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MONASH UNIVERSITY
THESIS ACCEPTED IN SATISFACTION OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

ON..... 2 September 2003

.....
Sec. Research Graduate School Committee

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ADDENDUM

Regretfully, in some references throughout the thesis, the following names may be spelt incorrectly: Gütlich, Schröder, Ōkawa and Mathionère. The most common misspellings are: Gutlich or Guetlich, Schroder or Schroeder, Okawa and Mathionere.

Acknowledgements

Page xv, line 5: "exemplary" for "supervision in his supervisory"

Chapter 1

Page 6, line 2: Before "metal ion" insert "d-block"

Page 8, Para. 1: Comment: J is used here in a general context and gains the appropriate subscript in a particular model, such as in the trinuclear model on p 414.

Page 16, line 5: Read "...gain control of the way molecules assemble..."

Page 22, line 25: Read "...TCNE has also been investigated."

Page 26, line 21: After "Simply stated," insert "apart from cases of 'accidental orthogonality',"

Page 27, line 9: " $t_{2g}^3 e_g^2$ " for " $t_{2g}^3 e_{2g}^2$ "

Page 30, line 13: "...Prussian-Blue like magnets is the series..." for " Prussian-Blue like magnets are the series..."

Page 37, line 5: "This group is in..." for "This group are in..."

Page 43, line 9: Delete "small"

Chapter 2

Page 87, line 12: "...to define a self-penetrated network..." for "to define an self-penetrated network..."

Page 100, Fig. 2.9: Comment: The sample is cooled in zero field and M is then measured within the field of 5 Oe as the sample is warmed, to yield the $ZFCM$ values.

Chapter 3

Page 132, line 15: "...dissolve and thus no longer possess..." for "...dissolve and are thus no longer possess..."

Page 133, line 5: After "...[Mn(salen)(dca)]_n," insert ", presumably by air oxidation."

Page 151, Table 3.6: Comment: E.s.d. values for g and J are ± 0.01 and ± 0.01 cm⁻¹ respectively.

Page 154, line 4: "...and the corresponding Schiff-base ligand. Except [Fe(salen)(dca)]_n, which..." for "...and the corresponding Schiff-base ligand, excepting [Fe(salen)(dca)]_n, which..."

Chapter 4

Page 167, line 4: "This is presumably..." for "This presumably..."

- Page 167, Sec. 4.2.2: Comment: Precautions were not taken to ensure all iron was Fe^{II} during synthesis. There may have in fact been some Fe^{III} present. The isolated product was observed to oxidise in air and was hence kept under nitrogen.
- Page 176, line 17: Delete "base" and read "acid"
- Page 194, line 7: Before "Perusal..." insert "The slight increase in μ_{eff} above 200 K in Fig. 4.18 might indicate orbital degeneracy effects."

Chapter 5

- Page 234, line 1: Insert reference 74 after "...Heisenberg chain model"

Chapter 6

- Page 253, line 9: "...was observed by the Murray group..." for "...was observed members of the Murray group..."

Chapter 7

- Page 278, line 9: Delete "The large ground state is a result of ferrimagnetism, the antiferromagnetic coupling of the four central Mn^{IV} ions ($S = 3/2$) and the eight perimeter Mn^{III} ions ($S = 2$) (Figure 7.2)." and read "The large ground state is due to ferrimagnetism (Figure 7.2), which is the result of the uncompensated spin arrangement involving antiferromagnetic coupling between the two spin subsets (perimeter and central cubane), which are themselves ferromagnetically coupled."

Chapter 8

- Page 374, line 11: Comment: E.s.d. values for g , J and θ are ± 0.01 , $\pm 0.1 \text{ cm}^{-1}$ and $\pm 0.01 \text{ K}$ respectively.
- Page 374, line 11: After "...+1.95 K." insert "The positive sign of θ results from a very rapid increase in χ_{M} ."

Chapter 9

- Page 394, Para. 1: Comment: The $\text{Mn}^{\text{III}}\text{-O}$ distance for the central manganese atom, Mn(1), of 2.169(3) Å is longer than the average $\text{Mn}^{\text{III}}\text{-Ligand}$ distance for $\{\text{Mn}_4\}$ or $[(\text{Me}_3\text{-tacn})\text{Mn}^{\text{III}}\{\mu\text{-dmg}\}_3\text{Mn}^{\text{II}}]\text{Mn}^{\text{III}}(\text{Me}_3\text{-tacn})](\text{ClO}_4)_2$,²⁸ both equal to 2.06 Å. As a consequence of the $\bar{3}$ symmetry at this site the expected Jahn-Teller distortion of the Mn^{III} ion is averaged throughout the crystal to produce the relatively long Mn-O distance of 2.169(3) Å.
- Page 425, Sec. 9.6.2: Comment: The most likely reason for the microanalytical data not being in good agreement with the calculated values is that the sample analysed may be contaminated with a small amount of the aforementioned fine brown solid.
- Page 426, line 16: Omit "The latter were most likely Me_4NClO_4 ."

**SYNTHESIS, STRUCTURE AND
MAGNETISM IN CLUSTERS AND
NETWORKS CONTAINING
DICYANAMIDE AND RELATED
LIGANDS**

DAVID JAMES PRICE

B.Sc. (HONS.)

A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

SCHOOL OF CHEMISTRY

MONASH UNIVERSITY

2003

"It was the best of times, it was the worst of times, it was the age of wisdom, it was the age of foolishness, it was the epoch of belief, it was the epoch of incredulity, it was the season of light, it was the season of darkness, it was the spring of hope, it was the winter of despair, we had everything before us, we had nothing before us, we were all going direct to heaven, we were all going direct the other way..."

An excerpt from A Tale of Two Cities by Charles Dickens

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SUMMARY

This thesis covers two main areas of interest. Firstly, molecule-based magnetic materials are described with the focus on new d-block metal dicyanamide frameworks (coordination polymers) containing various co-ligands. Secondly, polynuclear mixed valence manganese cluster complexes and single-molecule magnet (SMM) clusters are described. The compounds synthesised have been characterised in detail by means of single-crystal X-ray diffraction studies and magnetic susceptibility measurements. Much of the present work has been published or submitted for publication, details of which are given in Appendix 2.

A new spin-canted antiferromagnet (weak ferromagnet) was discovered, $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ (dca = dicyanamide, $\text{N}(\text{CN})_2^-$), which has an ordering temperature, T_N of 6.3 K. It possesses a novel 3D self-penetrating single network structure that can be considered as a structural compromise between the single rutile net of α - $[\text{Mn}(\text{dca})_2]$ and the doubly interpenetrated rutile-like $[\text{Mn}(\text{tcm})_2]$ species (tcm = tricyanomethanide, $\text{C}(\text{CN})_3^-$). Linear 1D chain dca complexes containing the co-ligand terpyridine, $[\text{Mn}^{\text{II}}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ and $\{[\text{Mn}^{\text{II}}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$, were formed as part of a study aimed at modifying metal-dca network structures and thus magnetic properties by incorporating chelating ligands. These two complexes display weak antiferromagnetic coupling and no long-range order.

$[\text{M}^{\text{III}}(\text{Schiff-base})(\text{dca})]_n$ (where $\text{M}^{\text{III}} = \text{Mn}$ and Fe ; Schiff-base (deprotonated) = salen^{2-} , sal-o-phen^{2-} and $(\pm)\text{-saltch}^{2-}$), complexes were formed and represent rare examples of trivalent metal-dca species. This series display very similar structures, consisting of linear 1D chains of planar $\text{M}^{\text{III}}(\text{Schiff-base})^+$ moieties bridged by $\mu_{1,5}$ -dca links, and displays very weak antiferromagnetic coupling.

The structures and magnetism of two new chiral 3D framework types containing neutral acetylacetone-derived Schiff-base ligands were investigated. The complexes, $[M^{II}(\text{acenH}_2)(\text{dca})_2]$, $M^{II} = \text{Mn}$ and Fe ; $\text{acenH}_2 = N,N'$ -ethylenebis(acetylacetoneimine), are isomorphous and consist of 3-fold helical motifs linked by $\mu_{1,5}$ -dca ligands to form a chiral 3D network. They are the first examples of single networks with the unusual 'dense' 7^59 topology. The second framework type is exhibited by the complexes $[M^{II}(\text{actchH}_2)(\text{dca})_2]$, $M^{II} = \text{Mn}$ and Fe ; $(\pm)\text{-actchH}_2 = (\pm)\text{-}N,N'\text{-trans-1,2-cyclohexanebis(acetylacetoneimine)}$. It consists of 2D square-grid (4,4) sheets of composition $[M(\text{dca})_2]$ that are connected in the third dimension by μ -actchH₂ ligands. This network type displays an unprecedented topology. These 3D network materials also display very weak antiferromagnetic coupling. The structure of a mononuclear complex, *trans*- $[\text{Mn}^{II}(\text{acenH}_2)_2(\text{dcnm})_2]$ (dcnm = dicyanonitrosomethanide, $\text{ONC}(\text{CN})_2$), was also investigated. It exhibits an unusual bis-chelating mode of acenH_2 .

Heteroleptic anionic dicyanamide dca network complexes were studied with the nitrite ligand. The chiral complexes, $\text{Ph}_4\text{P}[M^{II}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$, $M^{II} = \text{Co}$ and Ni , display 2D square-grid sheets structures with $\mu_{1,5}$ -dca and chelating *O,O*-nitrite groups. A side product was also discovered, $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$, which also possesses a chiral structure, consisting of linear anionic 1D helical chains of $[\text{Co}(\text{dca})\text{Br}_2]^-$. These complexes display very weak antiferromagnetic coupling. Traces of $\alpha\text{-}[M(\text{dca})_2]$ are thought to be responsible for long-range ordering effects observed in low fields in the nitrite containing complexes, but this is not definitive in the Co^{II} case.

While attempting to link Mn_3 or Mn_4 oxo-bridged clusters with dicyanonitrosomethanide (dcnm) to form extended network complexes, a new Mn^{III} complex, $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2] \cdot \text{HOAc} \cdot \text{H}_2\text{O}\}_n$, was discovered. The structure consists of infinite 1D linear chains that are hydrogen bonded to form 2D sheets. This compound

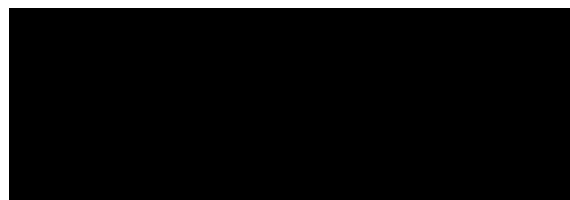
undergoes a magnetic phase transition, at $T_N = 6.1$ K, to an ordered antiferromagnetic phase, probably mediated by the hydrogen bonding pathways. There is also a metamagnetic transition at *ca.* 1000 Oe from the antiferromagnetic phase to a canted-spin antiferromagnetic (weak ferromagnetic) phase, brought about by increasing the applied field.

Similarly, work aimed towards forming extended network complexes between intact Mn_3 oxo-centred carboxylate clusters and bridging dca, led to the discovery of a new manganese(III/IV) carboxylate cluster, $[Mn_{16}O_{16}(OMe)_6(OAc)_{16}(MeOH)_3(H_2O)_3] \cdot 6H_2O$, and a new 1D linear manganese(III) complex, $[Mn(\mu-OAc)(OAc)_2]$. Detailed magnetic measurements have shown the Mn_{16} complex to be a new single-molecule magnet, while the linear chain complex displays weak antiferromagnetic coupling without long-range order.

Finally, related studies into extended network complexes containing the potentially bridging dcnm ligand led to ligand transformations and the formation of new trinuclear and tetranuclear mixed valent manganese complexes, $[Mn_3(mcoe)_6]NO_3 \cdot 2H_2O$ and $(Me_4N)_2[Mn_4O_2(cao)_4(MeCN)_2(H_2O)_6](NO_3)_4 \cdot 2H_2O$ (where mcoe = methyl(2-cyano-2-hydroxyimino)ethanimidate, $ONC(CN)C(NH)OCH_3$; and cao = cyanoacetamidoximate $ON=C(CN)(CONH_2)^-$). Separately, two mononuclear complexes were also isolated, $[Cu(mcoe)_2(MeOH)_2]$ and $[Ni(cao)_2(H_2O)_2]$. The chelating-bridging ligands mcoe and cao were formed, *in situ*, by nucleophilic addition of solvent to dcnm. The structural and magnetic properties of these compounds were investigated. Each of these complexes display inter-molecular hydrogen bonding interactions.

DECLARATION

This thesis contains no material that has been accepted for the award of any degree or diploma in any University and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text of the thesis.



David James Price

School of Chemistry

Monash University

April 2003

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Finally, thanks to my family and my Mum for love and support over the years.

ABBREVIATIONS

χ	Magnetic susceptibility
θ	Weiss constant
C	Curie constant
B.M., μ_B or β	Bohr magneton
μ_{eff}	Effective magnetic moment
N	Avogadro's number
k	Boltzmann constant
S	Spin value
S_z	Projection of S on z-axis
M_S	Magnetic quantum number
g	Spectroscopic or Lande splitting factor
ΔE or U_{eff}	Energy barrier to reversal of magnetisation
J	Coupling constant
T_C	Curie temperature
T_c	Critical temperature
T_N	Néel temperature
T_B	Blocking temperature
T	Tesla
T	Temperature
D	Axial zero-field splitting parameter
H	Magnetic field
M	Magnetisation
H_c	Coercive field
RM	Remnant magnetisation

M_{sat}	Saturation magnetisation
FCM	Field cooled magnetisation
$ZFCM$	Zero-field cooled magnetisation
Oe	Oersted
IR	Infrared
K	Kelvin
AC	Alternating current
DC	Direct current
S.I.	Système International d'Unités / International System of Units
χ' or χ_M'	In-phase AC susceptibility
χ'' or χ_M''	Out-of-phase AC susceptibility
S_T	Total spin value
H.S.	High spin
L.S.	Low spin
oct	Octahedral
tet	Tetrahedral
Å	Ångstrom
C_p	Specific heat capacity
F	Ferromagnetic
AF	Antiferromagnetic
FI	Ferrimagnetic
S-C AF	Spin-canted antiferromagnetic
SCM	Single chain magnet
SMM	Single molecule magnet
WOC	Water oxidation complex
PS II	Photosystem II
O4PE	Orthogonal four-fold phenyl embraces

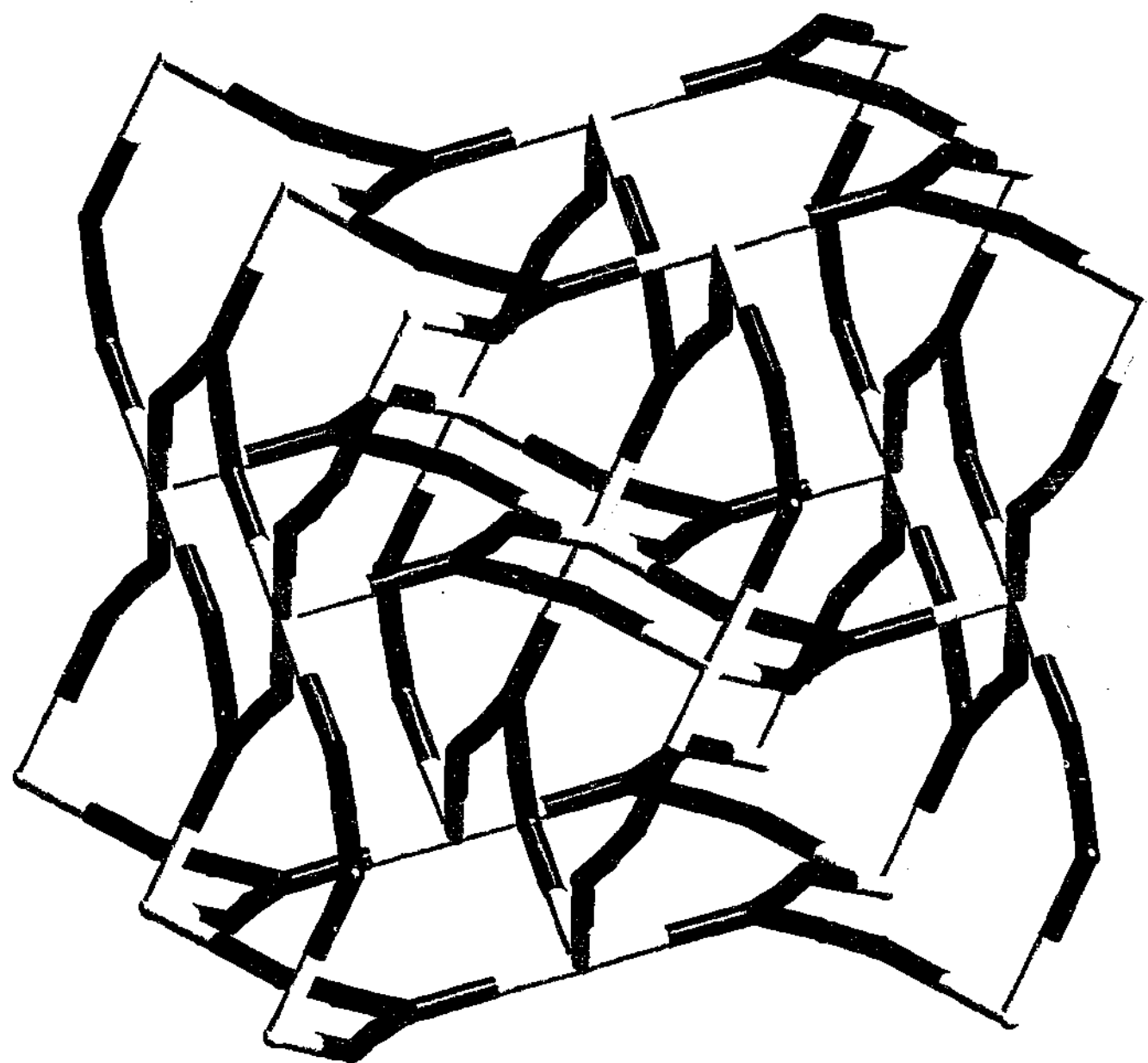
LIT4PE	Linear infinite chains of translational four-fold phenyl embraces
TGA	Thermogravimetric analysis
EXAFS	Extended X-ray absorption fine structure
XANES	X-ray absorption near edge structure
HFEPR	High-frequency/high-field electron paramagnetic resonance
NMR	Nuclear magnetic resonance
0D	Zero dimensional
1D	One dimensional
2D	Two dimensional
3D	Three dimensional
($\pm$)-actchH ₂	<i>N,N'</i> -($\pm$)- <i>trans</i> -1,2-cyclohexanebis(acetylacetoneimine)
($\pm$)-saltchH ₂	($\pm$)- <i>N,N'</i> - <i>trans</i> -cyclohexanebis(salicylideneimine)
(<i>S</i>)-pn	(<i>S</i>)-1,2-diaminopropane
1,1-dimen	1,1-dimethylenethylenediamine
2,2'-bipy or bipy	2,2'-bipyridine
2,5-Me ₂ pyz	2,5-dimethylpyrazine
3-MeO-salenH ₂	<i>N,N'</i> -ethylenebis(3-methoxysalicylideneimine)
3-MeO-salpentOH ²⁻	1,5-bis(3-methoxysalicylidenamino)pentan-3-ol
4,4'-bipy	4,4'-bipyridine
4,4'-Me ₂ dbmH	4,4'-dimethyldibenzoylmethane
5-Cl-salenH ₂	<i>N,N'</i> -ethylenebis(5-chlorosalicylaldimine)
6-Me-hmpH	6-methyl-2-hydroxymethylpyridine
acacH	acetylacetone
acenH ₂	<i>N,N'</i> -ethylenebis(acetylacetoneimine)
apym	2-aminopyrimidine
BEDT-TTF	bis(ethylenedithio)tetrathiafulvalene
biphen	2,2'-biphenoxide

bpe	1,4-bis(4-pyridyl)ethene
bpm	bis(1-pyrazolyl)methane
bpym	bipyrimidine
btaH	benzotriazole
Bu ⁿ or <i>n</i> -Bu	<i>neo</i> -butyl
Bu ^t or <i>t</i> -Bu	<i>tert</i> -butyl
BzO ⁻ /BzOH	benzoate/benzoic acid
cao	cyanoacetamidoximate
chp	6-chloropyridonato
chxn	<i>trans</i> -1,2-diaminocyclohexane
cit	citrate
Cl-hqnH	5-chloro-8-hydroxyquinoline
Cp [*]	pentamethylcyclopentadienyl
cyclam	1,4,8,11-tetraazacyclotetradecane
dbmH	dibenzoylmethane
dca	dicyanamide
dcnm	dicyanonitrosomethanide
DCNQIs	<i>N,N</i> -dicyanoquinone diimines
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethylsulfoxide
dpmH	dipivaloylmethane
dtc	<i>N,N</i> -diethyldithiocarbamate
en	1,2-diaminoethane
Et	ethyl
Et ₂ mal	2,2-diethylmalonate
Et ₂ O	diethylether
EtOH	ethanol

Etrad ⁺	2-(1-ethylpyridinium-4-yl)-4,4,5,5-tetramethylimidazolin-1-oxyl-3-oxide
H ₂ Bilm	2,2-biimidazole
H ₃ bzshz	<i>N</i> -phenylsalicylhydrazidine
H ₃ etheidi	<i>N</i> -(1-Hydroxymethylpropyl)iminodiacetic acid
H ₃ heidi	<i>N</i> -1-(hydroxyethyl)iminodiacetic acid
H ₃ metheidi	<i>N</i> -(1-Hydroxymethylethyl)iminodiacetic acid
HAT	1,4,5,8,9,12-hexaazatriphenylene
HCBD	hexacyanobutadiene
hepH	2-(hydroxyethyl)pyridine
Hhfac	hexafluoroacetylacetate
hmpH	2-(hydroxymethyl)pyridine
hqNH	8-hydroxyquinoline
<i>i</i> -PrOH	<i>iso</i> -propanol
JT	Jahn-Teller
mcoe	methyl(2-cyano-2-hydroxyimino)ethanimidate
Me	methyl
Me ₃ tacn	<i>N,N',N''</i> -trimethyl-1,4,7-triazacyclononane
MeCN	acetonitrile
MeOH	methanol
<i>m</i> -MPYNN ⁺	<i>m</i> - <i>N</i> -methylpyridinium nitronyl nitroxide
Mn ₁₂ -acetate	[Mn ₁₂ O ₁₂ (OAc) ₁₆ (H ₂ O) ₄]·2HOAc·4H ₂ O
Mn ₁₆ -acetate	[Mn ₁₆ O ₁₆ (OMe) ₆ (OAc) ₁₆ (MeOH) ₃ (H ₂ O) ₃]·6H ₂ O
moeH	methoxyethanol
mpdpH ₂	<i>m</i> -phenylenedipropionic acid
NITPh	2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl-3-oxide

NITPhOMe	4'-methoxy-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide
N-men	<i>N</i> -methylethylenediamine
<i>n</i> -PrOH	<i>normal</i> -propanol
OAc ⁻ /HOAc	acetate/acetic acid
opba	<i>ortho</i> -phenylenebis(oxamato)
ox	oxalate
paoH	pyridine-2-aldoxime
pbaOH	2-hydroxy-1,3-propylenebis(oxamato)
pdmH ₂	pyridine-2,6-dimethanol
Ph	phenyl
phen	1,10-phenanthroline
phth	phthalate
picH	picolinic acid
pn	1,2-diaminopropane
Por	porphyrin
ppoH	3-phenyl-3-pyrazolin-5-one
Pr ⁱ or <i>i</i> -Pr	<i>iso</i> -propyl
py	pyridine
pyz	pyrazine
pz	pyrazole
salenH ₂	<i>N,N'</i> -ethylenebis(salicylideneimine)
salH	salicylaldehyde
salOH ₂	salicylic acid
sal- <i>o</i> -phenH ₂	<i>N,N'</i> - <i>o</i> -phenylenebis(salicylideneimine)
salpnH ₂	<i>N,N'</i> -1,3-propylenebis(salicylideneimine)
saltmenH ₂	<i>N,N'</i> -(1,1,2,2-tetramethylethylene)bis(salicylidenedimine)

tach	1,3,5-triaminocyclohexane
tacn	1,4,7-triazacyclononane
tcm	tricyanomethanide
TCNE	tetracyanoethylene
TCNQs	7,7,8,8-tetracyano- <i>p</i> -quinodimethanes
terpy	2,2':6',2''-terpyridine
thmeH ₃	1,1,1-tris(hydroxymethyl)ethane
tpt	2,4,6-tris(4-pyridyl)-1,3,5-triazine
tren	tris(2-aminoethyl)amine
TTF	tetrathiafulvalene
TXPP	<i>meso</i> -tetrakis(4-halophenyl)porphyrinato



**CHAPTER 1: MOLECULE-BASED MAGNETISM,
A GENERAL INTRODUCTION**

This thesis covers two distinct but closely related areas of research, namely extended network complexes and single-molecule magnets (SMMs). Therefore this chapter, which is one of two introductions, deals with the background of molecule-based magnetism, theoretical concepts of magnetism, some of the significant literature in the field, and details of the present study (summarising the following chapters). The second introduction, Chapter 7, deals with the 'sub-topic' of single-molecule magnetism. It seeks to describe the background of SMMs, focussing on manganese cluster complexes. Chapter 7 also includes a brief treatment of the theoretical aspects of the physical properties of these species, and concludes with a discussion of non-manganese based SMMs.

1.1 Background

Magnetic materials have played a profoundly important role in the development of modern civilization. Their history can be traced back to ancient Greece with the discovery of naturally occurring magnets such as lodestone (Fe_3O_4), over 3000 years ago.^{1,2} Around the 11th Century, the Chinese invented the magnetic compass by rubbing lodestone on a steel needle.³ It wasn't for another 500 years or so that seafaring western civilisations used the compass as a navigational aid, making global trade and exploration possible as they were less reliant on good weather for navigation by stars and the sun. More recently, in the last hundred years or so, the use of magnets has become particularly widespread with the development of electricity. Today, magnets can be found in vital technologies including electric motors, generators, loudspeakers, frictionless bearings, magnetic switches, magnetic resonance imaging instruments, magnetic separators, and data storage found in the ubiquitous device of our times, the computer.

In 1832 Michael Faraday published the first diagram depicting magnetic field lines around a bar magnet.^{4,5} At that time, the magnet was undoubtedly made of iron. In the intervening 170 years, many advances have been made in materials that display

spontaneous magnetic ordering.⁴ The ferromagnetic metals, e.g. Fe and Co, were the mainstays until transition metal oxides, e.g. CrO_2 , were introduced in the period around World War II. Today, some of the most powerful and commercially successful magnets are rare earth based e.g. Co_2Sm , Co_5Sm , $\text{Co}_{17}\text{Sm}_2$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ materials.² These materials have high critical temperatures (T_c , see Table 1.1 for some examples) and the latter are particularly hard magnets (high coercivity, see Section 1.2.3). At the critical temperature (Curie temperature) the material undergoes a phase transition to a magnetically ordered state i.e. below this temperature it is a magnet. Traditional magnets are prepared by high temperature metallurgical techniques and are 'atom based', having *d*- or *f*-orbital spins ordering in at least two dimensions.^{1,3}

Table 1.1. Critical temperatures of some of today's magnets.²

Material	Critical Temperature T_c / K
Iron	1043
Cobalt	1394
Nickel	627
Fe_3O_4	858
CrO_2	387
SmCo_5	993
$\text{Nd}_2\text{Fe}_{14}\text{B}$	585

One of the earliest reports of a molecule-based magnet was in 1967 by Wickman *et al.*⁶⁻⁸ They reported ferromagnetic order below 2.5 K for the complex $[\text{Fe}^{\text{III}}(\text{dtc})_2\text{Cl}]$ (where $\text{dtc}^- = N,N$ -diethyldithiocarbamate). Reports appeared by Martin and Mitra and other groups in the subsequent decades dealing with ordered d-block phthalocyanines and

anionic Cu^{II} carbonates.⁹⁻¹² Subsequent research, by Day and co-workers into halide bridged d-block magnets,¹³⁻¹⁷ by Carlin and co-workers^{18,19} on weakly interacting mononuclear d-block salts, and by de Jongh and Miedema,²⁰ was also particularly important during the 1970-80 period.²¹ In 1985 Miller, Epstein and co-workers reported that $[\text{Fe}(\text{Cp}^*)_2][\text{TCNE}]$ (where Cp^* = pentamethylcyclopentadienyl; TCNE = tetracyanoethene) ordered ferromagnetically below a T_c value of 4.8 K.²²⁻²⁴ This exciting area of new materials research has grown rapidly since then, with many new molecule-based magnets being reported, a small number with T_c values above room temperature, which may lead to significant practical applications.^{25,26}

Currently the major disadvantages with molecular magnets include their brittleness (conventional magnets are usually quite malleable) and their generally lower T_c values. However, they may be prepared by comparatively mild solution-based organic/inorganic synthetic techniques as opposed to the high-temperature methods of atom-based magnets. Additionally, unlike their atom-based relatives, they are amenable to chemical modifications, which may be used to introduce other physical characteristics such as electrical or optical properties, not achievable with traditional magnets.^{1,27-29} Molecule-based magnets also bring together various research disciplines e.g. chemistry, materials science, physics and mathematics in the effort to explain some of the unusual (e.g. quantum) problems these materials present. It is this cooperation that may ultimately lead to the most fruitful and perhaps unexpected results of this research.

1.2 Magnetism, A Brief Overview

1.2.1 Paramagnetism in Mononuclear Coordination Complexes

The theory of magnetism as based on quantum mechanics was developed in the 1930s.³⁰⁻³³ The reader is directed to the books of Figgis,³⁴ Mabbs and Machin,³¹ Kahn³⁵

and Blundell³³ for in-depth treatments of magnetism as applied to ligand-field effects in transition metal complexes. What follows is an overview of the concepts of magnetism in an effort to illustrate the properties of paramagnets and molecule-based magnets.

Unpaired electrons are the fundamental basis of magnetism. Paramagnetism is a consequence of the interaction of orbital- and/or spin-angular momenta of unpaired electrons with the applied field.³¹ The electron spin can take two values $+\frac{1}{2}$ and $-\frac{1}{2}$, referred to as 'spin-up' and 'spin-down' respectively. If an atom, ion or molecule has two electrons in every orbital, their associated spin values will cancel, as the electrons must pair with opposite spins. The material will then be diamagnetic and be slightly repelled on application of a magnetic field. This may be understood in terms of Lenz's law by classical treatment of the paired electrons as a current loop.^{31,36} If a molecule has an odd number of electrons the molecule will have one (or more) unpaired spins and thus have a permanent magnetic dipole. Such a molecule is paramagnetic, and is attracted into a magnetic field. Examples of paramagnets include d- and f- block metal complexes and organic radicals. Paramagnets are referred to as magnetically dilute, meaning that the individual spin sites do not communicate (interact) throughout the bulk material. Without an applied magnetic field the spin directions are oriented randomly throughout the lattice due to thermal motion and hence net cancellation occurs and the magnetic moment is zero. When a strong magnetic field is applied the spins align parallel to the field direction. Once the field is removed the spins again randomise.

Paramagnets obey the Curie-Weiss law (Equation 1.1), which relates the magnetic susceptibility, χ , to the temperature, T , (where $\chi = M/H = \text{Magnetisation}/\text{Applied Field}$; C = the Curie constant; θ = the Weiss constant).^{31,35} Equation 1.1 is only valid when χ is independent of the applied field, H .³¹ Inorganic chemists commonly use a more convenient quantity, the effective magnetic moment, μ_{eff} , which is defined by Equation 1.2.^{31,35} This

magnetic moment has the non S.I. unit of Bohr Magneton (B.M., μ_B or β) and the advantage of being on a scale (~ 0.6 per metal ion) that lends itself to easy comparison. It should be noted that μ_{eff} is derived from an arbitrary definition and that magnetic susceptibility, χ , is the fundamental quantity.³¹ Many groups worldwide use the product, χT , rather than μ_{eff} .

$$\chi = \frac{C}{T - \theta} \quad \text{Equation 1.1}$$

$$\begin{aligned} \mu_{\text{eff}} &= \left(\frac{3k}{N\beta^2} \right)^{1/2} \sqrt{\chi T} \\ &= 2.828 \sqrt{\chi T} \end{aligned} \quad \text{Equation 1.2}$$

k = Boltzmann constant

N = Avogadro's number

The Weiss constant, θ , can be zero to negative for mononuclear paramagnetic metal complexes, with the magnitude depending on the nature of the ligand field ground-state and degree of distortion from perfect octahedral or tetrahedral symmetry.^{31,35} Thus, for orbitally non-degenerate ground-state systems (e.g. octahedral Ni^{II} , $^3\text{A}_{2g}$ ground-state) θ is close to zero and μ_{eff} remains independent of temperature as χ simplifies to C/T (the Curie law). In contrast, orbitally degenerate systems such as octahedral Co^{II} ($^4\text{T}_{1g}$) or V^{III} ($^3\text{T}_{1g}$) exhibit non-zero θ values, and consequently μ_{eff} decreases with decreasing temperature.

1.2.2 Short Range Coupling in Small Cluster Complexes

If two or more metal centres are in close proximity the unpaired spins on each centre can couple, that is, interact with each other so that one spin centre is 'aware' of, and is influenced by the presence of the other(s). The spins can align parallel to each other (ferromagnetic coupling) or antiparallel to each other (antiferromagnetic coupling). Hence,

as well as the ligand-field and orbital degeneracy consequences in mononuclear species mentioned in Section 1.2.1, the Weiss constant can also indicate the nature and strength of coupling between adjacent metal centres. Positive θ values indicate ferromagnetic coupling and thus μ_{eff} will increase with decreasing temperature, whereas negative θ values indicate antiferromagnetic coupling, in which case μ_{eff} will decrease with decreasing temperature. Larger θ values correspond to stronger coupling. Figure 1.1 shows plots of χ , $1/\chi$ and μ_{eff} versus temperature, T to illustrate the effects of the Weiss constant.

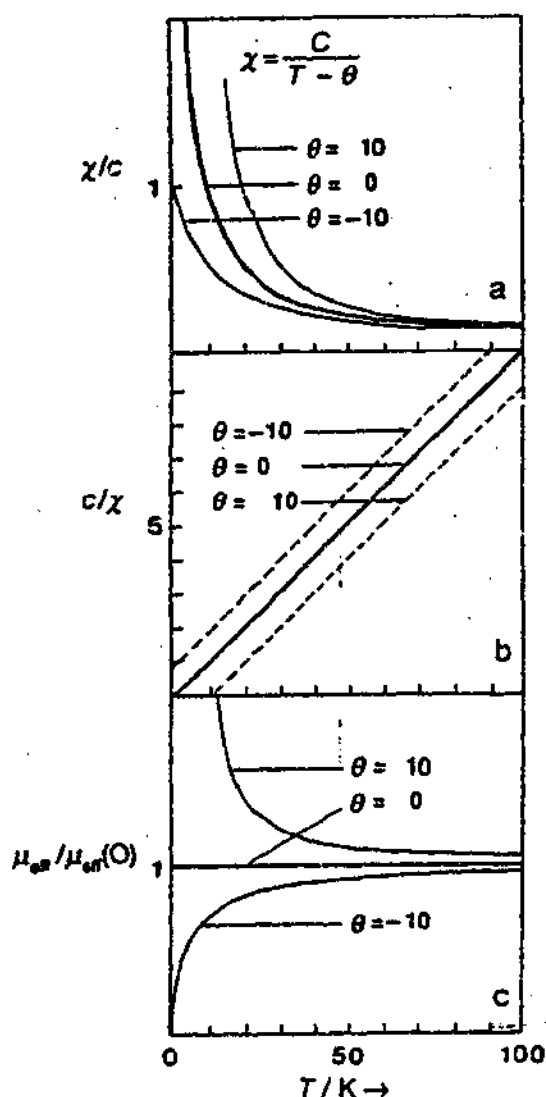


Figure 1.1 The effect the Weiss constant, θ , has on (a) χ , (b) $1/\chi$, and (c) μ_{eff} , versus temperature (reproduced from reference 2).

Coupling between metal centres is common in dinuclear, trinuclear and larger cluster complexes. This coupling is intra-molecular or short-range, as it does not extend beyond the finite clusters. For these systems the expression for χ is modified to include exponential $-2J/kT$ terms, where J , the spin-spin coupling constant, gives an indication of the type and magnitude of the magnetic coupling.^{31,35,37} The convention used here is that positive J values indicate ferromagnetic coupling, whereas negative J values indicate antiferromagnetic coupling. Various models have been developed for determining the coupling constants in different systems such as di-, tri- and tetra-nuclear complexes and also extended systems such as 1D chains.^{31,35} There are often multiple constants to represent the many individually considered interactions in multinuclear complexes. Care has to be taken in comparing literature J values since different authors use $-2/S_1 \cdot S_2$ or $-J S_1 \cdot S_2$ spin Hamiltonians. Most of these models assume that any orbital degeneracy on the metal ion is zero and thus spin-only formalism can be used. In cases such as $^4T_{1g}$ (Co^{II} oct) this is a gross approximation and more detailed models are required.³⁸

There are two commonly used mechanisms to account for the coupling: (a) direct interaction between d-orbitals, and (b) superexchange. The former situation, for example, exists in the copper(II) acetate monohydrate dimer, $[\text{Cu}^{\text{II}}(\text{OAc})_2(\text{H}_2\text{O})]_2$.³⁹ Weak overlap of the $d_{x^2-y^2}$ orbitals on each Cu^{II} ($S = 1/2$) centre leads to a diamagnetic ground-state.^{31,39} More commonly however, the ability of spin centres to couple can be associated with a 'superexchange' mechanism (or pathway), which is achieved through organic or inorganic bridges between the metal centres. This involves overlap of magnetic orbitals on the metal centres with the orbitals on the bridging ligands. The various superexchange models are explained in detail in reviews by Martin,⁴⁰ Ginsberg,⁴¹ and Kahn.^{35,42}

In molecule-based magnets, mechanisms of superexchange can include pathways *via* covalent bonds in diamagnetic (or paramagnetic radical) bridging ligands, hydrogen

bonds, or van der Waals interactions. Magnetic interactions can also occur by dipole-dipole through-space interactions or spin-polarisation mechanisms across appropriately substituted aromatic rings.⁴³

1.2.3 Long Range Order in Extended Network Coordination Complexes

In contrast with paramagnetic species and small coupled cluster complexes, which can display short-range magnetic coupling, magnetic materials can exhibit long-range coupling between spin centres throughout the entire solid. As such, they are known as magnetically concentrated. Long-range coupling, in special circumstances, can lead to long-range magnetic order with spontaneous magnetisation, which occurs abruptly in a magnetic phase transition to the ordered state below a critical temperature, T_c . Long-range order is a cooperative effect and is a property of the bulk solid, not of the individual atomic or molecular components.^{1,2,19,27,35,44-46} Figure 1.2 shows a schematic representation of the ways spins can align in a material.⁴⁴ Ferromagnetic (parallel spins) or antiferromagnetic (antiparallel spins) coupling can lead to long-range ferromagnetic or antiferromagnetic order respectively. Ferrimagnetic ordering is a special case of antiferromagnetism, where adjacent spins are of different magnitudes hence antiparallel alignment leads to a net moment.

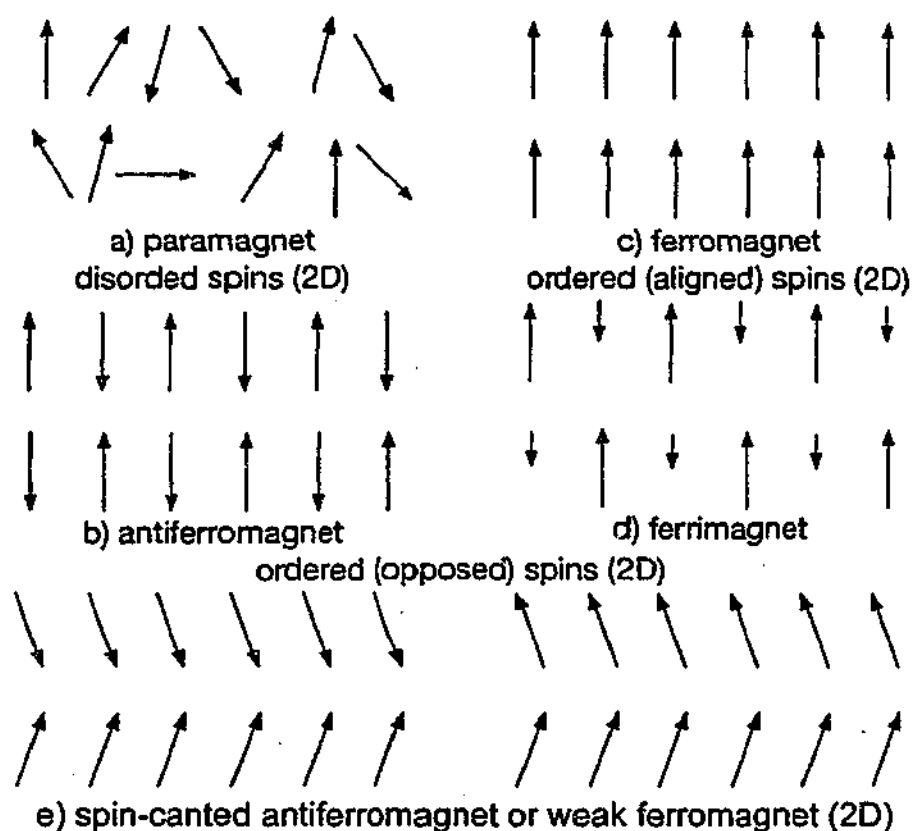


Figure 1.2 A schematic representation of spin-coupling behaviours in two dimensions, including (a) paramagnet disordered spins, (b) antiferromagnetic, (c) ferromagnetic, (d) ferrimagnetic and (e) spin-canted antiferromagnetic or weak ferromagnetic alignment of spins (reproduced from reference 2).

In addition to these magnetic behaviours, other ordering phenomena, such as metamagnetism, spin-canted antiferromagnetism (weak ferromagnetism) and spin-glass behaviour, may occur.⁴⁴ Metamagnetism occurs when a material that displays antiferromagnetic ordering transforms to a high-moment state (e.g. ferromagnetic or spin-canted antiferromagnetic) on the application of an external magnetic field. An example of a metamagnetic material is described in Chapter 6. Spin-canted antiferromagnetism, otherwise known as weak ferromagnetism, arises from a relative canting of spins resulting in a net moment, the size of which is dependent on the canting angle.^{44,47} A spin glass occurs where local alignment of spins exists, but long-range ordering does not. Whereas for a paramagnet the spin directions vary with time, for a spin glass they remain fixed or

change only very slowly.^{44,48} Figure 1.3 shows the magnetisation, M , versus applied field, H , for the various types of magnetic behaviour.

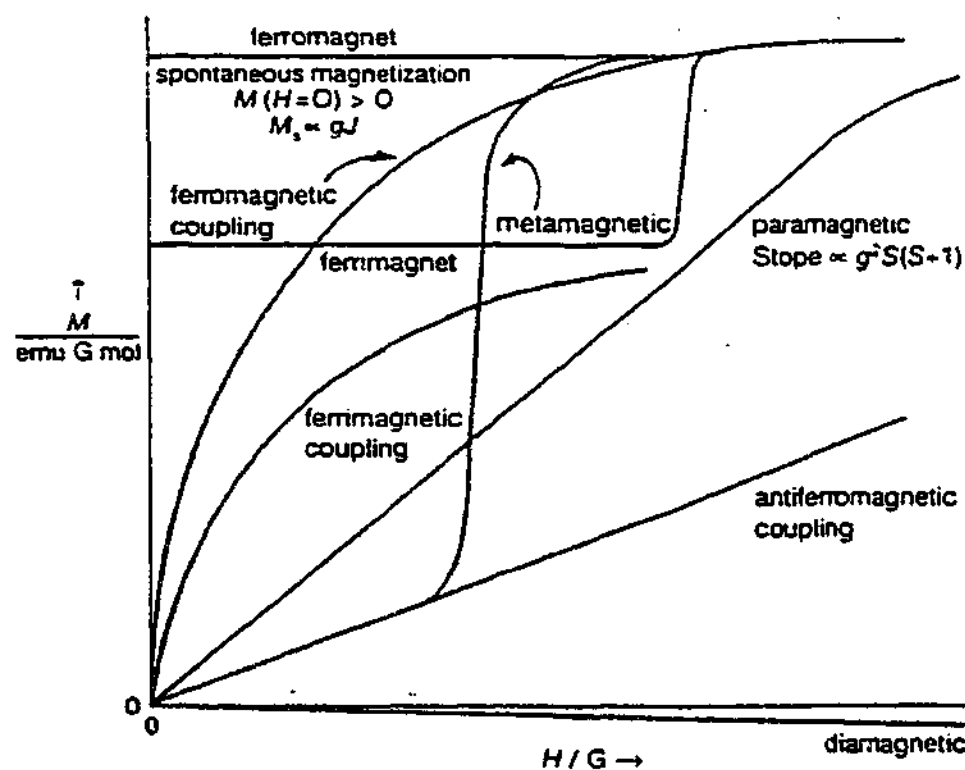


Figure 1.3 Schematic illustration of magnetisation (M) versus applied field (H) curves for different types of magnetic behaviour (reproduced from reference 2).

A magnet is said to display spontaneous magnetisation below a magnetic ordering, or critical, temperature T_c . For ferromagnets this is referred to as the Curie temperature, while for antiferromagnetic interactions or for spin-canting, it is known as the Néel temperature T_N .⁴⁴ The term 'spontaneous' can be a little misleading, as a small applied field is required to induce magnetisation. This is due to the presence of regions, or domains, where the spins are spontaneously ordered, but these domains are oriented randomly with respect to each other. Hence, the small applied field causes coalescence of the domains and magnetisation of the material. This situation is illustrated in Figure 1.4. When the external field is removed the magnetisation remains (remnant magnetisation,

RM) but will decrease slowly over time as the domain walls reform. If the direction of the field is reversed the magnetisation can be reduced to zero. The value of the applied field required to do this is called the coercive field, H_c . This history dependent $M(H)$ behaviour is known as hysteresis.⁴⁴ Magnets with coercive fields, $H_c > 1000$ Oe are referred to as 'hard' magnets, correspondingly 'soft' magnets have $H_c < 1000$ Oe. Magnetic data storage devices use hard magnets, and soft magnets are found in AC motors and magnetic shielding.^{2,26,27,44}

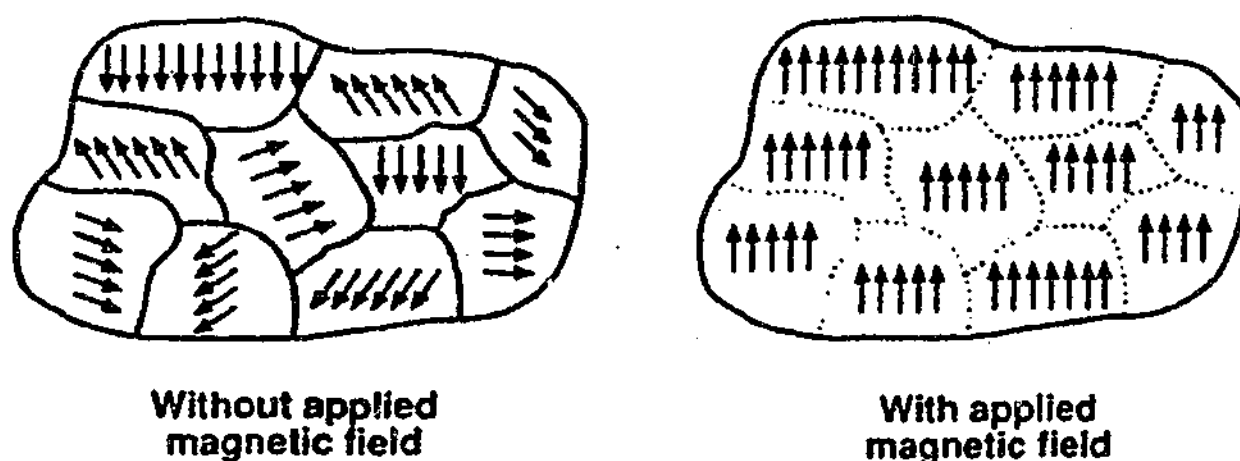


Figure 1.4 Schematic representation of magnetic domains without an applied field (left) and in the presence of a field (right). Reproduced from reference 2.

Above the critical temperature the thermal motion of the spins is enough to prevent long-range ordering. However, below the T_c the spin-alignment energy is enough to overcome the randomising effect of thermal motion, so the spins align throughout the solid.^{2,35,49,50}

1.2.4 Experimental Measurement of Long Range Magnetic Order

The first indication that a material may be a magnet can be seen in plots of χT or μ_{eff} versus temperature in DC fields of $H < 1$ Tesla (T). If χT (or μ_{eff}) increases to values

much higher than those expected for spin-only interactions, this can often indicate the occurrence of long-range magnetic order. This can be confirmed by various plots of magnetisation, M , versus temperature, a typical example of which is shown in Figure 1.5. This plot is generated from the following series of measurements. When the sample is cooled from room temperature in zero-field the magnetisation ($ZFCM$) is zero, then undergoes a small increase and maximum as the T_c is reached, but returns to near zero as domains are formed. Then the sample is returned to a temperature above T_c and a small field is applied, typically 5 Oe (NB. 1 T = 10,000 Oe). When the sample is cooled the magnetisation (FCM) increases abruptly at T_c , then reaches a plateau at low temperature. The field is removed and the sample warmed to above the T_c , the remnant magnetisation (RM) closely follows the field-cooled magnetisation (FCM , for materials with high RM), then above T_c returns to zero as the thermal energy causes the spins to randomise. This plot is used to determine the T_c of the material.

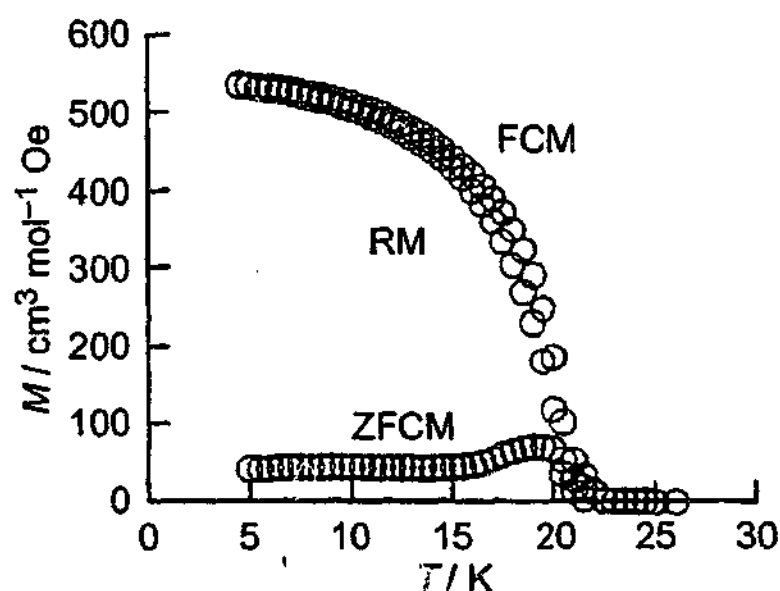


Figure 1.5 Typical plot of Magnetisation versus Temperature showing Field-Cooled Magnetisation (FCM), Zero-Field Cooled Magnetisation ($ZFCM$) and Remnant Magnetisation (RM) for a molecule-based magnet (specifically α -[Ni(dca)₂], a ferromagnet, $T_c = 21$ K). Reproduced from reference 51.

Other important measurements used to confirm the occurrence of long-range magnetic order include the in-phase (χ') and out-of-phase (χ'') components of the AC susceptibility. These give a sharp maximum at T_c . These are also used to demonstrate single-molecule magnetic behaviour, where frequency dependence of maxima in χ'' indicates slow relaxation of magnetisation. This subject is discussed in more detail in Chapter 7.

The nature of magnetic order is determined by measuring the field dependence of magnetisation for different temperatures below and above the T_c . The various types of magnetic behaviour give distinctive plots of M versus H , as shown in Figure 1.3. For example, materials that order ferromagnetically rapidly reach their saturation magnetisation plateau. Saturation magnetisation, $M_{\text{sat}} = 2S_T N\beta$ (where S_T = total spin value), can be used to differentiate between ferromagnetic and ferrimagnetic order in heterometallic systems with centres of unequal spins. For instance, a system with $S_1 = 5/2$ (e.g. H.S. oct Mn^{II}) and $S_2 = 1/2$ (e.g. oct Cu^{II}) will have M_{sat} values of $6N\beta$ ($S_T = 6/2$) or $4N\beta$ ($S_T = 4/2$) for ferromagnetic or ferrimagnetic ordering respectively.

As mentioned above, magnetic hysteresis is an important behaviour exhibited by magnets. It is used to determine the 'magnetic hardness' and memory of the material. At a given temperature below the T_c , the magnetisation, M , is plotted against applied field, H . As the field is increased from zero to large values, usually up to 5 T, the material typically reaches saturation magnetisation, M_{sat} . Then the field is reduced and the magnetisation does not follow the same curve, but due to domain formation has a remnant magnetisation, RM , at zero-field. The field is then increased in the opposite direction, and the magnetisation is reduced to zero at the value of field known as the coercive field, H_c . The

field is increased until M_{sat} is reached, then cycled back to zero and so on. Thus a symmetrical hysteresis loop is formed, an example of which is shown in Figure 1.6.

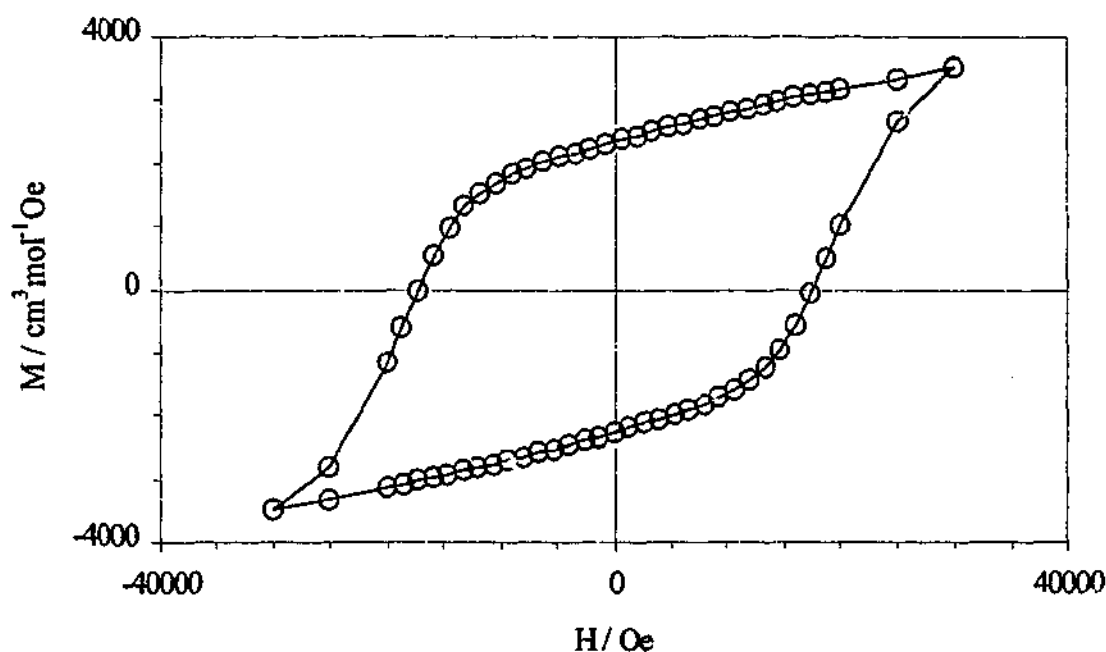


Figure 1.6 An hysteresis plot of a spin-canted antiferromagnet (specifically α -[Fe(dca)₂], embedded in Vaseline, $H_c = 17380$ Oe and $RM = 2330$ cm³mol⁻¹Oe). Reproduced from reference 52.

Another important technique to further confirm long-range magnetic order is heat capacity measurement. A plot of total specific heat, C_p , versus temperature will exhibit a maximum near the T_c indicating a phase change to a magnetically ordered state.^{47,53,54}

1.3 Crystal Engineering of Coordination Polymers

The overwhelming majority of molecule-based magnetic materials are coordination polymers, since suitable bridging ligands can facilitate superexchange interactions between unpaired spins on metal ions throughout the crystal lattice, thus potentially leading to long-range magnetic order. Hence the design of coordination

polymers and the associated network theory are highly relevant to the field of molecule-based magnetism. Some early coordination polymers were reported by J. C. Bailar many years ago.⁵⁵⁻⁵⁷

Crystal engineering involves the analysis and rational design of crystal structures, and ultimately aims to gain control the way molecules assemble in the solid state. There is much impetus to achieve the fully rational design of materials. As many of the physical properties of materials are largely dependent on their structure, control over the structure introduces the potential of constructing materials with desirable and useful properties. These include magnetic (long-range order, spin-crossover behaviour), electrical (conductivity, semiconductivity, superconductivity), optical (non-linear optical behaviour, transparency), physical (microporosity, hardness), and chemical (heterogeneous catalysis, solubility) properties.⁵⁸ For example, one could envisage synthesizing materials with large pores of predetermined size to be new catalysts tailor-made for specific processes. However, presently, the true crystal engineering of useful materials with predetermined structures remains an elusive goal. With some exceptions, many discoveries of new materials with interesting properties and structures have been made by accident or educated trial and error.

Towards the above goal, the crystal engineering of coordination polymers is currently a very active field of research that has seen rapid growth in recent years.⁵⁸⁻⁷³ It had its birth in 1990 in a paper by Hoskins and Robson, in which they describe the rational synthesis of new coordination polymers based on simple network prototypes.⁷⁴ For example, the structure of diamond consists of tetrahedral carbon atoms connected together to form a simple 3D network. By replacing the carbon atoms with tetrahedral metal centres (e.g. Cd^{II} , Zn^{II}) and the C-C bonds with linear bridging ligands (e.g. CN^-), one can construct new structures ($\text{Cd}(\text{CN})_2$, $\text{Zn}(\text{CN})_2$), which possesses the same topology as

diamond.⁷⁴ However, as the tetrahedral centres are no longer linked by C-C bonds (1.54 Å), but by the much longer M-CN-M bridges (5.46 (Cd) and 5.11 (Zn) Å), the resulting network is a much more open structure, thus allowing the interpenetration of a second identical, unconnected network.⁷⁴

Therefore, by controlling the geometry of metal ions and ligands it should in theory be possible to control the topology of the network formed. However, as stated above, reality can be unpredictable. Variables such as choice of solvent or counter ion can greatly influence the topology of the resulting network. In addition, even if the metal ions and ligands function as designed, different network topologies are possible for the same nodal geometry. For example, $\text{Cd}(\text{CN})_2$ or $\text{Zn}(\text{CN})_2$ needn't have formed diamond networks, as there are a number of other topologies it might have formed that also contain tetrahedral nodes (e.g. Lonsdaleite and Quartz networks).⁵⁸ The phenomena of polymorphism and pseudopolymorphism provide an illustration of the challenges facing the crystal engineer. Polymorphs contain the same chemical components but pack differently in the solid-state. For example, the α and β phases of $[\text{Cu}^{\text{I}}(\text{dca})(\text{bpe})]$ (bpe = 1,4-bis(4-pyridyl)ethene) possess 2D and 3D structures respectively, further complicated by the fact that they crystallise together with the addition of a third, as yet unidentified, phase.⁷⁵ Pseudopolymorphism is where the chemical compositions differ only in the amount and/or type of solvent included. Hence, a large element of uncertainty remains in crystal engineering. However, this can be a bonus since it is often the unexpected results, perhaps beyond the original imagination of the chemist, which can be more interesting than the intended structures.

One convenient way of defining the construction of a framework is based on the idea of a net.⁷⁶ Two particularly useful compendia of nets relevant to chemistry were compiled by Wells over twenty years ago.^{77,78} He defined crystal structures in terms of

their topology by reducing them to a series of points or nodes with certain topologies (3-connecting, 4-connecting, 6-connecting etc.) that are connected to a fixed number of other nodes. The resulting structures can be either discrete (zero-dimensional) polyhedra or infinite (1D, 2D or 3D) periodic nets.⁶³ Examples of simple infinite 2D nets given the symbols (6,3) and (4,4), are shown in Figure 1.7. One way of representing the topology or connectivity of any given net is in terms of the general symbol (n,p) , where p is the number of pathways or connections to neighbouring nodes that radiate from any centre or node, and n is the number of nodes in the smallest closed circuits in the net. Thus, the number 6 in the symbol (6,3) indicates that the shortest circuits in the net are hexagons and the number 3 indicates that the nodes are three-connecting. A 'shortest circuit' is defined as the shortest circuit possible that includes a given *pair of links* (outward and inward bound) from a node. Thus, each *pair of links* from a node has a 'shortest circuit' associated with it. For each link radiating (outward bound) from a p -connected node there are $(p-1)$ other links *via* which to return to the node (inward bound). Thus, for any node there are $p(p-1)/2$ 'shortest circuits'. The factor of $1/2$ is included so that each 'shortest circuit' is not counted twice, because it does not matter which direction the 'shortest circuit' is travelled. As strange as it may sound, for a given node, the 'shortest circuits' are not necessarily all the same size. The (n,p) notation strictly only applies when all $p(p-1)/2$ 'shortest circuits' originating from any node are n -gons (as is the case for the (6,3) nets in Figure 1.7(a)). Otherwise, the more complete Schläfli notation, $n^{p(p-1)/2}$, should be used. Thus, the symbol (4,4) for the net in Figure 1.7(b) is not strictly correct since two of the six 'shortest circuits' for each node involve six nodes (*trans* links), while the other four involve four nodes (*cis* links). The correct symbol is $4^4 6^2$, Wells having simplified this to 4^4 (or (4,4)) by arbitrarily ignoring 'shortest circuits' with collinear links.²¹ The (4,4) notation is used to describe a number of 2D networks presented in this thesis.

Two different geometric forms of the (6,3) net are shown in Figure 1.7(a), emphasising that nets may be distorted without changing connections and retain the same topology. For the same reason, in a topological sense square-planar and tetrahedral nodes should be regarded as simply 4-connecting centres. However, there are obvious chemical reasons for delineating between them.

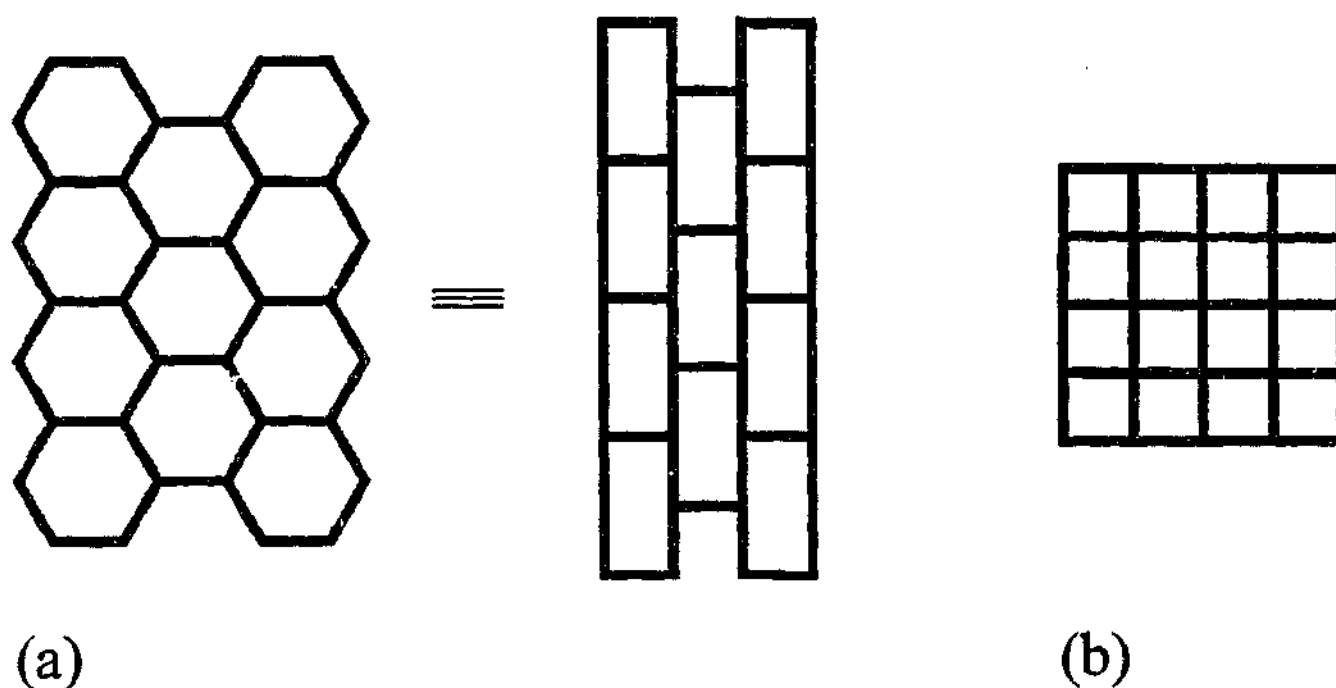


Figure 1.7 (a) Two different geometrical arrangements of the (6,3) net, and (b) the (4,4) net. Reproduced from reference 76.

Many infinite nets have real examples such as minerals, which can provide convenient names for the nets. On the other hand, some nets are only represented by a few real examples or remain theoretical entities.⁵⁹ For instance, Chapter 4 describes both, a net with a topology for which the first real example was reported in 1998,⁷⁹ and a net with an unprecedented topology. Some of the simplest infinite 3D nets include: the α -polonium (α -Po) net (with 6-connecting octahedral nodes - also known as the ReO_3 or NaCl net); the diamond, Lonsdaleite, quartz, feldspar-related and zeolite related nets (with four-

connecting tetrahedral nodes); the NbO net (involving 4-connecting square planar nodes with a 90° twist along each link); the PtS net (with tetrahedral and square planar nodes in 1:1 ratio); the rutile (TiO_2) net (with octahedral and trigonal nodes in a 1:2 ratio); the “ Pt_3O_4 ” net (with square planar and trigonal nodes in a 3:4 ratio); the Ge_3N_4 net (with tetrahedral and trigonal nodes in a 3:4 ratio) and various three-connected nets described by Wells,⁷⁸ the most symmetrical of which is the chiral (10,3)-a net.⁵⁹ When applying Schläfli notation to nets with more than one type of node, each node is treated separately with the same principles being used for each (see Chapter 2 for an example of this treatment).

Many coordination polymers form with large voids, cavities and/or channels in their networks. In such cases there are three main ways in which networks with such voids may maximise their packing efficiencies. The first is by intercalation, whereby ‘guest’ molecules occupy the cavities of the network (the ‘host’). This is often achieved by inclusion of solvent molecules (commonly disordered). The second is by interdigitation, which may occur for 1D and 2D systems, examples of which can be seen in Chapter 3. The third method is by interpenetration, whereby the voids are occupied by one or more, independent, usually identical frameworks. The key feature of these entangled systems is that they can only be disentangled by the breaking of bonds. This occurs when the rods of one network pass through the rings of another and *vice versa*.⁷⁶ Interpenetration is uncommon for 1D systems but very common for 2D and 3D systems where numerous examples have been observed with wide ranges of topologies.⁷⁶ Some examples of interpenetration are shown in Figure 1.8 for 2D and 3D frameworks. Chapter 2 describes an unusual self-penetrated or self-entangled structure, which is the polymeric equivalent of a molecular knot.⁸⁰

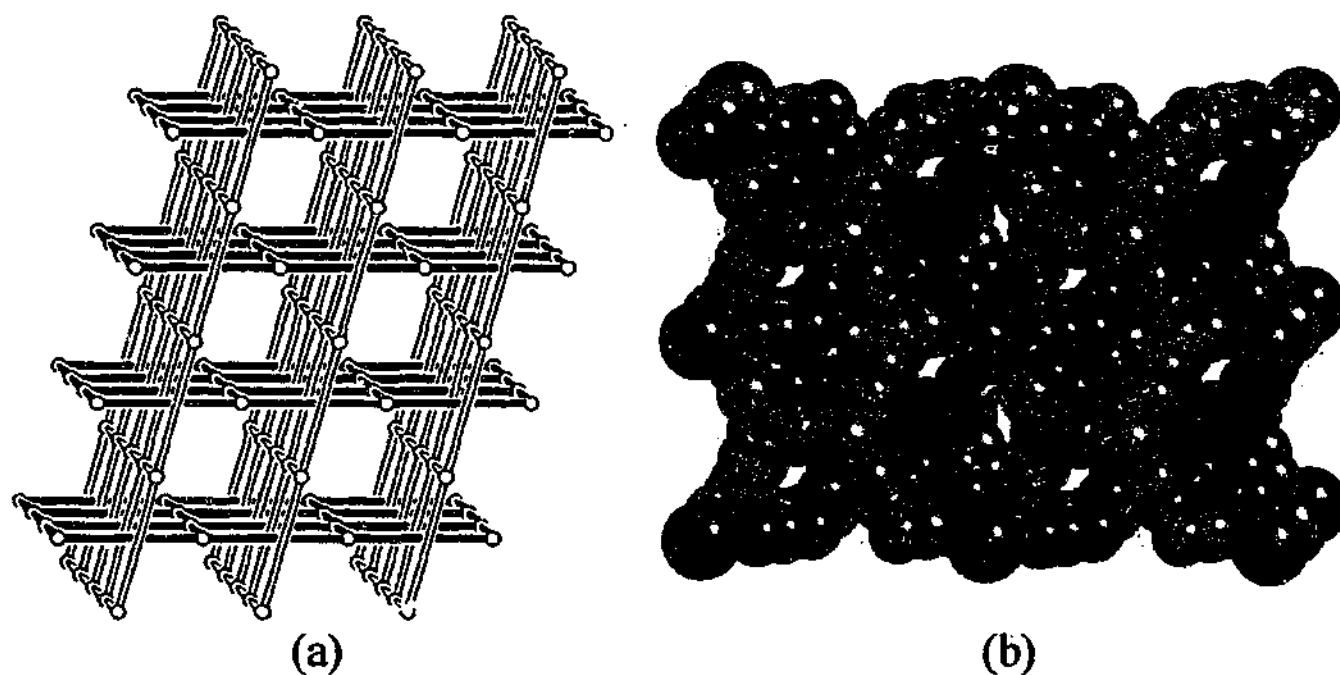


Figure 1.8 (a) One mode of inclined penetration for 2D (4,4) sheets and; (b) The two (2-fold) interpenetrating 3D nets of the rutilate-related $[M^{II}(C(CN)_3)_2]$ complexes. Reproduced from references 76 and 59 respectively.

1.4 Some Examples of Molecule-Based Magnets

The number of known molecule-based magnets is increasing rapidly due to the large amount of research attention that has been focused on this field over recent years by many groups worldwide. What follows is an introduction to the main families of molecule-magnets *via* the illustration of particular examples. They are categorised primarily on the basis of bridging ligand. The metal dicyanamides, which are most relevant to this thesis, are discussed in Section 1.4.7. Further details in the area of molecule-based magnetism (including purely organic molecule-based magnets, which are beyond the scope of this thesis) can be found in Kahn's book³⁵ and in excellent reviews and conference reports on the subject.^{2,27,29,50,81-85}

1.4.1 Donor-Acceptor Charge Transfer Complexes and Related Systems

In 1985 Miller *et al.* reported the molecule-based magnet, $[\text{FeCp}^*_2]^+[\text{TCNE}]^-$ (where $\text{Cp}^* = \text{pentamethylcyclopentadienyl}, \text{C}_5\text{Me}_5$; $\text{TCNE} = \text{tetracyanoethylene}, (\text{NC})_2\text{C}=\text{C}(\text{CN})_2$).²²⁻²⁴ The structure, which is shown in Figure 1.9, consists of chains of alternating radical ferrocenium cationic donors, $\text{D}^{+\bullet}$, and radical TCNE anionic acceptors, $\text{A}^{\bullet-}$, each of which carries a spin $S = 1/2$. The salt orders ferromagnetically below the T_c value of 4.8 K. Interestingly, this material is one of the few truly 'molecular magnets' in that there is no covalent bonding between the spin carriers. While it has been shown that the majority of the spin is localised on the Fe^{III} ion, spin polarisation is proposed to result in a spin of opposite sign on the Cp^* rings, which face the $\text{TCNE}^{\bullet-}$ anions. Ferromagnetic coupling is thought to occur *via* a spin exchange between the Cp^* rings and the $\text{TCNE}^{\bullet-}$.⁸⁶ This research into donor-acceptor salts has shown that covalent bonding between spin centres is not essential for long-range magnetic order to occur. However, the low T_c is attributable to the weakness of the through-space interaction in comparison to superexchange interactions observed in a coordination polymer network.

Since this work, several additional donor-acceptor and related molecule-based magnets have been reported.^{25,26,45,87-95} These materials show a range of magnetic behaviour. For instance, the series of compounds $[\text{Mn}^{\text{III}}\text{TXPP}][\text{TCNE}]$ (where $\text{TXPP} = \text{meso-tetrakis(4-halophenyl)porphyrinato}$, $\text{X} = \text{F, Br, I}$) display ferrimagnetic ordering as high as 28 K (for $\text{X} = \text{F}$).⁸⁸ However, in these compounds the $\text{TCNE}^{\bullet-}$ radicals act as bridging ligands between the $[\text{Mn}^{\text{III}}\text{TXPP}]^+$ moieties to form linear 1D coordination polymer chains. Thus, enhanced spin interactions may account for the higher T_c value compared to the donor-acceptor salt of $[\text{FeCp}^*_2]^+[\text{TCNE}]^-$.

A large series of related electron-transfer salt compounds with Mn^{III} -porphyrinato, $[\text{Mn}^{\text{III}}\text{Por}]$, and polycyano ligands similar to TCNE have also been investigated. These

include those containing TCNQs (7,7,8,8-tetracyano-*p*-quinodimethanes),⁹⁶⁻⁹⁹ HCBT (hexacyanobutadiene),¹⁰⁰⁻¹⁰⁴ and DCNQIs (*N,N*-dicyanoquinone diimines).⁹⁰

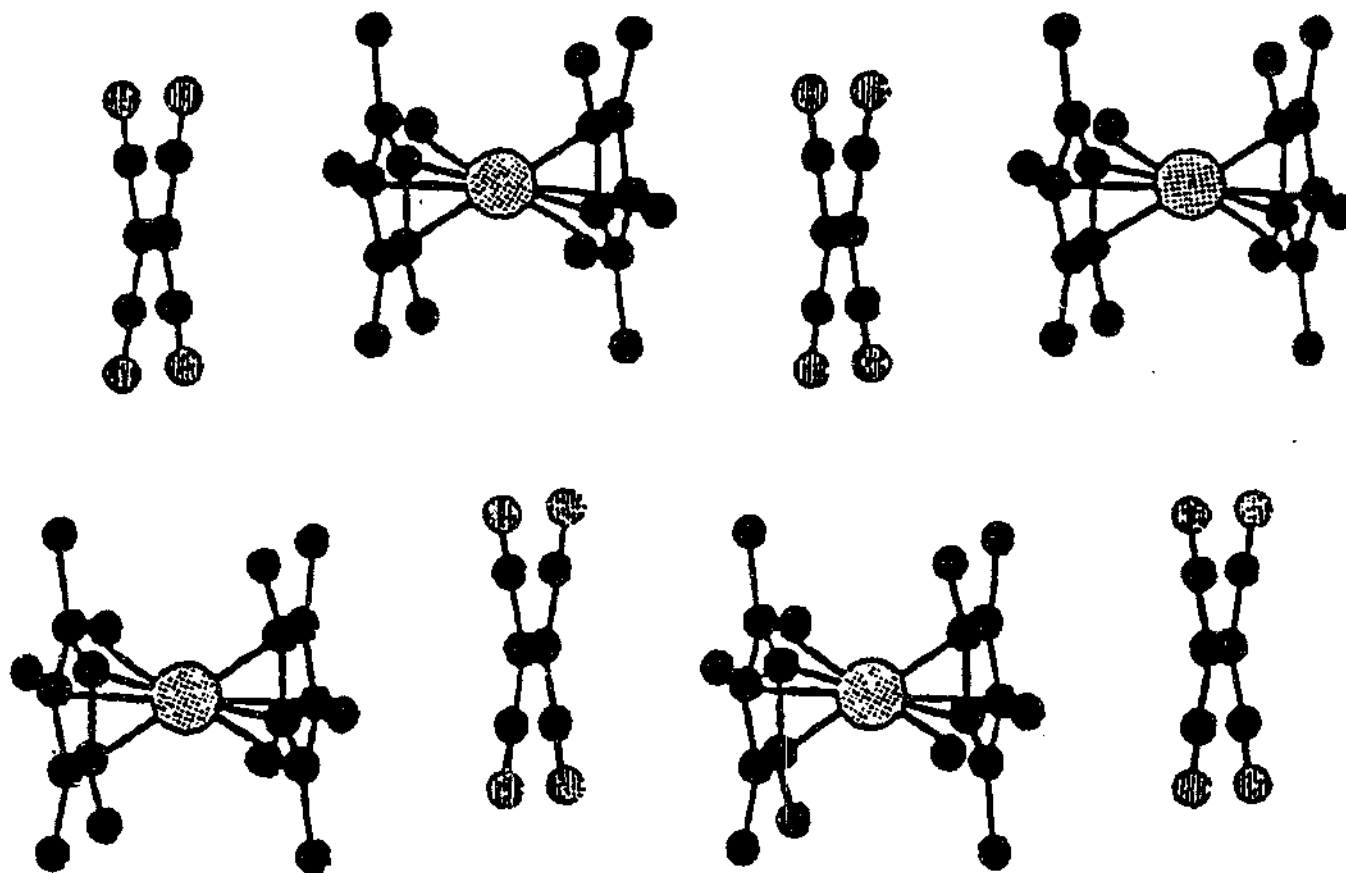


Figure 1.9 The chain structure of $[\text{FeCp}^*_2]^+[\text{TCNE}]^-$. Reproduced from reference 90.

In 1991 Miller *et al.* reported what is one of the most significant results of the field. They discovered the first room-temperature molecule-based magnet, $[\text{V}(\text{TCNE})_x] \cdot y(\text{solvent})$ (where solvent = CH_2Cl_2 ; $x \approx 2$; $y \approx 1/2$), which is a ferrimagnet with an extrapolated T_c value of ~ 400 K (higher than the thermal decomposition temperature of 350 K).^{25,26,105-108} It was found that due to extreme insolubility and air and water sensitivities, the composition and consequently magnetic properties are highly dependent on solvent and preparative conditions. For example, if MeCN was used, $[\text{V}(\text{TCNE})_x] \cdot y(\text{MeCN})$ was synthesised, whose T_c was found to be only 120 K (again dependent on the preparation). These materials are amorphous and considering the high T_c

values, are thought to consist of disordered coordination polymers. It is interesting to note, but perhaps coincidental, that a number of room-temperature molecule based magnets are disordered/non-stoichiometric, as is the case for some of the Prussian-Blue type materials discussed in Section 1.4.2. Miller *et al.* have also studied analogues of the vanadium complexes, $[M^{II}(\text{TCNE})_2] \cdot x(\text{CH}_2\text{Cl}_2)$, (where $M^{II} = \text{Mn, Fe, Co and Ni}$).¹⁰⁹ These compounds are metamagnets. The Fe compound, for example, has a T_c value of 121 K.

1.4.2 Prussian-Blue Analogues

Perhaps the most important family of molecule-based magnets is that of the Prussian Blue analogues and there are a number of excellent reviews covering the subject.^{50,110-116} Prussian Blue itself, $\text{Fe}^{III}_4[\text{Fe}^{II}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$ ($x \approx 14-15$), is perhaps the first known coordination compound and gives its name to this family of molecule-based magnets.¹¹³ It was discovered in 1704 by M. Diesbach when he obtained a bright blue pigment after boiling beef blood (!) in a strongly basic medium.¹¹⁷⁻¹¹⁹ It has since enjoyed wide use as a dyeing agent. This compound exhibits long-range ferromagnetic ordering below a T_c value of 5.6 K.¹²⁰⁻¹²² Ferromagnetic coupling occurs between the distant (10.18 Å apart)¹¹³ high-spin Fe^{III} centres *via* the low-spin diamagnetic Fe^{II} centres that are surrounded by the cyano-carbon donors.¹²³

The structure of Prussian Blue was first proposed by Keggin and Miles in 1936¹²⁴ and then reformulated by Ludi and Güdel in 1973.^{113,125,126} The Prussian Blue family contains a number of systems of general formulae $\text{C}_n\text{A}_p[\text{B}(\text{CN})_6]_q \cdot x\text{H}_2\text{O}$, where A and B are divalent or trivalent transition metal ions and C is a monovalent cation (e.g. Cs^+ , Na^+). The structure of the lattice is face-centred cubic (α -Po related), where A cations occupy the edges and centre of the cell, B occupies the corners and faces (octahedral sites) and C cations are inserted into part of the tetrahedral sites.¹¹³ Three typical examples are shown in Figure 1.10.

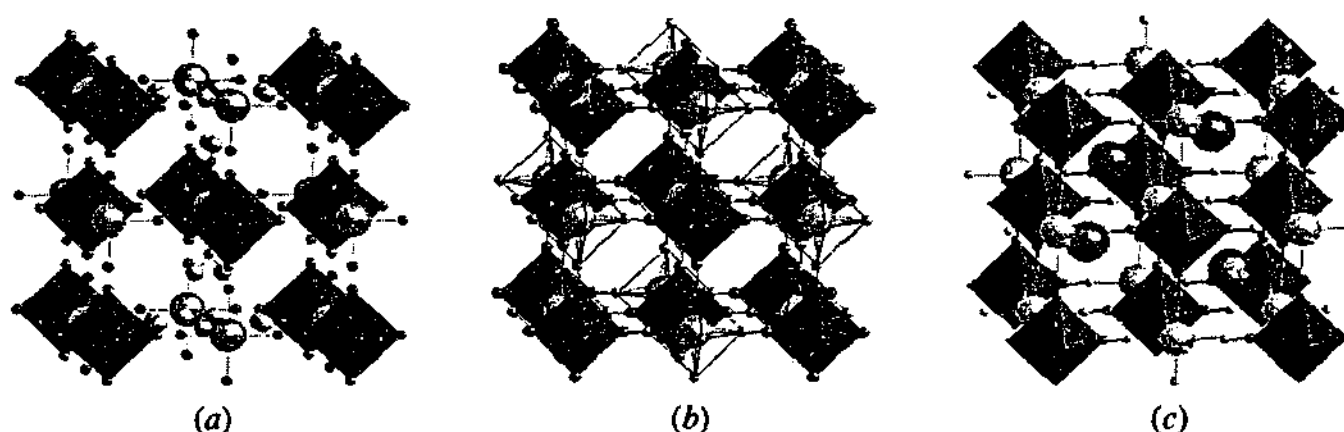
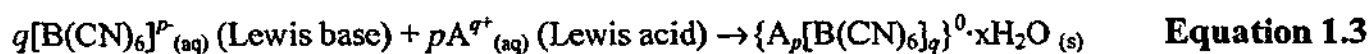


Figure 1.10 Typical cubic structures of Prussian-Blue analogues; (a) $A^{II}_3[B^{III}(CN)_6]_2 \cdot xH_2O$; (b) $A^{III}[B^{III}(CN)_6]$; (c) $C^I A^{II}[B^{III}(CN)_6]$. $[B^{III}(CN)_6]$ are the solid octahedra surrounded by CN^- (very small spheres); A are the small light spheres; C^I are the medium grey spheres at tetrahedral sites in (c); and finally in (a) the H_2O are shown as the smaller light grey spheres. Reproduced from reference 112.



The general reaction scheme to produce neutral Prussian-Blue analogues is given in Equation 1.3. When n , p and q are unity the cubic lattice is complete (Figure 1.10(c)). Each A^{II} metal ion is connected *via* cyanide bridges to six different B^{III} metal ions and *vice versa*. The B^{III} ions are coordinated by the cyanide carbon atoms and thus are low-spin, whereas the A^{II} ions are coordinated by the cyanide nitrogens and thus are usually high-spin. This lattice contains eight tetrahedral sites within the cell, and half of these are occupied by the C^I cations. Water molecules can occupy any vacant position in the lattice. In Prussian Blue itself there are no C^I cations, hence one quarter of the $[Fe^{II}(CN)_6]^{4-}$ sites are vacant to balance the charge. Each of these vacant sites is occupied by approximately 7 H_2O molecules (one coordinated to each of the six surrounding Fe^{III} centres that would

otherwise be coordinated by a cyanide nitrogen donor atom, plus the seventh H_2O between them). There are two tetrahedral sites within the cubic lattice per A atom, therefore for the four A metal atoms of Prussian Blue there are about eight H_2O molecules at tetrahedral sites, which gives a total of fifteen for the formula $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$.

Due to the structure of the Prussian-Blue system, great potential exists for the production of a wide range of magnetic materials. For instance, different combinations of paramagnetic A and B cations are possible, and the high symmetry allows a degree of control over the type and size of the magnetic interactions between A and B.¹¹³ Hence, a large number of these materials are now known.^{116,127-129}

The first low-temperature magnetic studies of Prussian-Blue analogues were performed by Bozorth and co-workers in the 1950s, where they reported magnetic ordering temperatures as high as 50 K.¹²¹ However, problems with sample purity meant their conclusions were in doubt.^{50,113} Later, during the 1980s, Klenze and co-workers¹³⁰ and then Babel and co-workers¹³¹⁻¹³³ reported several materials with T_c values up to 90 K, i.e. above liquid nitrogen.¹¹³ In more recent times the groups of Verdaguer^{113,128,124-142} and Girolami^{114,129,143-146} have undertaken a systematic approach using the principle of orthogonal orbitals (*vide infra*) in order to obtain materials with high critical temperatures.⁵⁰ They and others have demonstrated the ability to tune the magnetic properties of these materials using guiding rules, which are described below.

The type of ordering observed in these materials is explained by a superexchange mechanism based on the principle of orthogonal magnetic orbitals. Simply stated, coupling between orthogonal orbitals is ferromagnetic, whereas between non-orthogonal orbitals it is antiferromagnetic.^{35,50,111,112} This is most clearly observed for the highly symmetric Prussian Blues. For the paramagnetic A and B centres, the coupling interaction, $J(\text{AB})$ between the high-spin A centre with a configuration of $t_{2g}^x e_g^y$, and the low spin B centre

with a configuration t_{2g}^2 is a sum of two competing interactions. The $J(t_{2g}t_{2g})$ A-B interaction involving the t_{2g} orbitals of unpaired spins on A and B is an antiferromagnetic contribution, and the $J(e_g t_{2g})$ A-B interaction between the orthogonal e_g orbitals on A and the t_{2g} orbitals on B is a ferromagnetic contribution. When both contributions are present, antiferromagnetic usually dominates. When the spins on A and B (S_A and S_B) are equal this can lead to long-range antiferromagnetic ordering and when they are non-equal ferrimagnetic ordering may occur. To illustrate, $\text{CsNi}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$,¹³⁴ with A and B configurations of $t_{2g}^6 e_g^2$ and t_{2g}^3 (Ni^{II} and Cr^{III} respectively), is a ferromagnet with $T_c = 50$ K. $\text{CsMn}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot \text{H}_2\text{O}$,^{114,143} with its $t_{2g}^3 e_g^2$ and t_{2g}^3 centres, is a ferrimagnet with a $T_N = 90$ K.¹⁴⁷ Orthogonality of orbitals in Prussian Blues has led to the ability to predict the nature of the magnetic ordering according to the electronic configuration of the metal ions (see Table 1.2).^{50,112}

However, these predictions do not account for the magnitude of the A-B interactions and hence the values of the critical temperatures. There are a number of qualitative methods that have been applied to optimise these parameters. The superexchange pathway largely responsible for the A-B interaction is thought to be *via* the empty cyanide anti-bonding π^* orbitals.⁵⁰ The t_{2g} type orbitals of the B ion are delocalised towards these π^* orbitals. This delocalisation is more pronounced when the two orbitals are closer in energy. Increasing this antiferromagnetic $t_{2g}(\text{A})$ - $t_{2g}(\text{B})$ interaction is achieved by using B ions with high-energy 3d orbitals (which are more radially expanded), which is the case for the early transition metals in lower oxidation states.^{50,114,144,148}

Table 1.2 Prediction of the nature of magnetic ordering in the Prussian Blue-like phases according to the electronic configurations of the high-spin A and low-spin B ion (AF = antiferromagnetic, F = ferromagnetic and FI = ferrimagnetic). Reproduced from reference 50.

A	B		
	t_{2g}^1 and t_{2g}^5	t_{2g}^2 and t_{2g}^4	t_{2g}^3
$t_{2g}^1 e_g^0$	AF	FI	FI
$t_{2g}^2 e_g^0$	FI	AF	FI
$t_{2g}^3 e_g^0$	FI	FI	AF
$t_{2g}^3 e_g^1$	FI	FI	FI
$t_{2g}^3 e_g^2$	FI	FI	FI
$t_{2g}^4 e_g^2$	FI	FI	FI
$t_{2g}^5 e_g^2$	FI	FI	FI
$t_{2g}^6 e_g^2$	F	F	F
$t_{2g}^6 e_g^3$	F	F	F

A related consideration is that the early transition metals possess more unpaired electrons in the t_{2g} orbitals, which give rise to higher critical temperatures.¹⁴⁸ This can be illustrated in the isostructural series of ferromagnets $Ni^{II}_3[Fe^{III}(CN)_6]_2 \cdot 14H_2O$,¹⁴⁹ $Ni^{II}_3[Mn^{III}(CN)_6]_2 \cdot 12H_2O$,¹¹⁴ and $Ni^{II}_3[Cr^{III}(CN)_6]_2 \cdot 15H_2O$,¹³⁴ which have T_c values of 23, 30 and 53 K respectively. These values correlate with the number of unpaired electrons in the t_{2g} orbitals of the low-spin ions of 1, 2 and 3 for Fe^{III} , Mn^{III} and Cr^{III} respectively.¹⁴⁸

The principle of maximising antiferromagnetic interactions between unequal spins to yield ferrimagnets (*vide supra*) was successfully employed by Verdaguer *et al.* in the production of $Cs_{0.75}Cr^{II}_{1.125}[Cr^{III}(CN)_6] \cdot 5H_2O$ and $Cr^{II}_3[Cr^{III}(CN)_6]_2 \cdot 10H_2O$, which order at 190 and 240 K respectively.¹²⁸ In 1995 the same group reported the first room-temperature

Prussian Blue-like molecule based magnet, $V^{II}_{0.4}V^{III}_{0.6}[Cr(CN)_6]_{0.86} \cdot 3H_2O$, which orders ferrimagnetically below 315 K.¹³⁵ Verdaguer *et al.* subsequently reported the two amorphous ferrimagnets with nominal compositions of $V^{II}_{0.45}V^{III}_{0.53}[V^{IV}O]_{0.02}[Cr^{III}(CN)_6]_{0.69}(SO_4)_{0.23} \cdot 3.0H_2O \cdot 0.02K_2SO_4$ and $Cs^{I}_{0.82}V^{II}_{0.66}[V^{IV}O]_{0.34}[Cr^{III}(CN)_6]_{0.92}(SO_4)_{0.203} \cdot 3.6H_2O$, with T_N values of 310 and 315 K respectively.¹³⁹ It has been observed that ferrimagnetism gives the highest ordering temperatures of the Prussian Blues analogues.⁵⁰ Along these lines, Miller *et al.* also reported a non-stoichiometric Prussian Blue analogue $K_{0.058}V^{II/III}[Cr^{III}(CN)_6]_{0.79} \cdot (SO_4)_{0.058} \cdot xH_2O$, which has a T_N of 372 K.^{107,147} An interesting aspect to these materials is that their ordering temperatures are dependent on the amount of hydration present, i.e. they decrease when the materials are dehydrated. This phenomenon has particular relevance for the compound presented in Chapter 6 of this thesis.

At around the same time Girolami *et al.* reported the related stoichiometric compound $KV^{II}[Cr^{III}(CN)_6] \cdot 2H_2O$,¹⁴⁶ with a T_N value of 376 K. Ordering in this magnet is attributed to the presence of V^{III} impurities in the lattice.¹⁴⁷ Additionally, Girolami *et al.*¹²⁹ have investigated Prussian Blue analogues constructed from $[Cr^I(CN)_5NO]^{3-}$ anions as a route to high T_N ferrimagnets. The compounds, $K_{0.5}Mn[Cr^I(CN)_5NO]_{0.83} \cdot 4H_2O \cdot 1.5MeOH$, $Cs_{0.5}Cr[Cr^I(CN)_5NO]_{0.83} \cdot 2H_2O \cdot 0.6MeOH$, and $Cr[Cr^I(CN)_5NO]_{0.5} \cdot 2H_2O \cdot 1.8MeOH$ order below 31, 89 and 127 K respectively. However, the $[Cr^I(CN)_5NO]^{3-}$ anion gave materials with lower ordering temperatures than did the related $[Cr^{III}(CN)_6]^{3-}$ anion, which they attribute to the lower symmetry of the anion and the fewer unpaired electrons it contains.¹²⁹ Likewise the magnetic, electrical and optical properties of other substituted pentacyanometallate ($[Fe(CN)_5L]^n$, where $L = NO^+$, NH_3 , H_2O , SO_4^{2-} , or pseudohalide) containing materials have been investigated.¹⁵⁰⁻¹⁵²

Another Prussian Blue-related magnet reported by Entley and Girolami is $(\text{Et}_4\text{N})_{0.5}\text{Mn}^{\text{II}}_{1.25}[\text{V}^{\text{II}}(\text{CN})_5]\cdot 2\text{H}_2\text{O}$, which ferrimagnetically orders below a T_{N} value of 230 K.¹⁴⁴ However, it does not possess the face-centred cubic structure common to the Prussian Blue family. Previous reports by Babel *et al.* showed that inclusion of bulky cations, such as Me_4N^+ (as opposed to the alkali cations of the Prussian Blues) force the adoption of lower dimensionalities such as 2D sheets and 1D chains.^{131,133,153-156} For example the series $\text{CsMn}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]\cdot \text{H}_2\text{O}$,¹³¹ $(\text{Me}_4\text{N})\text{Mn}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$,¹⁵⁶ and $(\text{Me}_4\text{N})\text{Mn}^{\text{II}}[\text{Mn}^{\text{III}}(\text{CN})_6]\cdot 8\text{H}_2\text{O}$ ¹⁵⁵ have 3D cubic, 2D sheet, and 1D chain structures, and order ferrimagnetically below 90, 59 and 29 K, respectively. The decrease in ordering temperatures follows the reduction in magnetic interactions, due to lower dimensionality.¹⁴⁸ It is therefore believed, on the basis of the high ordering temperature, that $(\text{Et}_4\text{N})_{0.5}\text{Mn}^{\text{II}}_{1.25}[\text{V}^{\text{II}}(\text{CN})_5]\cdot 2\text{H}_2\text{O}$ possesses a 3D structure.¹⁴⁴

A particularly interesting family of Prussian Blue-like magnets are the series of $\text{A}_x\text{Co}_y[\text{Fe}(\text{CN})_6]\cdot x\text{H}_2\text{O}$ complexes, which display photo-induced magnetism. In 1996, Fujishima and Hashimoto *et al.*¹⁵⁷⁻¹⁶² first observed that ferrimagnetism could be enhanced in CoFe Prussian Blue analogues by photo-irradiation at low temperatures. The proposed mechanism involved a photo-induced electron transfer within pairs of diamagnetic $\text{Co}^{\text{III}}-\text{Fe}^{\text{II}}$ moieties within the structure to give $\text{Co}^{\text{II}}-\text{Fe}^{\text{III}}$ magnetic pairs, thus enhancing magnetisation.¹⁶³ Other groups including, Miller and Epstein,¹⁶⁴⁻¹⁶⁸ and Verdaguer^{127,169-173} have also investigated the magneto-optical properties of these and similar materials. For instance, $\text{Rb}_{1.8}\text{Co}_4[\text{Fe}(\text{CN})_6]_{3.30}\cdot 13\text{H}_2\text{O}$ reported by Verdaguer *et al.*,¹¹³ is essentially diamagnetic before being photo-excited in the near IR, after which it is a ferrimagnet with $T_{\text{N}} = 21$ K. Thermal decay of this excited state occurs above 108 K.¹⁷⁴

Fujishima and Hashimoto have also investigated the magnetic, electrical and optical properties of mixed valence chromium cyanide thin films.^{157,175,176} For example,

they demonstrated electrochemical tuning of the ordering temperature of such films, with T_c values ranging between 135 and 230 K for reduced and oxidised films respectively.¹⁴⁷

The nature and high-symmetry of the Prussian Blue-like phases has led to a wealth of molecule-based magnets being discovered and the ability to apply theoretical knowledge to tune the magnetic properties of these materials. However, the cubic symmetry of these phases means they are magnetically isotropic so that features of magnetically anisotropic systems are not observed. In addition, no group has been able to grow single crystals of Prussian Blue-like phases suitable for detailed magnetic measurements.¹⁷⁷ Hence, research has been focused on different cyanide-bridged species. Kahn and co-workers are interested in synthesising bimetallic compounds using the heptanuclear $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ precursor, which has a pentagonal bipyramidal structure and is incompatible with cubic symmetry.¹⁷⁷ Reacting this with Mn^{II} salts in aqueous solution, they grew single crystals of two phases, which both order ferromagnetically at a T_c value of 50 K.¹⁷⁸ The two phases, $\text{Mn}^{\text{II}}_2(\text{H}_2\text{O})_5[\text{Mo}^{\text{III}}(\text{CN})_7] \cdot 4\text{H}_2\text{O}$ (α -phase) and $\text{Mn}^{\text{II}}_2(\text{H}_2\text{O})_5[\text{Mo}^{\text{III}}(\text{CN})_7] \cdot 4.75\text{H}_2\text{O}$ (β -phase) both have similar local coordination environments of the metal sites, but differ in their 3D network structures. Single crystal magnetic measurements revealed that they also exhibit considerable magnetic anisotropy.^{53,179,180} More recently they have reported two 3D magnets, $[\text{Mn}^{\text{II}}_2(\text{tea})\text{Mo}^{\text{III}}(\text{CN})_7] \cdot \text{H}_2\text{O}$ ($T_c = 75$ K) and $[\text{Mn}^{\text{II}}_2(\text{tea})\text{Mo}^{\text{III}}(\text{CN})_7]$ ($T_c = 106$ K), (where tea = triethanolamine), with very similar topologies (the MoCN–Mn linkages are the same). The difference in their ordering temperature is attributed to the coordination sphere geometry of a Mn^{II} site found to be square-pyramidal and tetrahedral for the former and latter compounds respectively.¹⁸¹

Octacyanomethylate, $[\text{M}(\text{CN})_8]^{n-}$ ($\text{M} = \text{Mo}$ or W), precursors have been employed by Verdaguer and Hashimoto *et al.*¹⁴¹ to produce Prussian Blue analogues such as

$[\text{Mn}^{\text{II}}_6(\text{H}_2\text{O})_9][\text{W}^{\text{V}}(\text{CN})_8]_4 \cdot 13\text{H}_2\text{O}$.¹⁸² This compound, which possesses a (monoclinic) 3D network structure, orders ferrimagnetically below 54 K.

Recently, Miller *et al.* have utilised a tetrahedral precursor, the high-spin $[\text{Mn}^{\text{II}}(\text{CN})_4]^{2-}$ anion¹⁸³ to synthesise the compound $\text{Mn}^{\text{II}}[\text{Mn}^{\text{II}}(\text{CN})_4]$,¹⁸⁴ which powder diffraction data indicates possesses a 2-fold interpenetrated diamondoid (sphalerite) structure akin to the structures of $[\text{M}(\text{CN})_2]$, $\text{M}^{\text{II}} = \text{Cd}$ and Zn .⁷⁴ Magnetic measurements are consistent with all sites being high-spin Mn^{II} and show the compound to be an antiferromagnet with a T_N value of ~ 65 K.^{147,184}

Very recently, Beauvais and Long reported the synthesis and magnetic properties of $\text{Co}^{\text{II}}_3[\text{Co}^{\text{II}}(\text{CN})_5]_2 \cdot 8\text{H}_2\text{O}$,¹⁸⁵ a highly crystalline Prussian Blue analogue. Synthesised with the square-based pyramidal pentacyano precursor, $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$, the compound is a ferrimagnet with a T_N of 48 K. The dehydrated microporous material retains much of its crystallinity and is also a ferrimagnet with a slightly lower T_N of 38 K.

1.4.3 Multidimensional Molecule-Based Magnets from Hexacyanometallate and Metal-Chelate Precursors

The utilisation of hexacyanometallates as building blocks for molecule-based magnets is not limited to the Prussian Blue-like phases. Many research groups including those of Dunbar and Coronado,¹⁸⁶⁻¹⁸⁹ Mallah,¹⁹⁰ Ohba and Okawa,^{115,189,191-198} Miyasaka and Floriani,¹⁹⁹ Verdaguer,²⁰⁰ and Murray²⁰¹ have focused on using coordinatively unsaturated transition metal chelate complexes, instead of free metal ions, to react with hexacyanometallates to form new bimetallic compounds with lowered symmetry. Due to the variety of metal chelate complexes, and the inclusion of different counter cations and/or anions, there have been many such materials reported.¹¹⁵ What follows is a limited number of examples to illustrate this approach to molecule-based magnets.

In 1994 Ohba and Okawa *et al.* first reported the series of complexes, $[\text{Ni}(\text{en})_2]_3[\text{M}^{\text{III}}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ (where $\text{M}^{\text{III}} = \text{Cr}, \text{Mn}, \text{Fe}$ and Co).^{202,203} They are isomorphous, possessing fascinating rope-like 1D chain structures. The Fe^{III} complex, whose structure is shown in Figure 1.11, was first reported to be a ferromagnet with a T_c of 18.6 K.²⁰² Later work revealed single crystals did not order, but that the (rapidly precipitated) polycrystalline material displayed metamagnetic long-range order.^{203,204} It was thought likely that some disorder in the network forming quasi-2D and 3D domains is responsible for the magnetic behaviour.¹¹⁵

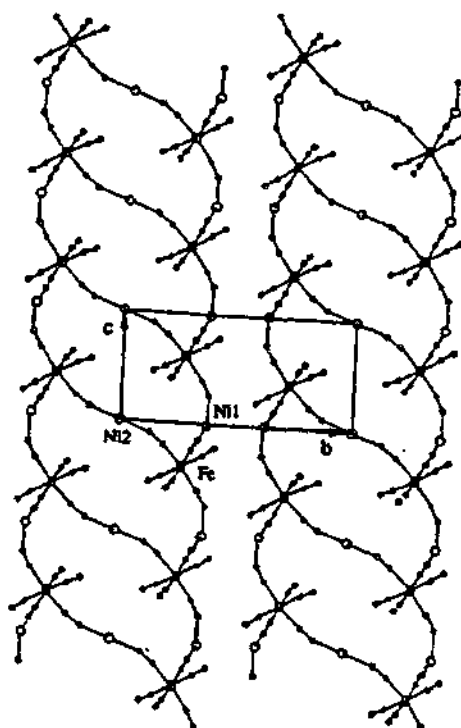


Figure 1.11 The rope-ladder crystal structure of $[\text{Ni}(\text{en})_2]_3[\text{Fe}^{\text{III}}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ in the bc -plane (en ligands and H_2O molecules are omitted for clarity). Reproduced from reference 202.

Ohba and Okawa *et al.* demonstrated the sensitivity of the structures of these compounds to alterations in the chelate ligands. For instance, *N*-methylethylenediamine (N-men), where a methyl substituent is introduced to ethylenediamine, was used to generate the series of compounds, $[\text{Ni}(\text{N-men})]_3[\text{M}^{\text{III}}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ (where $\text{M}^{\text{III}} = \text{Fe}$ and

Co; $n \approx 15$), which have 2D hexagonal (6,3) sheet structures.¹¹⁵ The Fe^{III} compound, whose structure is shown in Figure 1.12, orders ferromagnetically below 10.8 K. The dehydrated compound still shows ferromagnetic coupling but no long-range order is observed. In 1996 Verdaguer *et al.* reported the structure and magnetic properties of $[\text{Ni}(\text{cyclam})]_3[\text{Cr}^{\text{III}}(\text{CN})_6]_2 \cdot 20\text{H}_2\text{O}$ (where cyclam = 1,4,8,11-tetraazacyclotetradecane), which possesses a similar 2D hexagonal (6,3) sheet structure with numerous hydrogen-bonding interactions between the sheets. It showed ferromagnetic coupling but without long-range order.²⁰⁰ Very recently, Long *et al.*²⁰⁵ have reported a 2D hexagonal (6,3) network complex $[\text{Ni}(\text{cyclam})]_3[(\text{tach})\text{Cr}^{\text{III}}(\text{CN})_3]_2\text{I}_2$ (where tach = 1,3,5-triaminocyclohexane), in which three *fac* sites on the Cr^{III} centre are capped by the tach ligand. It was synthesised during work intended to produce high-nuclearity cyanide-bridged metal clusters (see Section 1.4.4 and Chapter 7). The authors suggest metamagnetic behaviour with long-range ordering for this complex, but do not report a critical temperature.

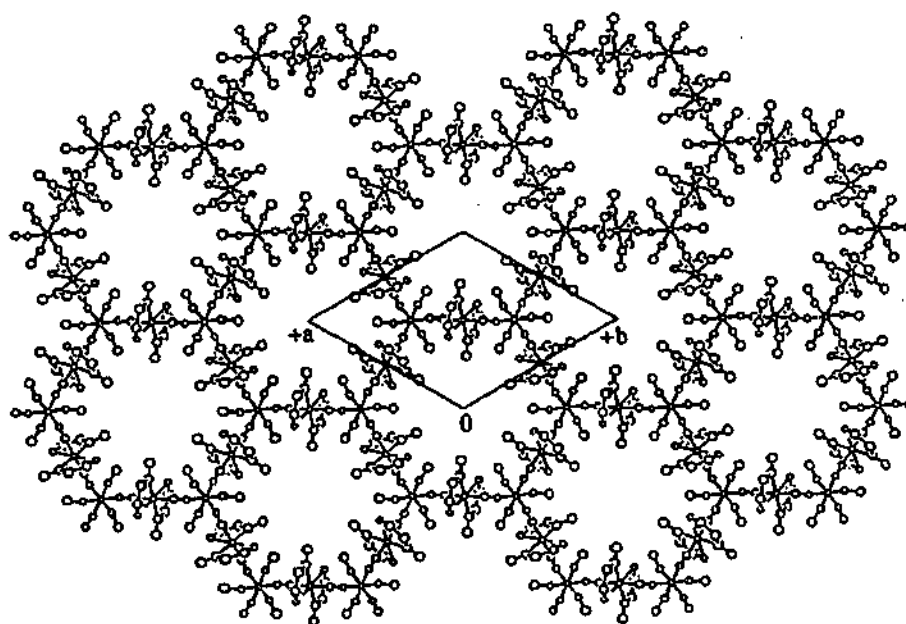


Figure 1.12 The 2D (6,3) hexagonal sheet lattice structure of $[\text{Ni}(\text{N-men})]_3[\text{Fe}^{\text{III}}(\text{CN})_6]_2 \cdot 15\text{H}_2\text{O}$ in the *ab*-plane (H_2O molecules are omitted for clarity). Reproduced from reference 115.

Likewise, Ohba and Okawa *et al.* reported the series of bimetallic compounds, $[\text{Ni}(\text{L})_2]_2[\text{Fe}^{\text{III}}(\text{CN})_6]\text{X}\cdot n\text{H}_2\text{O}$ (where $\text{L} = \text{pn}$, 1,1-dmen; X^- = various counter anions, e.g. ClO_4^- , BF_4^- and PF_6^- for pn , and those plus CF_3SO_3^- , BzO^- , NCS^- and others for 1,1-dmen; $\text{pn} = 1,2$ -diaminopropane, 1,1-dimen = 1,1-dimethylethylenediamine), which have 2D grid-like (4,4) sheet structures.^{206,207} Intra-sheet ferromagnetic coupling was observed for each compound. Inter-sheet separation, influenced by the diamine, counter-ion and the amount of hydration, was found to govern the type of long-range order. Small inter-sheet separations gave metamagnets due to inter-sheet antiferromagnetic coupling, and large inter-sheet separations gave ferromagnets. Furthermore, the ferromagnets became metamagnets on dehydration due to the reduction in inter-layer separation. For example, $[\text{Ni}(1,1\text{-dimen})_2]_2[\text{Fe}^{\text{III}}(\text{CN})_6]\text{OBz}\cdot 6\text{H}_2\text{O}$ orders below 10 K with a relatively large coercive field (for the series) of 750 Oe, which is attributable to a different packing mode of the sheets in comparison with the other similar compounds.²⁰⁷

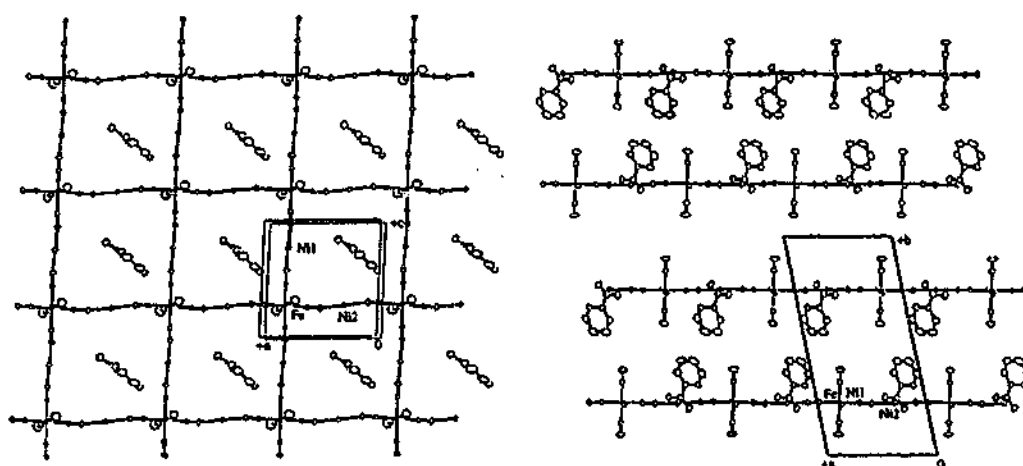


Figure 1.13 Two views of the 2D (4,4) grid sheet structure of $[\text{Ni}(1,1\text{-dimen})_2]_2[\text{Fe}^{\text{III}}(\text{CN})_6]\text{OBz}\cdot 6\text{H}_2\text{O}$ (1,1-dimen ligands and H_2O molecules are omitted for clarity). Left: projection in the ac -plane and, right: projection in the ab -plane. Reproduced from reference 207.

Miyasaka and Floriani *et al.* reported compounds of the type, $A[Mn(L)]_2[M^{III}(CN)_6] \cdot nH_2O$ (where A = univalent cation; $M^{III} = Fe, Mn, Cr, Co$; L^{2-} = tetradentate Schiff-bases),^{199,208-212} which similarly have 2D grid-like (4,4) sheet structures. For example, $(Et_4N)[Mn^{III}(5-Cl-salen)]_2[Fe^{III}(CN)_6]$ (where $5-Cl-salenH_2 = N,N'$ -ethylenebis(5-chlorosalicylaldehydeimine)) shown in Figure 1.14, is a metamagnet with ferrimagnetic layers and antiferromagnetic interlayer interactions, and with a T_N of 4.0 K.¹⁹⁹

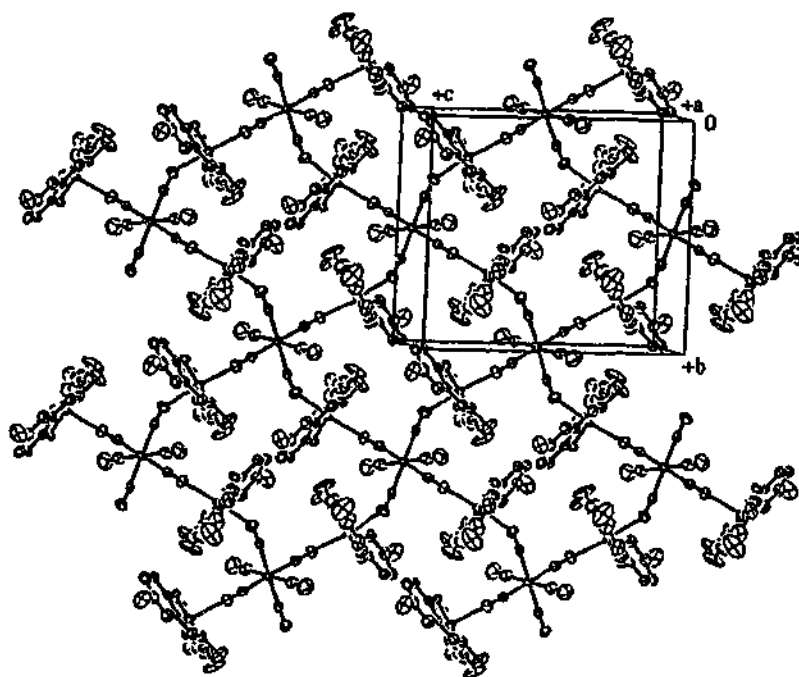


Figure 1.14 The 2D (4,4) sheet structure of $(Et_4N)[Mn^{III}(5-Cl-salen)]_2[Fe^{III}(CN)_6]$ (Et_4N^+ counter-ions are omitted for clarity). Reproduced from reference 199.

Recently, Dunbar and Coronado *et al.* and others have reported several bimetallic compounds with 2D layered structures.¹⁸⁶⁻¹⁸⁹ For instance, the layered ferromagnet $[Ni(chxn)_2]_3[Fe^{III}(CN)_6]_2 \cdot 2H_2O$ (where $chxn = trans$ -1,2-diaminocyclohexane) has a 2D distorted (4,4) sheet structure, and orders below 14 K.¹⁸⁶ The bulky cyclohexane ligands

produce a large inter-layer separation, possibly disavouring inter-layer antiferromagnetic interactions, as was observed previously for Ohba and Okawa (*vide supra*). This compound also has a large coercive field of 2.3 kOe at 2K and displays some unusual AC susceptibility behaviour.¹⁸⁶ Also of interest is the use of *trans*-1,2-diaminocyclohexane, which was employed here as a racemic mixture of the two enantiomers. This group are in the process of attempting to use enantiopure samples of the diamine to investigate magneto-optical effects of resulting networks.¹⁸⁶ This is particularly relevant to the chiral networks reported in Chapter 4 of this thesis where a Schiff-base derived from *trans*-1,2-diaminocyclohexane was used.

Dunbar *et al.*¹⁸⁷ have used Mn^{II} bipyrimidine (bpym) chelates with ferricyanide to produce a ferrimagnet, $\text{Mn}(\text{H}_2\text{O})_2[\text{Mn}(\text{bpym})(\text{H}_2\text{O})_2]_2[\text{Fe}^{\text{III}}(\text{CN})_6]_2 \cdot 9\text{H}_2\text{O}$, which has a 2D sheet structure and orders below 11 K.

A number of 3D bimetallic compounds using metal chelates and hexacyanometallates have also been reported with a variety of structures and magnetic behaviours.^{197,198,213,214} Inoue *et al.* recently reported an interesting example, the 3D chiral ferrimagnet $\text{K}_{0.4}[\text{Cr}^{\text{III}}(\text{CN})_6][\text{Mn}(\text{S})\text{-pn}](\text{S})\text{-pnH}_{0.6}$ (where (S)-pn = (S)-1,2-diaminopropane), which possesses an interesting structure of interconnected helical bimetallic loops, and orders below the T_N value of 53 K.

Very recently, Verdaguer *et al.* reported two isostructural 3D cyano-bridged bimetallic complexes using $[\text{Mn}^{\text{II}}_2(\mu\text{-bpym})(\text{H}_2\text{O})_8]^{4+}$ and the octacyanometallates $[\text{M}^{\text{IV}}(\text{CN})_8]^{4-}$, $\text{M}^{\text{IV}} = \text{Mo}$ and W , as precursors.²¹⁵ The complexes, $[(\text{Mn}^{\text{II}}_2(\text{H}_2\text{O})_4(\mu\text{-bpym}))][\text{M}^{\text{IV}}(\text{CN})_8]$, possess a complicated 3D structure shown in Figure 1.15. Magnetically, these complexes show weak antiferromagnetic coupling and no long-range magnetic order, which is partly due to the Mo and W centres being diamagnetic. They are presently studying possible analogues with paramagnetic octacyanometallate species.

Julve and Verdager *et al.*^{216,217} have used substituted cyanometallates, including $[\text{Fe}^{\text{III}}(\text{phen})(\text{CN})_4]^-$, where phen = 1,10-phenanthroline, to produce a new heterobimetallic linear chain complex $[\{\text{Fe}^{\text{III}}(\text{chel})(\text{CN})_4\}_2\text{Mn}^{\text{II}}(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ that displays ferrimagnetic behaviour but no ordering above 1.9 K.²¹⁷

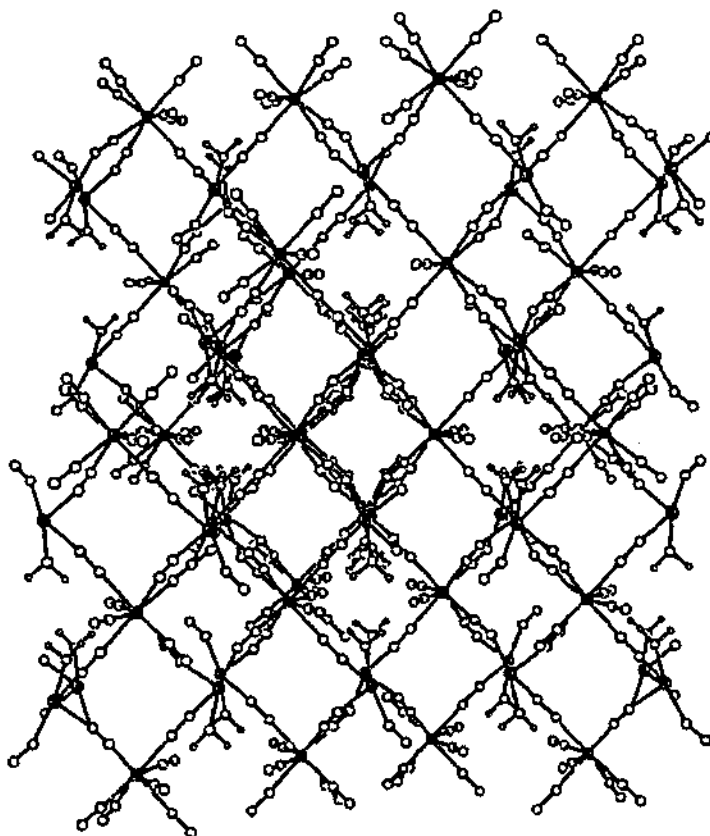


Figure 1.15 The crystal structure of $[(\text{Mn}^{\text{II}}_2(\text{H}_2\text{O})_4(\mu\text{-bpym}))][\text{M}^{\text{IV}}(\text{CN})_8]$ viewed along the *c*-axis direction (bpym ligands are omitted for clarity). Reproduced from reference 215.

1.4.4 Multinuclear Cyanide Bridged Clusters

Considerable recent research in transition metal cyanide chemistry has been focused on generating discrete high-spin cyano-bridged cluster complexes.^{113,201,218-228} Using an extension of the approach described above for the design of $[\text{M}(\text{CN})_6]^{n-}$ based networks with lower dimensionality than the Prussian Blue phases, one can produce zero-dimensional (0D) systems (clusters). This is achieved by reacting hexacyanometallates with A^{II} metal ions that have labile groups in one or two coordination sites, i.e.

$[A^{II}(L_4)(H_2O)_2]$ or $[A^{II}(L_5)(H_2O)_1]$, where L_4 and L_5 are tetra- and penta-dentate chelating 'capping' ligands, thus impeding the growth of extended network structures. By the suitable choice of metal ions, large clusters with high-spin ground states can be synthesised. Additionally, if significant magnetic anisotropy is introduced, for example by low structural symmetry, these species can exhibit the phenomenon of single-molecule magnetism. This latter topic is described in more detail in Chapter 7.

Parker *et al.*^{229,230} of Monash University reported the structure and magnetism of the heptanuclear clusters with $Cu^{II}_6Fe(CN)_6$ and $Mn^{II}_6Cr^{III}(CN)_6$ cores, which consist of a single hexacyanometallate surrounded by six capped transition metal ions.

Murray *et al.* have investigated the cluster $[Ni^{II}(bpm)_2]_3[Fe^{III}(CN)_6]_2 \cdot 7H_2O$ (where bpm = bis(1-pyrazolyl)methane),²⁰¹ which displays long range ferromagnetic order below a T_c of 23 K. This magnetic order is possibly facilitated by a 3D hydrogen bonding network that connects the clusters (Figure 1.16). The dehydrated material does not order magnetically, indicating the possible importance of the hydrogen bonding to the occurrence of long-range magnetic order. Similar results were shown by the compounds $[M^{II}(bipy)_2]_3[Fe^{III}(CN)_6]_2 \cdot nH_2O$ ($M^{II} = Ni$, $n = 13$; $M^{II} = Cu$, $n = 10$), which order below 11 and 13 K respectively.²³¹ Dunbar has questioned these results and believes something other than hydrogen bonded H_2O pathways between the clusters is responsible for the long-range order.²³² The effect of dehydration on magnetic behaviour has also been observed in $\{[Mn^{III}(\mu-OH)(\mu-OAc)_2] \cdot HOAc \cdot H_2O\}_n$ described in Chapter 6 in this thesis, and by Hashimoto *et al.* in Prussian Blue analogues.¹⁵²

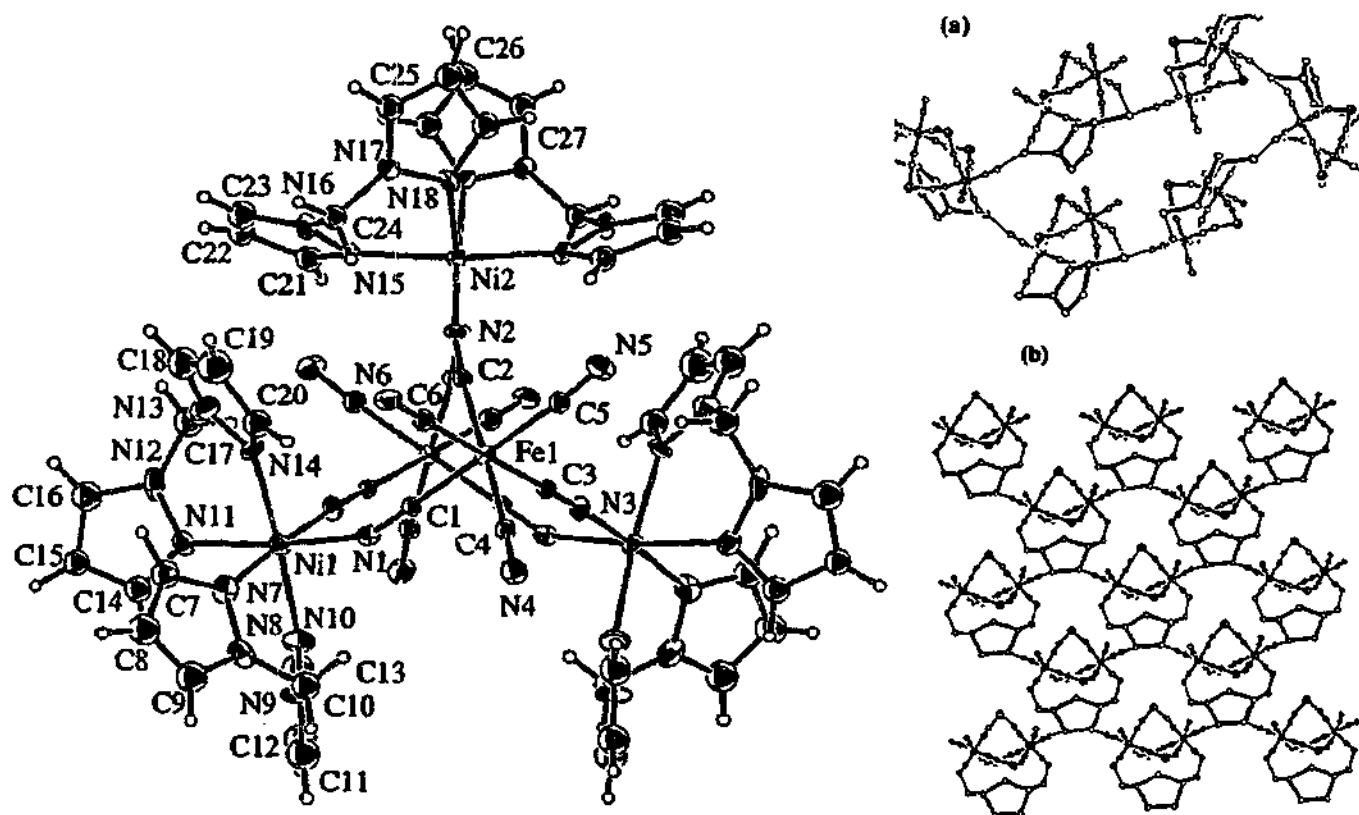


Figure 1.16 Left: the crystal structure of $[\text{Ni}^{\text{II}}(\text{bpm})_2]_3[\text{Fe}^{\text{III}}(\text{CN})_6]_2 \cdot 7\text{H}_2\text{O}$ (H_2O molecules omitted), and right: two different hydrogen bonding networks present in the structure (bpm ligands omitted). Reproduced from reference 201.

Some recent discoveries made in this field include those by Long *et al.*,^{205,225-228} Decurtins *et al.*,^{3,224} and Hashimoto *et al.*,²³³ For instance, $[\text{Mn}^{\text{II}}\{\text{Mn}^{\text{II}}(\text{MeOH})_3\}_8(\mu\text{-CN})_{30}\{\text{Mo}^{\text{V}}(\text{CN})_3\}_6] \cdot 5\text{MeOH} \cdot 2\text{H}_2\text{O}$ (Mn_9Mo_6), is reported to have a very high $S = 51/2$ ground state spin. This material shows ferromagnetic ordering below 44 K due to ferromagnetic inter-cluster coupling.²²⁴ The structurally analogous Mn_9W_6 cluster also has a high spin ground state ($S = 39/2$).²³³ These are prepared from octacyanomethylate precursors.

Recently, Long *et al.* reported two 'giant' nickel-chromium-cyanide clusters, the larger being $[(\text{Me}_3\text{tacn})_{14}\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}]\text{I}_{20} \cdot 70\text{H}_2\text{O}$ (where $\text{Me}_3\text{tacn} = N,N',N''$ -trimethyl-1,4,7-triazacyclononane).²²⁷ The structure consists of a double face-centred cubic unit

sharing a Ni vertex (Figure 1.17). They have also reported the first cyano-bridged single molecule magnet, a $\text{MnMo}_6(\text{CN})_{18}$ cluster (see also Chapter 7).²²⁸

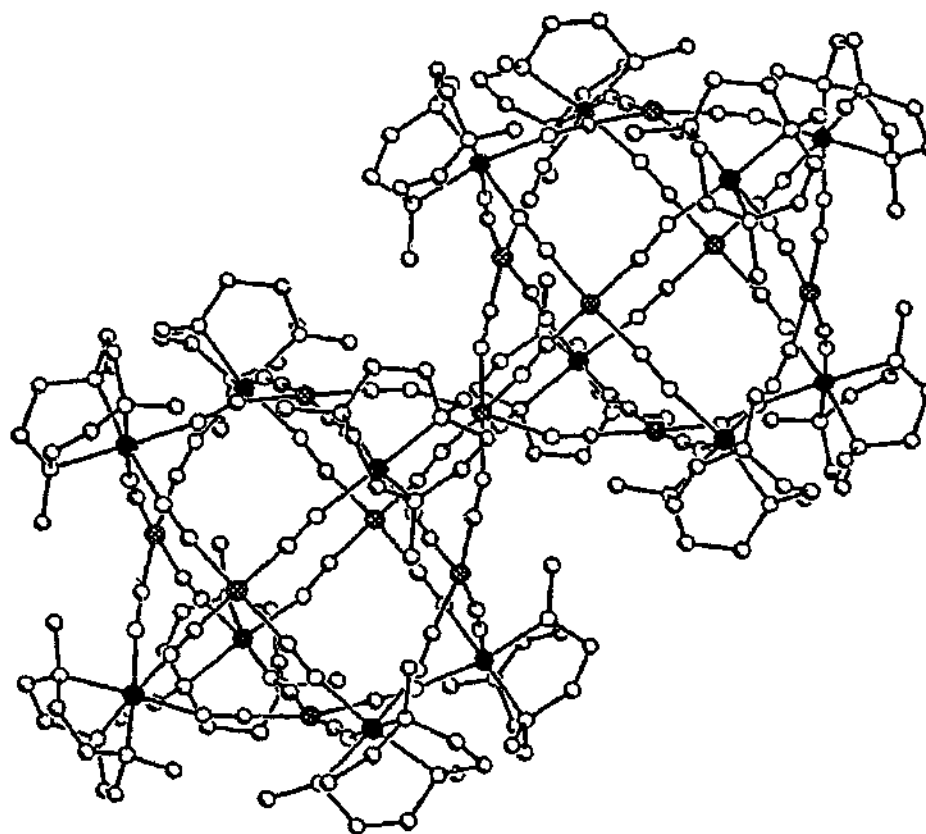


Figure 1.17 The crystal structure of $[(\text{Me}_3\text{tacn})_{14}\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}]^{20+}$. Black, crosshatched, shaded and white spheres correspond to Cr, Ni, C and N atoms respectively (hydrogen atoms are omitted for clarity). Reproduced from reference 227.

1.4.5 Oxalate-Bridged Networks and Related Systems

The planar bis-chelating anionic ligand oxalate, $(\text{C}_2\text{O}_4^{2-}, \text{ox})$, has been used quite extensively to produce homometallic and heterobimetallic extended network complexes that display interesting magnetic, optical and electrical properties, including, but not limited to, long-range magnetic order.^{50,234-261} The general synthetic approach to these materials involves the reaction of mononuclear tris(oxalato) transition metal precursors,

$[B^{III}(ox)_3]^{3-}$, with transition metal salts (A^{II}) in the presence of a suitable counter-cation to give anionic network species, $[A^{II}B^{III}(ox)_3]^-$.

Two general structural motifs have been regularly observed for oxalate-based networks, which are determined by the nature of the cation. The $[B^{III}(ox)_3]^{3-}$ anion is a chiral complex with two enantiomers (Δ and Λ configurations). When bulky achiral cations such as $n\text{-Bu}_4\text{N}^+$ or Ph_4P^+ are used with racemic mixtures of the $[B^{III}(ox)_3]^{3-}$ anion, 2D hexagonal (6,3) sheet structures are obtained, as shown in Figure 1.18. Metal centres include $A^{II} = \text{Mn, Fe, Co, Ni, and Cu}$; $B^{III} = \text{Cr, Fe and Ru}$.²⁵⁸ The handedness of each A^{II} and B^{III} centres alternate within the sheet. The layers are interleaved by the cations, which determine the inter-layer separation. These complexes behave as ferrimagnets with T_N values ranging from 5 to 44 K, and rather weak coercive fields, one of the largest being 320 Oe for the $\text{Fe}^{II}\text{Cr}^{III}$ complex.^{237,262-267}

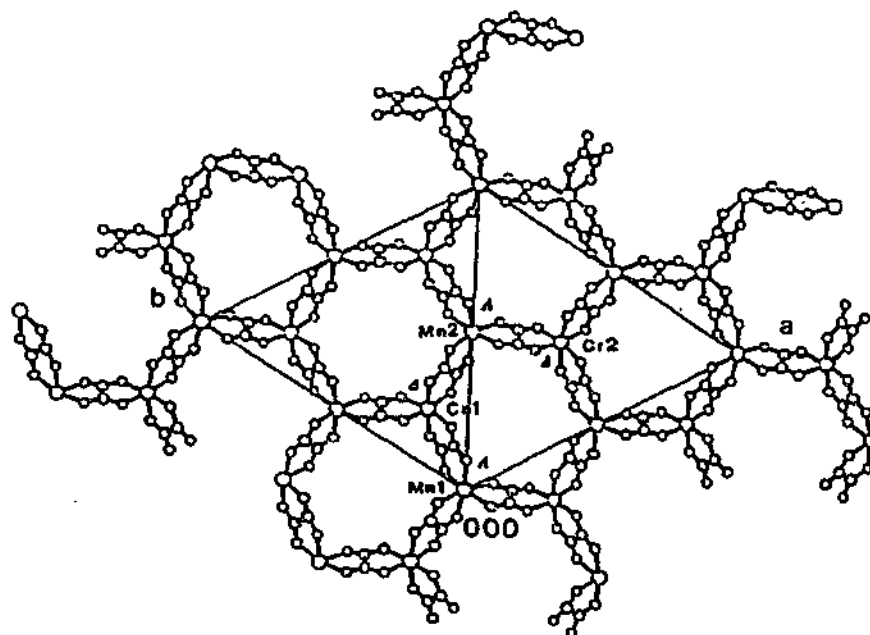


Figure 1.18 A single anionic 2D hexagonal (6,3) network in the structure of $\text{Ph}_4\text{P}[\text{Mn}^{II}\text{Cr}^{III}(\text{ox})_3]$ (reproduced from reference 50).

The second type of structure is the chiral 3D (10,3)-a anionic network, shown in Figure 1.19 ((10,3)-a denotes the most symmetric of the (10,3) nets), formed when the cations are chiral metal complexes such as $[Z^{II}(\text{bipy})_3]^{2+}$ (where $Z^{II} = \text{Ru, Fe, Co, Ni, Zn}$). Decurtins *et al.* first reported these phases in 1993.²⁶⁸ The 3D network has the general formula $[Z^{II}(\text{bipy})_3][M^I M^{III}(\text{ox})_3]$ or $[Z^{II}(\text{bipy})_3][M^{II} M^{II}(\text{ox})_3]$ (where $M^{II} = \text{Mn, Fe, Co, Cu}$; $M^{III} = \text{Cr, Fe}$; $M^I = \text{alkali metal, NH}_4^+$). The chirality of the resulting net is the same as the cation. If racemic mixtures of cations are used, racemic mixtures of crystals are produced, though each crystal is of a single hand. The cations and solvent molecules occupy cavities in the framework. The cavities can also accommodate small anions (X^-) such as ClO_4^- , BF_4^- or PF_6^- so that the range of compounds includes $[Y^{III}(\text{bipy})_3][X][M^I M^{III}(\text{ox})_3]$, $[Y^{III}(\text{bipy})_3][X][M^{II} M^{II}(\text{ox})_3]$ and $[Z^{II}(\text{bipy})_3][X][M^{II} M^{III}(\text{ox})_3]$ (where $Y^{III} = \text{Cr, Rh}$).^{239,257,269} Magnetically, these complexes are less interesting than the 2D phases. Where the complexes do show long-range magnetic order it is with lower critical temperatures, e.g. 6.6 K.²⁵⁷

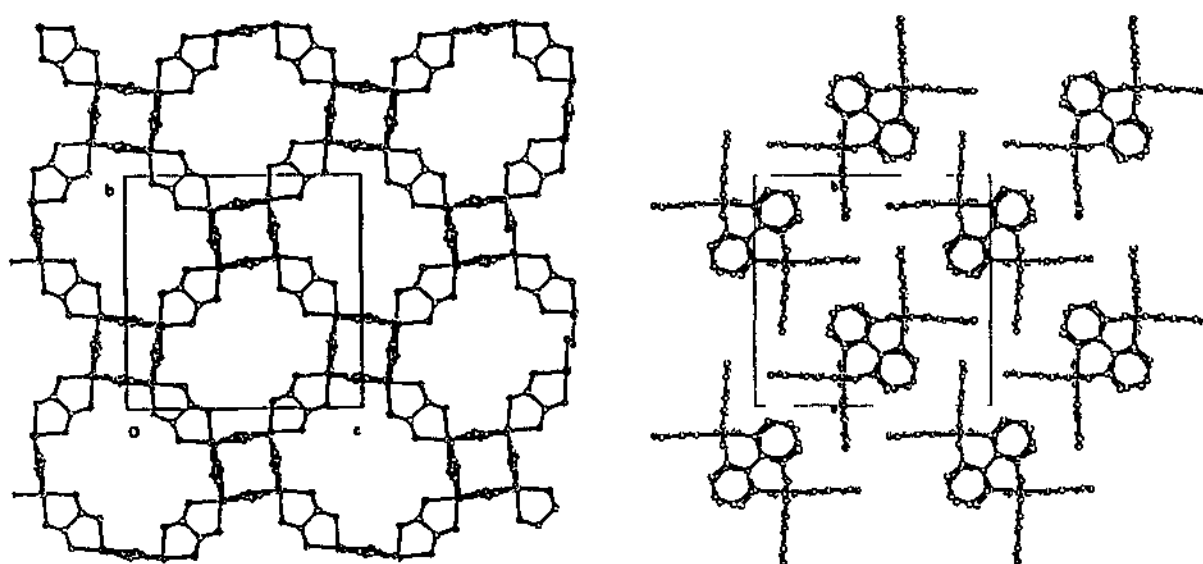


Figure 1.19 Two representations of the crystal structure of $[\text{Co}^{III}(\text{bipy})_3][\text{Co}^{II}_2(\text{ox})_3]\text{ClO}_4$. Left: the $[\text{Co}^{II}_2(\text{ox})_3]^{2-}$ network in the *bc*-plane and right: the $[\text{Co}^{III}(\text{bipy})_3]^{3+}$ cations (reproduced from reference 239).

Dance *et al.*²⁷⁰ have also reported the occurrence of a chiral 3D (10,3)-a net with the compound $(\text{Ph}_3\text{MeP})_2[\text{NaCr}^{\text{III}}(\text{ox})_3]$, which is the only published 3D oxalate-based net of its type to include an achiral monpositive cation. The cations also form a supramolecular (10,3)-a net, due to multiple π - π and $\text{CH}\cdots\pi$ interactions, which interpenetrates the anionic net. There are also supramolecular interactions between the two interpenetrated nets, which provide chiral recognition between the cation and anion lattices. Consequently, the two nets are of opposite chirality. The weak supramolecular interactions of these types are discussed further in Chapter 5 in relation to mixed-ligand anionic dca networks.

Many examples of oxalate-based coordination polymers are now known, with a variety of magnetic behaviours, with examples exhibiting ferro-, ferri-, antiferro- and metamagnetic ordering. Day *et al.* have observed negative magnetisation at low temperatures in some systems.^{241,267} The nature of magnetic ordering can be predicted by the principle of orthogonality of magnetic orbitals.³⁵

Recent work in the field has focused on adding new properties to these networks by incorporating interesting cations such as decamethylmetallocenium ($[\text{M}^{\text{III}}\text{Cp}^*_2]^+$, $\text{M}^{\text{III}} = \text{Co}, \text{Fe}$), and tetrathiafulvalene (TTF).^{251,252,258} For instance, an example incorporating the cation BEDT-TTF⁺ (bis(ethylenedithio)tetrathiafulvalene), which forms the basis of many molecular conductors and superconductors, has exhibited both conductivity and ferromagnetic order.²⁵¹ Figure 1.20 shows the structure of $[\text{FeCp}^*_2][\text{MnFe}(\text{ox})_3]$, which consists of alternating layers of the paramagnetic $[\text{FeCp}^*_2]^+$ ions and ferromagnetic $[\text{MnFe}(\text{ox})_3]^-$ networks. While it has been shown that the bulk magnetic properties of the networks were not significantly affected by replacing non-magnetic cations with paramagnetic ones, the packing of the anionic sheets is altered.²⁵²

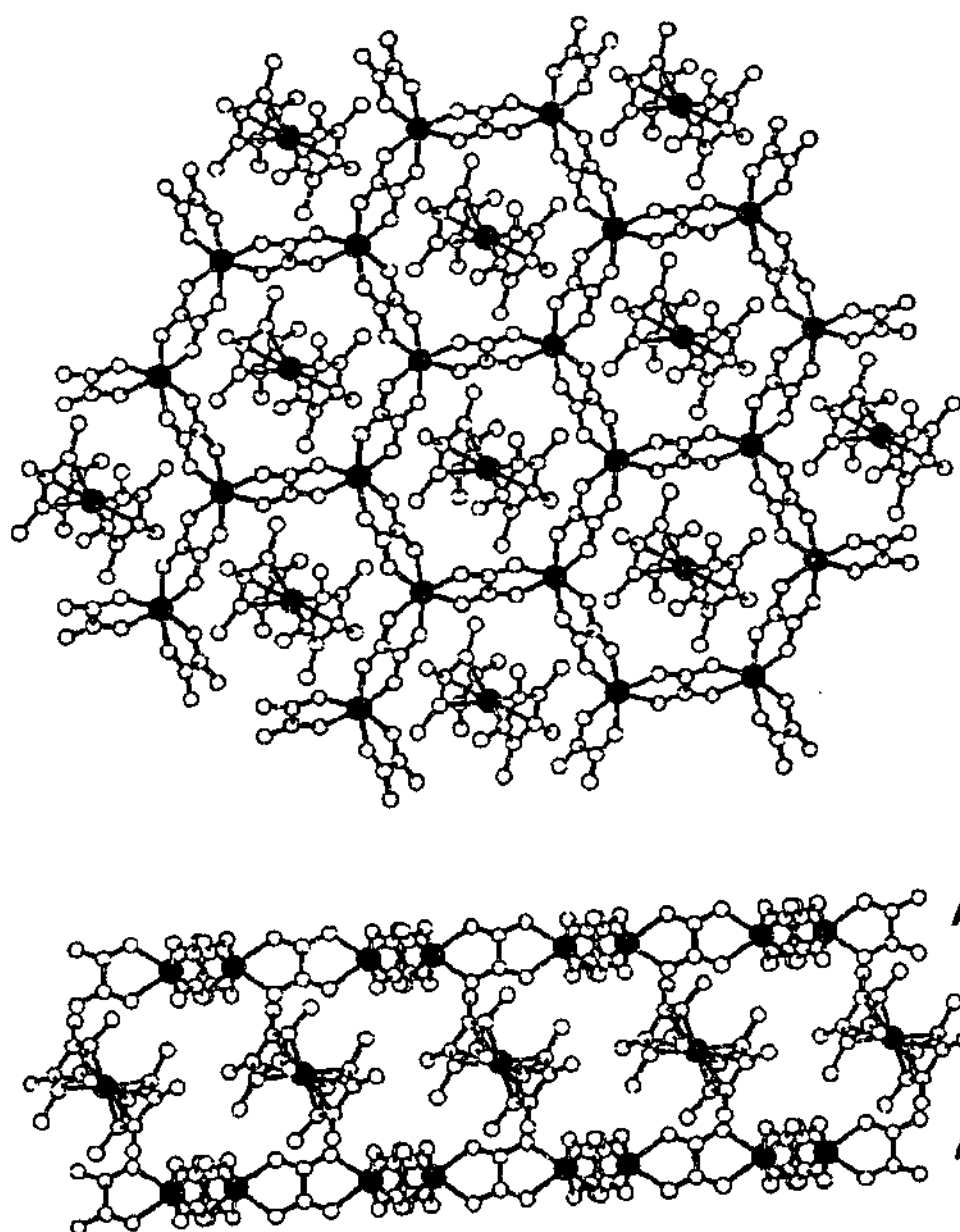


Figure 1.20 Two different views of the structure of $[\text{FeCp}^*_2][\text{MnFe}(\text{ox})_3]$ in the *ab*-plane (top) and the *ac*-plane (bottom). Reproduced from reference 252.

Recently, De Munno and Julve *et al.*²⁶¹ reported the compound $[\text{Fe}^{\text{II}}_2(\text{bpym})(\text{ox})_2] \cdot 5\text{H}_2\text{O}$, whose structure shown in Figure 1.21 consists of neutral 2D (6,3) hexagonal sheets related to those of the oxalate networks above, but includes bridging 2,2'-bipyrimidine (bpym) ligands. Intercalated water molecules form hydrogen bonding networks between the sheets. This compound exhibits intra-layer antiferromagnetic coupling between the high-spin Fe^{II} ions, but does not show long range-order. De Munno

and Julve *et al.*²⁷¹ also reported a chiral 3D Fe^{III} magnet $\{(\text{NH}_4)_2[\text{Fe}^{\text{III}}_2\text{O}(\text{ox})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}\}_n$, which orders below a T_c of 40 K. The chiral anionic network, shown in Figure 1.22, consists of Fe^{III} centres bridged by single $\mu\text{-O}^{2-}$ and bisbidentate oxalate ligands forming pseudohexagonal channels. The ammonium cations and water molecules occupy the channels.

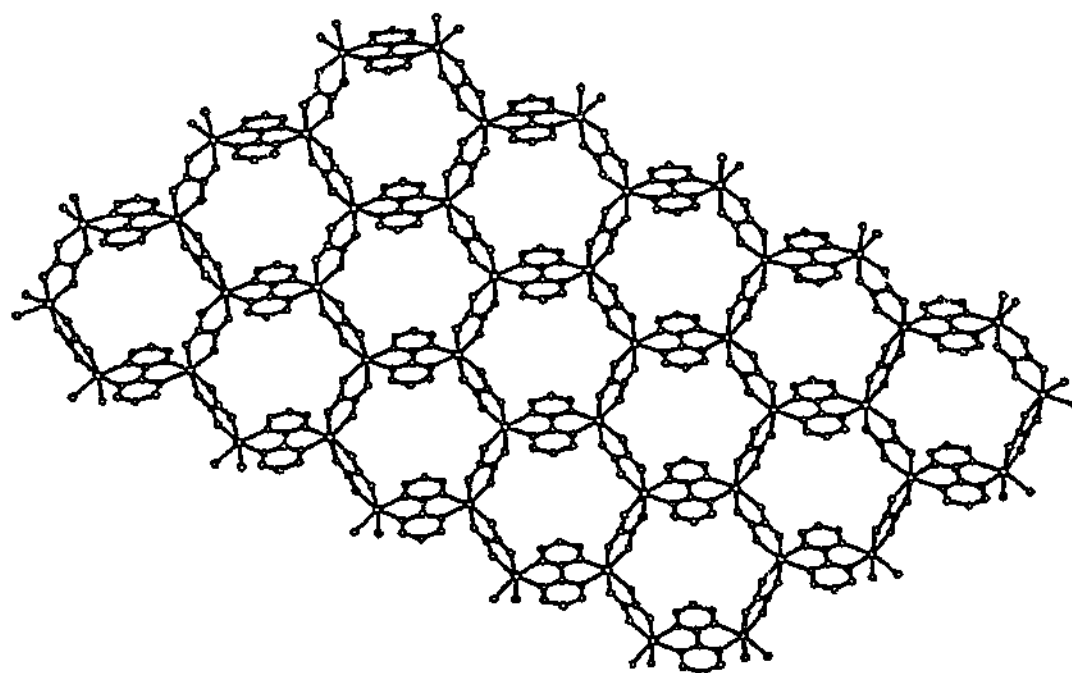


Figure 1.21 The crystal structure of $[\text{Fe}^{\text{II}}_2(\text{bpym})(\text{ox})_2]\cdot 5\text{H}_2\text{O}$ in the *ab*-plane (H_2O molecules omitted for clarity). Reproduced from reference 261.

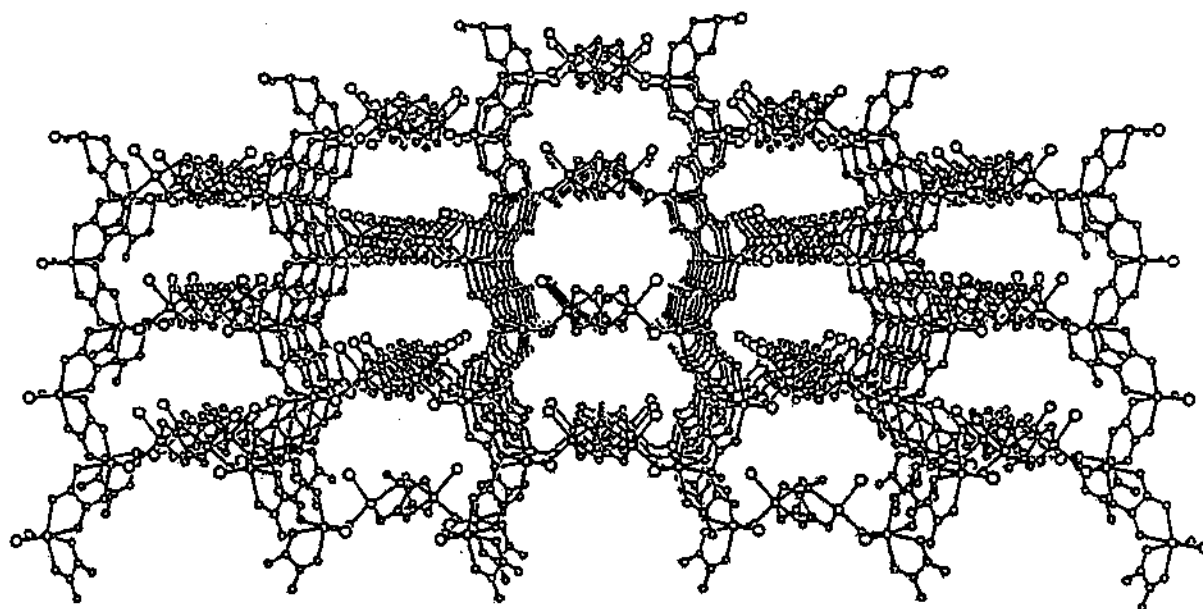


Figure 1.22 Structure of $\{(\text{NH}_4)_2[\text{Fe}^{\text{III}}_2\text{O}(\text{ox})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}\}_n$ viewed down the pseudohexagonal channels (reproduced from reference 271).

Other related bis-chelating ligands have also been used as precursors for magnetic materials. Kahn, Verdaguer and other groups have employed oxamato,^{234,249,253,272-276} oxamido,²⁷⁷⁻²⁸² oximato,^{283,284} and dithiooxalato²⁸⁵ ligands to synthesise bimetallic systems. For example, in 1988 Kahn *et al.*²⁸⁶ reported the ferromagnet $[\text{Mn}^{\text{II}}\text{Cu}^{\text{II}}(\text{pbaOH})(\text{H}_2\text{O})_3]$ (where $\text{H}_4\text{pbaOH} = 2\text{-hydroxy-1,3-propylenebis(oxamide)}$), which consists of linear bimetallic chains of alternating Mn^{II} and Cu^{II} ions. The intra-chain coupling is ferrimagnetic and inter-chain coupling is ferromagnetic, leading to ferromagnetic order below 4.6 K. Removing the water molecule coordinated to the Cu^{II} centre leads to a partially dehydrated material that orders at the higher T_c of 30 K.²⁷⁵ The increased ordering temperature was attributed to the fact that the chains are closer to each other than in the hydrated phase.²⁷⁵

Kahn *et al.* have also reported some fascinating examples containing three spin carriers by incorporation of a radical cation. For example, the isomorphous complexes $(\text{Etrad})_2[\text{M}^{\text{II}}_2\{\text{Cu}^{\text{II}}(\text{opba})\}_3(\text{DMSO})_x] \cdot 0.25\text{H}_2\text{O}$ (where $\text{M}^{\text{II}} = \text{Mn}$, $x = 0.5$; $\text{M}^{\text{II}} = \text{Co}$, $x = 1.5$; $\text{Etrad}^+ = 2\text{-(1-ethylpyridinium-4-yl)-4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide}$; and $\text{opba} = \text{ortho-phenylenebis(oxamato)}$).²⁴⁹ The structures consist of 2D anionic hexagonal (6,3) sheets, analogous to the oxalate networks, where the $\text{Cu}(\text{opba})$ units replace the oxalate ligands (Figure 1.23). Nearly perpendicular two-fold interpenetration of the sheets occurs. The Mn and Co complexes order magnetically below 22.8 and 37 K respectively. The latter is also quite a hard magnet with a coercive field, which is dependent on particle size, measured at 24 kOe at 6 K for very small crystals.²⁴⁹

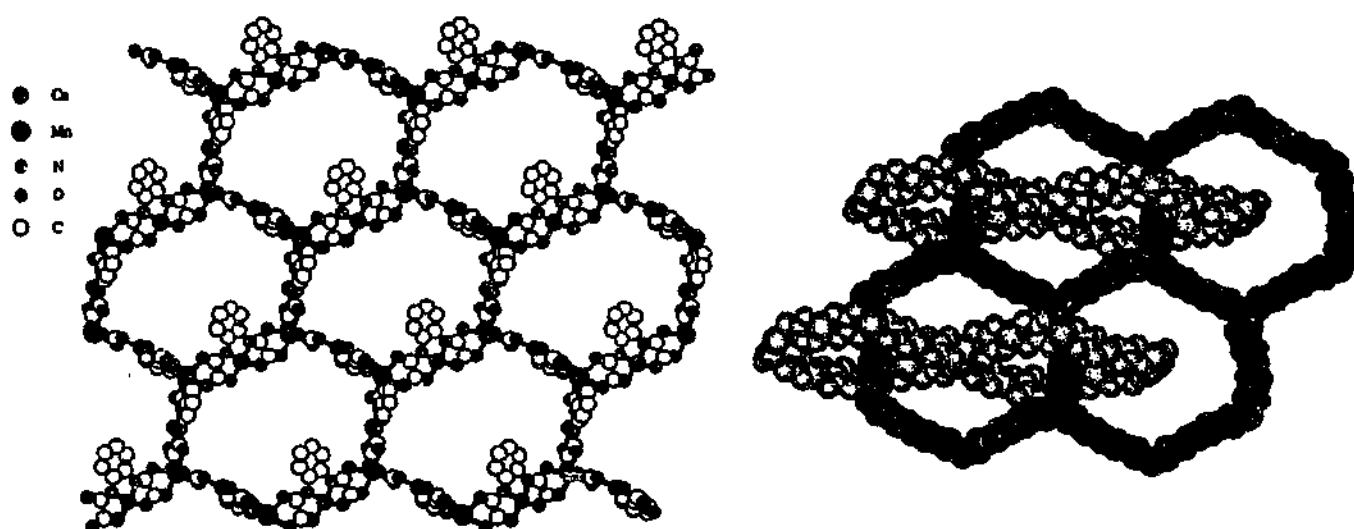


Figure 1.23 Left: the 2D hexagonal anionic sheet structure of $[\text{Mn}^{\text{II}}_2\{\text{Cu}^{\text{II}}(\text{opba})\}_3(\text{DMSO})_{0.5}]^{2-}$. Right: the overall interpenetrated structure of the sheets. Ettrad^+ cations, DMSO and H_2O molecules are omitted for clarity. Reproduced from reference 234.

1.4.6 Single-Chain Magnets

A relative newcomer to the field of molecule-based magnetism is the area of so-called ‘single-chain magnets’ or SCMs. It has evolved very recently, in the last few years, as an offshoot of the field of single-molecule magnets (SMMs), which is described in more detail in Chapter 7. Briefly, SMMs are zero-dimensional entities, often large multinuclear polyoxo metal clusters, with large ground state spin values, which can be magnetised at low temperatures. Due to an energy barrier between the ‘spin-up’ to ‘spin-down’ states they display slow relaxation of magnetisation, and hence are ‘trapped’ or ‘frozen’ in either one of the two states. Single-chain magnets are similar in that they display slow magnetisation relaxation, but as the name implies, are one-dimensional entities. They usually require 1D Ising-chain behaviour, which derives from orbitally degenerate ions such as octahedral Co^{II} .²⁸⁷ This phenomenon was first predicted in 1963 by Glauber.²⁸⁸ In 2001 Caneschi *et al.*²⁸⁹⁻²⁹¹ reported the compound $[\text{Co}^{\text{II}}(\text{hfac})_2(\text{NITPhOMe})]$ (where $\text{hfac} =$

hexafluoroacetylacetonate, NITPhOMe = 4'-methoxy-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide), which was the first experimental evidence to confirm Glauber's prediction. The complex has a spiral chain structure. Recently, Clérac *et al.*²⁹² have reported on the structure and SCM behaviour of a heterometallic chain complex, $[\text{Mn}^{\text{III}}_2(\text{saltmen})_2\text{Ni}^{\text{II}}(\text{pao})_2(\text{py})_2](\text{ClO}_4)_2$ (where $\text{saltmenH}_2 = N,N'$ -(1,1,2,2-tetramethylethylene)bis(salicylideneimine) and $\text{paoH} = \text{pyridine-2-al-doxime}$), which consists of trinuclear repeating units, shown in Figure 1.24.

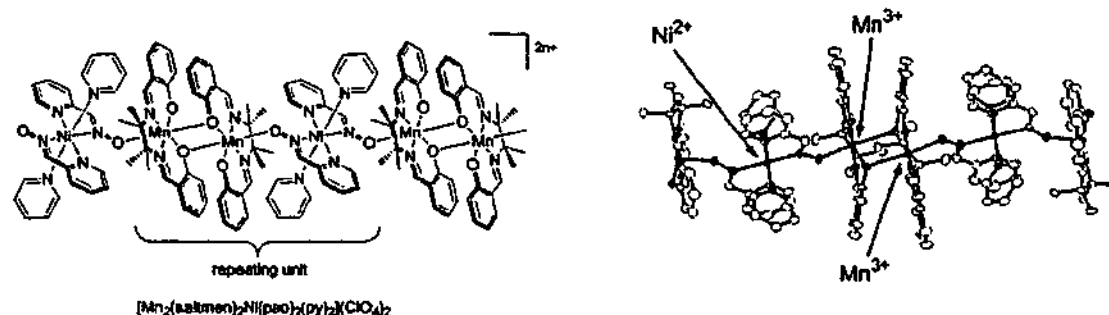


Figure 1.24 (Left) A schematic diagram of $[\text{Mn}^{\text{III}}_2(\text{saltmen})_2\text{Ni}^{\text{II}}(\text{pao})_2(\text{py})_2](\text{ClO}_4)_2$ and (Right) its crystal structure with Mn^{III} and Ni^{II} centres indicated (reproduced from reference 292).

1.4.7 Poly-Cyano Ligands: Dicyanamide, Tricyanomethanide and Dicyanonitrosomethanide

Research into the chemistry of cyano-based ligands has undergone a renaissance within the field of molecule-based magnetism. In particular, the observation of room-temperature magnetic ordering in several Prussian Blue phases and in vanadium TCNE compounds (*vide supra*) has seen researchers looking at ligands that contain non-radical cyano moieties, such as dicyanamide ($\text{N}(\text{CN})_2^-$, dca) and tricyanomethanide ($\text{C}(\text{CN})_3^-$, tcm).^{147,293,294} Their conjugated nature and their ability to bridge multiple metal centres, both of which are essential for the occurrence of long-range magnetic order, have led to

their significance. Despite this, compared to the oxalate and cyanide ligands, dca and tcm are relative newcomers to the field of molecule-based magnetism. However, dca and tcm transition metal complexes were first reported in the 1960s.²⁹⁵⁻³⁰¹ Since Batten *et al.* reported, in 1998, the occurrence of long-range ferromagnetic order in α -[M^{II}(dca)₂] (where M^{II} = Co and Ni, with T_c values of 9 and 20 K respectively), there has been much research focused on using dca and other such poly-cyano ligands as precursors for molecule-based magnets.^{147,293}

The structure of dca in its various resonance forms is shown in Figure 1.25. IR and Raman spectroscopic measurements and X-Ray structural analysis have shown that the dicyanamide ion has an angular planar structure, with a central C–N–C angle of approximately 120° and N–C–N angles of around 175°.³⁰¹

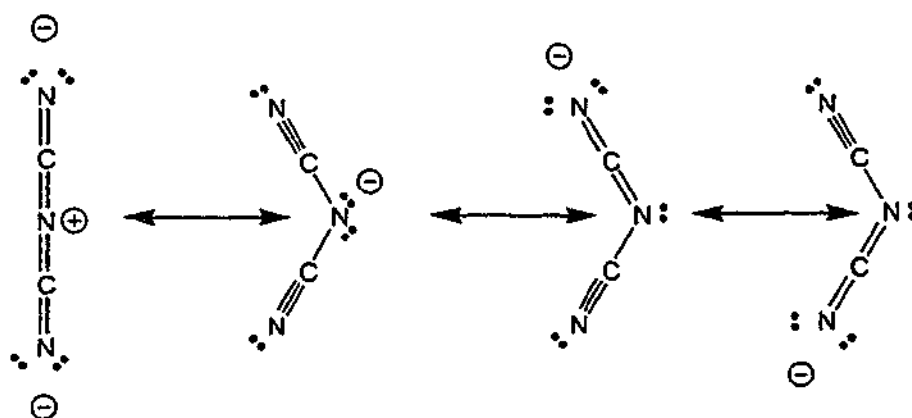


Figure 1.25 Resonance structures of dicyanamide (dca), the first linear structure is unfavourable.

Dicyanamide is capable of forming covalent and coordination bonds *via* the amide and/or nitrile nitrogens. The possible coordination modes of dca are shown in Figure 1.26. It has four lone pairs of electrons and thus it is possible for dca to act as a tetradentate

ligand. The rigid structure of dca and the disposition of donor atoms prevent metal chelation and favour multiple bridging.

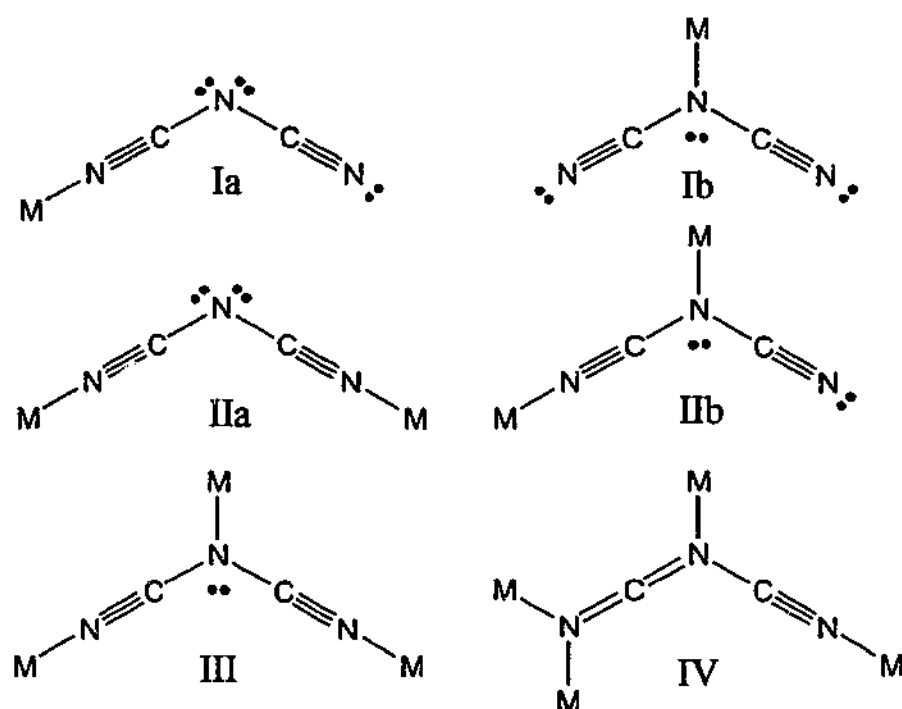


Figure 1.26 Some possible coordination modes of dicyanamide (dca).

The binary $[\text{M}(\text{dca})_2]$ complexes were first described by Köhler in the mid 1960s.^{297,298} He used spectroscopic studies to gain much insight into the structures of these compounds and their derivatives.³⁰¹ Two phases were reported: α - $[\text{M}(\text{dca})_2]$ (where $\text{M}^{\text{II}} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ and Cu) and β - $[\text{M}(\text{dca})_2]$ (where $\text{M}^{\text{II}} = \text{Mn}, \text{Co}$ and Zn). The α -phase contains octahedral metal centres and tridentate dca ligands, while the β -phase contains tetrahedral metal centres and bidentate dca ligands. It was not until 1998, when Batten *et al.* reported the crystal structure of α - $[\text{Cu}(\text{dca})_2]$, that the structure of this phase was unambiguously determined.⁵¹ The structure, shown in Figure 1.27, consists of a single rutile-like network, and is described in more detail along with that of the related two-fold interpenetrated rutile-like $[\text{M}(\text{tcm})_2]$ structure in Chapter 2 in relation to the self-penetrating structure of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$.

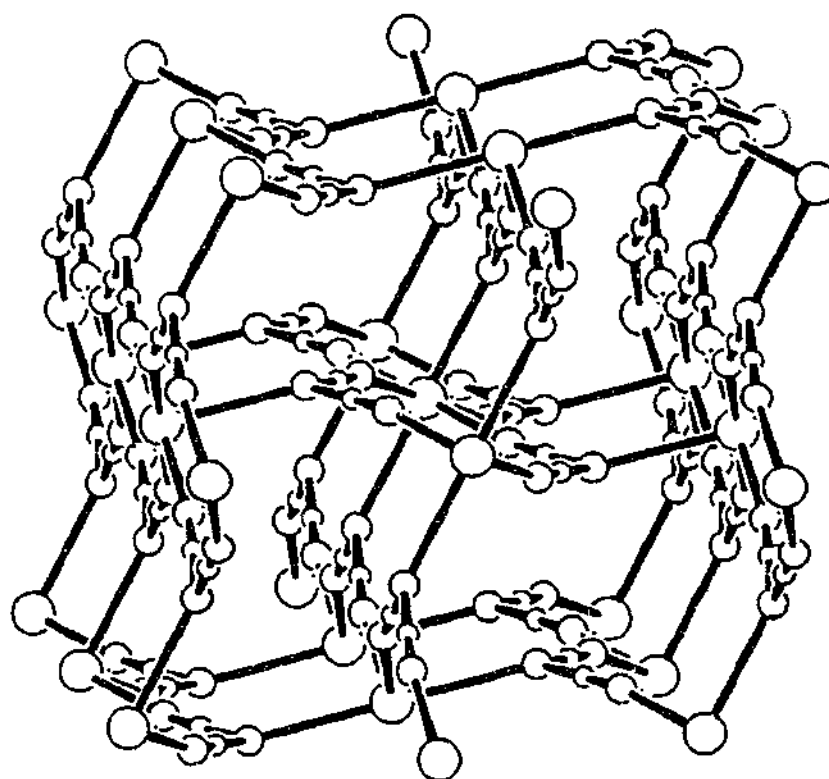


Figure 1.27 Rutile-like structure of α -[Cu(dca)₂]. Circles represent in order of decreasing size Cu, N, C (reproduced from reference 51).

In this paper Batten *et al.*⁵¹ reported the long-range ferromagnetic order exhibited by the α -[M(dca)₂], M^{II} = Co and Ni, complexes with T_c values of 9 and 20 K respectively. This was closely followed by reports of long-range order for the same and other rutile-like dca species,^{47,147,302-306} which are summarised in Table 1.3. α -[Cu(dca)₂] was thought until very recently not to order magnetically. This was believed to be due to the presence of Jahn-Teller distortion, which elongates the axial Cu-N_{amide} bonds, thus leading to weaker Cu...Cu magnetic interactions. Recently ferromagnetic order has been detected below 1.7 K.³⁰⁷

Table 1.3 Magnetic data summary for the rutile-like α -[M^{II}(dca)₂] series, where M^{II} = Cr, Mn, Fe, Co and Ni, (S-C AF = spin-canted antiferromagnetic and F = ferromagnetic).

M ^{II}	Type of Ordering	T_c or T_N / K	Coercive Field, H_c / Oe	ref
Cr	S-C AF	47	300	304
Mn	S-C AF	16	406 ^(a)	47
Fe	S-C AF	19	17800	303
Co	F	9	710	51
Ni	F	21	7975	303

(a) Miller *et al.*³⁰⁴ reported a value of 750 Oe

Köhler first reported the tetrahedral β -[M(dca)₂] series (where M^{II} = Mn, Co and Zn).^{297,301,308} In fact, Zn^{II} does not form the rutile-like phase. The tetrahedral Mn^{II} and Co^{II} complexes can be obtained from depyridination of the corresponding [M^{II}(dca)₂(py)₂] complexes.^{297,302,306} The crystal structure of β -[Zn(dca)₂] was recently reported,^{306,309} and consists of (interdigitated) corrugated 2D (4,4) sheets of [Zn(dca)₂] with $\mu_{1,5}$ -dca ligands (Figure 1.28). On the basis of powder X-ray diffraction data it is believed the tetrahedral Co^{II} complex adopts this same structure.³⁰⁶ Since Köhler's work no further reports of β -[Mn(dca)₂] have appeared.^{301,308}

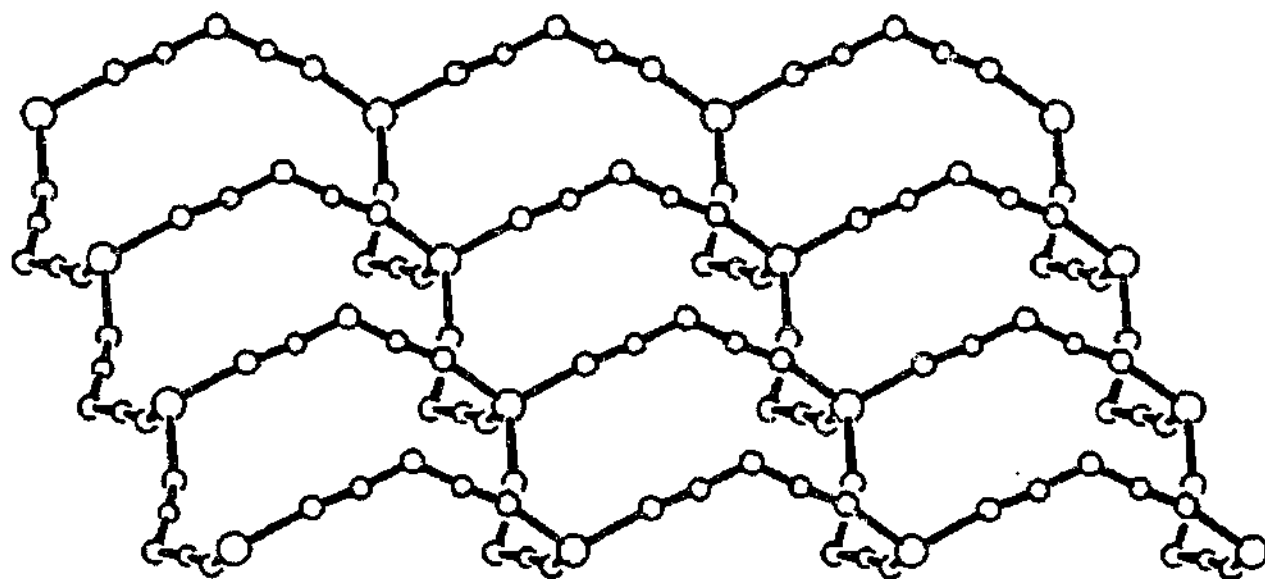


Figure 1.28 The crystal structure of a single 2D (4,4) sheet of β -[Zn(dca)₂] (reproduced from reference 306).

In recent years research groups worldwide have displayed immense interest in dca based coordination polymers with many containing co-ligands.^{310,311} In cases where such studies are particularly relevant to the present study, some of the recent literature will be discussed in the following chapters.

In recent papers by Schnick *et al.* on the alkaline earth dca compounds, [M(dca)₂] (where M^{II} = Mg, Ca, Sr, and Ba) and other dca related work,³¹²⁻³¹⁴ a different assignment of the IR spectrum of dca to that of Köhler's original work was used.³⁰¹ They swapped the asymmetric ($\nu_{as}(\text{C}\equiv\text{N})$) and symmetric nitrile stretching modes ($\nu_s(\text{C}\equiv\text{N})$). For consistency with previous work of Murray *et al.*, the assignment of Köhler is retained in this thesis.

Another ligand included in this investigation was the pseudochalcogenide anion dicyanonitrosomethanide ($\text{ONC}(\text{CN})_2^-$, dcnm), otherwise known as nitrosodicyanomethanide, shown in Figure 1.29. This ligand has also been known for some time,³¹⁵ with early work by Köhler *et al.*,³¹⁶⁻³²² Chow and Britton,^{323,324} Skopenko *et*

al.,^{320,321,325-330} and later research by Hvastijová and Jäger *et al.*³³¹⁻³⁴⁰ featuring prominently.

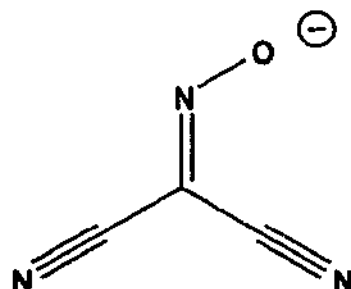


Figure 1.29 The dicyanonitrosomethanide (dcnm) anion.

The first structurally characterised dcnm compound was Ag(dcnm), reported by Chow and Britton in 1974.^{323,324} In the structure, which consists of two interpenetrating 3D nets, dcnm is tetradentate, bridging four Ag atoms *via* both nitrile nitrogens and the nitroso oxygen and nitrogen atoms.⁷⁶

Several other dcnm complexes have been investigated to date including lanthanide,^{326,330} main group,^{341,342} and transition metal complexes.^{335,343-349} From these structures it is clear that dcnm is an ambidentate ligand. Some of the coordination modes are shown in Figure 1.30. However, the structures of the simple binary compounds of the first row transition metals, $[M^{II}(\text{dcnm})_2]$, have not been reported. This may be partly due to the tendency of dcnm to undergo a nucleophilic addition (at one of the nitrile carbon atoms) of solvent molecules (e.g. H_2O and MeOH) upon coordination to form chelating ligands. Hvastijová *et al.*^{332,350} in particular have investigated this phenomenon, and it has been experimentally observed in the present study and is described in Chapter 9.

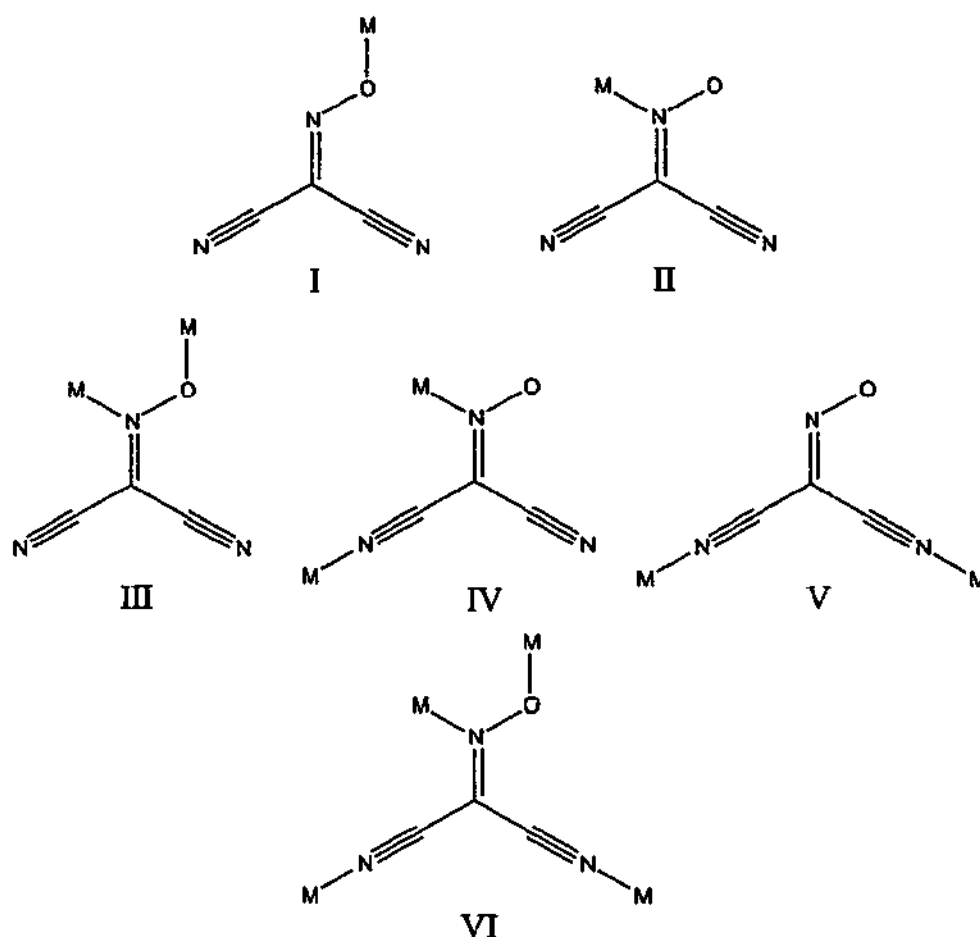


Figure 1.30 Some of the possible coordination modes of dicyanonitrosomethanide (dcnm) that have been structurally characterised: monodentate (I and II), bidentate (III, IV and V) and tetradentate (VI).

1.5 The Present Study

The encompassing theme of the present work is molecule-based magnetic materials. Initially, the project involved the synthesis, structural characterisation and magnetic properties of coordination polymers incorporating first row transition metals, dicyanamide or dicyanonitrosomethanide, and various co-ligands such as Schiff-bases. This work led to the discovery of several mixed valence manganese cluster complexes, which in turn led into the field of single-molecule magnets. This thesis is therefore broadly divided into two parts. Chapters 1 to 6 deal with polymeric coordination complexes, whereas Chapters 7 to 9 focus on the cluster studies. For the most part, each chapter is

designed to be self-contained with its own relevant introduction. As such, they need not be read sequentially. A brief summary of all subsequent chapters is provided below.

The majority of crystal structures presented in this thesis were solved by the candidate. For those solved by either Dr. Stuart Batten or Dr. Paul Jensen, due reference is made in the experimental section of each chapter where appropriate. Some crystallographic details, bond lengths and angles are given throughout the text, however full details (i.e. complete tables of bond lengths, angles, coordinates etc.) for all structures are to be found on the attached CD-ROM of Appendix 3.

Chapter 2 describes the structure and magnetic properties of a new molecule-based magnet $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$. A hydrated derivative of the parent rutile-like α - $[\text{Mn}(\text{dca})_2]$ species, this complex possesses an interesting self-penetrated single network structure that can be considered a structural compromise between the single rutile net of α - $[\text{M}(\text{dca})_2]$ and the doubly interpenetrated rutile-like $[\text{M}(\text{tcm})_2]$ series. $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ was discovered to exhibit long-range spin-canted antiferromagnetic order below a T_N value of 6.3 K. Additionally, the structures and magnetism of two closely related dca complexes containing terpyridine, $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ and $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$, are discussed. The former complex has a linear 1D chain structure, and the latter also a linear chain structure but hydrogen bonds with the non-coordinated dca ligands form a pseudo-sheet structure. These two complexes display weak antiferromagnetic coupling.

In Chapter 3 an isostructural series of 1D linear chain complexes containing salicylaldehyde derived Schiff-base ligands is investigated. The compounds are $[\text{M}^{\text{III}}(\text{L})(\text{dca})]_n$, where $\text{M}^{\text{III}} = \text{Mn}$ and Fe ; $\text{LH}_2 = \text{salenH}_2$ (*N,N'*-ethylenebis(salicylideneimine)), *sal-o-phenH*₂ (*N,N'*-*o*-phenylenebis(salicylideneimine)) and $(\pm)\text{-saltchH}_2$ ($(\pm)\text{-N,N'-trans-cyclohexanebis(salicylideneimine)}$). These complexes

display weak antiferromagnetic coupling and are some of the first M^{III} -dca compounds to be isolated and structurally characterised.

The structures and magnetism of two new chiral 3D framework types containing acetylacetone derived Schiff-based ligands are described in Chapter 4. The complexes $[M^{II}(\text{acenH}_2)(\text{dca})_2]$, $M^{II} = \text{Mn}$ and Fe ; $\text{acenH}_2 = N,N'$ -ethylenebis(acetylacetoneimine), are isomorphous and consist of 3-fold helical $\{[\text{Fe}(\mu\text{-acenH}_2)(\mu_{1,5}\text{-dca})]^+\}_n$ motifs that are linked by $\mu_{1,5}$ -dca ligands to form a chiral 3D network. They are the first examples of single networks with the unusual 'dense' 7^59 topology. The second framework type is exhibited by the complexes $[M^{II}(\text{actchH}_2)(\text{dca})_2]$, $M^{II} = \text{Mn}$ and Fe ; $(\pm)\text{-actchH}_2 = (\pm)\text{-}N,N'\text{-trans-1,2-cyclohexanebis(acetylacetoneimine)}$. It consists of 2D square-grid (4,4) sheets of composition $[M(\text{dca})_2]$ that are connected in the third dimension by $\mu\text{-actchH}_2$ ligands. These links are 2-fold helices. This network type possesses an unprecedented topology with the Schläfli symbol $4^8.5^4.6^3$, and is compared to the α -polonium type net. These materials also display weak antiferromagnetic coupling. The structure of a mononuclear complex, *trans*- $[\text{Mn}^{II}(\text{acenH}_2)_2(\text{dcnm})_2]$, was also investigated. It exhibits an unusual bis-chelating mode of acenH_2 .

Chapter 5 details the structures and magnetism of three anionic heteroleptic dca complexes. The first two compounds, $\text{Ph}_4\text{P}[M^{II}(\text{dca})_2(\text{NO}_2)]\cdot\text{MeCN}$, $M^{II} = \text{Co}$ and Ni , have 2D square-grid sheets structures with $\mu_{1,5}$ -dca and chelating nitrite groups. The compound $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$ also possesses a chiral structure, consisting of linear anionic 1D helical chains of $[\text{Co}(\text{dca})\text{Br}_2]^-$. It is the first air-stable tetrahedral cobalt(II) dca network complex. The magnetic properties of the $\text{Ph}_4\text{P}[M(\text{dca})_2(\text{NO}_2)]\cdot\text{MeCN}$, $M^{II} = \text{Co}$ and Ni , complexes are indicative of very weak antiferromagnetic exchange coupling occurring *via* $\mu_{1,5}$ -dca bridges. Traces of $\alpha\text{-}[M(\text{dca})_2]$ are thought to be responsible for long-range ordering

effects observed in low fields but this is not definitive in the Co^{II} case. $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$ displays very weak intra-chain antiferromagnetic coupling with no magnetic order.

A new manganese(III) complex, $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$, whose structure consists of infinite 1D linear chains that are hydrogen bonded to form 2D sheets, is described in Chapter 6. The complex displays weak intra-chain antiferromagnetic coupling at higher temperatures and a magnetic phase transition, at $T_N = 6.1$ K, to an ordered antiferromagnetic phase, probably mediated by the hydrogen bonding pathways. There is also a metamagnetic transition at *ca.* 1000 Oe from the antiferromagnetic phase to a canted-spin antiferromagnetic (weak ferromagnetic) phase, brought about by increasing the applied field.

The fields of polynuclear cluster complexes with an emphasis on manganese oxo clusters, and single-molecule magnets are reviewed in Chapter 7.

The structures and magnetism of a new manganese(III/IV) carboxylate cluster, $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_{16}(\text{MeOH})_3(\text{H}_2\text{O})_3]\cdot 6\text{H}_2\text{O}$, and a new 1D linear manganese(III) complex, $[\text{Mn}(\mu\text{-OMe})(\text{OAc})_2]$, are detailed in Chapter 8. Detailed magnetic measurements have shown the Mn_{16} complex to be a new single-molecule magnet. The linear chain complex displays weak antiferromagnetic coupling.

The final chapter, Chapter 9, investigates the structures and magnetic properties of trinuclear and tetranuclear mixed valent manganese complexes, $[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3\cdot 2\text{H}_2\text{O}$ and $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4\cdot 2\text{H}_2\text{O}$ (where *mcoe* = methyl(2-cyano-2-hydroxyimino)ethanimidate, $\text{ONC}(\text{CN})\text{C}(\text{NH})\text{OCH}_3^-$; and *cao* = cyanoacetamidoximate $\text{ON}=\text{C}(\text{CN})(\text{CONH}_2)^-$). Separately, two mononuclear complexes were also isolated, $[\text{Cu}(\text{mcoe})_2(\text{MeOH})_2]$ and $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$. These are also discussed. The chelating-bridging ligands *mcoe* and *cao* were formed *in situ* by nucleophilic addition of solvent to *dcnm*.

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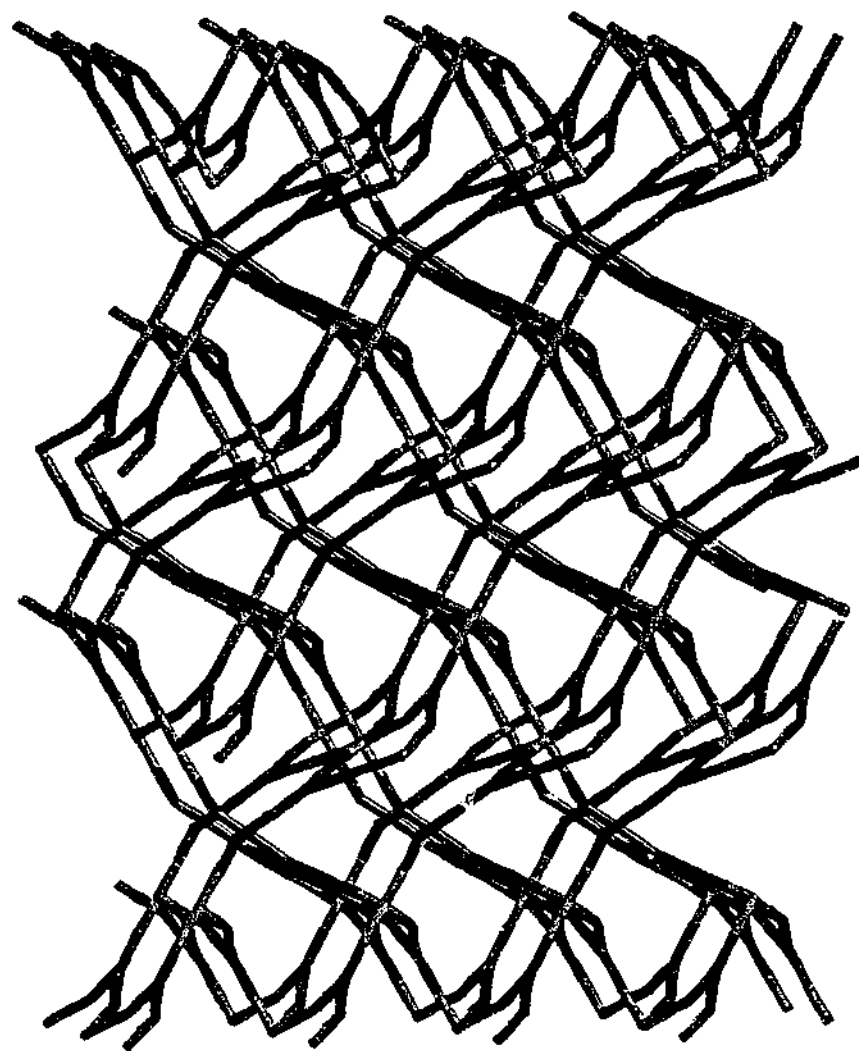
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CHAPTER 2: 1D, 2D AND 3D MANGANESE(II)

DICYANAMIDE

NETWORK COMPLEXES

2.1 A Molecule-Based Magnet, $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$, and Self-penetration – a Structural Compromise Between Single Networks and Interpenetration of Networks

2.1.1 Introduction

Work undertaken during the candidate's B.Sc. Honours year included studies of the rutile-like α - $[\text{Mn}(\text{dca})_2]$ species and a new, related hydrated species, $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$.¹ The discovery of this hydrated species seemed to answer some questions regarding the reported formula of $\text{Ni}(\text{dca})_2 \cdot 0.5\text{H}_2\text{O}$.^{2,3} It was proposed that a hydrated species analogous to that above as an impurity could be responsible for the formulation. However, the trihydrate lost water in air and transformed back into the parent rutile-like binary species. Could another hydrate be responsible? In addition to this, the magnetization *versus* temperature plots of α - $[\text{Mn}(\text{dca})_2]$ ($T_N = 16$ K) showed a small abrupt increase at 6 K that could not be explained as well as the main transition at 16 K.⁴ Subsequently, during the Ph.D. program, a new dicyanamide containing molecule-based magnet was discovered, $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$. This mono-hydrated analogue of the parent species behaves as a spin-canted antiferromagnet, ordering below 6.3 K thus explaining the magnetisation anomaly seen in the parent rutile-like α - $[\text{Mn}(\text{dca})_2]$, and is described here. Structurally $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ displayed a new self- or intra-penetrated 3,6-connected (2:1) network topology that can be related back to rutile. This new network can be thought of as a structural compromise between the two interpenetrated rutile-like networks of $[\text{M}(\text{tcm})_2]$ (where tcm = tricyanomethanide) and the single rutile-like network of α - $[\text{M}(\text{dca})_2]$. Indeed, an isostructural compound $[\text{M}(\text{dca})(\text{tcm})]$ can be formed in which tcm is topologically equivalent to the $\text{dca} \cdot \text{H}_2\text{O}$ moiety in $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$.⁵

Entangled systems have received considerable interest due to the interesting physical properties and topologies these species display.⁶ Entanglement on the molecular scale seen, for example, in rotaxanes and catenanes has been reported widely.⁷ Entanglement of ordered polymeric networks is known as interpenetration and many examples have been reported.⁶ Interpenetration occurs where two or more independent networks pass through each other such that they cannot be separated without the breaking of bonds.

The polymeric equivalent of a molecular knot is a self-penetrating (self-entangled or intra-penetrating) network. These single networks contain regions where rods pass through rings in a similar manner to interpenetrated systems. While rods and rings in any network may be chosen such that a rod passes through a ring, a useful and necessary restriction is to define a self-penetrated network as such only when the topological 'shortest circuits' are penetrated by rods of the same network.^{8,9} The magnetism of self-penetrated nets containing open-shell d ions was essentially unexplored at the onset of this work.

2.1.2 Synthesis and Characterisation of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$

Crystals of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ were obtained from either a solution of $[\text{Mn}(\text{dca})_2]$ in a mixture of wet methanol/ethanol or from an aqueous 1:2 solution of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}(\text{dca})$. Unlike $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, the crystals are not sensitive to solvent loss at room temperature. The infrared spectrum of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ shows a broad absorption at 3388 cm^{-1} and a sharp peak at 1625 cm^{-1} due to $\nu(\text{OH})$ and $\delta(\text{HOH})$ vibrations respectively, of the coordinated water. Absorptions due to dicyanamide occur at 2310, 2258, and 2185 cm^{-1} corresponding to $[\nu_{\text{as}}(\text{C}-\text{N}) + \nu_{\text{s}}(\text{C}-\text{N})]$, $\nu_{\text{as}}(\text{C}\equiv\text{N})$ and $\nu_{\text{s}}(\text{C}\equiv\text{N})$ vibrations respectively. These values are indicative of bidentate dicyanamide. However,

the absorptions at 1359 and 1326 cm^{-1} correspond to $\nu_{\text{as}}(\text{C}-\text{N})$ vibrations of bidentate and tridentate dicyanamide respectively. Likewise the absorptions at 956 and 937 cm^{-1} are due to $\nu_{\text{s}}(\text{C}-\text{N})$ of tridentate and bidentate dicyanamide respectively. Two different types of dicyanamide i.e. bidentate and tridentate coordination modes are inferred from this spectroscopic evidence, and this was further confirmed by single-crystal X-ray crystallographic analysis (see next section). Microanalytical results on samples prepared by the different routes (see Experimental Section 2.4.1) were consistent with the formulation $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$.

2.1.3 Crystal Structure of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$

X-Ray structural analysis was performed by Dr. P. Jensen on a single crystal prepared by the candidate. Table 2.1 contains a summary of crystallographic details and Table 2.2 (see page 98) contains selected interatomic distances and angles. The atom labelling scheme for $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ is shown in Figure 2.1. The structure consists of a 3D network containing Mn^{II} atoms coordinated in a near octahedral arrangement by (on average) five dca ligands and one water molecule. There are two types of dca ligand – one (dca1) is tridentate, coordinating to three Mn^{II} atoms *via* both nitrile nitrogens ($\text{Mn}(1)-\text{N}(1) = 2.191(4) \text{ \AA}$) and the amide nitrogen ($\text{Mn}(1)-\text{N}(2^{\text{ii}}) = 2.417(4) \text{ \AA}$). The other (dca2) is bidentate, coordinating directly to two Mn^{II} atoms *via* the nitrile nitrogens only ($\text{Mn}(1)-\text{N}(3) = 2.171(5)$ and $\text{Mn}(1)-\text{N}(5^{\text{i}}) = 2.190(4) \text{ \AA}$). The dca2 ligand also forms a hydrogen bond *via* the amide nitrogen to the coordinated water molecule coordinated to an adjacent Mn^{II} atom. This moiety $\text{dca2}\cdot\text{H}_2\text{O}$ is, however, disordered over two positions related by a mirror plane (Figure 2.2). One nitrile group ($\text{N}(3)$ and $\text{C}(2)$) and the amide nitrogen ($\text{N}(4)$) of dca2 (and the Mn^{II} atom coordinated by the nitrile group) lie on the mirror plane, whereas the other nitrile group and water ligand do not. The latter, in fact,

have symmetry-related positions that superimpose on each other so that the nitrogen and oxygen atoms have been given the same positional and thermal parameters. Consequently the O...N hydrogen-bonding distance is constrained to be equivalent to the NCN distance of the dca2 ligand ($O(1)\cdots N(4) = 2.633(7) \text{ \AA}$), and the position of the nitrile carbon atom is the only site not fully occupied by a non-hydrogen atom. The result of this disorder is the creation of a trigonal pseudo-tridentate 'ligand' $dca2 \cdot H_2O$, which is structurally almost identical to tcm (see below) and thus the formula of the complex could be written as $[Mn(dca1)(dca2 \cdot H_2O)]$.

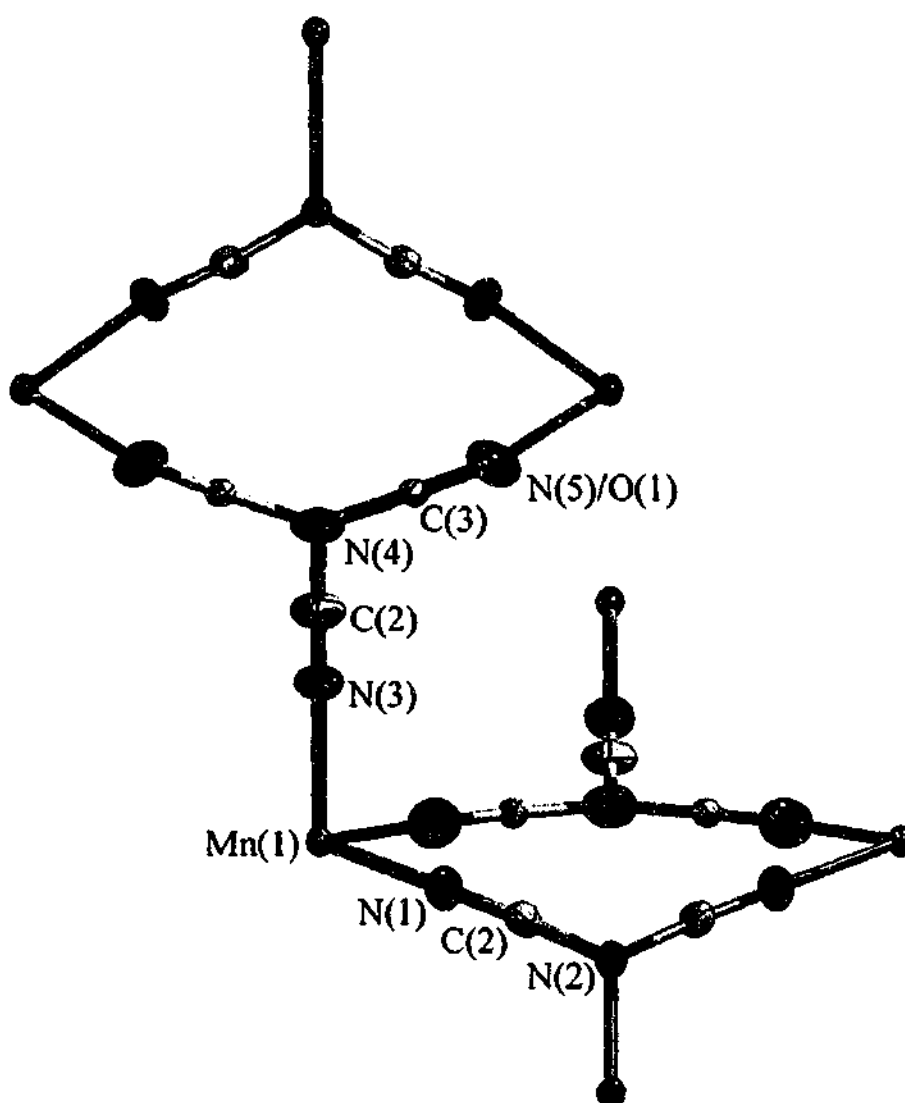


Figure 2.1 $[Mn(dca)_2(H_2O)]$ atom labelling scheme (thermal ellipsoids shown at 50 % probability).

Table 2.1 Summary of crystal data for $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$.

Compound	$[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$
Formula	$\text{C}_4\text{H}_2\text{MnN}_6\text{O}$
M	205.06
Crystal system	Orthorhombic
Space group	$Ama2$
$a/\text{\AA}$	7.5743(2)
$b/\text{\AA}$	17.4533(7)
$c/\text{\AA}$	5.6353(2)
$U/\text{\AA}^3$	744.97(4)
Z	4
$\rho_{\text{calc}} / \text{gcm}^{-3}$	1.828
T/K	293(2)
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	1.728
θ range / $^\circ$	3.56 – 30.03
Index ranges	$0 \leq h \leq 9,$ $-24 \leq k \leq 0,$ $0 \leq l \leq 7$
Completeness to $2\theta = 55^\circ / \%$	98.8
Data collected	5465
Unique data (R_{int})	611 (0.037)
Observed reflections [$I > 2\sigma(I)$]	554
Parameters	68
Final R_1, wR_2 [$I > 2\sigma(I)$] ^(a)	0.0262, 0.0571
(all data)	0.0333, 0.0615
Goodness of fit, S	1.199

^(a) $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$

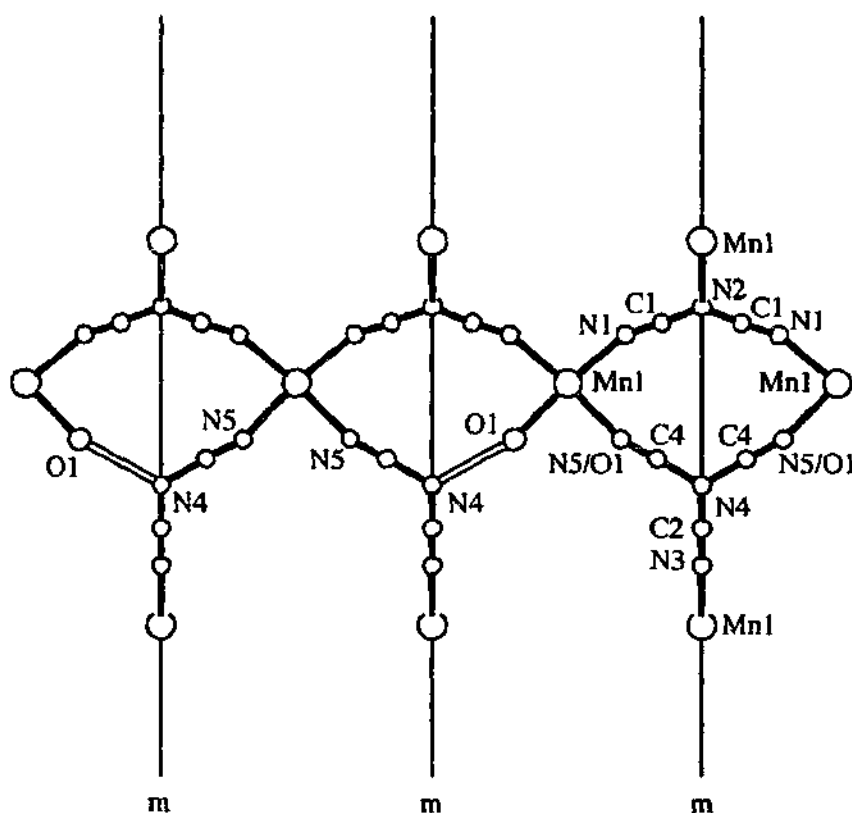


Figure 2.2 A chain in the structure of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ showing the disorder of the $\text{dca}_2 \cdot \text{H}_2\text{O}$ moiety over the mirror plane. The two different orientations of the system are shown on the left and the resultant sum on the right. Hydrogen bonds are denoted by open bonds, and the atom labelling scheme is given without distinction of symmetry related atoms.

To effectively describe the topology of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$, one must first recognize its close relationship with the rutile-like structures of $\alpha\text{-}[\text{M}(\text{dca})_2]$ (single net) and $[\text{M}(\text{tcm})_2]$ (two identical interpenetrating nets). The structure of rutile (TiO_2) consists of octahedral Ti^{IV} atoms (six-connectors) and trigonal O^{2-} atoms (three-connectors) in a 1:2 ratio (Figure 2.3) and can be described in terms of square channels in which the three-connecting centres form the sides of the channels and the six-connecting centres occupy the corners. These channels can be constructed by cross-linking four adjacent TiO_2 chains oriented perpendicular to each other. The sides of the channels contain six-membered rings

(alternating three- and six-connectors), which are the second smallest rings in the structure. The smallest rings are four-membered rings within the aforementioned chains that also contain alternating three- and six-connectors ($\text{Ti}-(\text{O}_2)-\text{Ti}$). Both the four- and six-membered rings are however considered 'smallest circuits' in the topological sense.

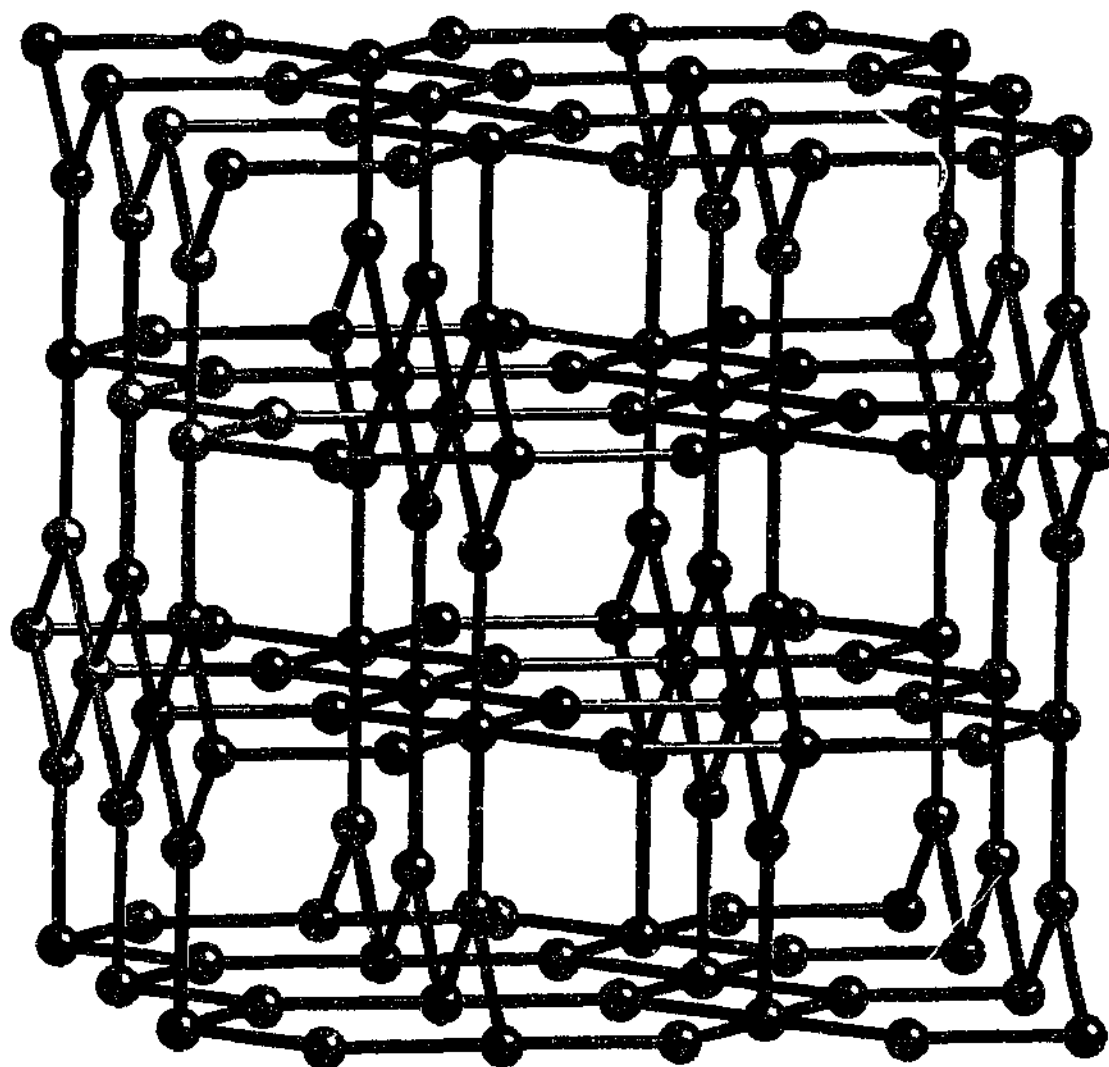


Figure 2.3 The TiO_2 rutile framework. Octahedral Ti centres are represented by blue spheres and trigonal O centres are red spheres. A square channel is highlighted in the centre by purple bonds (the four separate chains) and the green bonds (connections between chains that form the channels). A four-membered ring (left) and a six-membered ring (top left) are also highlighted by green bonds.

In the $[M(\text{tcm})_2]$ structures, the distance between the trigonal centres (the central carbon atom of tcm) and the octahedral centres (metals) (*ca.* 4.5-5.0 Å) is much greater than for TiO_2 . This results in a much larger open framework, thus allowing interpenetration of a second network. Interpenetration occurs by the passing of one of the rods (M-NC-C) of one net through the six-membered ring of the other. The four-membered rings are too sterically crowded to permit interpenetration (Figure 2.4).

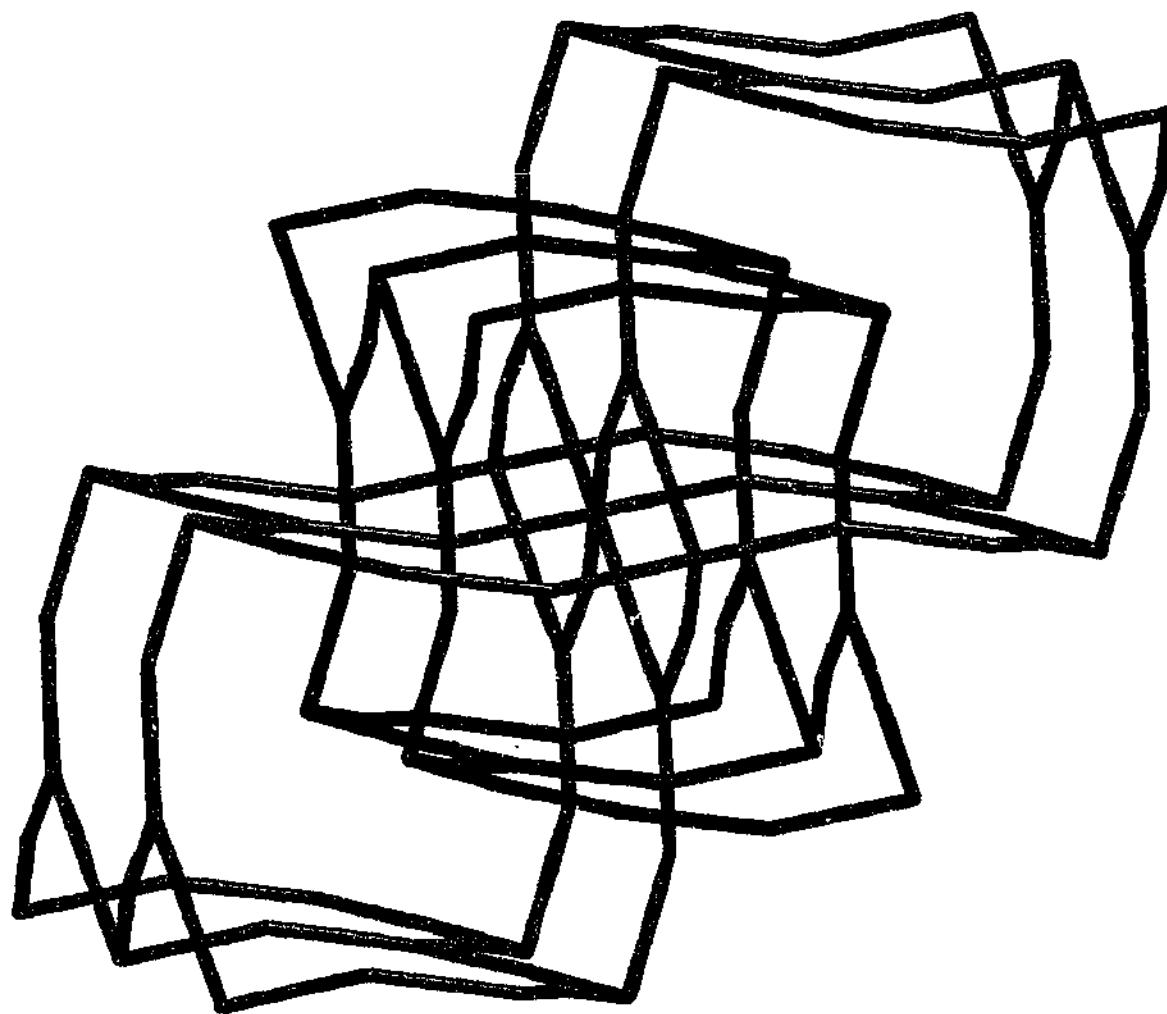


Figure 2.4 A square channel of $[M(\text{tcm})_2]$ network (blue) interpenetrated by a second identical network (red).

In the rutile-like structures of $\alpha\text{-}[M(\text{dca})_2]$ two thirds of the trigonal to octahedral node connections are of a similar length to those in the $[M(\text{tcm})_2]$ structures, however one third, the $\text{M-N}_{\text{amide}}$ links, are considerably shorter. Consequently the links between the

chains are shorter, so that the channels are smaller than those of the $[M(\text{tcm})_2]$ structures. The result is a collapsed, denser network (Figure 2.5). Structurally, the size of the four-membered rings remain relatively unchanged, however the six-membered rings, through which pass the rods of the second net in the $[M(\text{tcm})_2]$ structures, are considerably decreased in size. Hence it would appear interpenetration of a second net is not favoured and does not occur.

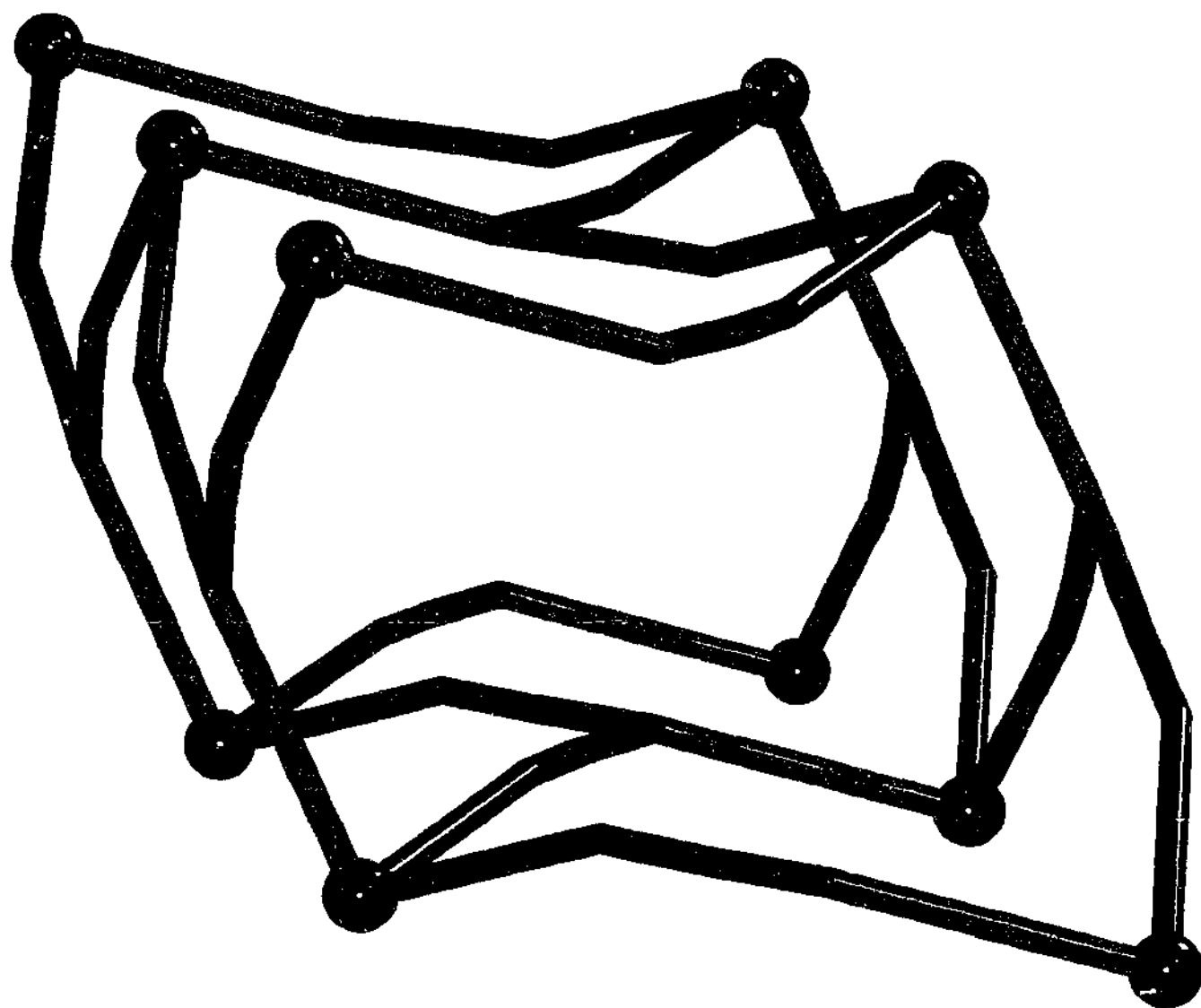


Figure 2.5 A single square channel in the structure of rutile-related α - $[M(\text{dca})_2]$. The M-N_{amide} links (green bonds) are significantly shorter than equivalent links in $[M(\text{tcm})_2]$ structures.

In the structure of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ we combine the two different ligands, dca1 (with one short and two long links) and $\text{dca}2\cdot\text{H}_2\text{O}$ (with three equivalent long links). As in the $\alpha\text{-}[\text{M}(\text{dca})_2]$ structures the short link of dca1 again occurs between the ML_2 chains. If we examine the connections between four adjacent chains analogous to those that form the square channels in the previous two rutile-related structures, the similarities and differences of this new network to rutile will become apparent. The chains, all of which are crystallographically equivalent, have the formula $[\text{Mn}(\text{dca}1)(\text{dca}2\cdot\text{H}_2\text{O})]$ with dca1 ligands on one side of the chain and $\text{dca}2\cdot\text{H}_2\text{O}$ on the other. Again, adjoining chains are mutually inclined to one another, and are connected by the third link of the three connecting centres to the axial positions on the manganese centres. The requirement that the $\text{Mn}\cdots\text{Mn}$ distance within the chains must be the same for the dca1 and $\text{dca}2\cdot\text{H}_2\text{O}$ bridges means the dca1 inter-chain link must be the $\text{Mn}-\text{N}_{\text{amide}}(\text{N}(2))$ bond. The $\text{dca}2\cdot\text{H}_2\text{O}$ inter-chain link is the $\text{Mn}-\text{N}_{\text{nitrile}}(\text{N}(3))$ bond that lies on the mirror plane. The result is that the two inter-chain linkages of three-connecting centres to six-connecting centres are of different lengths, depending on whether the ligand is dca1 or $\text{dca}2\cdot\text{H}_2\text{O}$. The structural consequences of this are shown in Figure 2.6. Moving along the network we can see that the first two inter-chain linkages are of the long $\text{dca}2\cdot\text{H}_2\text{O}$ type. The next two linkages are of the shorter dca1 type. Therefore, while the four chains in rutile connect to form a square channel, the network of interconnected chains in $[\text{Mn}(\text{dca}1)(\text{dca}2\cdot\text{H}_2\text{O})]$ fails to meet back at its starting point, and folds back on itself in the spiral manner shown in Figure 2.6. The interpenetration seen here is similar to that in the $[\text{M}(\text{tcm})_2]$ complexes. The $\text{N}(4)-\text{C}(2)\equiv\text{N}(3)-\text{Mn}(1)$ rods of $\text{dca}2\cdot\text{H}_2\text{O}$ (structurally similar to tcm) penetrate the six-membered rings of $\text{Mn}_3(\text{dca}1)(\text{dca}2\cdot\text{H}_2\text{O})_2$ (structurally similar to M_3tcm_3 rings). However, in this instance we have a single network folding such that it penetrates itself – hence self- or intra-penetration.

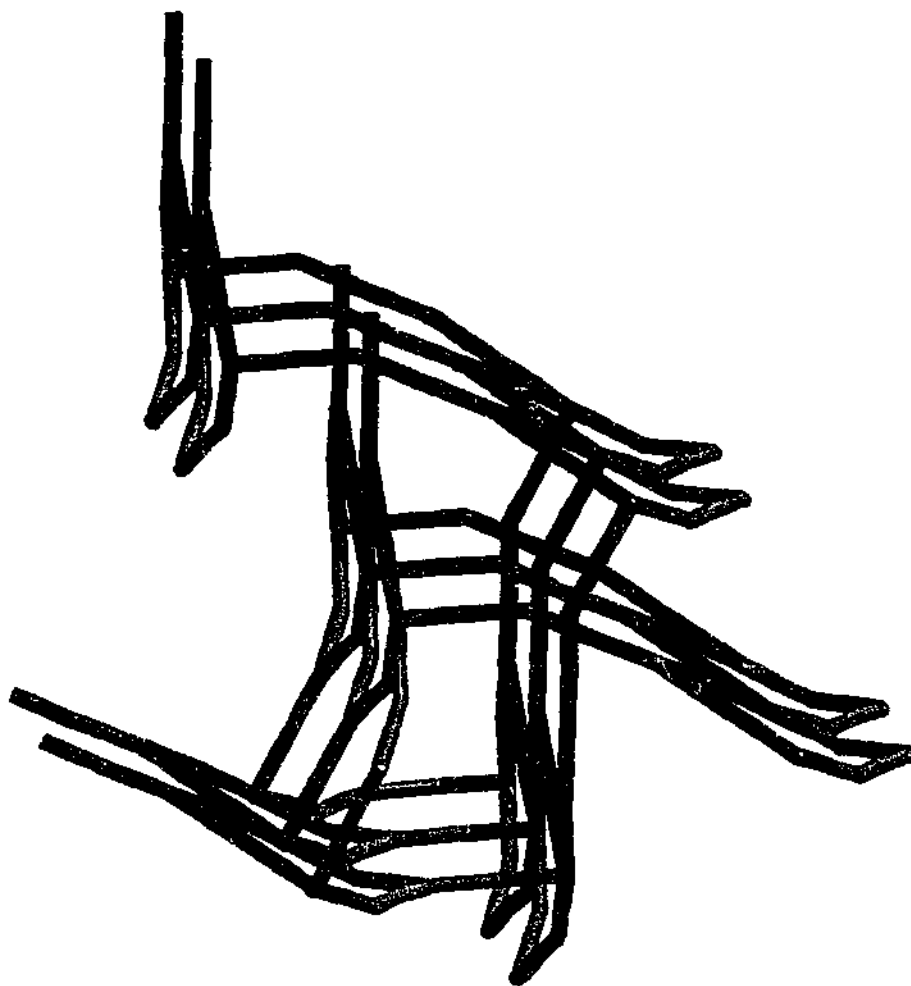


Figure 2.6 The connections of four adjacent orthogonal chains in the structure of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ (the $\text{dca}\cdot\text{H}_2\text{O}$ moieties are shown in blue) showing the self-penetration of the network.

The overall network is shown in Figure 2.7. The importance of 'shortest circuits' in the topology of a network for defining a self-penetrating network was discussed in Chapter 1. Inspection of the rutile network (Figure 2.3) shows that there are 15 smallest circuits that start from a six-connected centre ($p = 6$): two four-membered rings, ten six-membered rings and three eight-membered rings. The smallest circuits radiating out from the three-connecting centres ($p = 3$) are one four-membered ring and two six-membered rings. In the self-penetrated network of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$, the distribution and size of the smallest rings are the same as rutile: four-, six- and eight-membered rings (2:10:3) for the six-connecting nodes, and four- and six-membered rings (1:2) for each of the two types of

three-connecting nodes (dca1 and dca2·H₂O). Thus, although rutile and [Mn(dca)₂(H₂O)] have different topologies, they have the same Schläfli notation: $(4^2.6^{10}.8^3)(4^1.6^2)$.

Recently, a number of other self-penetrating networks have been reported.^{8,9} [Mn(dca)₂(H₂O)] is a new example of a self-penetrating network. This structure also represents a new topology for a network containing three- and six-connectors in a ratio of 2:1. Previously described topologies include the afore mentioned rutile and that of [Hg(tpt)₂(ClO₄)₂]·6C₂H₂Cl₄ (tpt = 2,4,6-tris(4-pyridyl)-1,3,5-triazine).¹⁰

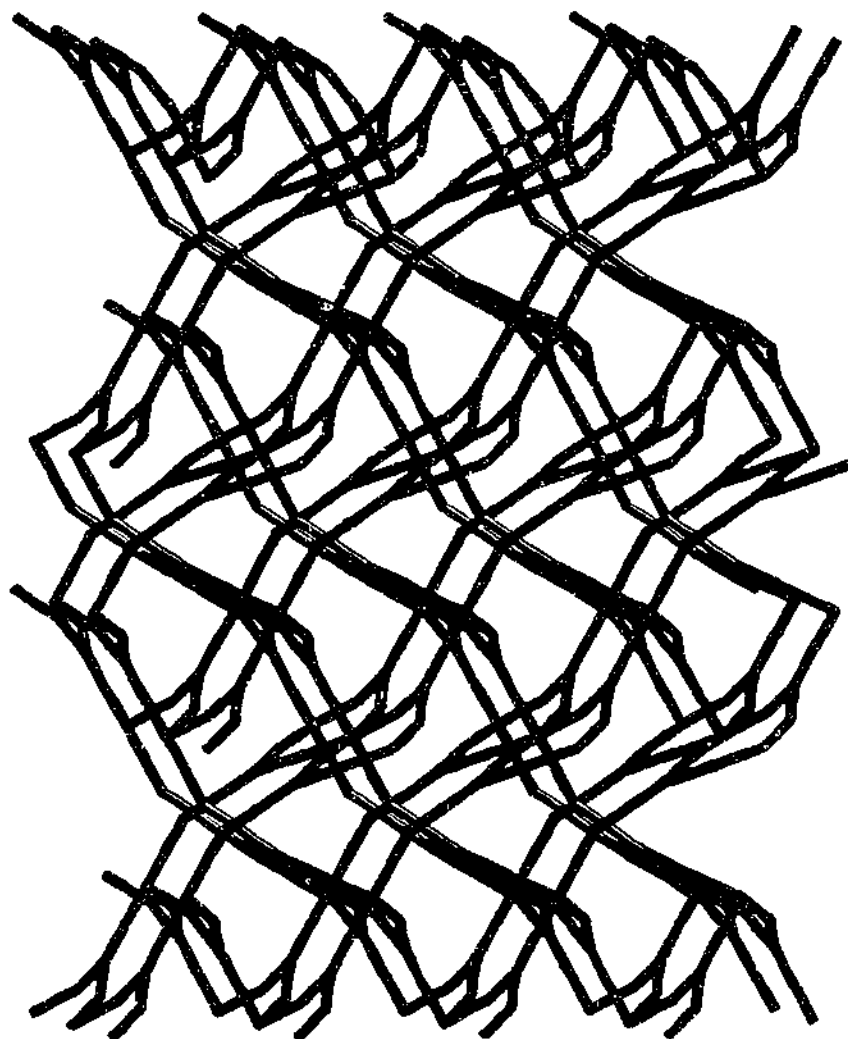


Figure 2.7 Overall view of [Mn(dca)₂(H₂O)] with Mn shown in red, dca1 (green) and dca2·H₂O (blue).

The shortest Mn...Mn distance is through space between a manganese(II) atom of a self-penetrating rod and that of a ring and is equal to the unit cell length c (5.6353(2) Å). The next shortest Mn...Mn distance is *via* the Mn-N $\equiv$ C-N-Mn dca1 link (6.2368(7) Å) and is the shortest Mn-ligand-Mn distance. From previous work,^{4,11-13} it is believed that this particular magnetic exchange pathway of the tridentate dca is important in any observed long-range order. However, it would not appear to be absolutely necessary. For example, β -[Co(dca)₂],¹⁴ Ph₄E[Ni(dca)₃] (E = P or As)^{15,16} and α -[Mn(dca)₂(pyz)]^{17,18} display long-range order despite possessing no M-N_{amide} links. The intra-chain Mn...Mn distance is equal to the unit cell length a (7.5743(2) Å).

Table 2.2 Selected interatomic distances (Å) and angles (°) for [Mn(dca)₂(H₂O)].

Mn(1)–N(1)	2.191(4)	Mn(1)–N(3)	2.171(5)
Mn(1)–N(2 ⁱⁱ)	2.417(4)	Mn(1)–N(5 ⁱ)/O(1 ⁱ)	2.190(4)
N(1)–C(1)	1.148(4)	N(3)–C(2)	1.146(7)
C(1)–N(2)	1.307(4)	C(2)–N(4)	1.325(8)
N(4)–C(3)	1.460(7)	C(3)–N(5)	1.175(6)
N(4)···O(1)	2.633(7)		
N(3)–Mn(1)–N(1)	94.8(2)	N(1)–Mn(1)–N(5 ⁱ)/O(1 ⁱ)	87.8(1)
N(3)–Mn(1)–N(5 ⁱ)/O(1 ⁱ)	96.5(1)	N(1)–Mn(1)–N(1 ⁱⁱⁱ)	95.9(2)
N(3)–Mn(1)–N(2 ⁱⁱ)	178.7(3)	N(1)–Mn(1)–N(5 ^{iv})/O(1 ^{iv})	167.7(2)
N(3)–Mn(1)–N(1 ⁱⁱⁱ)	94.8(2)	N(2 ⁱⁱ)–Mn(1)–N(5 ⁱ)/O(1 ⁱ)	84.4(2)
C(1)–N(1)–Mn(1)	157.3(4)	C(3)–N(4)–C(3 ⁱⁱⁱ)	119.2(7)
C(1)–N(1)–C(1 ^v)	118.3(4)	C(3)–N(5)–Mn(1 ^{vii})	161.7(4)
C(1)–N(2)–Mn(1 ^{vi})	120.6(2)	N(1)–C(1)–N(2)	174.5(4)
C(2)–N(3)–Mn(1)	162.9(5)	N(3)–C(2)–N(4)	178.4(6)
C(2)–N(4)–C(3)	118.0(3)	N(5)–C(3)–N(4)	176.2(6)

Symmetry transformations: (i) $-x, -y, z-1$; (ii) $-x, 1/2-y, z-1/2$; (iii) $1/2-x, y, z$; (iv) $x+1/2, -y, z-1$; (v) $-x-1/2, y, z$; (vi) $-x, 1/2-y, z+1/2$; (vii) $-x, -y, z+1$.

2.1.4 Magnetism of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$

$[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ is a new example of a growing class of homometallic spin-canted antiferromagnets, otherwise known as weak ferromagnets, which includes its parent, the rutile-like α - $[\text{Mn}(\text{dca})_2]$.^{4,12,19-24} In a field of 0.3 T the $\mu_{\text{per Mn}}$ at 300 K of $5.64 \mu_{\text{B}}$ ($\chi_{\text{M}}T = 3.98 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) decreases gradually to $2.62 \mu_{\text{B}}$ ($\chi_{\text{M}}T = 0.86 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) as the temperature is decreased to 4.2 K (Figure 2.8).

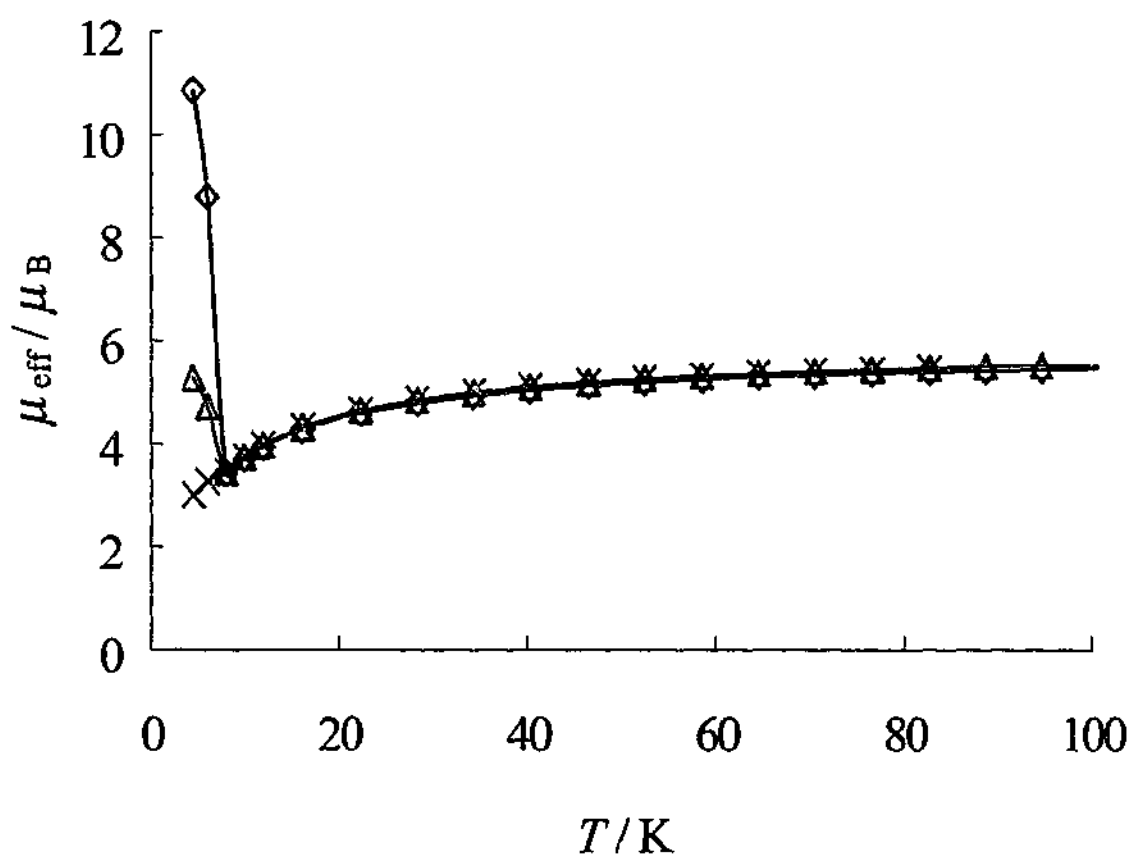


Figure 2.8 Plots of magnetic moment, $\mu_{\text{per Mn}}$, versus temperature for $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ in different applied fields; 20 Oe (◇), 100 Oe (Δ) and 3000 Oe (×).

The Weiss constant, θ , from the χ vs. $1/T$ plot is -4.2 K indicating antiferromagnetic coupling. In field values below about 200 Oe the magnetic moment shows an abrupt increase at approximately 6 K due to the onset of long-range magnetic order ($\mu_{\text{per Mn}}$ is $10.9 \mu_{\text{B}}$ at 4.2 K in a field of 20 Oe). The T_{N} value of 6.3 K was confirmed

by measuring zero-field cooled (*ZFCM*) and field cooled magnetization (*FCM*, $H = 5$ Oe), see Figure 2.9. These diverge at the ordering temperature, 6.3 K.

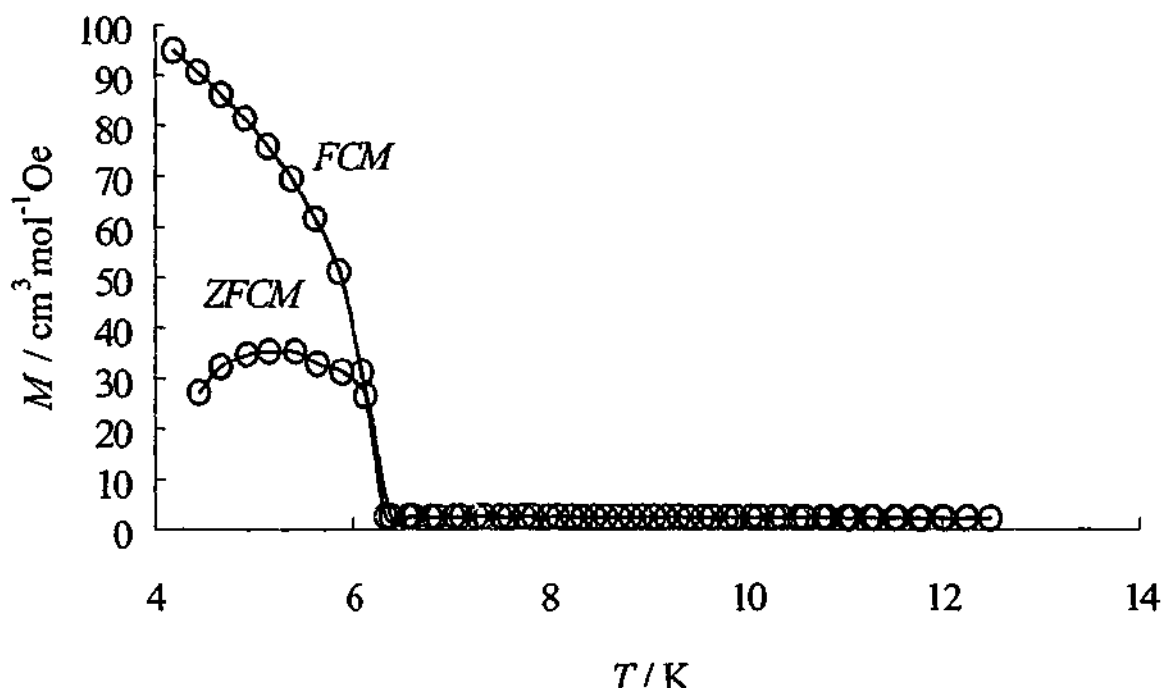


Figure 2.9 Plots of magnetization of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$, M , versus temperature with zero-field cooled (*ZFCM*) and field cooled (*FCM* $H = 5$ Oe) measurements.

The AC in-phase susceptibility, χ' , versus T plot (Figure 2.10) shows a very sharp maximum at 6.3 K indicative of a weak ferromagnet (spin-canted antiferromagnet). M vs. H hysteresis measurements on a neat powder at 2 K gave a remnant magnetization (RM) of $112 \text{ cm}^3 \text{ mol}^{-1} \text{ Oe}$ and a coercive field, H_c , of 250 Oe, values typical of a soft magnet (Figure 2.11). High field magnetization measurements made at temperatures above and below the ordering temperature, show behaviour consistent with spin-canted antiferromagnetism such as linear plots with low values of M even in the highest fields employed. For example, at 2 K and in 5 T $M = 1.7 N\beta$ (M_{sat} for Mn^{II} is $5 N\beta$).

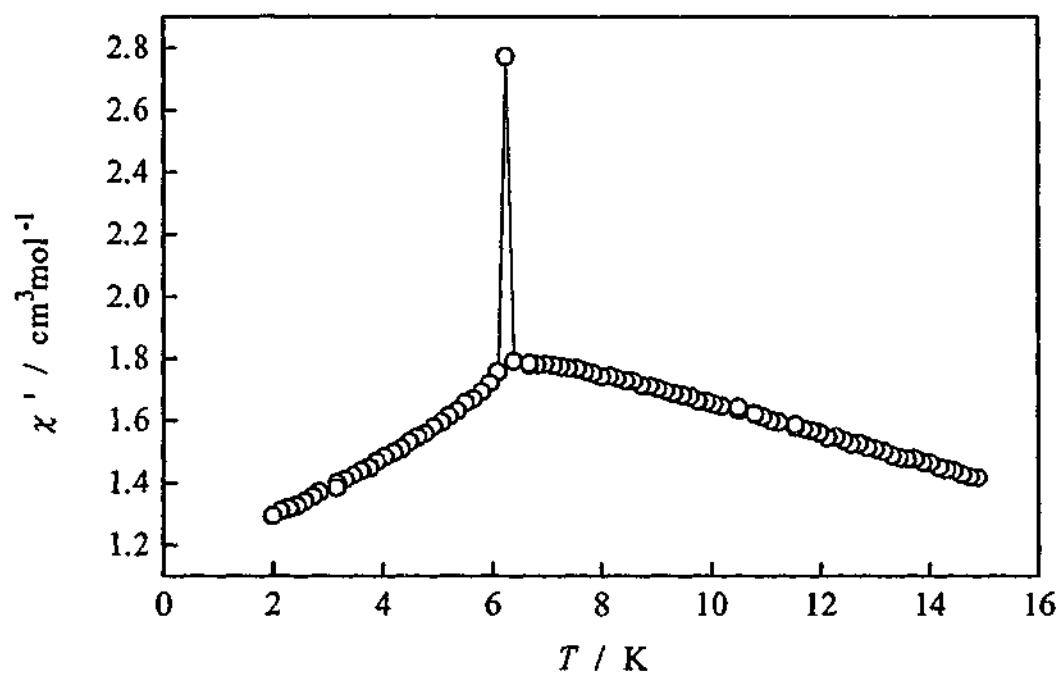


Figure 2.10 Plot of in-phase, χ' , AC susceptibility *versus* temperature in a field of 1 Oe oscillating at 20 Hz.

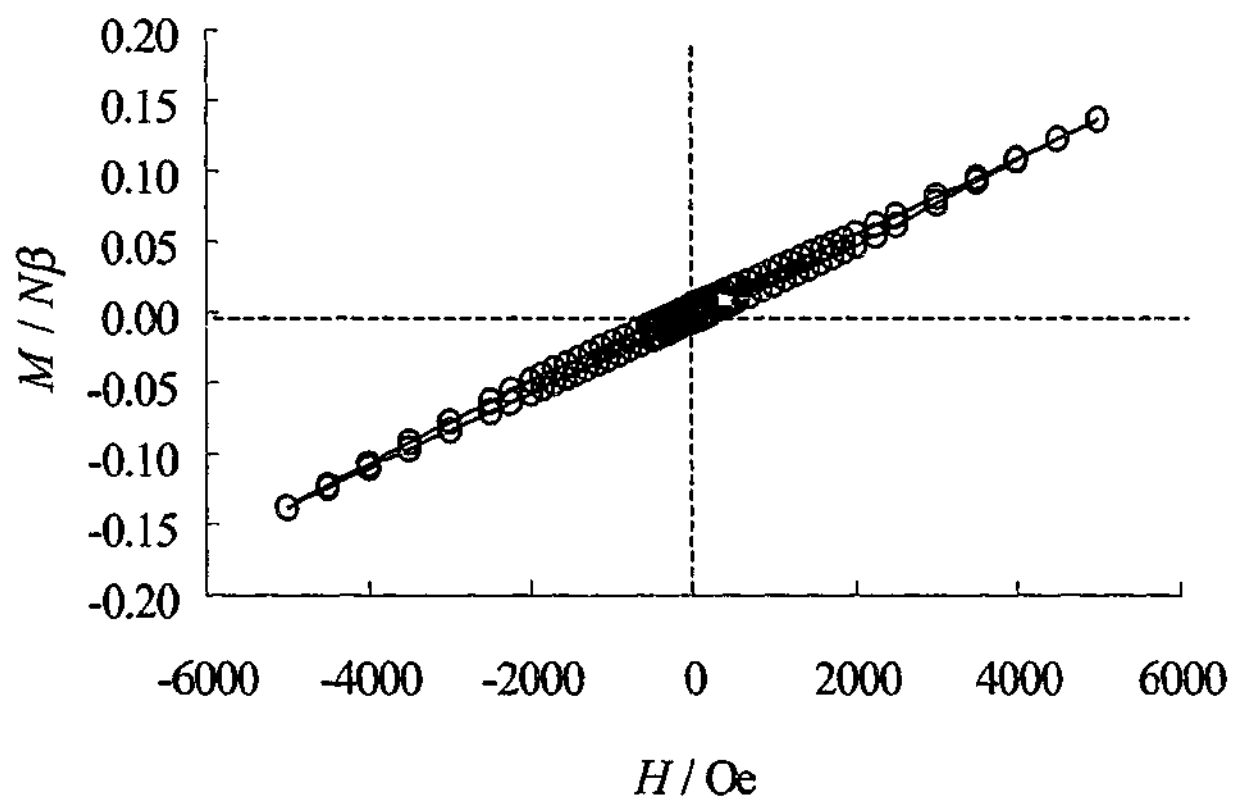


Figure 2.11 Hysteresis loop for $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ of a powder sample at 2 K.

Antiferromagnetic coupling is thought to arise from super-exchange *via* the M-NC-N-CN-M pathways of bidentate dicyanamide coordinating through their nitrile nitrogens between Mn^{II} centres as in the cases of $\alpha\text{-[Mn(dca)}_2\text{]}$ and the $[\text{Mn(dca)}_2\text{L}_2]$ chain complexes (L = e.g. pyridine).^{4,12,25} Use of Rushbrooke and Wood theory²⁶ for the coupling of $S = 5/2$ centres led to a set of best-fit parameters of the 0.3 T susceptibility data of $g = 1.93$ and $J = -0.19 \text{ cm}^{-1}$, although agreement below 30 K was poor. The J value is similar to those seen in the $[\text{Mn(dca)}_2\text{L}_2]$ chain complexes.^{4,12}

The occurrence of long-range order from spin-canting is believed to arise from a complex combination of the super-exchange pathway $\text{M-N}\equiv\text{C-N-M}$ i.e. *via* bonding through the amide nitrogen and orientation of the Mn^{II} centre chromophores 60.6° to each other along those same exchange pathways.

2.2 Two linear Mn^{II} chain complexes containing dicyanamide and terpyridine: $[\text{Mn(dca)(NO}_3\text{)(terpy)}]_n$ and $\{[\text{Mn(dca)(H}_2\text{O)(terpy)}](\text{dca})\}_n$

2.2.1 Introduction

In recent years research in polymeric coordination complexes containing dicyanamide has undergone rapid growth.^{13,16,27-37} Of particular interest is the potential of dicyanamide to act as a bridging ligand in molecule-based magnetic materials, particularly in response to the tridentate bridging mode seen in the series of rutile-related complexes $\alpha\text{-[M(dca)}_2\text{]}$, $\text{M}^{\text{II}} = \text{Cr, Mn, Fe, Co, Ni and Cu}$, which display long-range magnetic order.

Much work has been undertaken to modify the structures and properties of dicyanamide containing networks by the incorporation of co-ligands giving 3D, 2D and 1D complexes of the general formula $[\text{M(dca)}_2\text{L}_2]$, where L can be a terminal ligand, for

example, DMF, pyridine,⁴ 4-benzoylpyridine³⁸ or 2-aminopyridine.³⁹ The resulting structures often have 1D chain (e.g. L = pyridine, 4-benzoylpyridine and DMF) or 2D sheet structures (e.g. L = EtOH) or in the case of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ both chain and sheet structural types exist in the one material.⁴ The complexes $[\text{M}(\text{dca})_2(\text{apym})]$ ($\text{M}^{\text{II}} = \text{Co}$ and Ni , apym = 2-aminopyridine), reported by Jensen *et al.*,³⁹ have a 1D linear tubular structure.³⁹ In the above examples dicyanamide bridges through both nitrile nitrogen atoms in the $\mu_{1,5}$ mode, except the apym complexes, which has dicyanamide in the tridentate $\mu_{1,3,5}$ mode bridging through both nitrile and central amide nitrogens, as well as dca ligands in the $\mu_{1,5}$ mode. In fact, the tubular structures of the apym complexes can be described as single square channels of the rutile-like α - $[\text{M}(\text{dca})_2]$ complexes 'coated' by the monodentate apym ligands.³⁹

When L_2 is a linear bridging ligand, for example pyrazine (pyz) or 4,4'-bipyridine,^{17,18,39-42} the resulting complexes can have doubly interpenetrating α -Po related 3D network structures.¹⁷ Polymorphs also exist such as β - $[\text{Cu}(\text{dca})(\text{pyz})]$, which possesses a 2D square grid structure.⁴³ Long-range antiferromagnetic order has been reported in α - $[\text{Mn}(\text{dca})_2(\text{pyz})]$ ^{18,40} and in $[\text{Cu}_2(2,5\text{-Me}_2\text{pyz})(\text{dca})_4]$, 2,5-Me₂pyz = 2,5-dimethylpyrazine, at very low temperatures.³⁰ N-heterocyclic chelating ligands, both bridging and terminal, have also been employed to modify the structures and consequently the properties of dicyanamide containing coordination polymers. Some examples include the two-dimensional $[\text{Fe}_2(\text{dca})_4(\text{bpym})] \cdot \text{H}_2\text{O}$ and $[\text{Fe}_2(\text{dca})_4(\text{bpym})(\text{H}_2\text{O})_2]$ where bpym = 2,2'-bipyrimidine is also bridging Fe^{II} centres in a bis-chelating fashion,³⁴ and the one-dimensional complexes $[\text{M}(\text{dca})_2(\text{bpym})(\text{H}_2\text{O})]$, $\text{M} = \text{Mn}^{\text{II}}$, Fe^{II} and Co^{II} ,⁴⁴ $[\text{M}(\text{dca})_2(\text{phen})]$, $\text{M} = \text{Mn}^{\text{II}}$ and Cu^{II} , phen = 1,10-phenanthroline,⁴⁵ and $[\text{Co}_3(\text{HAT})(\text{dca})_6(\text{H}_2\text{O})_2]$, HAT = 1,4,5,8,9,12-hexaazatriphenylene, where the tris-chelated trinuclear $\text{Co}_3(\text{HAT})$ units are further bridged by $\mu_{1,5}$ -dca ligands.³¹

The present study using terpyridine as a terminal chelate forms part of an extensive study using terminal and bridging co-ligands bonded to $\text{Mn}^{\text{II}}(\text{dca})_2$.⁴ While the candidate was in the process of solving the structures of the following two $\text{Mn}^{\text{II}}(\text{dca})_2$ -terpy species, Escuer *et al.* reported the same compounds.⁴⁶ It follows on from their related Mn^{II} -azide adduct chemistry.⁴⁷⁻⁴⁹

2.2.2 Synthesis and Characterisation of $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$

This compound and that described in section 2.2.3 were initially obtained in the same reaction. To obtain them separately, crystals of $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ were prepared by reaction of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with terpy, in methanol followed by subsequent addition of a methanolic solution of $\text{Na}(\text{dca})$ (1:1:2 molar ratio). This route for $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ is similar to that reported by Escuer *et al.*⁴⁶ The infrared spectrum of $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ shows that absorptions due to dicyanamide occur at 2294, 2243, and 2177 cm^{-1} corresponding to $[\nu_{\text{as}}(\text{C}-\text{N}) + \nu_{\text{s}}(\text{C}-\text{N})]$, $\nu_{\text{as}}(\text{C}\equiv\text{N})$ and $\nu_{\text{s}}(\text{C}\equiv\text{N})$ vibrations respectively. These values are indicative of bidentate dicyanamide bridging through both nitrile nitrogens ($\mu_{1,5}$). Elemental microanalysis supported the above formulation.

2.2.3 Synthesis and Characterisation of $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$

Crystals of $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ were prepared by a two step reaction. First, $\text{Mn}(\text{terpy})\text{Cl}_2$ was prepared by reaction of MnCl_2 with terpyridine in ethanol. This solid was then reacted with a solution of $\text{Na}(\text{dca})$ in a methanol/water mixture. This contrasts with the synthesis of $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ reported by Escuer *et al.* where they used Mn^{II} triflate to prevent the formation of $[\text{Mn}(\text{dca})_2(\text{NO}_3)(\text{terpy})]_n$.⁴⁶ The infrared spectrum of $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ shows a strong absorption at 3296 cm^{-1} due to $\nu(\text{OH})$ of the coordinated water. Hydrogen bonding (*vide infra*) is responsible for the relative sharpness of the peak. Evidence of two different dicyanamides can be seen

clearly in the $\nu_s(\text{C}\equiv\text{N})$ absorption, as it is split into two peaks at 2166 and 2143 cm^{-1} . The former is consistent with $\mu_{1,5}$ dicyanamide and the latter lower wavenumber value is due to the free uncoordinated, albeit hydrogen-bonded, dicyanamide. In comparison, $\text{Ph}_4\text{P}(\text{dca})$, which has unbound dca and shows $\nu_s(\text{C}\equiv\text{N})$ at 2130 cm^{-1} , whereas $\text{Na}(\text{dca})$, in which dca is bound to the Na^+ atoms shows $\nu_s(\text{C}\equiv\text{N})$ at 2182 cm^{-1} . These spectroscopic data were supported by X-ray crystallographic analysis (see Section 2.2.5). Elemental microanalysis supported the above formulation.

2.2.4 Crystal Structure of $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$

Crystallographic details for $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ are given in Table 2.3 (see page 109) and selected bond distances and angles are given in Table 2.4 (see page 110). $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ crystallizes in the monoclinic space group $P2_1/n$ with the asymmetric unit containing one formula unit. The structure (Figure 2.12) consists of zigzag chains of manganese atoms linked by single $\mu_{1,5}$ -dca bridges ($\text{Mn}-\text{N} = 2.221(1)$ and $2.196(1)$ Å). Each manganese atom is seven-coordinate with an approximately pentagonal bipyramidal environment around the metal. The equatorial plane contains the three nitrogens of the chelating terpyridine ligand ($\text{Mn}-\text{N} = 2.301(1)$, $2.278(1)$ and $2.319(1)$ Å) and two oxygen atoms of a chelating nitrate ligand ($\text{Mn}-\text{O} = 2.366(1)$ and $2.399(1)$ Å). The bridging dca nitrile nitrogens fill the axial coordination sites, so that they are in a *trans* arrangement. The average bond distance to the axial ligands ($2.208(2)$ Å) is approximately 0.12 Å shorter than the average equatorial bond distance ($2.333(5)$ Å). The smallest chelating angle ($\text{O}(1)-\text{Mn}(1)-\text{O}(2) = 54.93(4)^\circ$) is that subtended by the nitrate ligand. A mean plane defined by the five equatorial donor atoms gave the greatest deviation as 0.1918(9) Å for N(2) (of the central pyridine ring) towards N(21). The manganese atom deviates 0.0721(6) Å away from this plane towards N(25^b). The terpyridine ligand is not

entirely planar. The angle between the mean plane of the coordination environment and that of the central pyridine ring is $26.75(7)^\circ$, being bent towards N(21). The angles the other two pyridine rings make to the central one are $17.0(1)$ and $15.0(1)^\circ$ for the planes containing N(1) and N(3) respectively.

Recently Escuer *et al.* reported a very similar complex, $[\text{Mn}(\text{dca})(\text{OAc})(\text{terpy})]_n$, which is essentially isostructural with a chelating acetate instead of the chelating nitrate.⁵⁰ It has comparable Mn–N_{dca} and Mn–N_{terpy} bond distances, but slightly shorter chelate bond distances of Mn–O_{acetate} = 2.300(4) and 2.269(4) Å. The chelating angle of the acetate is slightly larger at $57.1(1)^\circ$.

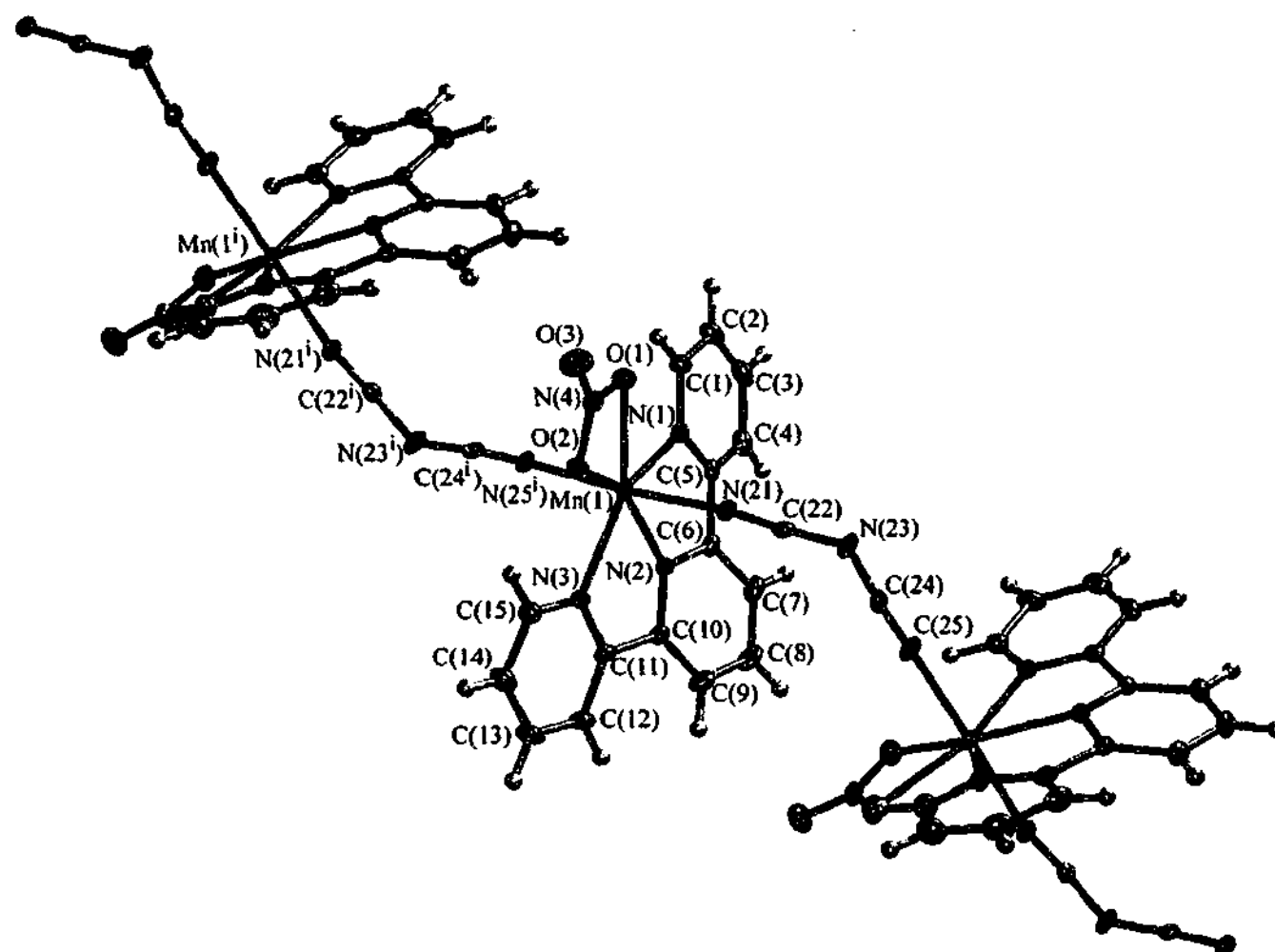


Figure 2.12 The crystal structure of $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ with atom labelling scheme (thermal ellipsoids shown at 50 % probability).

The chains propagate parallel to the $[101]$ lattice vector. The intra-chain Mn...Mn distance is $8.1713(1)$ Å. The Mn...Mn distance between adjacent chains in the a -axis direction is equal to the unit cell length a ($8.7458(1)$ Å). The chains interdigitate with adjacent chains in the ac -plane (Figure 2.13) *via* weak π - π stacking interactions, with closest separation of 3.67 Å and a pyridyl centroid...centroid distance of 3.803 Å, forming sheets. The chains also participate in weak π - π interactions, with adjacent chains in the b -axis direction, with closest separation of 3.49 Å and a pyridyl centroid...centroid distance of 3.759 Å (Figure 2.14). The Mn...Mn distance between these adjacent chains is $8.6093(5)$ Å.

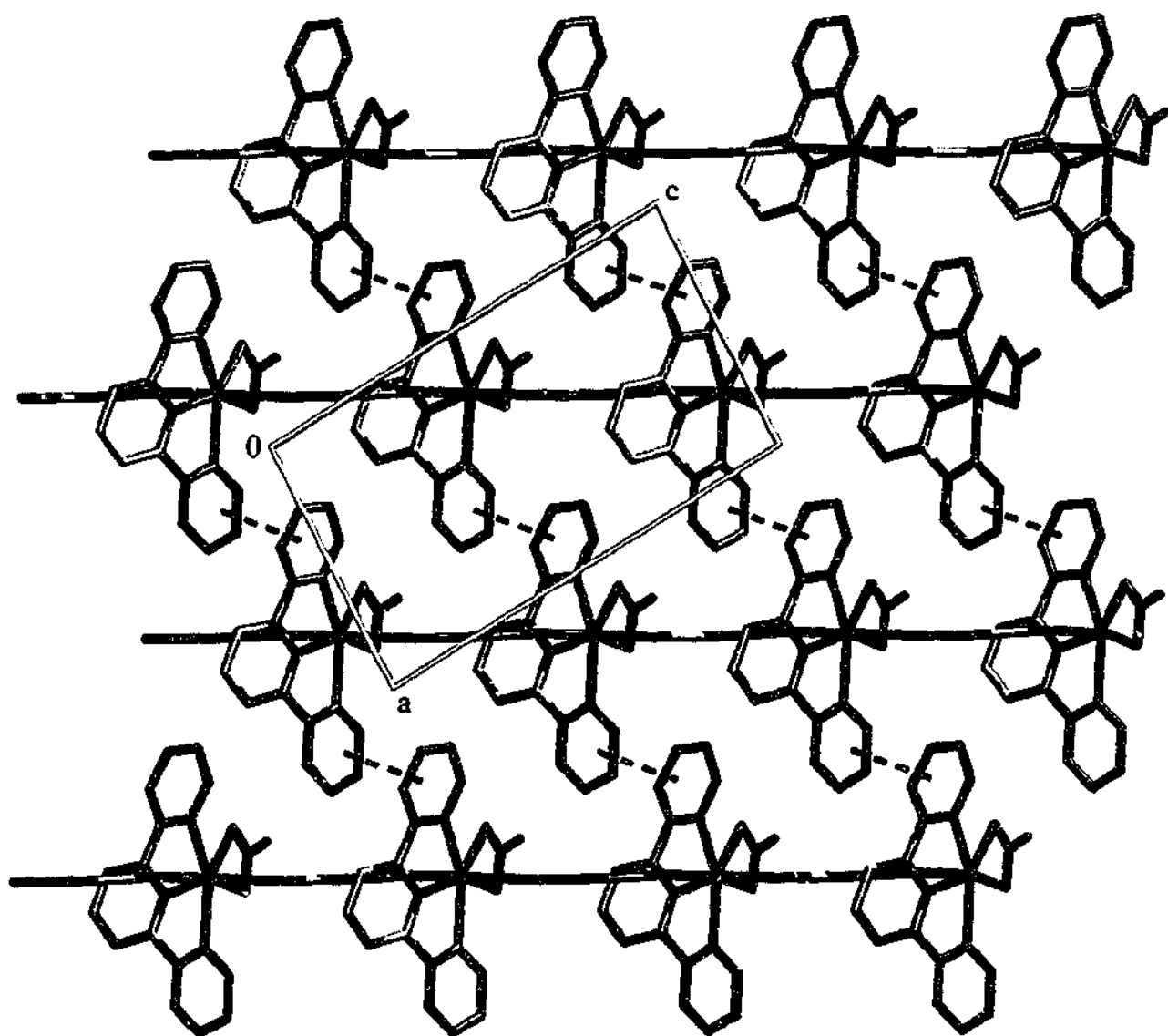


Figure 2.13 Packing diagram of $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ in the ac -plane showing weak π - π interactions (dashed green).

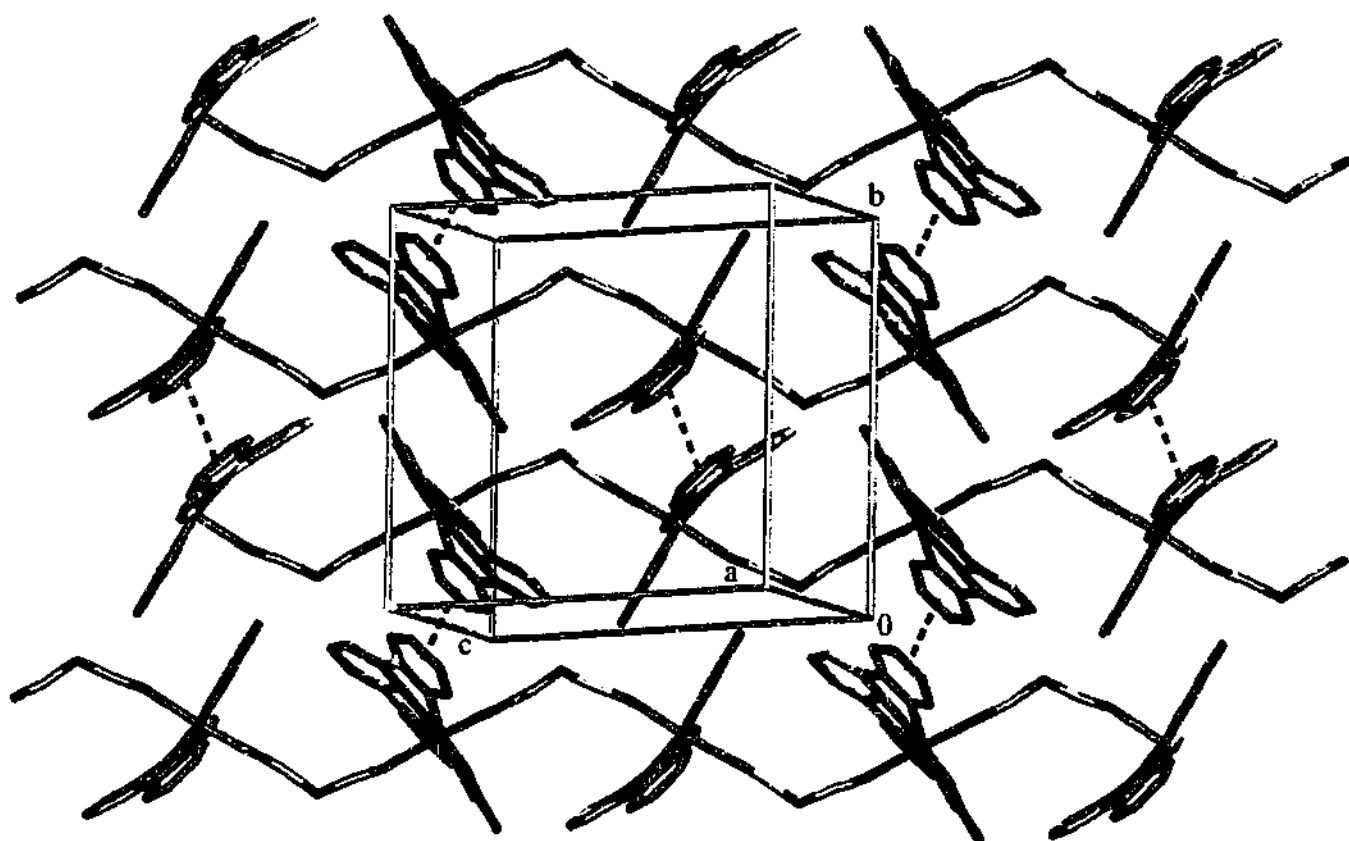


Figure 2.14 Packing diagram of $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ showing weak π - π interactions (dashed pink/red).

Table 2.3 Summary of crystal data for $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ and $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$.

Compound	$[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$	$\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$
Formula	$\text{C}_{17}\text{H}_{11}\text{MnN}_7\text{O}_3$	$\text{C}_{19}\text{H}_{13}\text{MnN}_9\text{O}$
<i>M</i>	416.27	438.32
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
<i>a</i> /Å	8.7458(1)	7.5461(2)
<i>b</i> /Å	13.7690(2)	8.7787(3)
<i>c</i> /Å	14.7029(2)	14.7849(5)
$\alpha/^\circ$		78.309(1)
$\beta/^\circ$	95.759(1)	79.923(2)
$\gamma/^\circ$		81.269(2)
<i>U</i> /Å ³	1761.60(4)	937.41(5)
<i>Z</i>	4	2
$\rho_{\text{calc}} / \text{g cm}^{-3}$	1.570	1.553
<i>T</i> /K	123(2)	123(2)
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	0.785	0.737
Index ranges	$-11 \leq h \leq 11,$ $-18 \leq k \leq 18,$ $-19 \leq l \leq 19$	$-9 \leq h \leq 9,$ $-11 \leq k \leq 11,$ $-19 \leq l \leq 19$
Completeness to $2\theta = 55^\circ/\%$	99.9	99.4
Data collected	31142	17431
Unique data (<i>R</i> _{int})	4344 (0.0543)	4241 (0.0790)
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	3281	3005
Parameters	253	279
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^(a)	0.0339, 0.0628	0.0427, 0.0762
(all data)	0.0596, 0.0692	0.0821, 0.0920
Goodness of fit, <i>S</i>	1.033	1.020

^(a) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

Table 2.4 Selected interatomic distances (Å) and angles (°) for $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$.

Mn(1)–N(1)	2.301(1)	O(1)–N(4)	1.263(2)
Mn(1)–N(2)	2.778(1)	O(2)–N(4)	1.268(2)
Mn(1)–N(3)	2.319(1)	N(4)–O(3)	1.227(2)
Mn(1)–O(1)	2.366(1)	N(21)–C(22)	1.151(2)
Mn(1)–O(2)	2.299(1)	C(22)–N(23)	1.311(2)
Mn(1)–N(21)	2.221(1)	N(23)–C(24)	1.308(2)
Mn(1)–N(25 ⁱ)	2.196(1)	C(24)–N(25)	1.151(2)
N(2)–Mn(1)–N(1)	71.02(5)	N(25 ⁱ)–Mn(1)–N(3)	89.92(5)
N(2)–Mn(1)–N(3)	70.08(5)	N(21)–Mn(1)–N(1)	90.28(5)
N(1)–Mn(1)–N(3)	140.18(5)	N(21)–Mn(1)–N(2)	83.34(5)
O(1)–Mn(1)–N(1)	84.25(4)	N(21)–Mn(1)–N(3)	93.39(5)
O(1)–Mn(1)–N(2)	153.42(4)	N(25 ⁱ)–Mn(1)–O(1)	88.30(5)
O(1)–Mn(1)–N(3)	135.50(4)	N(25 ⁱ)–Mn(1)–O(2)	90.91(5)
O(2)–Mn(1)–N(1)	139.15(4)	N(21)–Mn(1)–O(1)	87.29(5)
O(2)–Mn(1)–N(2)	148.37(4)	N(21)–Mn(1)–O(2)	86.76(5)
O(2)–Mn(1)–N(3)	80.66(4)	Mn(1)–N(21)–C(22)	167.0(1)
O(1)–Mn(1)–O(2)	54.93(4)	N(21)–C(22)–N(23)	174.6(2)
N(25 ⁱ)–Mn(1)–N(21)	175.59(5)	C(22)–N(23)–C(24)	119.4(1)
N(25 ⁱ)–Mn(1)–N(1)	89.03(5)	N(23)–C(24)–N(25)	173.5(2)
N(25 ⁱ)–Mn(1)–N(2)	100.55(5)	C(24)–N(25)–Mn(1 ⁱⁱ)	177.1(1)

Symmetry transformations: (i) $x+1/2, -y+1/2, z+1/2$; (ii) $x-1/2, -y+1/2, z-1/2$.

2.2.5 Crystal Structure of $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$

Crystallographic details for $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ are given in Table 2.3 and selected interatomic distances and angles are given in Table 2.5 (see page 115).

$\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ crystallizes in the triclinic space group $P\bar{1}$. The structure

(Figure 2.15) consists of linear zigzag chains, which propagate along the *a*-axis direction, of manganese atoms linked by single $\mu_{1,5}$ -dca bridges. The second dca is non-coordinating and links adjacent chains *via* hydrogen bonds through the nitrile nitrogens, in the *b*-axis direction, to the coordinated water on each manganese centre. Thus the overall structure consists of 2D (4,4) sheets in the *ab*-plane (Figure 2.16). Each manganese atom is six coordinate, having three sites filled by the chelating terpyridine ligand (Mn–N = 2.288(2), 2.235(2) and 2.297(2) Å), two sites are occupied by the nitrile nitrogens of two $\mu_{1,5}$ -dca ligands (Mn–N = 2.177(2) and 2.167(2) Å) and the sixth site is filled by the water molecule (Mn(1)–O(1) = 2.219(2) Å). The nitrile atom (N(25)) of one of the bridging dca ligands occupies a position in approximately the same plane as the terpyridine ligand and the other (N(21)) perpendicular to this, so that they are in a *cis* arrangement. The terpyridine ligand is more planar than it is in [Mn(dca)(NO₃)(terpy)]_n, where the angles the two outer rings make with the central ring are 5.9(1) and 3.5(1)° for the rings containing N(1) and N(3) respectively. Due to this planarity, the coordination mode of the manganese atom is distorted octahedral.

The intra-chain Mn···Mn distance is equal to the *a* unit cell length (7.5461(2) Å), being significantly shorter than the equivalent for [Mn(dca)(NO₃)(terpy)]_n. The inter-chain Mn···Mn distance along the chain of hydrogen bonds is equal to the *b* unit cell length (8.7787(3) Å). The shortest inter-chain distance, which is also the shortest metal-to-metal distance, is 6.9946(7) Å, between Mn^{II} atoms in adjacent hydrogen bonded sheets. The sheets pack in a “back-to-back” *AB* fashion (Figure 2.17).

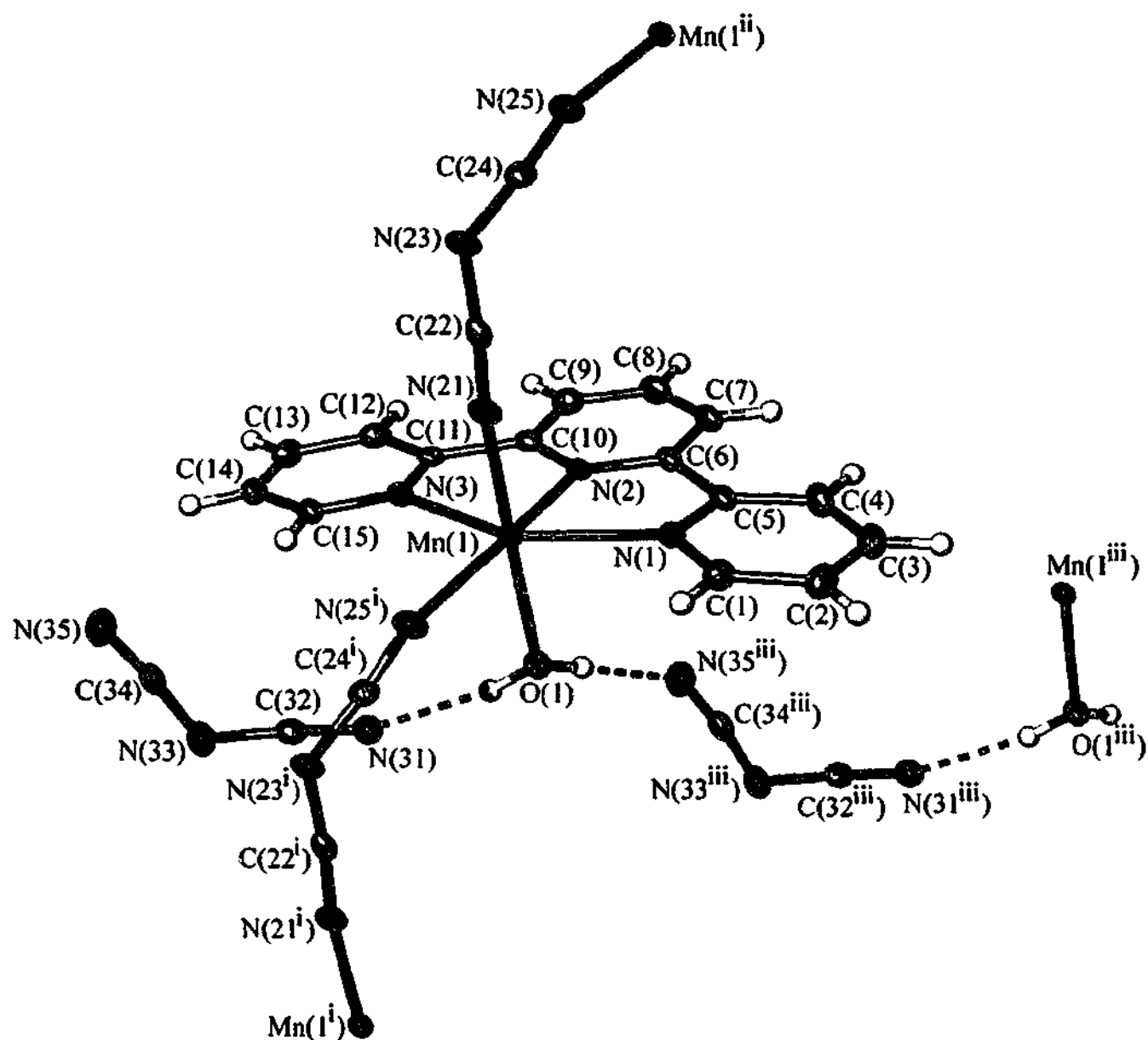


Figure 2.15 A segment of the crystal structure of $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ with atom labelling scheme (thermal ellipsoids shown at 50 % probability).

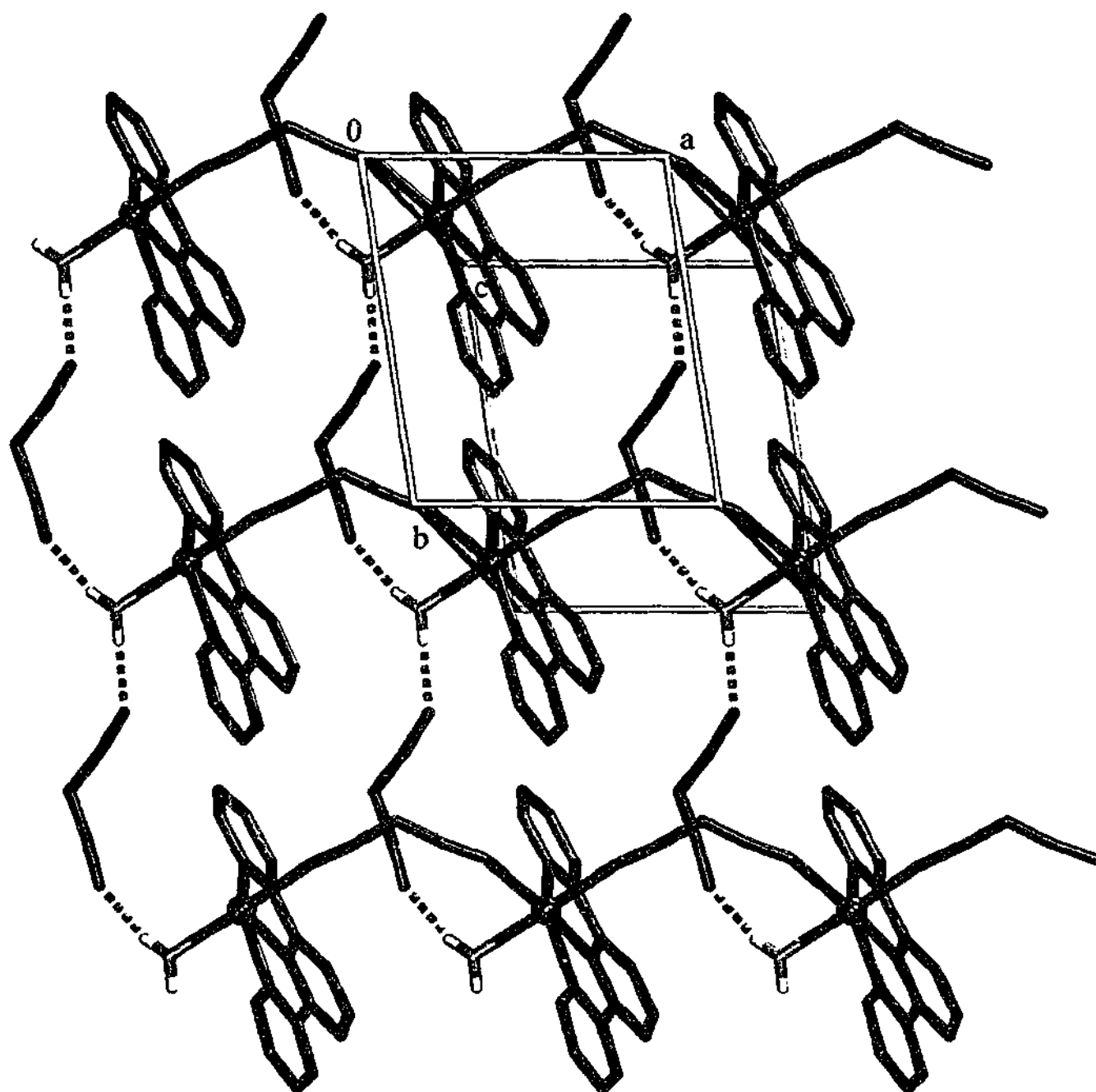


Figure 2.16 Hydrogen bonded sheets of $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ showing the water and hydrogen bonds (orange) to lattice dicyanamide ligands (blue).

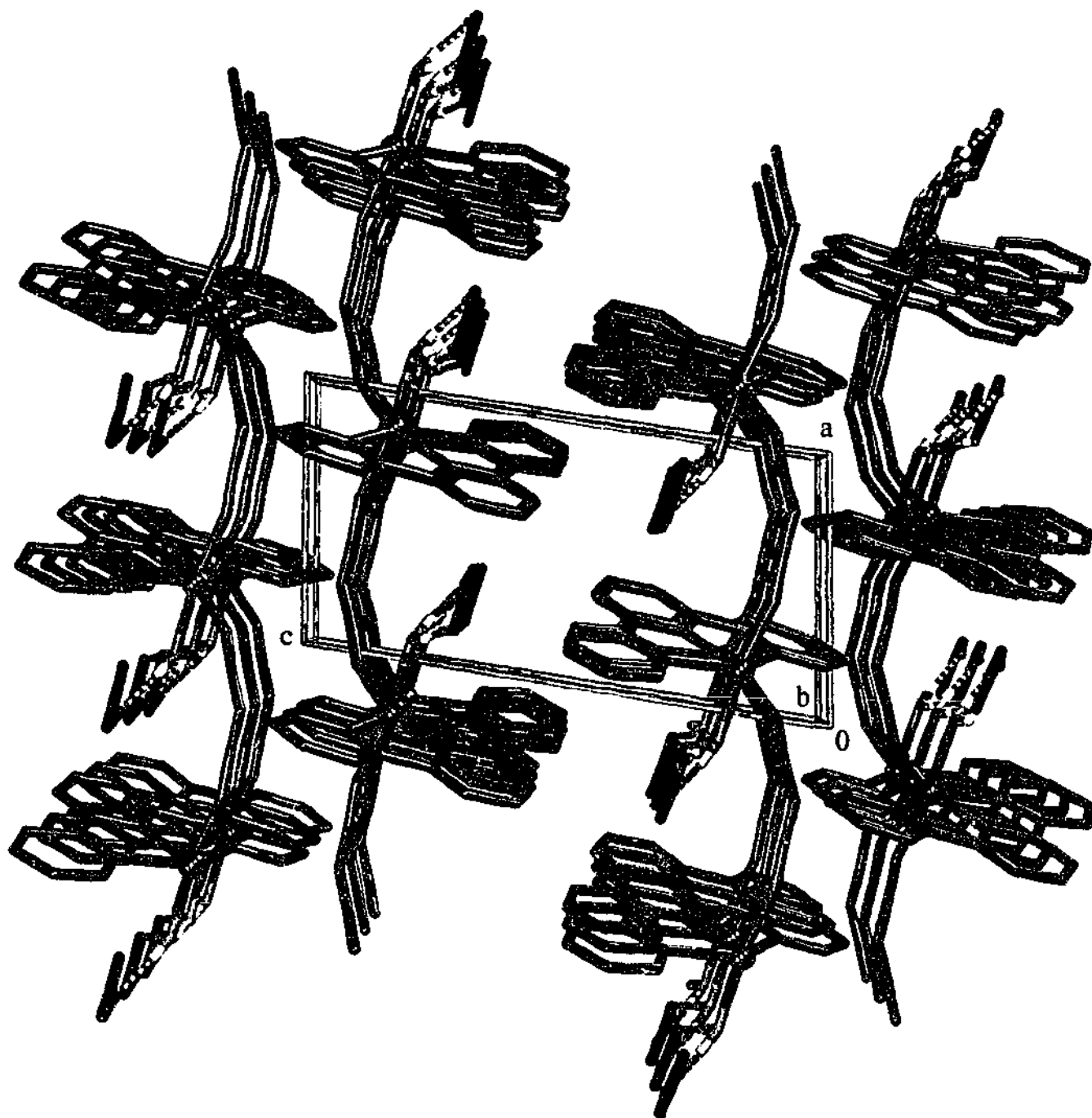


Figure 2.17 Packing diagram of $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ viewed along the b -axis direction.

Table 2.5 Selected interatomic distances (Å) and angles (°) for $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$.

Mn(1)–N(1)	2.288(2)	Mn(1)–N(21)	2.177(2)
Mn(1)–N(2)	2.235(2)	Mn(1)–N(25 ⁱ)	2.167(2)
Mn(1)–N(3)	2.297(2)	Mn(1)–O(1)	2.219(2)
N(21)–C(22)	1.154(3)	N(31)–C(32)	1.156(3)
C(22)–N(23)	1.310(3)	C(32)–N(33)	1.315(3)
N(23)–C(24)	1.302(3)	N(33)–C(34)	1.308(3)
C(24)–N(25)	1.159(3)	C(34)–N(35)	1.158(3)
N(2)–Mn(1)–N(1)	71.76(7)	N(25 ⁱ)–Mn(1)–N(2)	161.16(7)
N(2)–Mn(1)–N(3)	71.26(7)	N(25 ⁱ)–Mn(1)–N(3)	94.04(7)
N(1)–Mn(1)–N(3)	143.03(7)	N(21)–Mn(1)–O(1)	172.90(7)
O(1)–Mn(1)–N(1)	85.05(7)	N(25 ⁱ)–Mn(1)–O(1)	81.58(7)
O(1)–Mn(1)–N(2)	87.30(7)	N(21)–Mn(1)–N(25 ⁱ)	94.03(7)
O(1)–Mn(1)–N(3)	92.81(7)	Mn(1)–N(21)–C(22)	164.0(2)
N(21)–Mn(1)–N(1)	92.63(7)	N(21)–C(22)–N(23)	173.9(3)
N(21)–Mn(1)–N(2)	98.36(7)	C(22)–N(23)–C(24)	120.1(2)
N(21)–Mn(1)–N(3)	93.07(7)	N(23)–C(24)–N(25)	174.2(3)
N(25 ⁱ)–Mn(1)–N(1)	121.93(7)	C(24)–N(25)–Mn(1 ⁱⁱ)	155.8(2)
N(31)–C(32)–N(33)	174.3(2)	Mn(1)–O(1)–H(16)	121(2)
C(32)–N(33)–C(34)	119.6(2)	Mn(1)–O(1)–H(17)	117(2)
N(33)–C(34)–N(35)	173.7(3)	H(16)–O(1)–H(17)	108(3)
Hydrogen bonds			
O(1)–H(17)	0.86(2)	O(1)–H(16)	0.86(2)
H(17)···N(31)	1.98(2)	H(16)···N(35 ⁱⁱⁱ)	1.93(2)
O(1)···N(31)	2.814(3)	O(1)···N(35 ⁱⁱⁱ)	2.791(3)
O(1)–H(17)···N(31)	166(3)	O(1)–H(16)···N(35 ⁱⁱⁱ)	176(3)

Symmetry transformations: (i) $x-1, y, z$; (ii) $x+1, y, z$; (iii) $x, y+1, z$

2.2.6 Magnetism of $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ and $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ Complexes

The magnetic moment μ_{eff} versus temperature plots for $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ and $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ are shown in Figure 2.18 and Figure 2.19, respectively. The magnetic properties of the two complexes are very similar and indicative of overall weak antiferromagnetic coupling. At 300 K, in a field of 1 T, $\mu_{\text{per Mn}} = 5.90 \mu_{\text{B}}$ and $5.80 \mu_{\text{B}}$ ($\chi_{\text{M}}T = 4.35$ and $4.20 \text{ cm}^3\text{mol}^{-1}\text{K}$) for $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ and $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ respectively. The moments decrease very gradually to $5.85 \mu_{\text{B}}$ and $5.72 \mu_{\text{B}}$ ($\chi_{\text{M}}T = 4.27$ and $4.09 \text{ cm}^3\text{mol}^{-1}\text{K}$) at around 50 K, then more rapidly to reach 4.57 and $3.58 \mu_{\text{B}}$ ($\chi_{\text{M}}T = 2.61$ and $1.60 \text{ cm}^3\text{mol}^{-1}\text{K}$) at 2 K. This rapid decrease arises from a combination of antiferromagnetic coupling and zero-field splitting of the ${}^6\text{A}_{1\text{g}}$ ions.⁵¹ Since the latter is expected to be weaker than the spin coupling it is not included in the analysis.

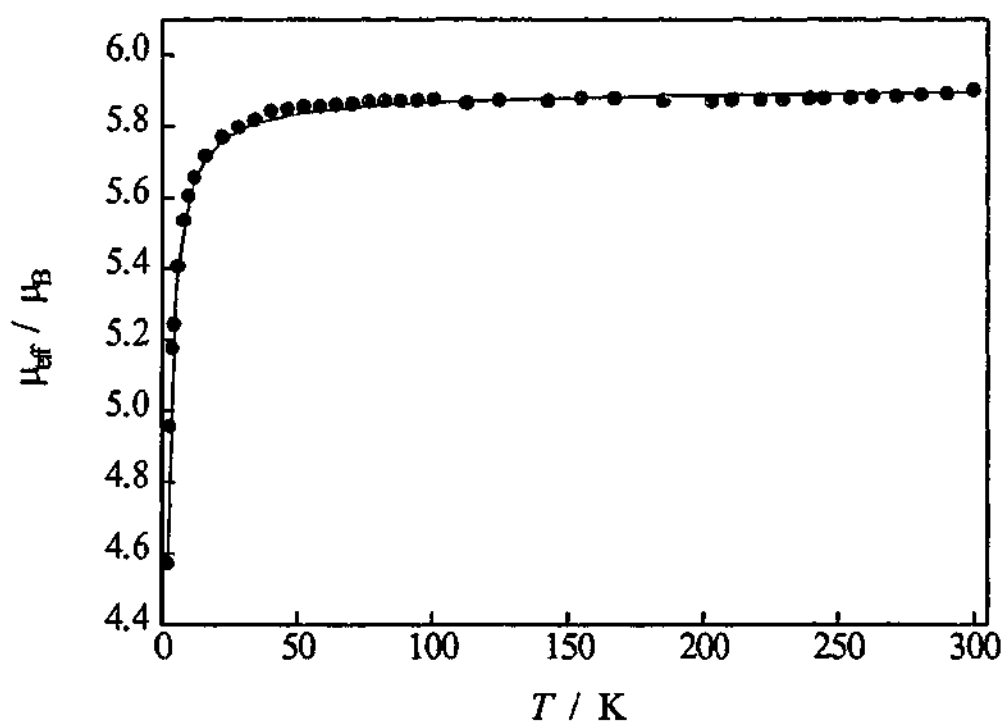


Figure 2.18 Plot of μ_{eff} versus T in a field of $H = 1$ T for $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$, the solid line shows the best-fit theoretical curve (see text).

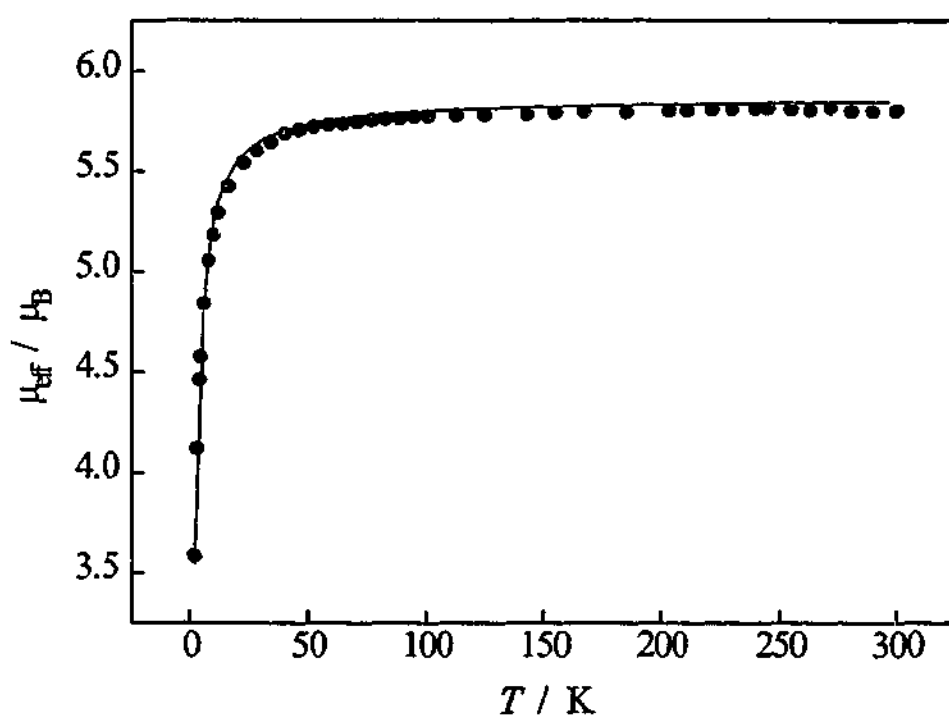


Figure 2.19 Plot of μ_{eff} versus T in a field of $H = 1$ T for $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$, the solid line shows the best-fit theoretical curve (see text).

The magnetic data were fitted to a 1D Heisenberg chain model ($S = 5/2$ $\{-2JS_iS_j\}$) derived by Fisher, given by Equation 2.1,⁵² yielding the best fit parameters shown in Table 2.6. Those derived by Escuer *et al.* are given for comparison. The values of g and J are similar for both determinations. The value of J for $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ (-0.06 cm^{-1}) is approximately half that for $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ (-0.13 cm^{-1}). This may be due to hydrogen bonding interactions between the chains, thus increasing the overall antiferromagnetic coupling.

$$\chi = \frac{N\beta^2 g^2}{3kT} S(S+1) \left(\frac{1+u}{1-u} \right) \quad \text{Equation 2.1}$$

$$u = \coth \frac{-2JS(S+1)}{kT} - \frac{2JS(S+1)}{kT}$$

Table 2.6 Best-fit parameters g and J for compounds $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ and $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ using the Fisher chain model⁵² with those reported by Escuer *et al.*⁴⁶ for the same compounds for comparison.

Compound	This work		Escuer <i>et al.</i> ^(a)	
	g	J / cm^{-1}	g	J / cm^{-1}
$[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$	1.99	-0.06	2.00(1)	-0.06(1)
$\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$	1.98	-0.13	2.00(1)	-0.10(1)

^(a) Figures reported by Escuer *et al.* divided by 2 for comparison as that group used the Hamiltonian $H = -JS_iS_j$

2.3 Conclusions

The new hydrated phase $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$, displays a fascinating rare 3D self-penetrated structure containing both tridentate ($\mu_{1,3}$) and bidentate ($\mu_{1,5}$) dicyanamide. The bidentate dicyanamide is further hydrogen bonded to a coordinated water molecule, thus forming a pseudo 3-connecting ligand. $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$, like its parent non-hydrated phase α - $[\text{Mn}(\text{dca})_2]$, is a spin-canted antiferromagnet with a T_N value of 6.3 K. This leads us to believe that this compound is responsible, as a trace impurity, for a weak transition, at 6 K, seen in the variable temperature magnetization plot of the parent species, α - $[\text{Mn}(\text{dca})_2]$, $T_N = 16$ K.⁴

The two complexes $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ and $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ were synthesised and structurally elucidated prior to them being reported by Escuer *et al.*⁴⁶ The structures of each are similar, in that they both consist of linear zigzag chains of manganese(II) atoms linked by $\mu_{1,5}$ -dca ligands. In the structure of $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$

weak π - π interactions between the terpy ligands of adjacent chains that influence the packing of the chains. In the structure of $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ non-coordinated dicyanamide ligands hydrogen bond to the coordinated water molecules, thus forming hydrogen-bonded 2D (4,4) sheets. They were initially synthesised in the same reaction using conditions similar to those used separately for the synthesis of $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$.

The long-range magnetic order shown by $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ and the lack of it observed in $[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$ and $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ is consistent with our understanding that bidentate dicyanamide, bridging through both the nitrile nitrogens ($\mu_{1,5}$ -dca), is a very poor super-exchange pathway and complexes containing only these links are unlikely to display long-range magnetic order. Escuer *et al.* recently published MO calculations that go towards explaining this, by comparing orbital interactions with the more efficient exchange mediator, $\mu_{1,3}$ -azide. From the presence of long-range order in the rutile-like α - $[\text{M}(\text{dca})_2]$ and $[\text{M}(\text{dca})(\text{tcm})]_n^5$ (excluding Cu in the dca/tcm compound), and $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ species, it is believed tridentate dicyanamide, bridging through both nitrile nitrogens and the amide nitrogen, is important for the occurrence of order. The Jahn-Teller elongation of the $\text{M}-\text{N}_{\text{amide}}$ bond in the copper complexes, which weakens magnetic exchange, the lack of magnetic order in the $[\text{Cu}(\text{dca})(\text{tcm})]$ compound,⁵ and the occurrence of ferromagnetic order in α - $[\text{Cu}(\text{dca})_2]$ at the very low temperature of $T_c = 1.7 \text{ K}^{53}$ may back this assertion. However, recent results for the compounds $(\text{Ph}_4\text{E})[\text{Ni}(\text{dca})_3]$, $\text{E} = \text{P}$ and As ,¹⁵ β - $[\text{Co}(\text{dca})_2]$,¹⁴ and α - $[\text{Mn}(\text{dca})_2(\text{pyz})]^{17,18}$ have cast doubt on this conclusion. These compounds display long-range magnetic order at 20 K, 9 K and 2.7 K respectively, yet the structures of each contain dicyanamide present only in the $\mu_{1,5}$ -dca coordination mode. Clearly the exchange pathways of bridging co-ligands also play an important role and future work yet needs to be done to explain these observations.

2.4 Experimental

2.4.1 Synthesis of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$

Method A: $\text{Mn}(\text{dca})_2$ (30 mg, 0.16 mmol) was dissolved in 5 mL of hot methanol. On cooling this solution to room temperature, 5 mL of ethanol was added. Crystals of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ suitable for X-ray diffraction were afforded by slow evaporation of this solution over a period of several months. The majority of crystals were triangular in habit and insensitive to solvent loss. I.R. (cm^{-1} , Nujol): 3611 vw,sh, 3577 vw, 3521 w, 3389 w,br, 3113 vw, 2310 s, 2258 s, 2185 s, 1626 m, 1359 m, 1326 m, 955 vw, 937 vw, 679 vw, 668 vw. Anal. (%): Found: C, 23.6; H, 0.8; N, 41.3. Calculated for $\text{C}_4\text{H}_2\text{MnN}_6\text{O}$: C, 23.4; H, 1.0; N, 41.0.

Method B: Aqueous solutions (5 mL each) of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.362 g, 1.0 mmol) and $\text{Na}(\text{dca})$ (0.178 g, 2.0 mmol) were combined. Slow evaporation over 2 weeks yielded several crystal aggregates and a small number of mainly irregularly shaped single crystals (some were of triangular habit) that were filtered and washed with ethanol. Yield 0.082 g, 40 %. I.R. (cm^{-1} , Nujol): 3520 m, 3388 m,br, 3222 w,sh, 3111 w, 2309 s, 2257 s, 2183 s, 1625 s, 1359 s, 1324 s, 1057 vw, 1006 vw, 956 w, 938 w, 681 w,sh, 667 w,sh. Anal. (%): Found: C, 23.5; H, 0.8; N, 41.4. Calculated for $\text{C}_4\text{H}_2\text{MnN}_6\text{O}$: C, 23.4; H, 1.0; N, 41.0. The powder XRD pattern matches that calculated from the crystal structure data.

2.4.2 Synthesis of $[\text{Mn}(\text{dca})_2(\text{NO}_3)(\text{terpy})]_n$

A methanolic solution (5 mL) of terpyridine (0.117 g, 0.5 mmol) was added to a methanolic solution (20 mL) of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.126 g, 0.5 mmol) and a pale yellow solution formed immediately. A methanolic solution (5 mL) of $\text{Na}(\text{dca})$ (1.0 mmol, 0.089 g) was then added to this yellow solution. After about three hours a yellow, crystalline solid had formed. It was subsequently collected by vacuum filtration, washed briefly with

methanol and dried in air. Yield 0.14 g, 66 %. I.R. (cm^{-1} , Nujol): 3583w, 3093vw, 2294s, 2244s, 2177s, 1774vw, 1741vw, 1595m, 1578m, 1470s, 1438s, 1404m, 1349s, 1308s, 1240w, 1185w, 1160w, 1096w, 1074vw, 1053w, 1040w, 1012m, 934vw, 909vw, 833vw, 818w, 799w, 774s, 752vw, 738w, 652m, 634m. Anal. (%): Found: C, 49.2; H, 2.5; N, 23.6. Calc. for $\text{C}_{17}\text{H}_{11}\text{MnN}_7\text{O}_3$: C, 49.0; H, 2.7; N, 23.6.

2.4.3 Synthesis of $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$

Part A: Synthesis of $\text{Mn}(\text{terpy})\text{Cl}_2$

Terpyridine (0.233 g, 1.0 mmol) was added to a hot stirred solution of MnCl_2 (0.126 g, 1.0 mmol) in ethanol (20 mL). A yellow precipitate formed immediately. The resultant mixture was stirred and heated for a further 15 minutes. The solid was filtered hot and washed briefly with ethanol and dried with ether (2×10 mL). Yield 0.34 g, 96 %, assuming the above formulation. This solid was used in Part B.

Part B: Synthesis of $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$

A solution of $\text{Na}(\text{dca})$ (0.11 g, 1.2 mmol) in methanol/water (5 mL/1 mL) was added to a stirred suspension of $\text{Mn}(\text{terpy})\text{Cl}_2$ (0.172 g, 0.48 mmol, from Part (a)) in methanol (7 mL). 3 mL of water was added to this suspension after which the $\text{Mn}(\text{terpy})\text{Cl}_2$ had largely dissolved. The solution was filtered to remove a small amount of undissolved residue. After one day many pale yellow block-like crystals had formed. The mother liquor was decanted into another vessel. The crystals were washed with acetone and dried with ether. Yield 50 mg, 23 %. I.R. (cm^{-1} , Nujol): 3599vw, 3296s, 3096vw, 3036vw, 2312s, 2250s, 2208s, 2166s, 2143s, 1644w, 1598m, 1581m, 1572m, 1478m, 1452s, 1440s, 1407m, 1366s, 1323s, 1246w, 1190w, 1164m, 1102w, 1074vw, 1052vw, 1021m, 1012m, 976vw, 938vw, 912vw, 777s, 754vw, 736w, 652m, 638m. Anal. (%): Found: C, 52.2; H, 3.0; N, 28.8. Calc. for $\text{C}_{19}\text{H}_{13}\text{MnN}_9\text{O}$: C, 52.1; H, 3.0; N, 28.8.

2.4.4 X-Ray Crystallography of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$, $[\text{Mn}(\text{dca})_2(\text{NO}_3)(\text{terpy})]_n$ and $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$

Data were collected using a Nonius KappaCCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), using ϕ and ω rotations with 1° frames. Integration was carried out by the program DENZO-SMN,⁵⁴ and data were corrected for Lorentz polarisation effects and for absorption using the program SCALEPACK.⁵⁴ Solutions were obtained by direct methods followed by successive Fourier difference methods using SHELXS 97⁵⁵ for $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ and teXsan⁵⁶ for $[\text{Mn}(\text{dca})_2(\text{NO}_3)(\text{terpy})]_n$ and $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$, while the final full matrix least squares refinements on F_{obs}^2 were performed using SHELXL 97⁵⁵ with the aid of the graphical interface program X-SEED.⁵⁷ All non-hydrogen atoms were refined anisotropically.

For $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ the hydrogen atoms were neither located nor assigned. Atoms C(3), O(1) and N(5) were refined at half occupancy due to the disorder over the mirror plane and O(1) and N(5) were constrained to have identical x , y , z and U_{ij} parameters. The structure was refined as a racemic twin. The structure of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ was also solved in $P1$, which indicated that the disorder was present even in the absence of any crystallographically imposed symmetry.

For $[\text{Mn}(\text{dca})_2(\text{NO}_3)(\text{terpy})]_n$ and $\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$ all terpy hydrogen atoms were assigned to calculated positions with isotropic thermal parameters 1.2 times the U_{eq} of the adjoining carbon atom. The water hydrogen atoms of the latter structure were located in the Fourier difference map and refined isotropically with the O–H bonds distances restrained to be $0.84(2) \text{ \AA}$ with the DFIX instruction.⁵⁸

2.4.5 X-Ray Powder Diffraction of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$

Powder X-ray diffraction data for $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ were collected by Mr. Rod Mackie (School of Physics and Materials Engineering, Monash University, Clayton) on a Scintag Automated Powder Diffractometer using a $\text{Cu-K}\alpha$ monochromatic radiation source ($\lambda = 154.059 \text{ pm}$), a solid state Ge detector, 2 mm divergence slit and a 3 mm receiving slit at room temperature. The programs Crystal Diffract⁵⁹ and Unit Cell⁶⁰ were used by Dr. Stuart Batten (School of Chemistry, Monash University, Clayton) to confirm that the single crystal was representative of the bulk sample.

2.5 References

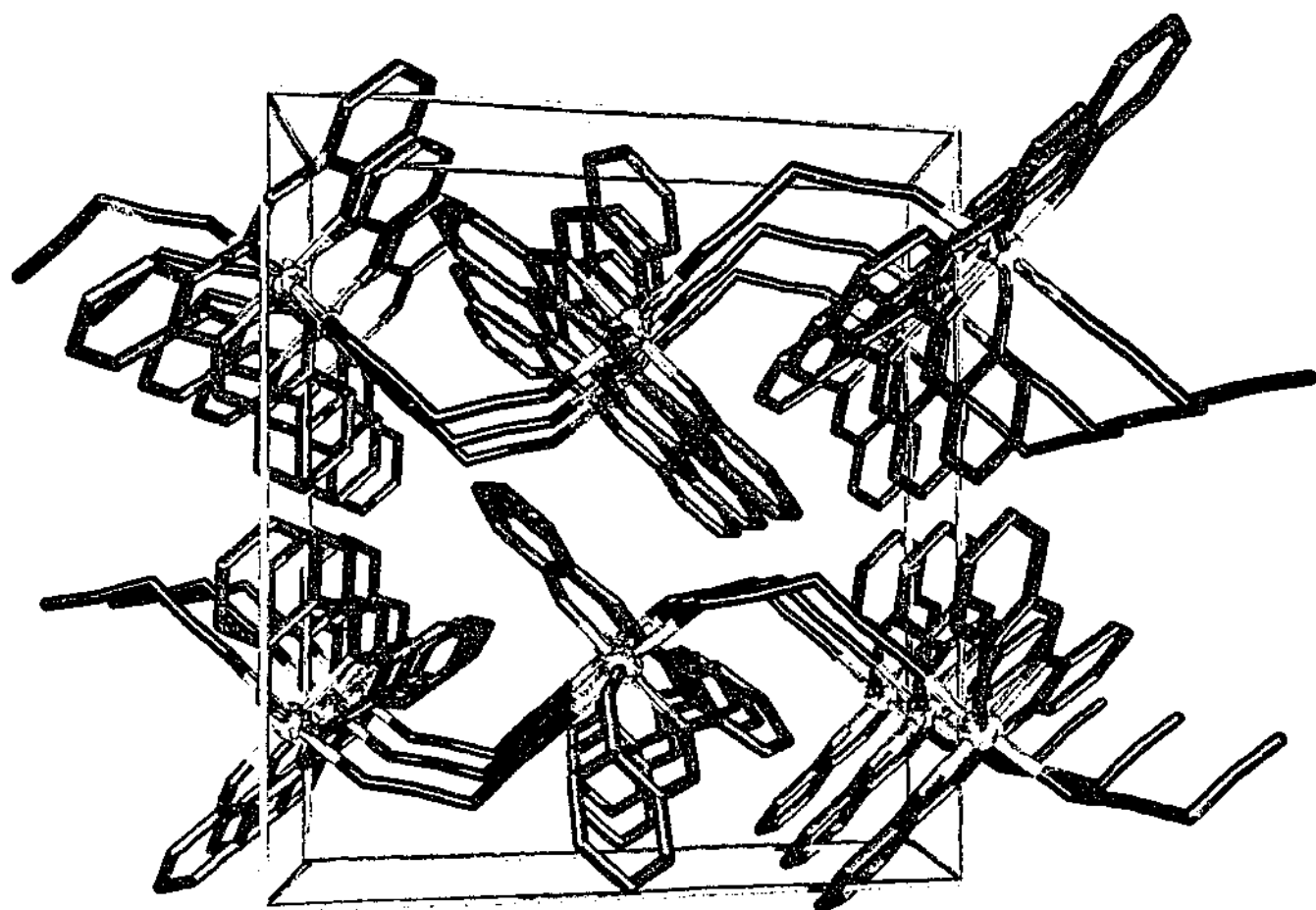
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**CHAPTER 3: 1D MANGANESE(III) AND
IRON(III) COORDINATION POLYMERS
CONTAINING SCHIFF-BASE LIGANDS AND
DICYANAMIDE**

3.1 Introduction

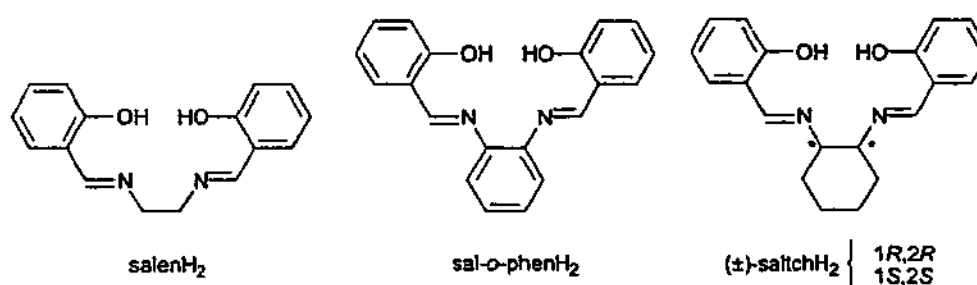
Studies of polymeric coordination complexes, and how the bridging ligands affect magnetic coupling and long-range order, have increased rapidly in recent years. The bridging ligands CN^- , $\text{C}_2\text{O}_4^{2-}$ and RCO_2^- ¹⁻¹¹ and poly-cyano ligands such as dicyanamide ($\text{N}(\text{CN})_2^-$, dca)^{3,12,13} have received most attention. Since the discovery, by our group and others, that the rutile-like binary complexes of dicyanamide, $\alpha\text{-[M(dca)}_2\text{)]}$, $\text{M}^{\text{II}} = \text{Cr, Mn, Fe, Co and Ni}$,^{12,14,15} display long-range magnetic order, we have been undertaking a wide investigation of molecule-based magnetic materials containing terminal and bridging co-ligands and the dicyanamide ligand.^{12,14,16-25} The present study of ternary transition metal dicyanamide networks containing tetradentate Schiff-base ligands is part of this investigation. It complements the results, described in Chapter 4, with novel dicyanamide chiral 3D network complexes with the acetylacetone derived Schiff-base ligands, acenH₂ (*N,N'*-ethylenebis(acetylacetoneimine)) and $(\pm)\text{-actchH}_2$ ($(\pm)\text{-N,N'-trans-1,2-cyclohexanebis(acetylacetoneimine)}$). Interestingly, the networks containing the achiral Schiff-base ligand are chiral and the crystals are spontaneously resolved.

Metal Schiff-base complexes continue to attract attention in magnetochemical work, either in their own right, or as building blocks in heterometallic molecule based magnetic materials. For instance, Floriani and Miyasaka *et al.* have incorporated metal-Schiff-base moieties into 'molecular' Prussian-blue CN^- bridged magnetic materials. For example, they have combined Schiff-base ligands and hexacyanometallates in the complex $[\text{NEt}_4][\text{Mn(5-Cl-salen)}]_2[\text{Fe(CN)}_6]$, which consists of $[\text{Mn(5-Cl-salen)}]^+$ moieties linked with ferricyanide forming a 2D sheet structure. This complex is a metamagnet with $T_N = 4.0 \text{ K}$.²⁶ This is one of many such studies by this group; $[\text{Fe(salen)}]^+$ has also been

employed.²⁷ More recently Miyasaka *et al.* also reported using Mn^{III} Schiff-base dimers as possible components in magnetic materials as the dimers display ferromagnetic coupling.²⁸

Outside of their magnetochemical interest, manganese(III/IV) Schiff-base complexes are also relevant as models for the water oxidation complex (WOC) of photosystem II (PS II) of green plants and cyanobacteria.²⁹⁻³³ Homo-chiral manganese(III) Schiff-base complexes have been used extensively as enantioselective catalysts for the epoxidation of olefins.³⁴⁻³⁷ The best known of these is Jacobsen's catalyst.³⁸ In addition, chiral Schiff-base complexes have also been demonstrated to display non-linear optical properties.^{39,40}

Described in this chapter are six new linear chain complexes of the general formula, $[M(\text{Schiff-base})(\text{dca})]_n$, $M^{\text{III}} = \text{Mn}$ and Fe . These are some of the first trivalent M^{III} -dca complexes to be reported, and the first to be structurally characterised.⁴¹ The tetradentate Schiff-base ligands chosen for this study were salenH₂ (*N,N'*-ethylenebis(salicylideneimine)), sal-*o*-phenH₂ (*N,N'*-*o*-phenylenebis(salicylideneimine)) and (±)-saltchH₂ ((±)-*N,N'*-*trans*-cyclohexanebis(salicylideneimine)) (Scheme 3.1). Initially salenH₂ was chosen, followed by two variations of salenH₂. By selecting the ligand sal-*o*-phenH₂, we could observe the effect that introducing the rigidity of the phenyl ring, as the bridge component of the Schiff-base ligand, may have on the structural and magnetic properties. The (±)-saltchH₂ ligand also possesses a six membered ring as the bridge component, however, it is flexible like salenH₂ and is also a chiral ligand, similar to that in Jacobsen's catalyst and related complexes. However, in this case a racemic mixture of (±)-saltchH₂ was employed.



Scheme 3.1 Schiff-base ligands salenH_2 , $\text{sal-}o\text{-phenH}_2$ and $(\pm)\text{-saltchH}_2$.

Several $[\text{M}(\text{salen})(\mu\text{-X})]_n$ linear chain 1D complexes have been reported previously, where $\text{M}^{\text{III}} = \text{Mn}$ or Fe and X is a short anionic bridging ligand including OAc^- ,⁴²⁻⁴⁵ NO_3^- ,⁴⁶ N_3^- ,⁴⁷ or CN^- (which has alternating high and low spin Mn^{III} ions)⁴⁸ or a longer bridging ligand such as $\text{N-4-pyridylglycinato}$, $4\text{-(pyridylthio)acetato}$,⁴⁹ or $1,4\text{-bis(1-imidazolyl)butane}$.⁵⁰ Such compounds are generally weakly exchange coupled, magnetic ordering not being a common feature. However, Rajasekharan *et al.* very recently reported the 1D helical polymer $[\text{Mn}^{\text{III}}(\text{salpn})(\text{NCS})]_n$ (where $\text{salpnH}_2 = \text{N,N'-Bis(salicylidene)-1,3-diaminopropane}$), which exhibits spin-canted antiferromagnetic ordering below 7 K.⁵¹

During the writing of this thesis, the structures and some physical properties of the compounds $[\text{M}(\text{salen})(\text{dca})]_n$, $\text{M}^{\text{III}} = \text{Mn}$ and Fe , were reported by Shi *et al.*⁵² However, there are serious shortcomings in this paper. They reported markedly different variable temperature magnetism of the Fe^{III} complex compared to our observations (*vide infra*) and proposed that it contains low-spin Fe^{III} with strong antiferromagnetic coupling. They measured electronic spectra and cyclic voltammetry on solutions of the complexes. As these complexes are polymeric, by necessity they must break up to dissolve and are thus no longer possess the reported structures in solution.

3.2 Synthesis and Characterisation of $[M(L)(dca)]_n$ Complexes;

$M^{III} = Mn$ and Fe ; $LH_2 = salenH_2$, $sal-o-phenH_2$ and $(\pm)$ -

$saltchH_2$

Reaction of $salenH_2$ and sodium dicyanamide with manganese(II) nitrate in air in a molar ratio of 1:1:1 in methanol led to the formation of $[Mn(salen)(dca)]_n$. Reaction of $Fe(salen)Cl$ with sodium dicyanamide in methanol in a molar ratio of 1:1 in methanol led to the formation of $[Fe(salen)(dca)]_n$. $[Mn(sal-o-phen)(dca)]_n$ was prepared in an analogous reaction to the synthesis of $[Mn(salen)(dca)]_n$, replacing $salenH_2$ with $sal-o-phenH_2$, and $[Fe(sal-o-phen)(dca)]_n$ was prepared in a similar reaction to $[Mn(sal-o-phen)(dca)]_n$, replacing the manganese(II) salt with iron(II) tetrafluoroborate. Reaction of $(\pm)$ - $saltchH_2$ with sodium dicyanamide and manganese(II) nitrate in a molar ratio of 1:2:1 in a methanol/acetone mixture led to the formation of $[Mn((\pm)-saltch)(dca)]_n$. $[Fe((\pm)-saltch)(dca)]_n$ was prepared by a similar reaction to the synthesis of $[Mn((\pm)-saltch)(dca)]_n$ except the manganese(II) salt was replaced by iron(II) tetrafluoroborate and a methanol/DMF solvent mixture was used. No base was needed to deprotonate the $salenH_2$, $sal-o-phenH_2$ or $(\pm)$ - $saltchH_2$ ligands.

As indicated above, Shi *et al.*⁵² very recently reported the synthesis of $[Mn(salen)(dca)]_n$ and $[Fe(salen)(dca)]_n$ from $Mn(OAc)_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$, respectively. In each case the $salenH_2$ ligand was formed *in situ* by reaction of the metal salt with salicylaldehyde and ethylenediamine. Problems with by-products ($Fe(salen)Cl$) in the synthesis of the Fe^{III} complex were also reported. By using $salenH_2$ as a reagent in the present work, rather than forming it *in situ*, or using $Fe(salen)Cl$ itself, to form the $[M(salen)(dca)]_n$ complexes, has reduced the potential of such by-product formation.

Some characteristic vibrational absorptions of the dicyanamide ligand and Schiff-base ligands for the $[M(\text{Schiff-base})(\text{dca})]_n$ complexes are listed in Table 3.1. It can be seen that the selected dicyanamide vibrations have lower wavenumber values for the $[\text{Mn}(\text{Schiff-base})(\text{dca})]_n$ complexes compared to the $[\text{Fe}(\text{Schiff-base})(\text{dca})]_n$ complexes (for equivalent Schiff-base). These values are consistent with bidentate dicyanamide ligands bridging through both the nitrile nitrogens in the $\mu_{1,5}$ -dca mode. There are no significant differences in the $[\text{M}(\text{salen})(\text{dca})]_n$ $\nu_{\text{as}}(\text{C}\equiv\text{N})$ or $\nu_{\text{s}}(\text{C}\equiv\text{N})$ values here compared to those reported by Shi *et al.*⁵²

Table 3.1 Selected assigned dicyanamide and Schiff-base IR absorptions.

Complex	dicyanamide			Schiff-base	
	$\nu_{\text{as}}(\text{C}-\text{N}) + \nu_{\text{s}}(\text{C}-\text{N})$	$\nu_{\text{as}}(\text{C}\equiv\text{N})$	$\nu_{\text{s}}(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$
$[\text{Mn}(\text{salen})(\text{dca})]_n$	2285	2226	2162	1622	1601
$[\text{Fe}(\text{salen})(\text{dca})]_n$	2317	2246	2179	1625	1598
$[\text{Mn}(\text{sal-}o\text{-phen})(\text{dca})]_n$	2284	2230	2161	1605	1576
$[\text{Fe}(\text{sal-}o\text{-phen})(\text{dca})]_n$	2316	2249	2174	1605	1579
$[\text{Mn}((\pm)\text{-saltch})(\text{dca})]_n$	2278	2229	2164	1620	1598
$[\text{Fe}((\pm)\text{-saltch})(\text{dca})]_n$	2315	2248	2182	1618	1594

3.3 Crystal Structures of $[M(\text{L})(\text{dca})]_n$ Complexes; $M^{\text{III}} = \text{Mn}$ and Fe ; $\text{LH}_2 = \text{salenH}_2$, $\text{sal-}o\text{-phenH}_2$ and $(\pm)\text{-saltchH}_2$

Crystal data for the $[M(\text{Schiff-base})(\text{dca})]_n$ complexes are summarised in Table 3.2. The structures of these complexes are all very similar. They consist of linear 1D zigzag chains of $[M(\text{Schiff-base})]^+$ moieties linked by $\mu_{1,5}$ -dca ligands *via* the nitrile nitrogens. In each case the high-spin M^{III} atom is coordinated in a near octahedral

environment by the imine nitrogens, (M–N = 1.991(2) - 2.024(3) Å (Mn), and 2.105(2) - 2.127(2) Å (Fe)), and phenolate oxygens, (M–O = 1.872(1) - 1.888(2) Å (Mn), 1.880(1) - 1.902(2) Å (Fe)), of the appropriate Schiff-base ligand in the equatorial plane and by two nitrile nitrogens of two bridging dicyanamide ligands in the axial positions (M–N = 2.252(3) - 2.297(2) Å (Mn), and 2.125(2) - 2.167(2) Å (Fe)). These distances are comparable to other M^{III} salen complexes. For instance, in [M^{III}(salen)(OAc)]_n, M^{III} = Mn,⁴⁵ and Fe,⁴⁴ the equatorial M^{III}–N_{imine} distances are 1.989 and 2.108(3) Å for Mn and Fe, respectively, and M^{III}–O_{phenolate} distances are 1.888 and 1.894(2) Å for Mn and Fe, respectively. In [Mn^{III}(salen)(μ_{1,3}-N₃)]_n⁴⁷ the Mn^{III}–N_{azide} distances are 2.280(2) and 2.334(2) Å, where the latter distance is significantly longer than the Mn^{III}–N_{dca} distances of the present structures.

In Chapter 4 the structures of [M^{II}(L)(dca)₂], M^{II} = Mn and Fe; L = acenH₂ and (±)-actchH₂, are reported. The M^{II}–N_{dca} distances range from 2.204(4) to 2.248(2) Å (Mn), and 2.112(4) to 2.200(4) Å (Fe). The M–N_{dca} distances for the Mn^{II} complexes are shorter than those for the Mn^{III} complexes presented here (although they do overlap within error) because the latter show Jahn-Teller elongation in the axial Mn^{III}–N_{dca} bonds (as expected for a d⁴ ion in near octahedral geometry). The M–N_{dca} distances for the present Fe^{III} complexes are, however, within the ranges of those distances for the Fe^{II} complexes in Chapter 4.

The asymmetric unit for each complex consists of one octahedral M^{III} atom, one Schiff-base ligand and one dicyanamide ligand.

Table 3.2 Crystal data for the [M(Schiff-base)(dca)]_n complexes.

Complex	[M(salen)(dca)] _n		[M(sal- <i>o</i> -phen)(dca)] _n		[M((±)-saltch)(dca)] _n	
	Mn	Fe	Mn	Fe	Mn	Fe
Formula	C ₁₈ H ₁₄ MnN ₅ O ₂	C ₁₈ H ₁₄ FeN ₅ O ₂	C ₂₂ H ₁₄ MnN ₅ O ₂	C ₂₂ H ₁₄ FeN ₅ O ₂	C ₂₂ H ₂₀ MnN ₅ O ₂	C ₂₂ H ₂₀ FeN ₅ O ₂
<i>M</i>	387.28	388.19	435.32	436.23	441.37	442.28
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Pbca</i>	<i>Pbca</i>	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>a</i> /Å	11.2285(3)	11.3538(2)	7.5424(1)	7.7017(1)	8.6890(1)	8.7045(2)
<i>b</i> /Å	16.8379(8)	16.4929(2)	16.7964(2)	16.9869(3)	15.7419(3)	15.9663(3)
<i>c</i> /Å	17.5396(8)	17.7377(4)	15.3008(2)	14.9862(2)	14.2566(2)	14.0241(3)
<i>β</i> /°			103.8472(6)	104.2021(8)	92.111(1)	90.973(1)
<i>U</i> /Å ³	3316.1(2)	3321.5(1)	1882.05(4)	1900.69(5)	1948.71(5)	1948.77(7)
<i>Z</i>	8	8	4	4	4	4
<i>T</i> /K	123(2)	123(2)	123(2)	123(2)	123(2)	123(2)
<i>μ</i> (Mo-Kα)/mm ⁻¹	0.820	0.932	0.732	0.824	0.708	0.804
Crystal dimensions/mm	0.4 × 0.15 × 0.075	0.24 × 0.21 × 0.06	0.3 × 0.15 × 0.15	0.23 × 0.2 × 0.05	0.13 × 0.13 × 0.1	0.25 × 0.1 × 0.1
Index ranges	-12 ≤ <i>h</i> ≤ 14; -22 ≤ <i>k</i> ≤ 22; -23 ≤ <i>l</i> ≤ 23	-14 ≤ <i>h</i> ≤ 14; -20 ≤ <i>k</i> ≤ 20; -23 ≤ <i>l</i> ≤ 23	-9 ≤ <i>h</i> ≤ 9; -22 ≤ <i>k</i> ≤ 22; -20 ≤ <i>l</i> ≤ 20	-10 ≤ <i>h</i> ≤ 10; -22 ≤ <i>k</i> ≤ 22; -19 ≤ <i>l</i> ≤ 19	-11 ≤ <i>h</i> ≤ 11; -20 ≤ <i>k</i> ≤ 21; -21 ≤ <i>l</i> ≤ 21	-11 ≤ <i>h</i> ≤ 11; -20 ≤ <i>k</i> ≤ 21; -18 ≤ <i>l</i> ≤ 18
Data collected	46338	43185	25139	29664	25930	25795
Unique data (<i>R</i> _{int})	4002 (0.1325)	3933 (0.0897)	4625 (0.0299)	4697 (0.0582)	4795 (0.0600)	4805 (0.0882)
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	2568	3033	3913	3519	3650	3267
Parameters	275	275	327	327	351	351
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^(a)	0.0698, 0.1214	0.0520, 0.0989	0.0341, 0.0970	0.0362, 0.0727	0.0470, 0.0920	0.0493, 0.1118
(all data)	0.1373, 0.1402	0.0793, 0.1072	0.0434, 0.1083	0.0653, 0.0811	0.0750, 0.1007	0.0917, 0.1264
Goodness of fit, <i>S</i>	1.108	1.053	1.114	1.020	1.028	1.057

^(a) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

3.3.1 $[M(\text{salen})(\text{dca})]_n$, $M^{\text{III}} = \text{Mn, Fe}$

The complexes $[M(\text{salen})(\text{dca})]_n$, $M^{\text{III}} = \text{Mn}$ and Fe , (Figure 3.1) are isomorphous and crystallize in the orthorhombic space group $Pbca$. Table 3.3 contains selected interatomic distances and angles (see page 140). The salen ligand is non-planar, such that the phenyl rings of the ligand are bent slightly away from the equatorial coordination plane (defined by mean plane of MN_2O_2) and are at $23.4(2)^\circ$ (Mn) and $24.0(1)^\circ$ (Fe) with respect to each other. The equatorial coordination planes along the chains, which run parallel to the b -axis direction, are at acute angles of $52.38(6)^\circ$ (Mn) and $50.70(4)^\circ$ (Fe) to each other. Intra-chain $M\cdots M$ distances are $8.4596(4)$ Å (Mn) and $8.3137(1)$ Å (Fe). The former distance is significantly longer due to the Jahn-Teller elongation in this direction. The inter-chain $M\cdots M$ distances of $7.4959(7)$ and $7.5830(8)$ Å (Mn), and $7.6169(5)$ and $7.6055(5)$ Å (Fe) are, interestingly, significantly shorter than the intra-chain $M\cdots M$ distances.

Shi *et al.* determined their structures of the $[M(\text{salen})(\text{dca})]_n$ complexes at 293 K, whereas the present structures were determined at 123 K. The structures at the two temperatures are isomorphous (same crystal system and space group), although the unit cell parameters of the former structures are slightly longer (differences of ~ 0.04 to 0.2 Å). The coordination bond lengths are the identical (within error) for the equivalent Mn and Fe structures at the two temperatures, with the exception of the $\text{Mn}^{\text{III}}-\text{N}_{\text{dca}}$ distances, which are ~ 0.05 Å longer at 293 K.

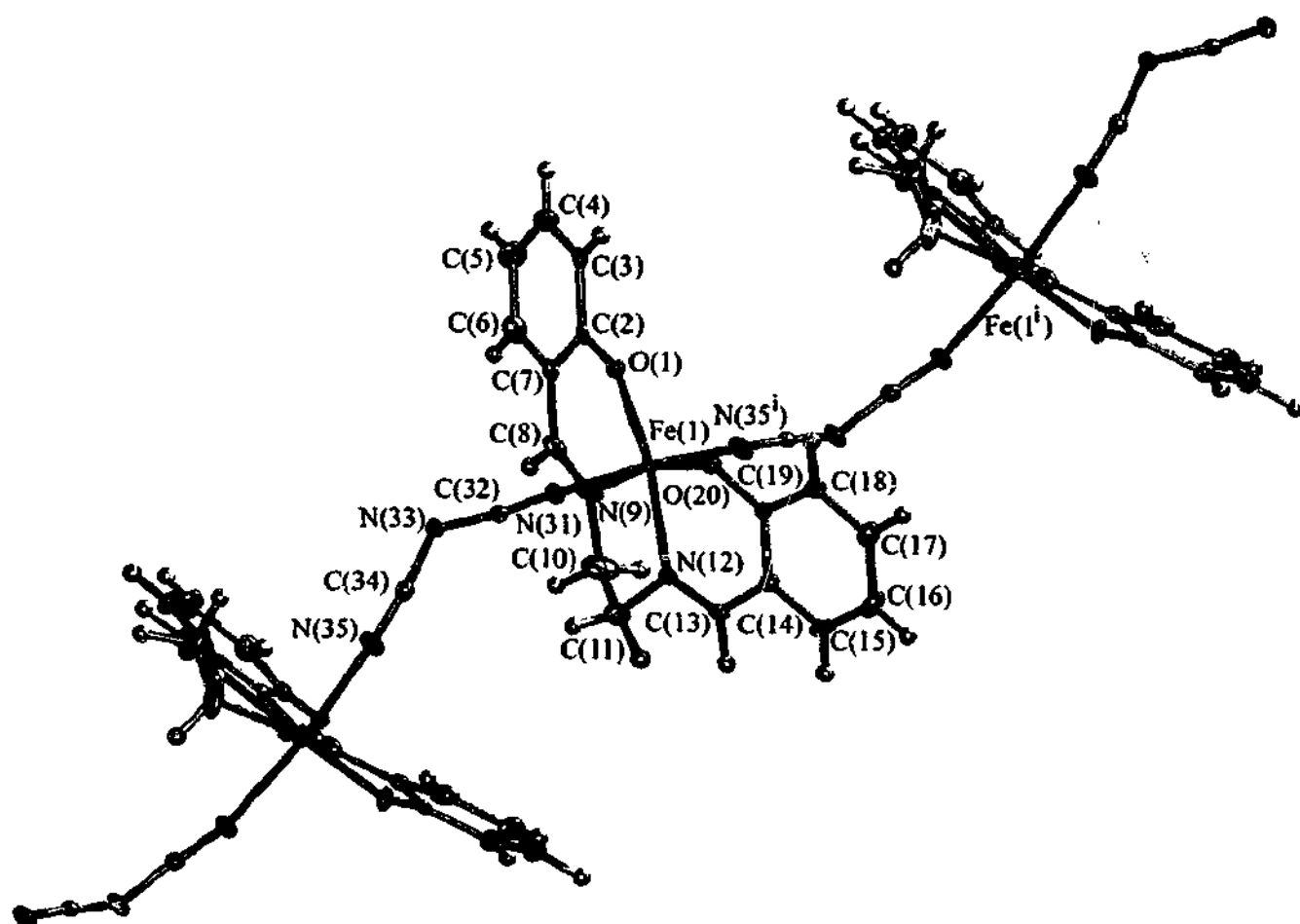


Figure 3.1 The crystal structure of $[\text{Fe}(\text{salen})(\text{dca})]_n$ with atom labelling scheme (thermal ellipsoids shown at 50 % probability). $[\text{Mn}(\text{salen})(\text{dca})]_n$ is isomorphous.

The $[\text{M}(\text{salen})(\text{dca})]_n$ chains interdigitate with adjacent chains in the bc -plane (Figure 3.2) *via* weak π - π interactions, with closest $\text{C}\cdots\text{C}$ contacts of 3.494(6) Å (Mn) and 3.443(4) Å (Fe) and phenyl centroid $\cdots$ centroid distances of 3.828 Å (Mn) and 3.772 Å (Fe), thus forming π -stacked sheets. The longer π - π distances for the manganese(III) structures are due to the Jahn-Teller elongation.

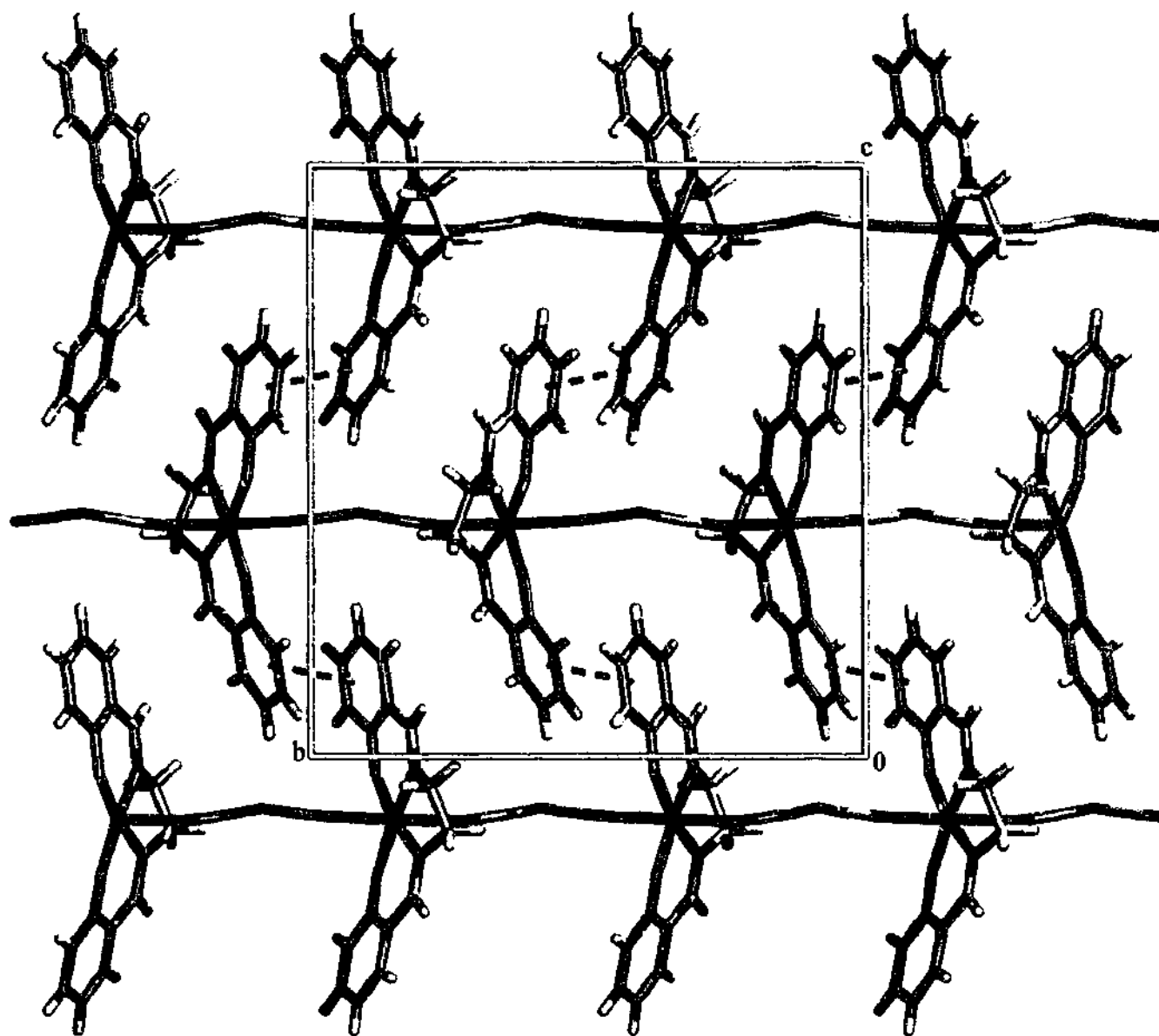


Figure 3.2 Packing diagram of $[\text{Fe}(\text{salen})(\text{dca})]_n$, showing interdigitating chains in the *bc*-plane, and π - π stacking interactions (dashed green).

Table 3.3 Selected interatomic distances (Å) and angles (°) of $[M(\text{salen})(\text{dca})]_n$, $M^{\text{III}} = \text{Mn}$ and Fe.

	Mn	Fe		Mn	Fe
M(1)–O(1)	1.882(3)	1.894(2)	M(1)–N(12)	2.024(3)	2.105(2)
M(1)–O(20)	1.883(3)	1.894(2)	M(1)–N(31)	2.252(3)	2.152(2)
M(1)–N(9)	2.018(3)	2.114(2)	M(1)–N(35 ⁱ)	2.253(4)	2.167(2)
M(1)···M(1 ⁱ)	8.4596(4)	8.3137(1)			
	Mn	Fe		Mn	Fe
O(1)–M(1)–N(9)	90.8(1)	88.62(9)	N(35 ⁱ)–M(1)–O(1)	91.5(1)	92.42(9)
N(9)–M(1)–N(12)	80.3(1)	77.7(1)	N(35 ⁱ)–M(1)–N(9)	88.0(2)	85.8(1)
N(12)–M(1)–O(20)	90.5(1)	88.32(9)	N(35 ⁱ)–M(1)–N(12)	88.4(1)	87.90(9)
O(20)–M(1)–O(1)	98.4(1)	105.46(8)	N(35 ⁱ)–M(1)–O(20)	90.8(1)	90.93(9)
N(31)–M(1)–O(1)	91.9(1)	91.90(9)	O(1)–M(1)–N(12)	171.1(1)	166.21(9)
N(31)–M(1)–N(9)	88.7(2)	88.6(1)	O(20)–M(1)–N(9)	170.8(1)	165.69(9)
N(31)–M(1)–N(12)	87.7(1)	86.55(9)	N(31)–M(1)–N(35 ⁱ)	175.3(1)	172.87(9)
N(31)–M(1)–O(20)	91.9(1)	93.38(9)			

Symmetry transformation: (i) $1/2-x, y-1/2, z$.

3.3.2 $[M(\text{sal-}o\text{-phen})(\text{dca})]_n$, $M^{\text{III}} = \text{Mn, Fe}$

The complexes $[M(\text{sal-}o\text{-phen})(\text{dca})]_n$, $M^{\text{III}} = \text{Mn}$ and Fe, (Figure 3.1) are isomorphous and crystallize in the monoclinic space group $P2_1/n$. Table 3.4 contains selected interatomic distances and angles (see page 144). While the phenyl groups of the salen ligand in the $[M(\text{salen})(\text{dca})]_n$ complexes are bent away from the coordination plane in a roughly symmetrical fashion, this is not the case for sal-*o*-phen. One of the phenyl rings is bent $3.9(1)^\circ$ (Mn) and $6.0(1)^\circ$ (Fe), while the other makes an angle with the

coordination plane of $24.88(8)^\circ$ (Mn) and $23.08(9)^\circ$ (Fe). In contrast to the $[M(\text{salen})(\text{dca})]_n$ complexes, the sal-*o*-phen equatorial coordination planes on adjacent M^{III} atoms are at the larger angles of $78.31(3)^\circ$ (Mn) and $73.64(4)^\circ$ (Fe) to each other. The chains run parallel to the $[101]$ lattice vector.

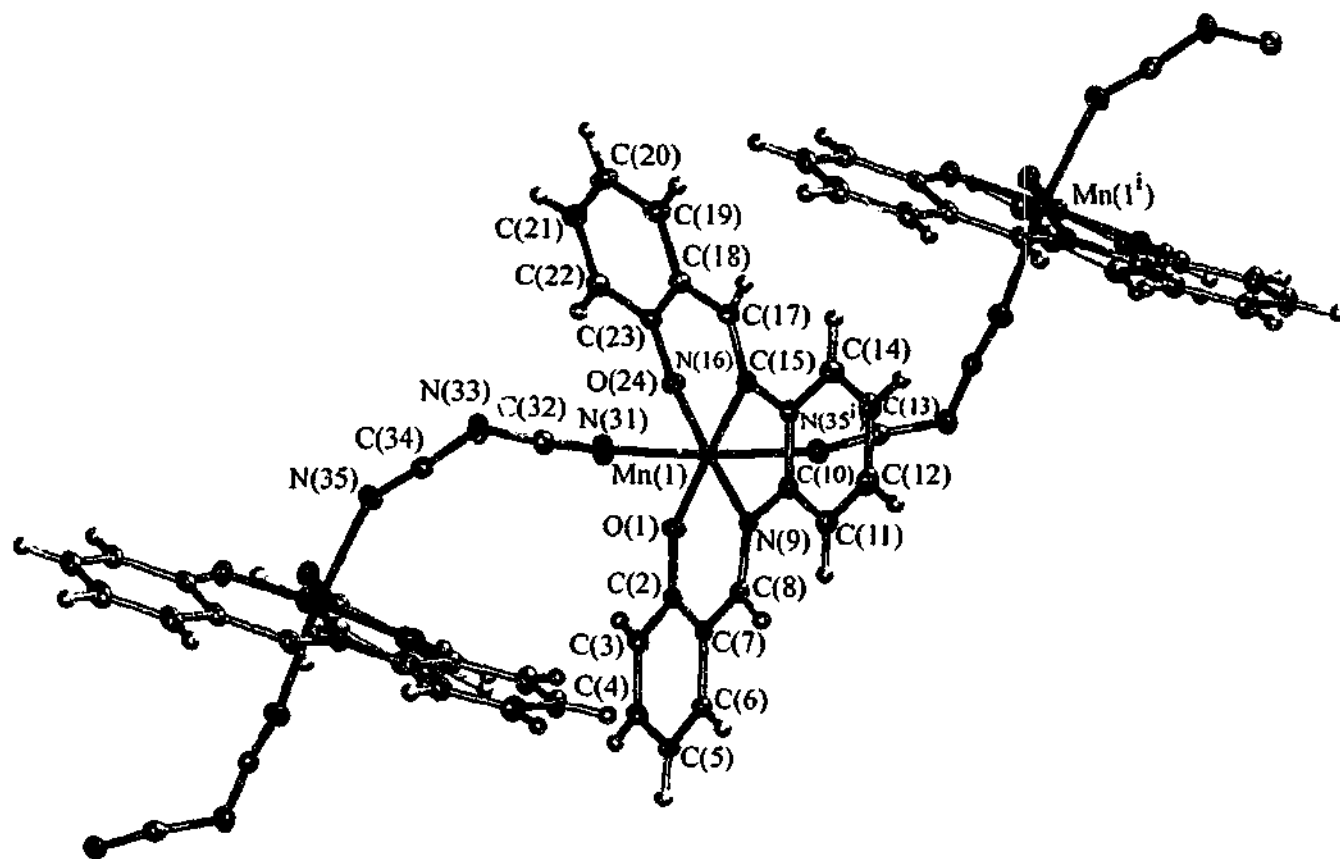


Figure 3.3 The crystal structure of $[\text{Mn}(\text{sal-}o\text{-phen})(\text{dca})]_n$ with atom labelling scheme (thermal ellipsoids shown at 50 % probability). $[\text{Fe}(\text{sal-}o\text{-phen})(\text{dca})]_n$ is isomorphous.

The intra-chain $M \cdots M$ distances of $7.7893(1) \text{ \AA}$ (Mn) and $7.6974(2) \text{ \AA}$ (Fe), are almost $1 \text{ \AA}$ shorter than those of the $[M(\text{salen})(\text{dca})]_n$ complexes. A contributing factor to the more pronounced angular zigzag nature of the chains described above may be the presence of $\text{CH} \cdots \pi$ interactions between a hydrogen atom (H(14)) on the bridge phenyl ring of sal-*o*-phen and one of the phenyl rings (C(2)-C(7)) of the salicylaldehyde moiety (Figure 3.4), with $\text{CH} \cdots \text{centroid}$ distances of $2.593 \text{ \AA}$ (Mn) and $2.630 \text{ \AA}$ (Fe). One of the

inter-chain $M\cdots M$ distances is equal to the unit cell length a (7.5424(1) Å (Mn) and 7.7017(1) Å (Fe)), and the next shortest $M\cdots M$ distances are 7.4666(5) Å (Mn) and 7.2516(5) Å (Fe). As in the $[M(\text{salen})(\text{dca})]_n$ complexes, these distances are shorter than the intra-chain $M\cdots M$ distances.

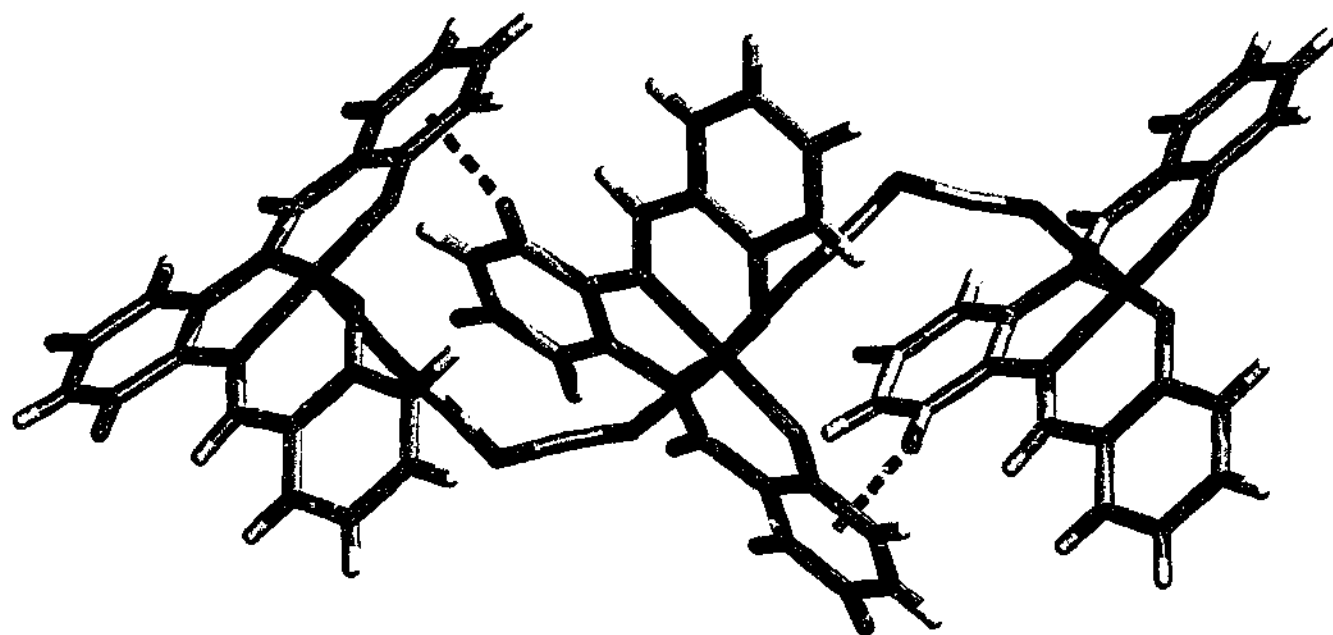


Figure 3.4 The structure of $[M(\text{sal-}o\text{-phen})(\text{dca})]_n$ showing intra-chain $\text{CH}\cdots\pi$ interactions (dashed green).

The $[M(\text{sal-}o\text{-phen})(\text{dca})]_n$ chains interdigitate with adjacent chains in the ac -plane (Figure 3.5). The bridge phenyl rings associate with one of the phenyl rings (C(18)-C(23)) of the salicylaldimine moiety of sal-*o*-phen *via* weak π - π interactions, with closest $\text{C}\cdots\text{C}$ contacts of 3.433(3) Å (Mn) and 3.376(3) Å (Fe), and phenyl centroid $\cdots$ centroid distances of 4.069 Å (Mn) and 3.969 Å (Fe).

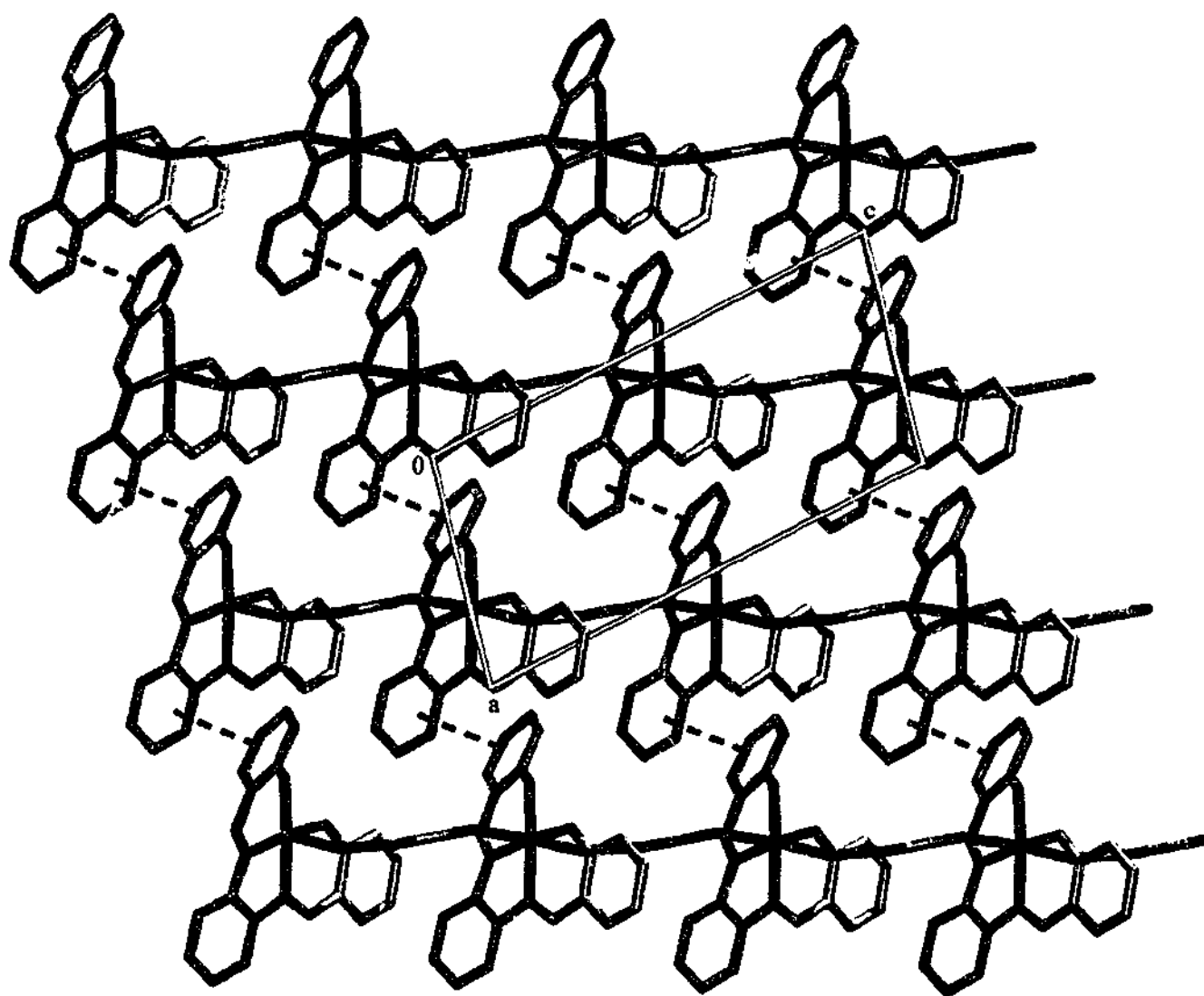


Figure 3.5 A packing diagram of $[M(\text{sal-}o\text{-phen})(\text{dca})]_n$, showing interdigitating chains in the ac -plane, and weak π - π stacking interactions (dashed green). Hydrogen atoms are omitted for clarity.

Table 3.4 Selected interatomic distances (Å) and angles (°) for $[M(\text{sal-}o\text{-phen})(\text{dca})]_n$, $M^{\text{III}} = \text{Mn}$ and Fe .

	Mn	Fe		Mn	Fe
M(1)–O(1)	1.872(1)	1.880(1)	M(1)–N(16)	1.994(1)	2.113(2)
M(1)–O(24)	1.881(1)	1.894(1)	M(1)–N(31)	2.275(2)	2.155(2)
M(1)–N(9)	2.007(1)	2.127(2)	M(1)–N(35 ⁱ)	2.277(2)	2.125(2)
M(1)···M(1 ⁱ)	7.7893(1)	7.6974(2)			
	Mn	Fe		Mn	Fe
O(1)–M(1)–N(9)	92.93(6)	89.83(6)	N(35 ⁱ)–M(1)–O(1)	95.16(6)	96.46(6)
N(9)–M(1)–N(16)	81.64(6)	77.46(6)	N(35 ⁱ)–M(1)–N(9)	89.00(6)	88.64(6)
N(16)–M(1)–O(24)	92.44(5)	89.93(6)	N(35 ⁱ)–M(1)–N(16)	86.74(6)	86.05(6)
O(24)–M(1)–O(1)	92.94(5)	102.66(6)	N(35 ⁱ)–M(1)–O(24)	91.76(6)	92.53(6)
N(31)–M(1)–O(1)	91.47(6)	92.09(6)	O(1)–M(1)–N(16)	174.23(6)	167.01(6)
N(31)–M(1)–N(9)	88.82(6)	86.61(6)	O(24)–M(1)–N(9)	173.98(6)	167.23(6)
N(31)–M(1)–N(16)	86.49(6)	84.57(6)	N(31)–M(1)–N(35 ⁱ)	173.11(6)	170.21(6)
N(31)–M(1)–O(24)	89.73(6)	90.24(6)			

Symmetry transformation: (i) $x-1/2, 1/2-y, z-1/2$.

3.3.3 $[M((\pm)\text{-saltch})(\text{dca})]_n$, $M^{\text{III}} = \text{Mn, Fe}$

The complexes $[M((\pm)\text{-saltch})(\text{dca})]_n$, $M^{\text{III}} = \text{Mn}$ and Fe , are also isomorphous and crystallize in the monoclinic space group $P2_1/n$. Table 3.5 contains selected interatomic distances and angles (see page 149). The asymmetric unit contains one R,R -saltch ligand (Figure 3.6). The chains however, which run parallel to the $[\bar{1}01]$ lattice vector, consist of alternating R,R -saltch and S,S -saltch ligands, resulting in an overall centrosymmetric structure. Thus the $(\pm)$ -saltch notation indicates the presence of both enantiomers in the

structure. The coordination planes of the saltch ligands on adjacent M^{III} centres along the chains make angles with respect to each other of $44.87(5)^\circ$ (Mn) and $42.22(7)^\circ$ (Fe) – smaller than those of the previous complexes. Like sal-*o*-phen, the phenyl rings of the ($\pm$)-saltch ligand are bent away from the coordination plane at different angles. One phenyl ring makes an angle of $5.7(1)^\circ$ (Mn) and $4.5(2)^\circ$ (Fe), while the other makes an angle with the coordination plane of $16.6(1)^\circ$ (Mn) and $16.0(1)^\circ$ (Fe).

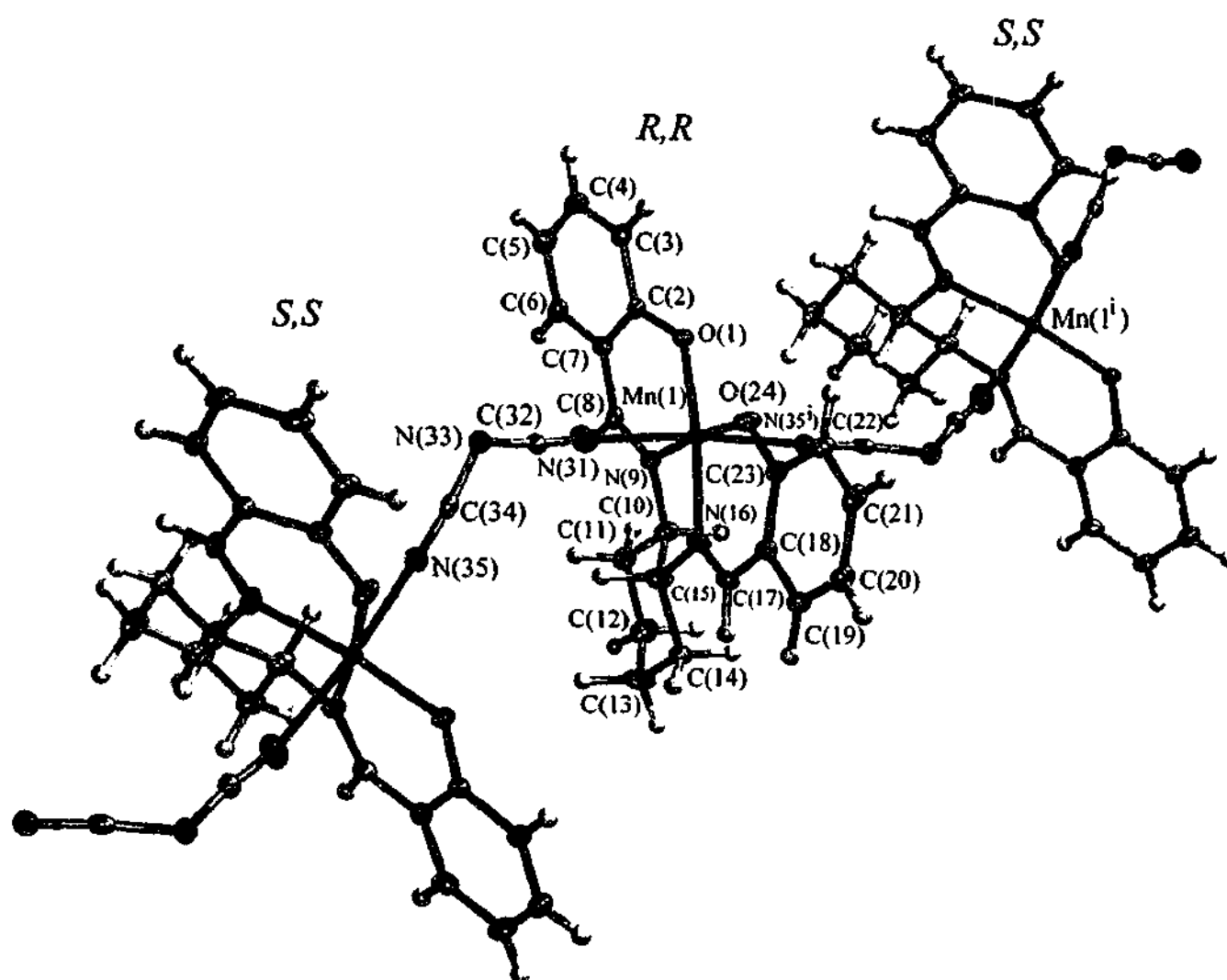


Figure 3.6 The crystal structure of $[Mn((\pm)\text{-saltch})(dca)]_n$ with atom labelling scheme and the enantiomeric forms of the saltch ligands indicated (thermal ellipsoids shown at 50 % probability). $[Fe((\pm)\text{-saltch})(dca)]_n$ is isomorphous.

The intra-chain M...M distances are 8.5297(1) Å (Mn) and 8.3790(2) Å (Fe). Unlike the previous complexes, only one of the inter-chain M...M distances, 7.8754(7) Å (Mn) and 7.7264(8) Å (Fe), is shorter than the intra-chain M...M distances. This observation may be due to the larger steric bulk of the cyclohexyl bridge of the saltch ligand hindering closer packing of the chains.

The chains again interdigitate *via* a series of weak π - π and CH... π interactions. Firstly, the phenyl ring (C(2)-C(7)) π -stacks with its symmetry equivalent in an adjacent chain, with C...C closest contacts of 3.465(4) Å (Mn) and 3.453(4) Å (Fe) and phenyl centroid...centroid distances of 3.624 Å (Mn) and 3.608 Å (Fe), and a hydrogen atom (H(14A)) on the cyclohexyl ring on the adjacent chain is directed towards the phenyl ring, with CH...centroid distances of 2.821 Å (Mn) and 2.774 Å (Fe). These interactions result in the formation of sheets in the (101) plane (Figure 3.7). Secondly, the other phenyl ring of the saltch ligand (C(18)-C(23)) associates with a hydrogen atom (H(12B)) on a cyclohexyl ring on an adjacent chain, with CH...centroid distances of 2.817 Å (Mn) and 2.730 Å (Fe), forming sheets in the *ac*-plane (Figure 3.8).

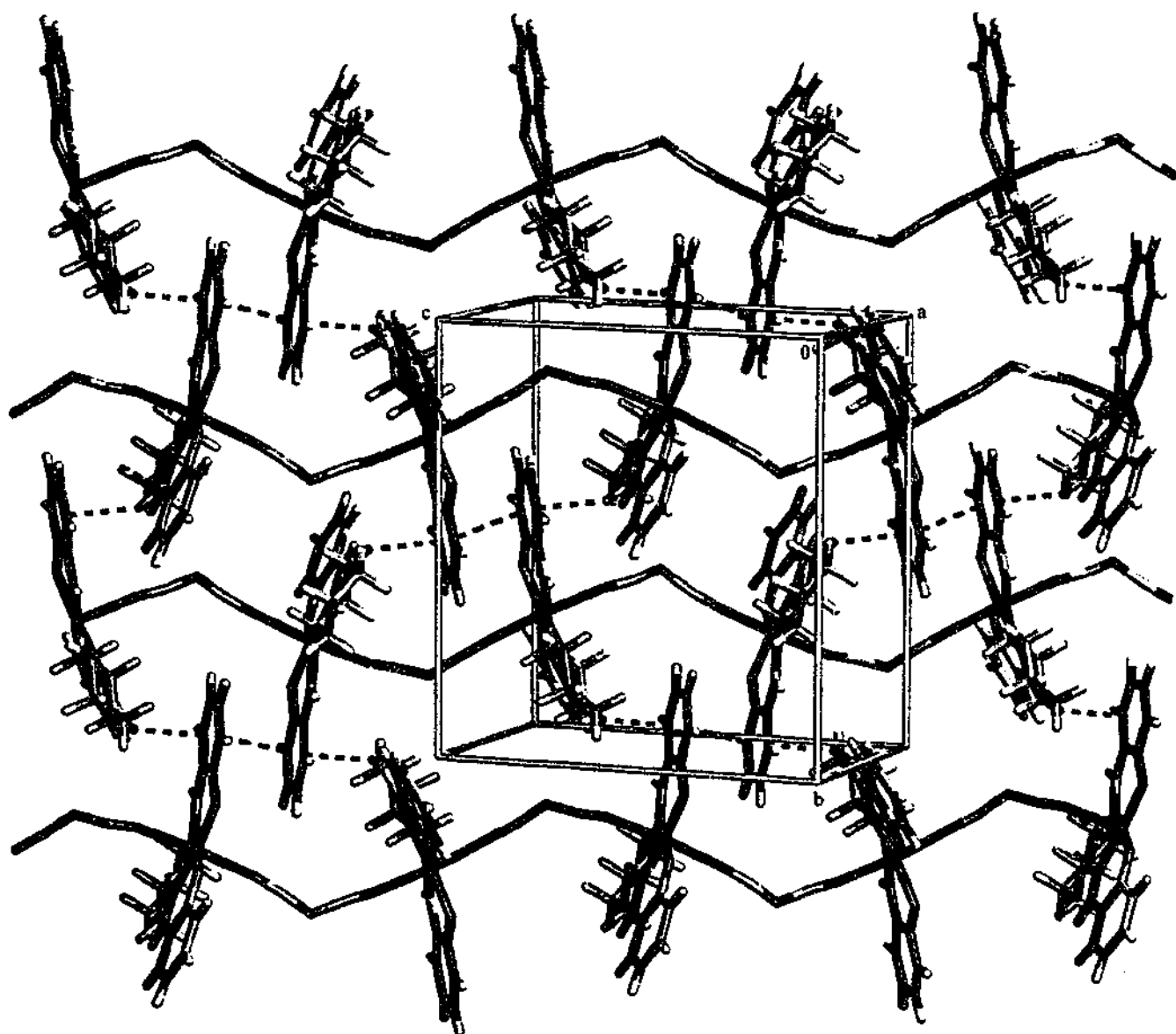


Figure 3.7 A packing diagram of $[M((\pm)\text{-saltch})(\text{dca})]_n$, showing π -stacking (dashed green) and $\text{CH}\cdots\pi$ (dashed pink/red) interactions forming sheets in the (101) plane.

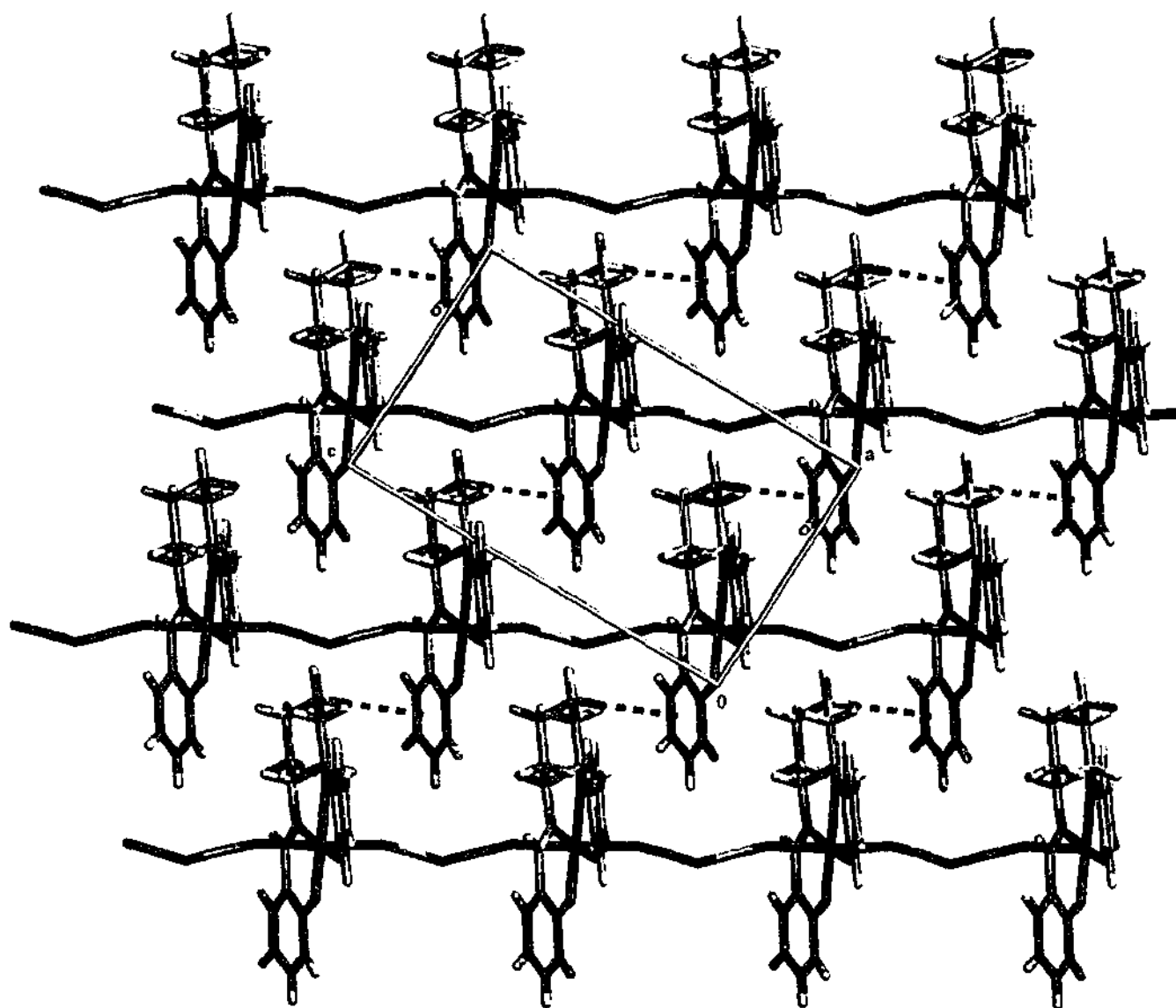


Figure 3.8 A packing diagram of $[M((\pm)\text{-saltch})(\text{dca})]_n$ in the ac -plane $\text{CH}\cdots\pi$ (dashed pink/red) interactions.

Table 3.5 Selected interatomic distances (Å) and angles (°) for $[M((\pm)\text{-saltch})(\text{dca})]_n$, M^{III} = Mn and Fe.

	Mn	Fe		Mn	Fe
M(1)–O(1)	1.875(2)	1.883(2)	M(1)–N(16)	2.002(2)	2.118(2)
M(1)–O(24)	1.888(2)	1.902(2)	M(1)–N(31)	2.295(2)	2.154(3)
M(1)–N(9)	1.991(2)	2.107(2)	M(1)–N(35 ⁱ)	2.297(2)	2.148(2)
M(1)···M(1 ⁱ)	8.5297(1)				
	Mn	Fe		Mn	Fe
O(1)–M(1)–N(9)	91.20(7)	88.51(9)	N(35 ⁱ)–M(1)–O(1)	96.15(7)	97.59(9)
N(9)–M(1)–N(16)	82.16(8)	78.03(9)	N(35 ⁱ)–M(1)–N(9)	88.41(8)	86.94(9)
N(16)–M(1)–O(24)	92.44(7)	92.44(7)	N(35 ⁱ)–M(1)–N(16)	87.50(8)	87.29(9)
O(24)–M(1)–O(1)	94.37(7)	103.69(8)	N(35 ⁱ)–M(1)–O(24)	88.59(8)	88.93(9)
N(31)–M(1)–O(1)	89.01(8)	89.93(9)	O(1)–M(1)–N(16)	172.35(7)	165.45(9)
N(31)–M(1)–N(9)	89.56(9)	89.9(1)	O(24)–M(1)–N(9)	173.93(8)	167.54(9)
N(31)–M(1)–N(16)	87.15(8)	84.60(9)	N(31)–M(1)–N(35 ⁱ)	174.49(8)	171.75(9)
N(31)–M(1)–O(24)	92.95(9)	92.6(1)			

Symmetry transformation: (i) $1/2+x$, $1/2-y$, $z-1/2$.

3.4 Magnetism of $[M(L)(\text{dca})]_n$ Complexes; M^{III} = Mn and Fe; LH_2 = *salenH*₂, *sal-o-phenH*₂ and $(\pm)\text{-saltchH}_2$

It can be seen from Figure 3.9 to Figure 3.14 (see pages 151 to 154) that the μ_{eff} vs. temperature behaviour for all the $[M^{\text{III}}(\text{Schiff-base})(\text{dca})]_n$ (M^{III} = Mn, Fe; Schiff-base = *salen*²⁻, *sal-o-phen*²⁻, *saltch*²⁻) series is rather similar and indicative of very weak antiferromagnetic coupling combined, perhaps, with weak zero-field splitting on the Mn^{III}

(5E_g ; d^4) and Fe^{III} ($^6A_{1g}$; d^5) centres. The corresponding χ vs. T plots are Curie-Weiss like, without any maxima (above 2 K). The approximation was made that z.f.s. is zero and Heisenberg chain models were used for $S = 2$ (Mn^{III}) and $S = 5/2$ (Fe^{III}).⁵³ The best-fit parameters are given in Table 3.6. Good agreement is obtained with the J values obtained by Shi *et al.*⁵² for $[Mn(salen)(dca)]_n$. Their $[Fe(salen)(dca)]_n$ data are clearly wrong and the assumed spin-state S of $1/2$ is not compatible with their quoted Fe–ligand distances. Their data are likely to be due, at least in part, to an impurity of the strongly antiferromagnetically coupled $[\{Fe(salen)\}_2(\mu-O)]$.⁵⁴ All the J values in Table 3.6 are less than 1 cm^{-1} , which is characteristic of $\mu_{1,5}$ -dca bridged M^{II} species.¹² This bridging mode provides a poor superexchange pathway and, in the Jahn-Teller elongated Mn^{III} species, involves σ -overlap of dca with the d_z , “magnetic” orbital on Mn^{III} ($t_{2g}^3 e_g(d_z^2)^1$). Similar overlap occurs in the Fe^{III} ($t_{2g}^3 e_g^2$) compounds.

Somewhat larger negative J values were found for related acetato-bridged chain structures such as $[Mn(salen)(OAc)]_n$, $J = -1.8\text{ cm}^{-1}$, reflecting the enhanced superexchange properties of acetate bridging. A recent $[Mn^{III}(salpn)(NCS)]_n$ helical (zig-zag) chain has $J = -1.6\text{ cm}^{-1}$ with ordering to a spin-canted antiferromagnet occurring below $T_N = 7\text{ K}$.⁵¹ The anisotropy on Mn^{III} (negative D) contributes to the spin canting.

There is not a big enough spread in J values in the present compounds to make a search for magnetostructural trends worthwhile. The shorter $M\cdots M$ distances in the $[M(sal-o-phen)(dca)]_n$ chains do appear to give larger J values. It is not possible to extract any relationship to π - π or CH- π interactions.

Table 3.6 Best-fit parameters for $[M^{III}(\text{chelate})(\text{dca})]_n$ series obtained using Fisher chain models ($S = 2$, Mn^{III} ; $S = 5/2$, Fe^{III}).

Complex	g	J / cm^{-1}
$[Mn(\text{salen})(\text{dca})]_n$	1.91 (1.99) ^a	-0.12 (-0.12) ^a
$[Mn(\text{sal-}o\text{-phen})(\text{dca})]_n$	1.88	-0.19
$[Mn(\text{saltch})(\text{dca})]_n$	1.95	-0.19
$[Fe(\text{salen})(\text{dca})]_n$	1.92 (2.01) ^b	-0.12 (-7.6) ^b
$[Fe(\text{sal-}o\text{-phen})(\text{dca})]_n$	1.90	-0.72
$[Fe(\text{saltch})(\text{dca})]_n$	1.87	-0.03

(a) ref: Shi *et al.*⁵² (b) ref: Shi *et al.*⁵² assuming $S = 1/2$ Fe^{III}

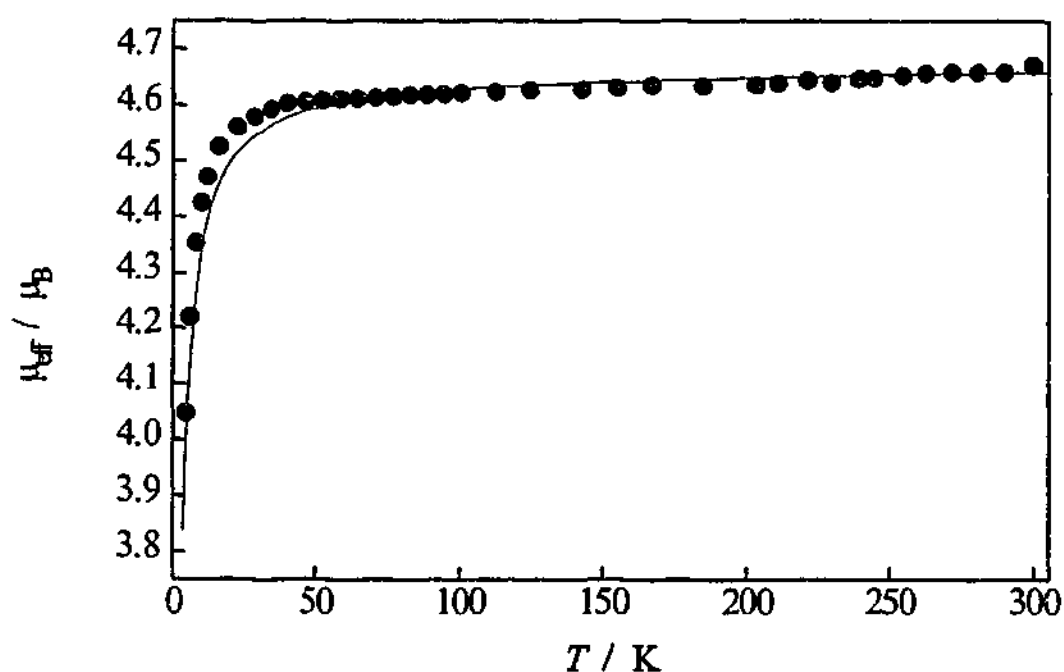


Figure 3.9 Plot of μ_{eff} versus temperature for $[Mn(\text{salen})(\text{dca})]_n$. For this and the following plots, the applied field is $H = 1$ T and the solid line indicates the line of best-fit.

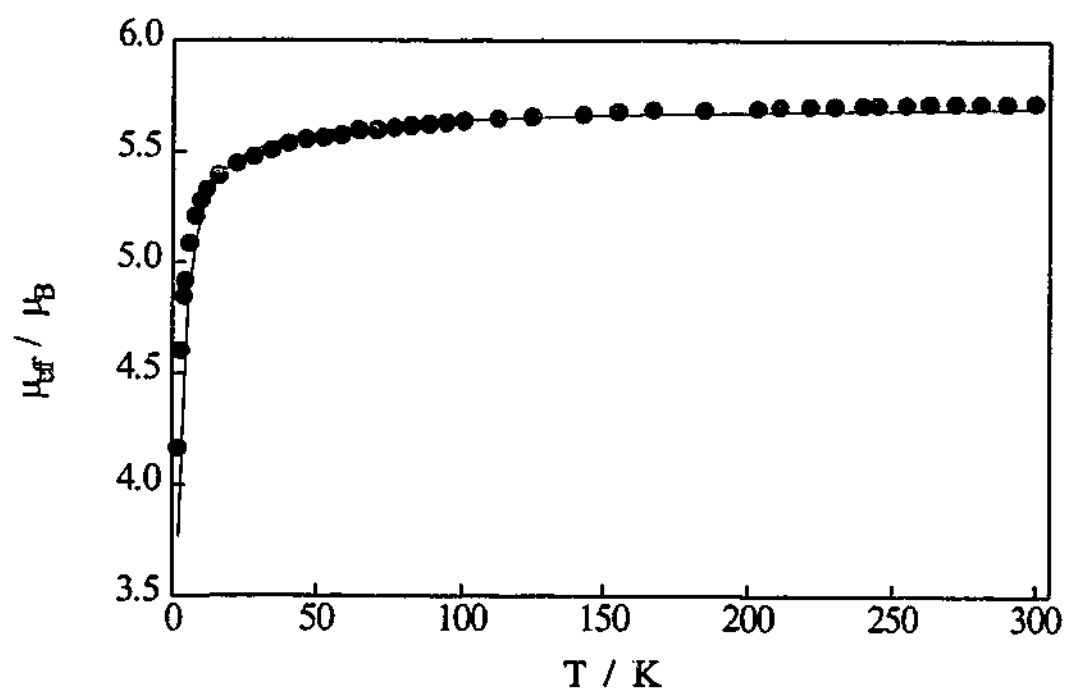


Figure 3.10 Plot of μ_{eff} versus temperature for $[\text{Fe}(\text{salen})(\text{dca})]_n$.

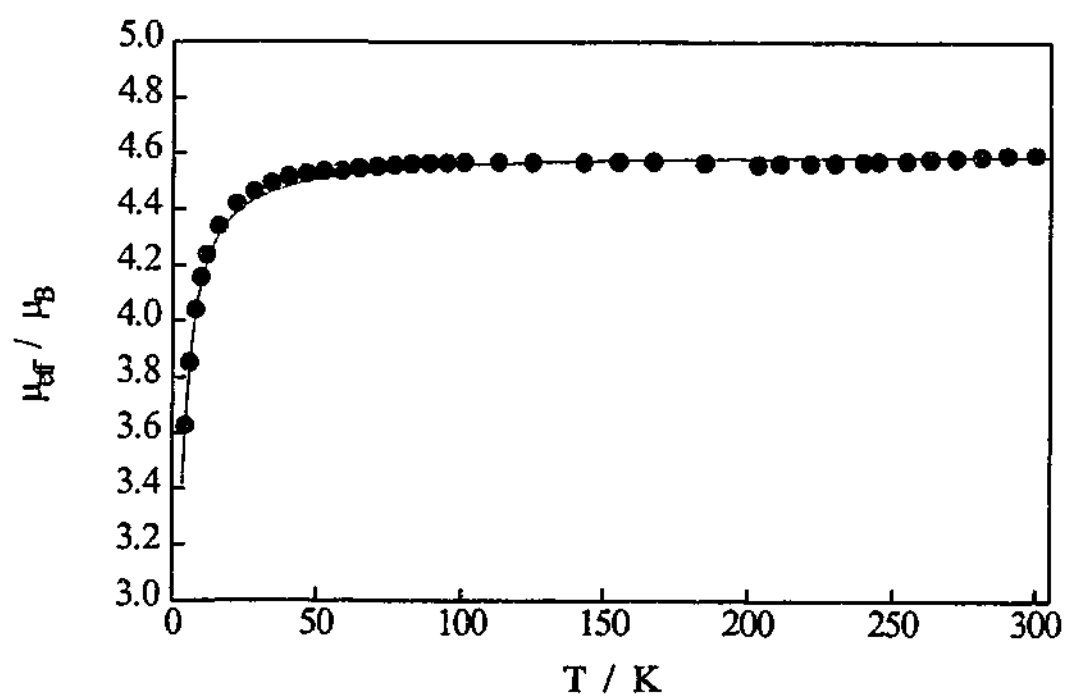


Figure 3.11 Plot of μ_{eff} versus temperature for $[\text{Mn}(\text{sal-}o\text{-phen})(\text{dca})]_n$.

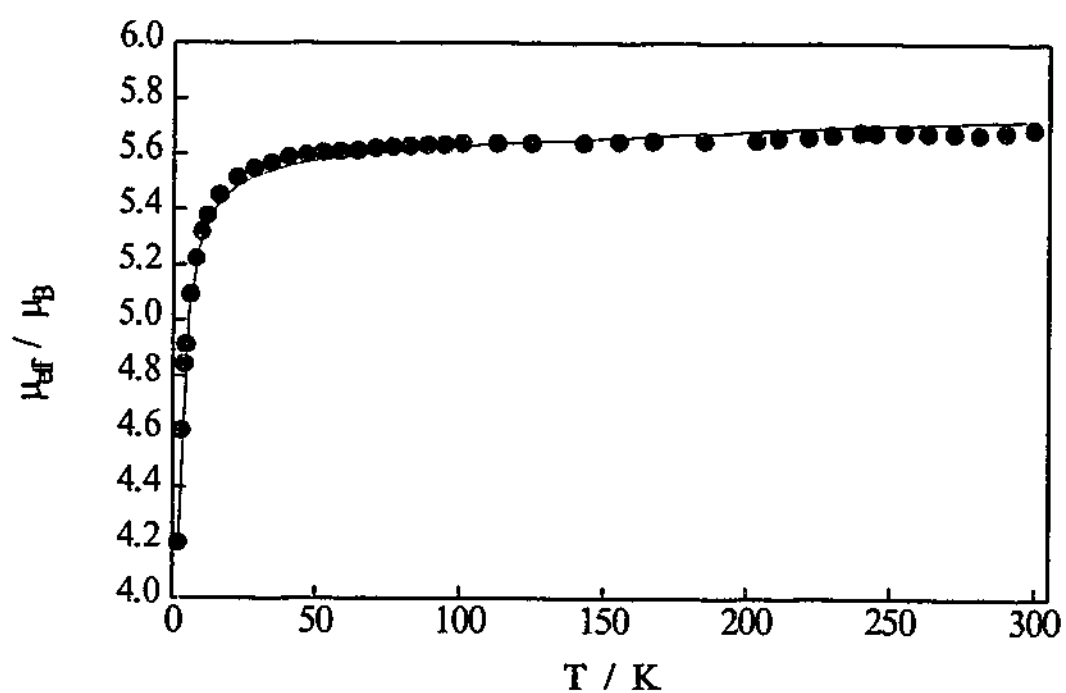


Figure 3.12 Plot of μ_{eff} versus temperature for $[\text{Fe}(\text{sal-}o\text{-phen})(\text{dca})]_n$.

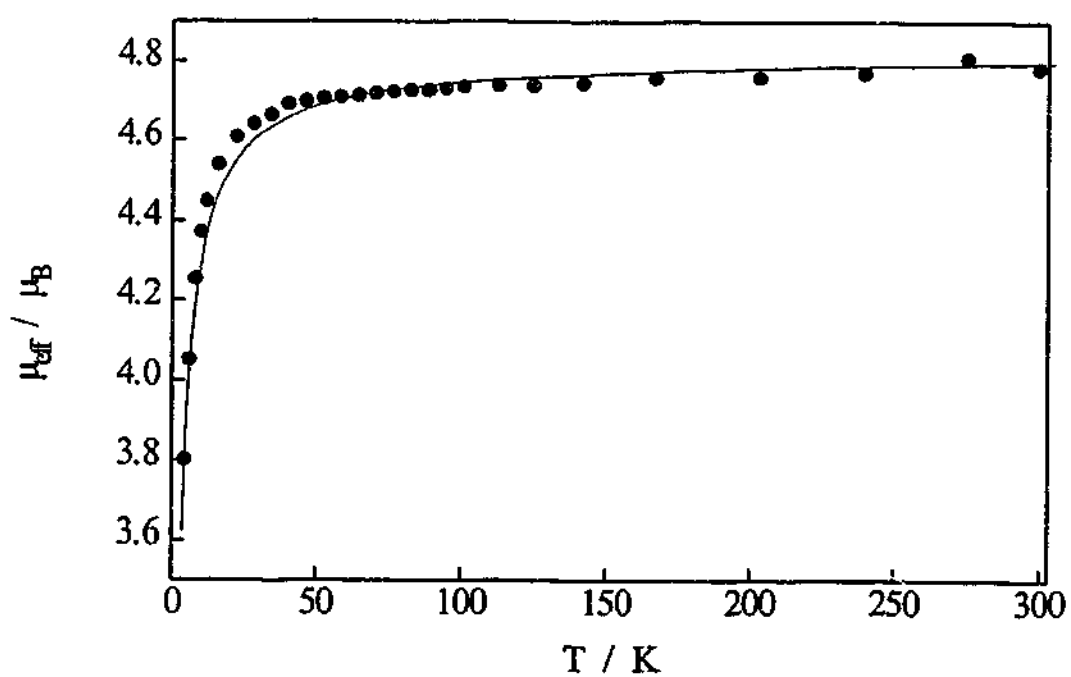


Figure 3.13 Plot of μ_{eff} versus temperature for $[\text{Mn}(\text{saltch})(\text{dca})]_n$.

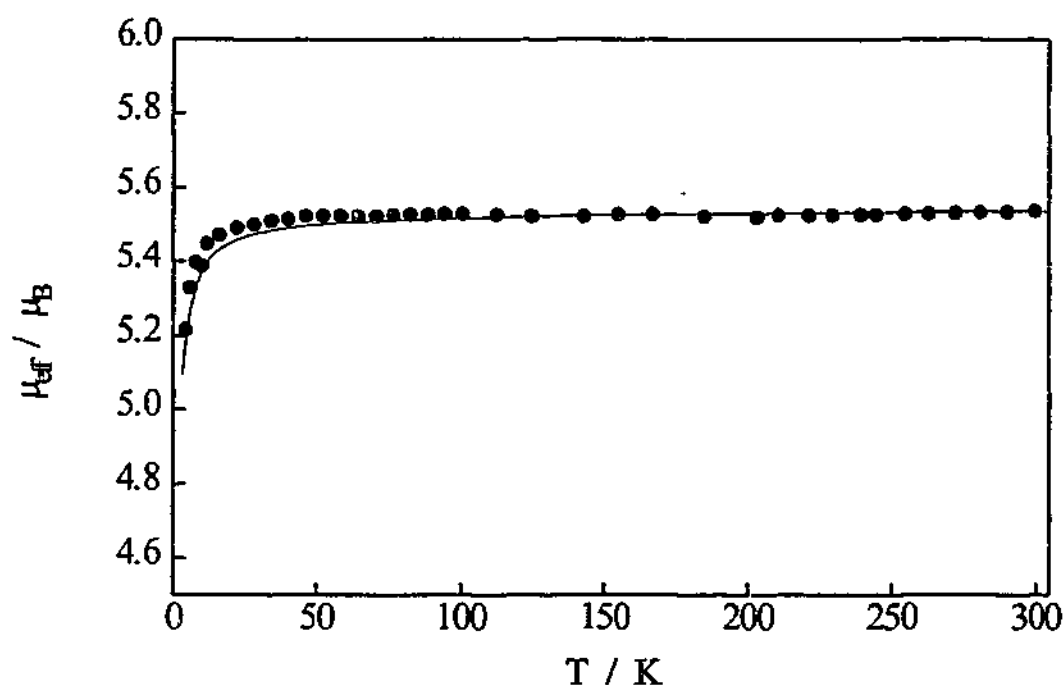


Figure 3.14 Plot of μ_{eff} versus temperature for $[\text{Fe}(\text{saltch})(\text{dca})]_n$.

3.5 Conclusions

The 1D coordination polymers, $[\text{M}(\text{L})(\text{dca})]_n$, $\text{M}^{\text{III}} = \text{Mn}$ and Fe ; $\text{LH}_2 = \text{salenH}_2$, $\text{sal-}o\text{-phenH}_2$ and $(\pm)\text{-saltchH}_2$, were synthesised, in most cases by reaction of a M^{II} salt with dca and the corresponding Schiff-base ligand. Except $[\text{Fe}(\text{salen})(\text{dca})]_n$, which was prepared from $\text{Fe}(\text{salen})\text{Cl}$ and dca. The complexes consist of octahedral high-spin M^{III} atoms coordinated in the equatorial plane by the tetra-chelating Schiff-base ligand and coordinated in the axial positions by single $\mu_{1,5}$ -dca bridges, forming infinite linear zigzag chains. The chains of the complexes interdigitate in a parallel fashion with adjacent chains, *via* weak π -stacking. Variable temperature magnetic susceptibility measurements (2–300 K; $H = 1$ T) showed that these compounds display very weak antiferromagnetic coupling, and consequently no long-range magnetic order was observed under these conditions. The data were fitted to Heisenberg chain models ($S = 2$, Mn^{III} ; $S = 5/2$, Fe^{III}) and J values obtained

ranged from -0.03 to -0.72 cm^{-1} . No significant magnetostructural relationships could be drawn due to all the complexes studied displaying very similar magnetic behaviour.

3.6 Experimental

The Schiff-base ligands salenH₂, sal-*o*-phenH₂ and ($\pm$)-saltchH₂ ligands were prepared by the condensation reaction of salicylaldehyde with the appropriate diamine; ethylenediamine, *o*-phenylenediamine and *trans*-($\pm$)-diaminocyclohexane respectively in a 2:1 molar ratio. Fe(salen)Cl was prepared according to the literature.⁵⁵

3.6.1 Synthesis of [Mn(salen)(dca)]_n

Na(dca) (0.089 g, 1.0 mmol) and salenH₂ (0.268 g, 1.0 mmol) were dissolved in a mixture of 5 mL ethanol and 10 mL methanol by heating to boiling and stirring for approximately 5 minutes. This was subsequently allowed to cool, causing some salenH₂ to recrystallise. This mixture was stirred and heated to gentle reflux at which point a methanolic solution (5 mL) of Mn(NO₃)₂·4H₂O (0.251 g, 1.0 mmol) was added. An instant colour change to a dark brown/black occurred on addition. The recrystallised salenH₂ redissolved soon after addition. Less than one third of the solution was placed in a conical flask to evaporate. The remaining solution was placed in a sealed vial. After approximately two weeks the solution in the conical flask had evaporated to dryness leaving behind some black material, and a small amount of red crystalline material. The latter is likely to be [(Mn(salen))₂(μ -O)]. The other two thirds of the solution was then allowed to slowly evaporate. After a month, a precipitate of black crystals had formed which was subsequently collected and washed several times with small amounts of methanol, once with water and followed by more methanol. (Yield 0.17 g, 44 %). IR (Nujol, cm⁻¹): 3575w, 3056w, 2360vw, 2285s, 2226s, 2162s, 1696vw, 1622s, 1601s, 1542s, 1466s, 1389m, 1359m, 1292s, 1243vw, 1202m 1150m, 1133m, 1090m, 1054m, 1036m, 985m, 973w,

962vw, 948vw, 932vw, 905m, 854w, 799m, 759m, 750m, 649m, 630s, 596msh. Anal. (%): Found: C, 55.9; H, 3.7; N, 18.3. Calc. for $C_{18}H_{14}MnN_5O_2$: C, 55.8; H, 3.6; N, 18.1.

3.6.2 Synthesis of $[Fe(salen)(dca)]_n$

A methanolic solution (5 mL) of $Fe(salen)Cl$ (0.358 g, 1.0 mmol) was added to a methanolic solution (5 mL) of $Na(dca)$ (0.089 g, 1.0 mmol). After a period of a week, black crystals suitable for X-ray diffraction analysis had formed. They were filtered and washed with ethanol and dried with diethyl ether. (Yield 0.14 g, 35 %). IR (Nujol, cm^{-1}): 3620vw, 2317s, 2246m, 2179s, 1625s, 1598s, 1547s, 1446s, 1383s, 1340m, 1297s, 1245w, 1199w, 1149m, 1129w, 1090w, 1054w, 1036w, 985w, 974vw, 958vw, 944vw, 907m, 854w, 797m, 759m, 749m, 595vw. Anal. (%): Found: C, 55.6; H, 3.5; N, 17.9. Calc. for $C_{18}H_{14}FeN_5O_2$: C, 55.7; H, 3.6; N, 18.0.

3.6.3 Synthesis of $[Mn(sal-o-phen)(dca)]_n$

A solution of $Mn(OAc)_2 \cdot 4H_2O$ (0.245 g, 1.0 mmol) in methanol (10 mL) was added to a stirred refluxing suspension of $sal-o-phenH_2$ (0.316 g, 1.0 mmol) and $Na(dca)$ (0.089 g, 1.0 mmol) in methanol (20 mL). On addition the solution went deep red/brown. The solution was then left to cool to room temperature and subsequently filtered to remove a fine brown precipitate. After a few days black crystals had formed. Most of the mother liquor was then decanted and the crystals collected by filtration. (Yield 0.01 g, 3 %). IR (Nujol, cm^{-1}): 2284m, 2230m, 2161s, 1605s, 1576s, 1531s, 1490vw, 1442m, 1347w, 1286w, 1254vw, 1232vw, 1193m, 1152m, 1130w, 1031vw, 968vw, 925vw, 871vw, 857vw, 810m, 754s, 672vw, 630w. Anal. (%): Found: C, 60.8; H, 2.7; N, 16.1. Calc. for $C_{22}H_{14}MnN_5O_2$: C, 60.7; H, 3.2; N, 16.1.

3.6.4 Synthesis of $[\text{Fe}(\text{sal-}o\text{-phen})(\text{dca})]_n$

$\text{Na}(\text{dca})$ (0.089 g, 1.0 mmol) was dissolved in a suspension of $\text{sal-}o\text{-phenH}_2$ (0.316 g, 1.0 mmol) in 15 mL of methanol stirred at gentle reflux. A methanolic (5 mL) solution of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.338 g, 1.0 mmol) was filtered into this suspension. The resulting mixture instantly turned a dark brown/black colour, and was stirred for a further 20 minutes at gentle reflux, after which time the $\text{sal-}o\text{-phenH}_2$ had dissolved/reacted. The solution was then left to stand at room temperature to slowly evaporate. After a few days, black crystals had appeared. These were filtered, washed quickly with methanol and dried in air (Yield 0.089 g, 20 %). IR (Nujol, cm^{-1}): 3607vw, 3073vw, 2316s, 2249s, 2174s, 1605s, 1579s, 1538s, 1445s, 1384s, 1338w, 1314s, 1255vw, 1230vw, 1189m, 1152m, 1127w, 1108vw, 1054vw, 1032w, 970w, 922m, 870w, 811m, 756m, 752s, 662w, 620m. Anal. (%): Found: C, 60.0; H, 3.1; N, 15.9. Calc. for $\text{C}_{22}\text{H}_{14}\text{FeN}_5\text{O}_2$: C, 60.6; H, 3.2; N, 16.1.

3.6.5 Synthesis of $[\text{Mn}((\pm)\text{-saltch})(\text{dca})]_n$

A solution of $(\pm)\text{-saltchH}_2$ (0.322 g, 1.0 mmol) and $\text{Na}(\text{dca})$ (0.178 g, 2.0 mmol) in a 7 mL/3 mL methanol/acetone mixture was added to a methanolic solution (5 mL) of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.251 g, 1.0 mmol). The resulting solution changed colour to dark brown/black after about 5-10 minutes. After a couple of days many black crystals were present. The crystals were collected, washed quickly with methanol and dried in air (Yield 0.210 g, 48 %). IR (Nujol, cm^{-1}): 3562vw, 3069vw, 2278s, 2229s, 2164s, 1620s, 1598sh, 1542s, 1450s, 1389m, 1341s, 1311s, 1285s, 1242vw, 1222m, 1200m, 1150s, 1128m, 1096vw, 1039vw, 1030w, 1020m, 972w, 907s, 858w, 851w, 810s, 786vw, 753s, 740w, 688w, 624s, 569m. Anal. (%), Found: C, 59.4; H, 4.6; N, 16.0. Calc. for $\text{C}_{22}\text{H}_{22}\text{MnN}_2\text{O}_2$:

C, 59.9; H, 4.6; N, 15.9. A suitable crystal for X-Ray diffraction was selected from a sample prepared by an analogous reaction to the preparation of $[\text{Mn}(\text{sal-}o\text{-phen})(\text{dca})]_n$.

3.6.6 Synthesis of $[\text{Fe}((\pm)\text{-saltch})(\text{dca})]_n$

A methanolic solution (5 mL) of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.338 g, 1.0 mmol) was added to a solution of $(\pm)\text{-saltchH}_2$ (0.322 g, 1.0 mmol) and $\text{Na}(\text{dca})$ (0.178 g, 2.0 mmol) in a 5 mL/5 mL methanol/DMF mixture. The resulting solution immediately changed colour to dark brown/black. After several days a black crystalline solid had formed. It was collected and washed quickly with methanol (Yield 0.071 g, 16 %). IR (Nujol, cm^{-1}): 3616 vw, 2315m, 2248w, 2182s, 1618s, 1594m, 1545m, 1342vw, 1330vw, 1312m, 1249w, 1218vw, 1193w, 1148w, 1123vw, 1032vw, 1016w, 977vw, 930vw, 908w, 750m, 738w, 620w. Anal. (%): Found: C, 59.1; H, 4.5; N, 15.8. Calc. for $\text{C}_{22}\text{H}_{22}\text{FeN}_2\text{O}_2$: C, 59.4; H, 5.0; N, 15.8.

3.6.7 X-Ray Crystallography

Data were collected using a Nonius KappaCCD diffractometer with graphite monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Integration was carried out by the program DENZO-SMN,⁵⁶ and data were corrected for Lorentz polarisation effects and for absorption using the program SCALEPACK.⁵⁶ Solutions were obtained by direct methods (SHELXS 97)⁵⁷ followed by successive Fourier difference methods, and refined by full matrix least squares on F_{obs}^2 (SHELXL 97)⁵⁷ with the aid of the graphical interface program X-SEED.⁵⁸ All non-hydrogen atoms were refined anisotropically (unless otherwise stated). Secondary CH_2 hydrogen atoms were included at calculated positions for $[\text{Fe}(\text{salen})(\text{dca})]_n$ with isotropic thermal parameters 1.2 times U_{eq} of the adjoining carbon atom. The equivalent hydrogen atoms for $[\text{Mn}(\text{salen})(\text{dca})]_n$ were not included due to the disorder present on one of the CH_2 carbon atoms (*vide infra*). All remaining hydrogen

atoms of $[M(\text{salen})(\text{dca})]_n$, $M^{\text{III}} = \text{Mn, Fe}$, and all those for the complexes $[M(\text{sal-}o\text{-phen})(\text{dca})]_n$, $[M((\pm)\text{-saltch})(\text{dca})]_n$, $M^{\text{III}} = \text{Mn and Fe}$, were found in the Fourier difference map and refined isotropically.

The methylene carbon, C(10), of complex $[\text{Mn}(\text{salen})(\text{dca})]_n$ was found to be disordered over two positions. It was modelled as two atoms, C(10A) and C(10B), which were refined with isotropic thermal parameters. Site occupancies of 0.37 and 0.63 (1-0.37) for C(10A) and C(10B) respectively. Hydrogen atoms on C(10A) and C(10B) or C(11) were not included due to the disorder present.

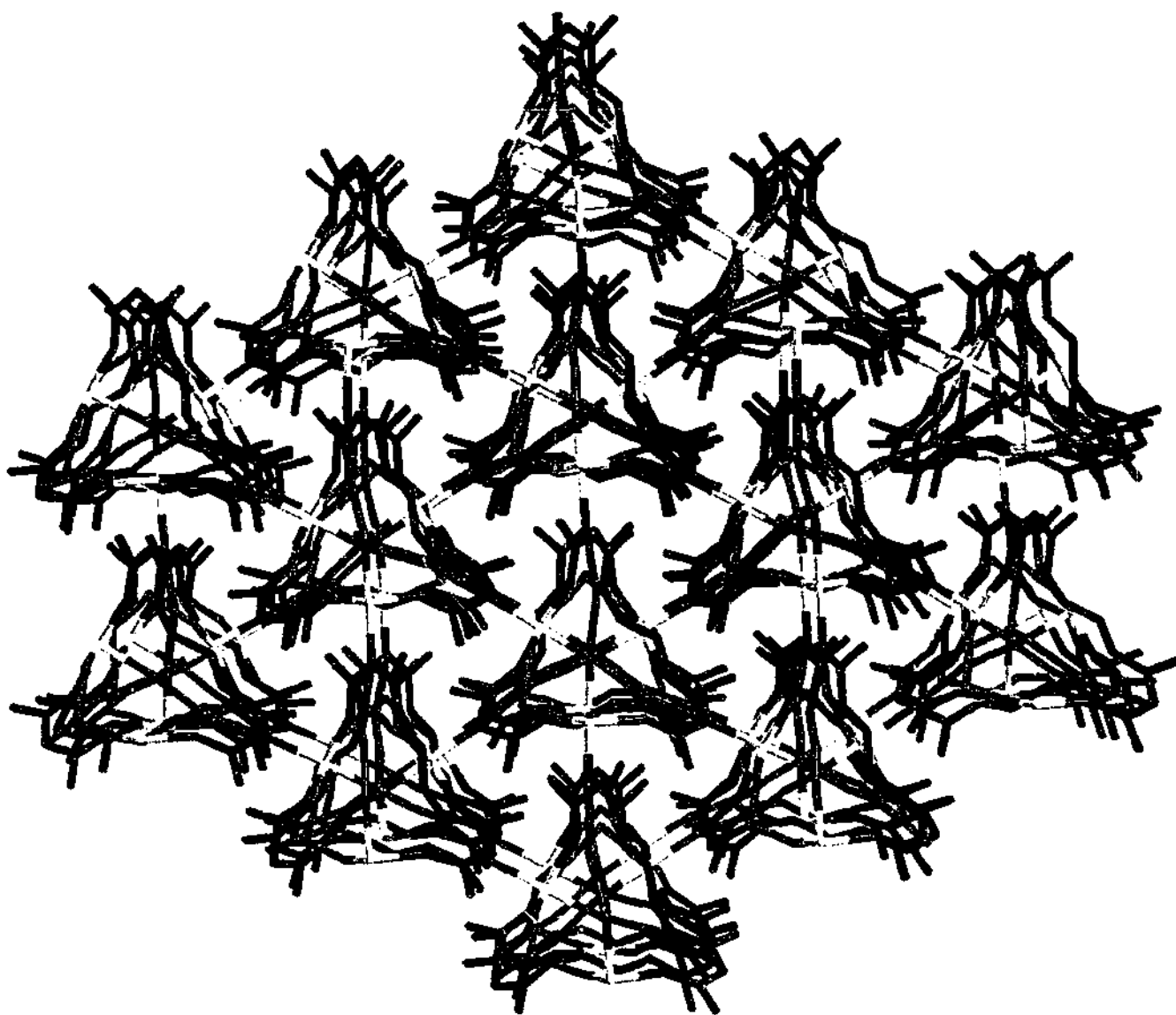
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**CHAPTER 4: CHIRAL 3D MANGANESE(II) AND
IRON(II) DICYANAMIDE NETWORKS
CONTAINING SCHIFF-BASE LIGANDS**

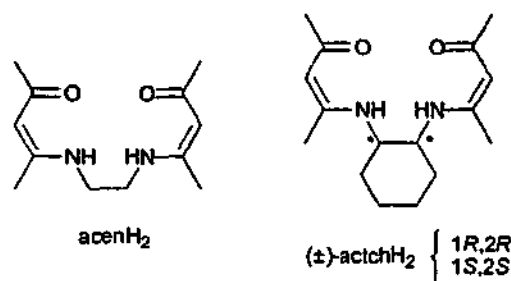
4.1 Introduction

The work presented in this chapter is part of a wider investigation of molecule-based magnetic materials containing terminal and bridging co-ligands and the dicyanamide ligand.¹⁻¹² The present study of chiral 3D transition metal dicyanamide networks containing acetylacetonate derived Schiff-base ligands complements work on the 1D linear chain complexes, $[M^{III}(L)(dca)]_n$, $M = Mn$ and Fe , with the salicylaldehyde derived Schiff-base ligands, $LH_2 = salenH_2$ (N,N' -ethylenebis(salicylideneimine)), $sal-o-phenH_2$ (N,N' -*o*-phenylenebis(salicylideneimine)) and $(\pm)$ -saltchH₂ ($(\pm)$ - N,N' -*trans*-cyclohexanebis(salicylideneimine)) described in Chapter 3.

From a synthetic chemical perspective, homo-chiral manganese(III) Schiff-base complexes have been used extensively as enantioselective catalysts for the epoxidation of olefins.¹³⁻¹⁶ The best known of these is Jacobsen's catalyst.¹⁷ In addition, chiral Schiff-base complexes have also been demonstrated to display non-linear optical properties.^{18,19} There is considerable current interest in synthesising and studying the properties of chiral molecule based magnets. For instance, Coronado *et al.* have recently reported chiral layered ferromagnets of $[Ni(chxn)_2]_3[Fe(CN)_6]_2 \cdot 2H_2O$ in two enantiopure forms, *1S,2S* and *1R,2R*.²⁰ Other recent papers are cited in this report.

Presented in this chapter are four new 3D transition metal dicyanamide network complexes of the general formula $[M(\text{Schiff-base})(dca)_2]$, $M^{II} = Mn$ and Fe . The Schiff-base ligands (Scheme 4.1) chosen for this study were $acenH_2$ (N,N' -ethylenebis(acetylacetonateimine)) and the chiral ligand, $(\pm)$ -actchH₂ ($(\pm)$ - N,N' -*trans*-1,2-cyclohexanebis(acetylacetonateimine)), the latter used as a racemic mixture. Initially, $acenH_2$ was used. The structures of the dicyanamide $acenH_2$ complexes with Mn^{II} and Fe^{II} were discovered to be chiral and individual crystals were spontaneously resolved into the

separate enantiomers. Following this isolation of a chiral network from achiral components, it was decided to explore the effect of deliberately introducing chirality by way of a structurally similar chiral Schiff-base ligand (i.e. ($\pm$)-actchH₂). The magnetic properties of these complexes were investigated.



Scheme 4.1 The Schiff-base ligands acenH₂ and ($\pm$)-actchH₂, drawn in conventional tetradentate enamineketone forms.

The pseudochalcogenide ligand dicyanonitrosomethanide (dcnm, ⁻ONC(CN)₂) was also investigated as a potential bridging ligand for molecule-based magnets by the candidate. Presented here is the structure of a mononuclear species *trans*-[Mn^{II}(acenH₂)₂(dcnm)₂] that was obtained during an effort to produce an analogous complex to [Mn(acenH₂)(dca)₂] with dcnm. As only a few crystals of this product were isolated, no further characterisation was performed.

4.2 Synthesis and Characterization

4.2.1 [M(acenH₂)(dca)₂], M^{II} = Mn and Fe

Aerobic reaction of sodium dicyanamide, acenH₂ and manganese(II) acetate or iron(II) perchlorate/tetrafluoroborate in methanol in the mole ratio of 1:1:1 or 2:1.5:1 led to the formation of the compounds [M(acenH₂)(dca)₂], M^{II} = Mn and Fe. The formation of by-products such as α -[Fe(dca)₂] and the solvated species [Fe(dca)₂(MeOH)₂], in the

synthesis of $[\text{Fe}(\text{acenH}_2)(\text{dca})_2]$, led to the use of a slight excess of acenH_2 in order to obtain a single phase of the product. No analogous by-products were observed in the synthesis of $[\text{Mn}(\text{acenH}_2)(\text{dca})_2]$. Interestingly, the oxidation state of the M^{II} ion remained at M^{II} , which contrasts with the $[\text{M}^{\text{III}}(\text{salen})(\text{dca})]_n$ species of Chapter 3. This presumably related to a different reduction potential exhibited by $[\text{M}^{\text{III}}(\text{salen})(\text{dca})]_n$, containing the N_2O_2 salen^{2-} ligand, compared to $[\text{M}(\text{acenH}_2)(\text{dca})_2]$, which contains neutral O-donor acenH_2 groups. The N-donor $\text{M}(\text{dca})_2$ components presumably dominate the reduction potential in the acenH_2 species. Solubility differences in the polymeric products will also play a part. Mole ratios of reagents are approximately the same in both series.

The infrared spectra of the complexes $[\text{M}(\text{acenH}_2)(\text{dca})_2]$, $\text{M}^{\text{II}} = \text{Mn}$ and Fe , show two absorptions assignable to $\nu_s(\text{C}\equiv\text{N})$ at 2184, 2171 and 2188, 2172 cm^{-1} respectively, implying slight differences in dicyanamide coordination environments within each structure. These values are indicative of bidentate dicyanamide, bridging through both nitrile nitrogens. Subsequent structural data (*vide infra*) confirmed two distinct, albeit similar, bidentate dicyanamide environments. The $\nu(\text{C}=\text{O})$ (acenH_2) position of 1592 (Mn) and 1598 (Fe) cm^{-1} for each complex is consistent with the enamineketone tautomeric form for this type of ligand. Structural studies of acenH_2 ²¹ and other such acetylacetone derived Schiff-base ligands²²⁻²⁵ have shown them to exist in the solid state in the enamineketone form shown in Scheme 4.1. Single crystals suitable for X-ray crystallographic experiments were grown by slow evaporation of dilute methanol solutions of the reactants.

4.2.2 $[\text{M}(\text{actchH}_2)(\text{dca})_2]$, $\text{M}^{\text{II}} = \text{Mn}$ and Fe

Aerobic reaction of sodium dicyanamide and actchH_2 with manganese(II) nitrate or iron(II) perchlorate/tetrafluoroborate in methanol in 2:1:1 or 2:1.5:1 mole ratio led to the formation of $[\text{M}(\text{actchH}_2)(\text{dca})_2]$, $\text{M}^{\text{II}} = \text{Mn}$ and Fe . As in the synthesis of $[\text{Fe}(\text{acenH}_2)(\text{dca})_2]$, a slight excess of the Schiff-base ligand, actchH_2 , was used to favour

the formation of the desired product, rather than by-products such as α -[Fe(dca)₂] and/or [Fe(dca)₂(MeOH)₂].

The infrared spectra of the complexes, [M(actchH₂)(dca)₂], M^{II} = Mn and Fe, show $\nu_s(\text{C}\equiv\text{N})$ at 2171 and 2172 cm⁻¹ respectively. These values are indicative of bidentate dicyanamide bridging through both nitrile nitrogens. Unlike in the infrared spectra of the [M(acenH₂)(dca)₂] complexes, no discernable splitting of these bands was observed, thus implying identical, or at least very similar, dicyanamide coordination environments. The $\nu(\text{C}=\text{O})$ (actchH₂) position of ~1594 cm⁻¹ for both complexes is (within instrumental error) the same as $\nu(\text{C}=\text{O})$ (1600 cm⁻¹) for the free ligand. Previous structural studies²² indicate the free ligand exists in the solid state as the enamineketone form as shown in Scheme 4.1. Crystals suitable for X-ray diffraction were obtained from the nitrate and tetrafluoroborate salts of manganese(II) and iron(II). [Fe(actchH₂)(dca)₂] was observed to oxidise in air so was kept under an atmosphere of nitrogen.

The chirality of these complexes (*vide infra*) is introduced by a racemic mixture (*R,R*- and *S,S*) of the ($\pm$)-actchH₂ ligand. In order to synthesise a homochiral product, a chirally pure sample of *S,S-trans*-diaminocyclohexane was kindly donated by Prof. G. B. Deacon (Monash University). Unfortunately, attempts to synthesise the Schiff-base ligand and the subsequent crystallisation of a coordination polymer, however, were unsuccessful, yielding brown oils for both ligand and coordination polymer syntheses.

4.2.3 [Mn^{II}(acenH₂)₂(dcnm)₂]

Reaction of Mn(OAc)₂·4H₂O with acenH₂ and Me₄N(dcnm) in methanol in a molar ratio of 1:1:1 led to a major product that was a dark brown residue, which was not characterised and a minor product - a very small amount of orange crystals of *trans*-

$[\text{Mn}^{\text{II}}(\text{acenH}_2)_2(\text{dcm})_2]$ that were characterised solely by single crystal X-ray diffraction. No further attempts were made to synthesise this product in higher yields.

4.3 Crystal Structures

4.3.1 $[\text{M}(\text{acenH}_2)(\text{dca})_2]$, $\text{M}^{\text{II}} = \text{Mn}$ and Fe

Crystal data for the complexes $[\text{M}(\text{acenH}_2)(\text{dca})_2]$, $\text{M}^{\text{II}} = \text{Mn}$ and Fe , are summarised in Table 4.1 and selected interatomic distances and angles are listed in Table 4.2 (see page 179). The structures of the two are isomorphous and exist in the trigonal crystal system. The crystals selected had opposite handed chiral space groups, $P3_2$ (Mn) and $P3_1$ (Fe), and were each racemically pure, as indicated by the Flack parameters²⁶ of zero (see Experimental Section 4.6.8, page 202) for each respective structure refinement. However, as none of the components are themselves chiral, it is assumed that the bulk samples are racemic mixtures of $P3_1$ and $P3_2$ crystals.

The atom labelling scheme for $[\text{Fe}(\text{acenH}_2)(\text{dca})_2]$ is shown in Figure 4.1. The asymmetric unit contains three metal atoms, three μ -acenH₂ ligands (bridging *via* the carbonyl oxygen donor atoms), and six $\mu_{1,5}$ -dca ligands (bridging *via* both nitrile nitrogens). Despite being crystallographically distinct the three metal ions and acenH₂ ligands are in very similar environments. The six $\mu_{1,5}$ -dca ligands are of two types. The first type bridge *two* metal centres and generate unique helices. The three different μ -acenH₂ ligands also bridge the same metal centres, forming three separate double bridges. The resulting three unique $\{[\text{M}(\mu\text{-acenH}_2)(\mu\text{-dca})]^+\}_n$ helical chains run parallel to the *c*-axis direction. One such helix is shown in Figure 4.2 (see also Figure 4.4). The second type of $\mu_{1,5}$ -dca ligands cross-link these helices in the *ab*-plane to form a single 3D network. The overall 3D structure is shown in Figure 4.3.

Table 4.1 Crystal data for $[M(\text{acenH}_2)(\text{dca})_2]$, $M^{\text{II}} = \text{Mn}$ and Fe .

Complex	Mn	Fe
Formula	$\text{C}_{16}\text{H}_{20}\text{MnN}_8\text{O}_2$	$\text{C}_{16}\text{H}_{20}\text{FeN}_8\text{O}_2$
M	411.34	412.25
Crystal system	Trigonal	Trigonal
Space group	$P3_2$	$P3_1$
$a/\text{\AA}$	15.1415(2)	15.0317(3)
$b/\text{\AA}$	15.1415(2)	15.0317(3)
$c/\text{\AA}$	22.8225(2)	22.7014(2)
$U/\text{\AA}^3$	4531.39(9)	4442.2(1)
Z	9	9
T/K	123(2)	123(2)
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	0.683	0.792
Crystal dimensions/mm	$0.4 \times 0.3 \times 0.26$	$0.13 \times 0.13 \times 0.13$
Index ranges	$-19 \leq h \leq 19,$ $-19 \leq k \leq 19,$ $-29 \leq l \leq 21$	$-19 \leq h \leq 19,$ $-19 \leq k \leq 19,$ $-29 \leq l \leq 21$
Completeness to $2\theta = 55^\circ / \%$	99.7	99.9
Data collected	60719	61722
Unique data (R_{int})	12995 (0.0424)	12875 (0.0821)
Observed reflections [$I > 2\sigma(I)$]	12364	10181
Parameters	753	730
Final R_1 , wR_2 [$I > 2\sigma(I)$] ^(a)	0.0637, 0.1334	0.0700, 0.1371
(all data)	0.0676, 0.1356	0.0974, 0.1468
Goodness of fit, S	1.120	1.062

^(a) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

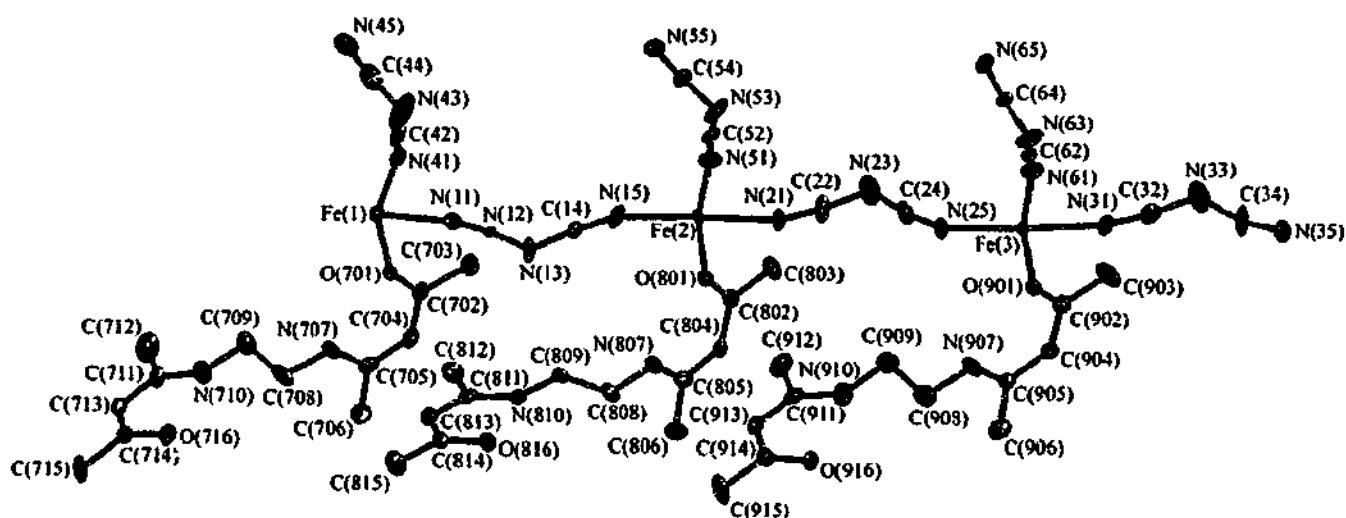


Figure 4.1 The asymmetric unit for $[\text{Fe}(\text{acenH}_2)(\text{dca})_2]$ with atom labelling scheme (thermal ellipsoids shown at 50 % probability and hydrogen atoms omitted for clarity). $[\text{Mn}(\text{acenH}_2)(\text{dca})_2]$ is isomorphous.

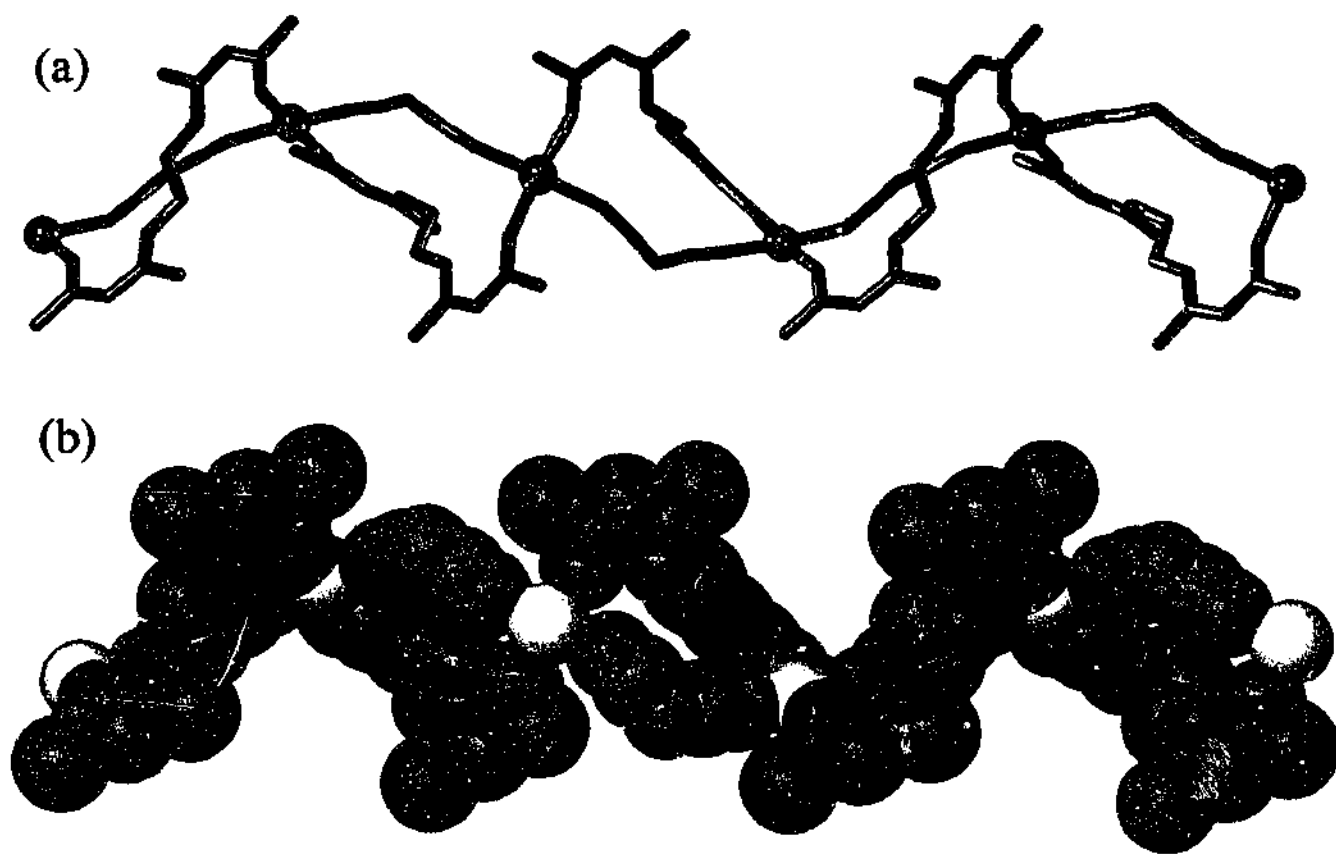


Figure 4.2 (a) A single $\{[\text{Fe}(\mu\text{-acenH}_2)(\mu\text{-dca})]^+\}_n$ helix in the structure of $[\text{Fe}(\text{acenH}_2)(\text{dca})_2]$ (the vacant *trans* coordination sites are occupied by cross-linking dca ligands); and (b) a space-filling representation, where metal centres, helix $\mu_{1,5}$ -dca and μ -acenH₂ ligands are yellow, red and green respectively.

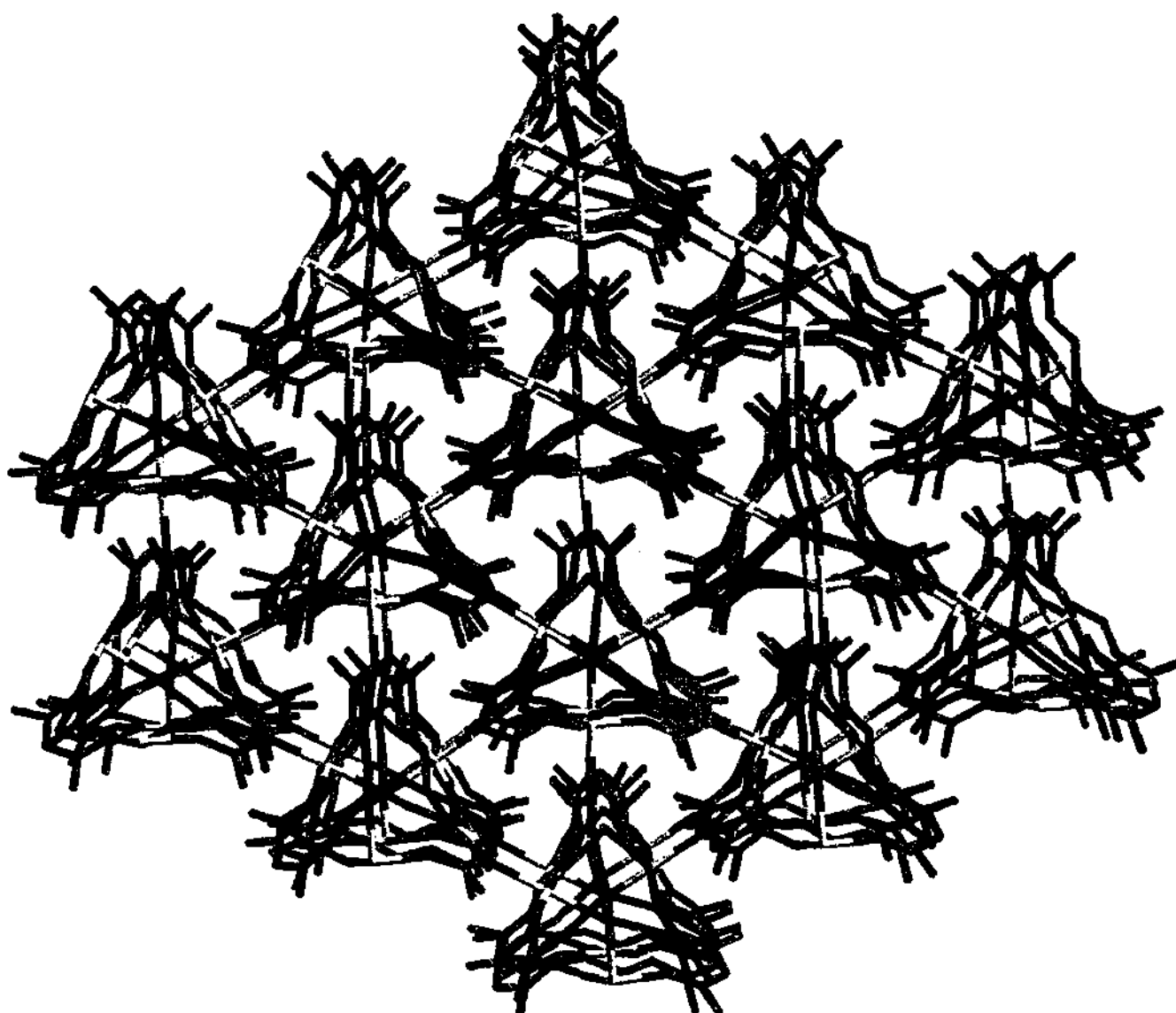


Figure 4.3 The 3D network structure of $[\text{Fe}(\text{acenH}_2)(\text{dca})_2]$ viewed down the c -axis direction. Colours are as in Figure 4.2 and cross-linking $\mu_{1,5}$ -dca ligands are purple.

The cross-linking $\mu_{1,5}$ -dca bridges form linear $\{[\text{M}(\text{dca})]_n\}^+$ chains that exist in 'layers' parallel to the ab -plane. Following these layers down the c -axis direction, the next layer is rotated 120° about the c -axis to the one above it, thus the layers show an ABC type packing sequence (Figure 4.4). In a topological sense, the helix $\mu_{1,5}$ -dca and μ -acenH₂ bridges can be treated together as a single link between the metal ions. Thus each metal centre is a 4-connecting node with square planar geometry. The net is then reduced to a 3D network of (topologically) identical square planar centres. Figure 4.5 shows a topological

representation. The resulting 3D chiral network type has been described by O'Keefe²⁷ as having the 'dense' 7⁵9 topology. The first real example of this previously theoretically predicted net²⁷ was observed recently by Ciani and co-workers in a (three-fold interpenetrated) Cu^{II} coordination polymer with the linear bridging ligand 1,2-bis(4-pyridyl)ethyne.²⁸ The structures reported here are the first examples of single, non-interpenetrating networks possessing this topology.

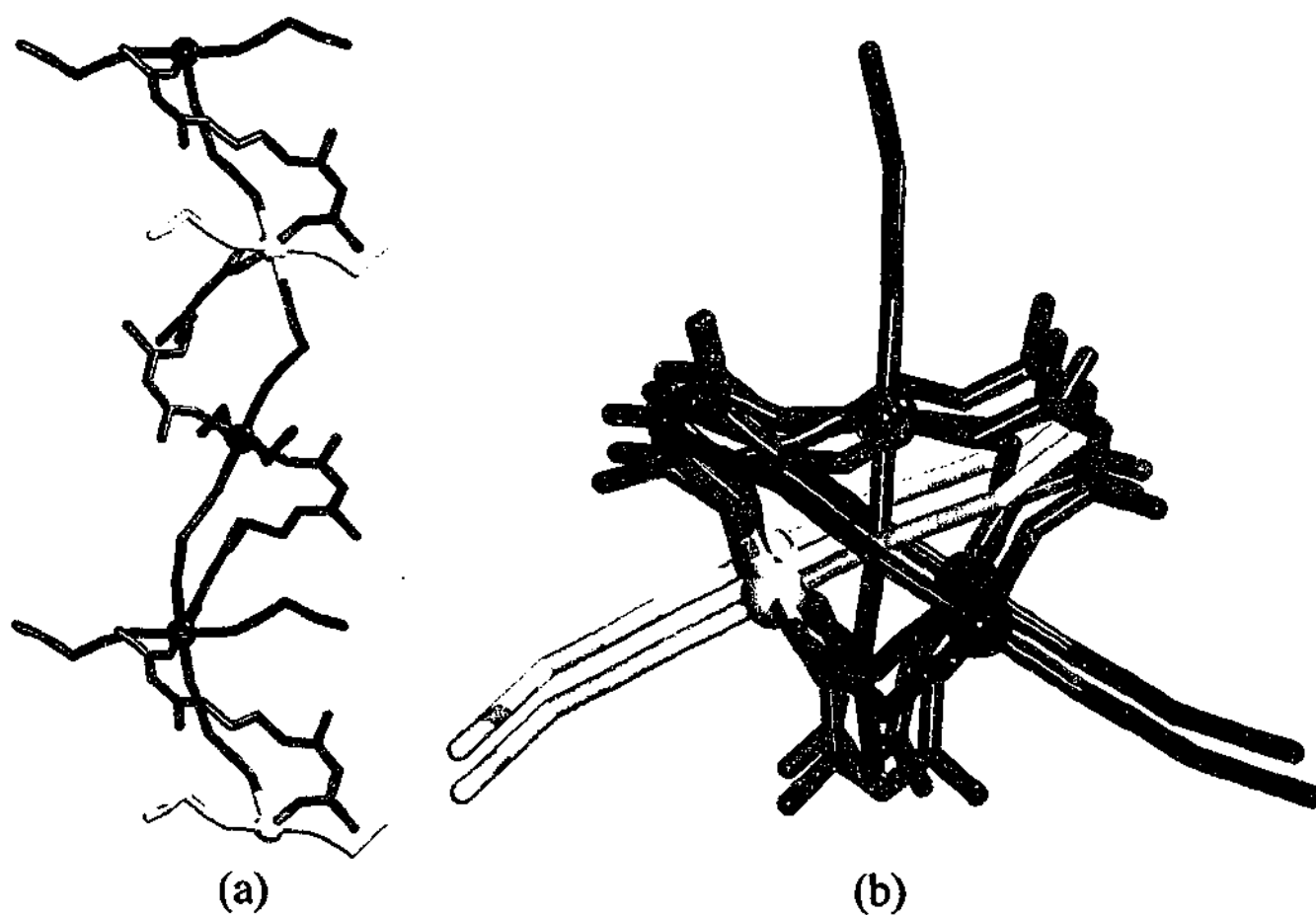


Figure 4.4 (a) A side-on and (b) a top view of a single helix in the structure of [Fe(acenH₂)(dca)₂] with cross-linking $\mu_{1,5}$ -dca ligands shown (different colours are used to indicate the ABC stacking sequence).

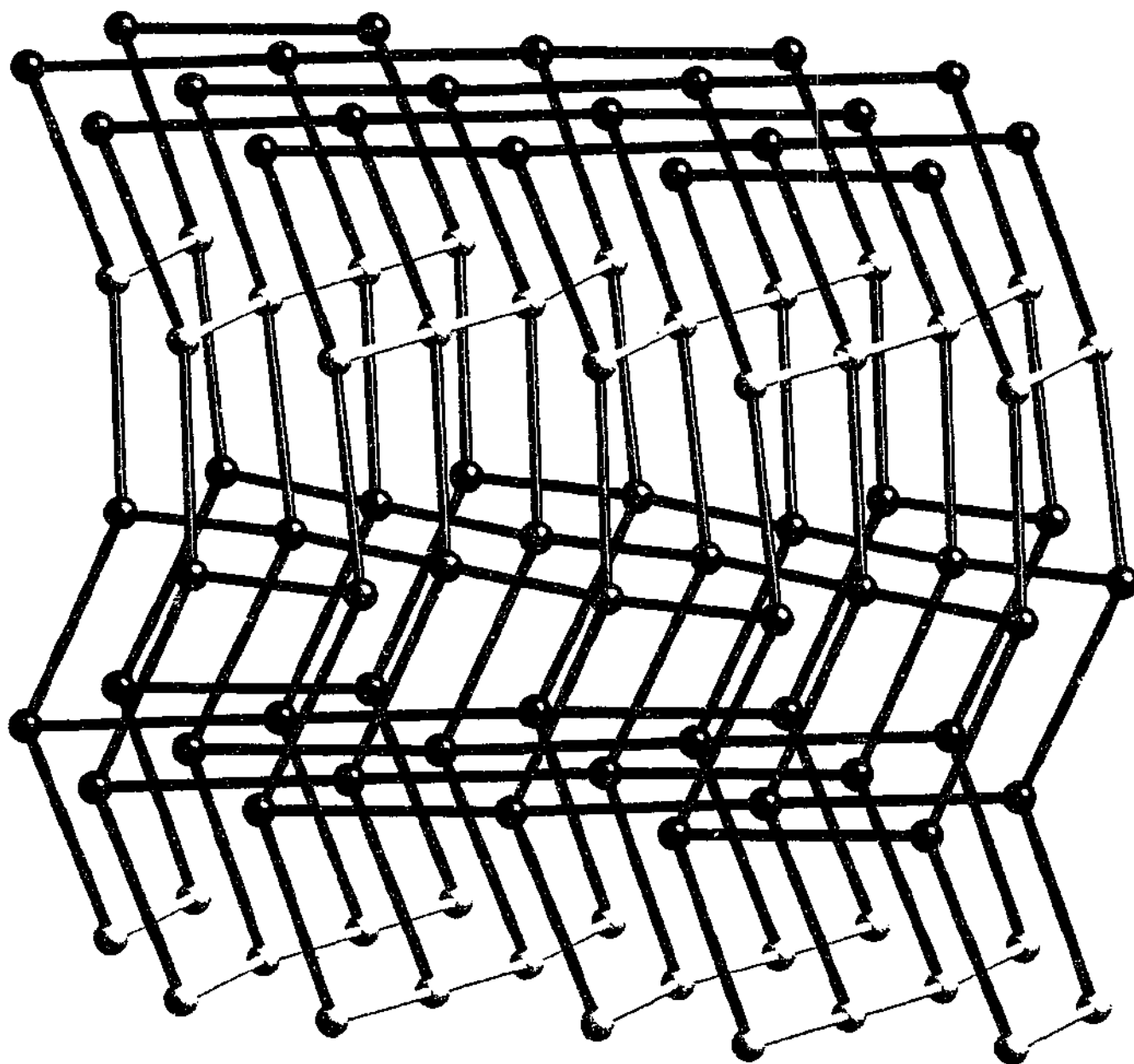


Figure 4.5 A schematic representation of the $[\text{Fe}(\text{acenH}_2)(\text{dca})_2]$ dense 7^5_9 network topology. Only metal centres are shown. Helix dca and acenH₂ connections have been reduced to the single red bonds and cross-links between helices are coloured as in Figure 4.4 to indicate repeating layers.

The local coordination environment of each metal ion is distorted octahedral. The equatorial coordination plane contains the nitrile nitrogens of four $\mu_{1,5}$ -dca ligands – two helix and two cross-linking dca ligands. The two helix dca ligands are symmetry related and are *trans* oriented ($\text{M}-\text{N}_{\text{dca}} = 2.204(4) - 2.234(4) \text{ \AA}$ (Mn), and $2.147(4) - 2.200(4) \text{ \AA}$

(Fe)). The cross-linking dca ligands are similarly *trans* oriented ($M-N_{dca} = 2.168(4) - 2.214(4) \text{ \AA}$ (Mn), and $2.112(4) - 2.162(5) \text{ \AA}$ (Fe)). The axial coordination sites are occupied by the carbonyl oxygen donor atoms of the acenH₂ ligand ($M-O_{acen} = 2.152(3) - 2.174(3) \text{ \AA}$ (Mn), and $2.074(3) - 2.092(3) \text{ \AA}$ (Fe)). Interestingly, in these structures the acenH₂ ligand is in its neutral protonated form with the hydrogens attached to the nitrogen atoms. Intra-ligand hydrogen bonding (Figure 4.6) occurs between the amine N-H and the coordinating carbonyl oxygen forming a pseudo six membered ring (average N...O distance is $2.62(3) \text{ \AA}$). Presumably the formation of intra-ligand hydrogen bonding may, in combination with the flexibility of the ligand backbone, influence or stabilise the bridging mode of acenH₂, which involves coordination of the oxygen donor atoms alone.

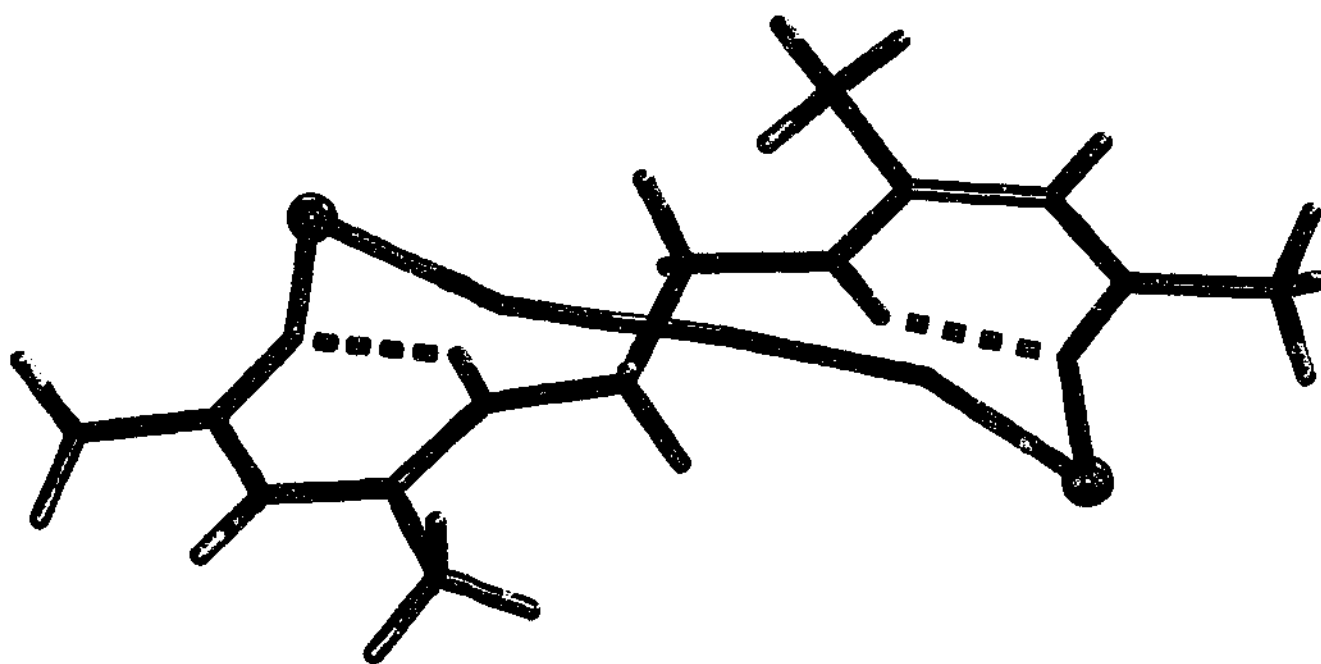


Figure 4.6 A single $\{M(\mu\text{-acenH}_2)(\mu\text{-dca})M\}$ helix moiety showing the intra-molecular hydrogen bonding of the acenH₂ ligand (green dashed bonds).

The crystal structure of the free ligand, acenH₂, was published in 1979 by Calligaris *et al.*²¹ Their data indicate the molecule is in the enamineketone form as shown

in Scheme 4.1, with intra-molecular hydrogen bonding of the same type observed here. In addition, they note the significant amount of delocalisation across the enamineketone groups. This is supported by the almost planar-trigonal nature of the amine group, as is also the case here, where the N bond angles sum to approximately 360° .

To the best of the candidate's knowledge, this bridging mode of acenH₂ had not been reported at the time of the present syntheses and characterisations. During the preparation of this thesis, Junk and Smith published the structures of four isostructural lanthanide coordination polymers, $\{Ln^{III}(NO_3)_3(acenH_2)_2\}[C_6H_{12}]\}_n$ (where $Ln^{III} = La, Pr, Nd$ and Sm),²⁹ in which acenH₂ adopts two distinct modes of coordination. The first is identical to that observed here, where acenH₂ acts as a bis-monodentate bridge *via* both oxygen atoms, with intra-ligand hydrogen bonding also present. The second mode involves a single acenH₂ chelating *via* the oxygen atoms only, thus forming a 14 membered chelate ring.²⁹ This mode is also observed in a mononuclear Mn^{II} complex reported here (see section 4.3.3, page 190). The complexation of the lanthanides by the acenH₂ ligands by oxygen atoms alone is explained by the hard acid/base relationship - oxygen coordination is preferred over that of nitrogen owing to the former being the harder Lewis base. However, Mn^{II} is an intermediate base, equally favouring O- or N-donors. A number of examples of Schiff-base ligands adopting bis-bidentate bridging modes have been reported.³⁰⁻³² For instance, in the dinuclear copper(I) complex, $[\{(Ph_3P)_2Cu\}_2(\mu-acen)] \cdot MePh$,³³ (Figure 4.7(b)) and in $[Co_2(3-MeO-salen)_3] \cdot 2H_2O \cdot 2DMSO$ (3-MeO-salenH₂ = *N,N'*-ethylenebis(3-methoxysalicylideneimine)),³² the Schiff-base acts as a bis-bidentate ligand occupying two coordination sites on each metal centre.

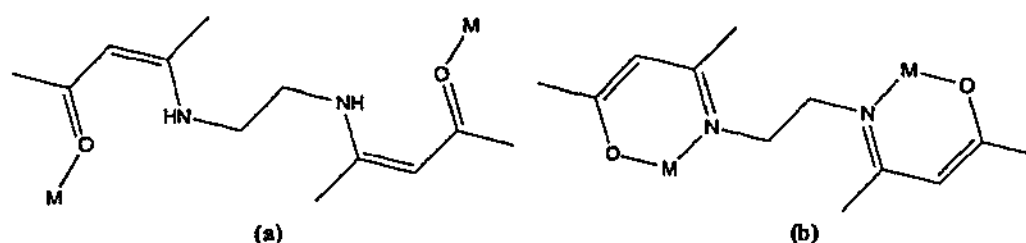


Figure 4.7 (a) The bridging mode of acenH₂ in the [M^{II}(acenH₂)(dca)₂] complexes and, (b) acen²⁻ in the structure of [{(Ph₃P)₂Cu}₂(μ-acen)]·MePh.³³

In the present case, the intra-helix M...M distances are 8.4111(5) - 8.4176(4) Å (Mn), and 8.3511(5) - 8.3601(5) Å (Fe). The inter-helix M...M distances are significantly longer, ranging from 8.7489(9) to 8.7508(9) Å (Mn), and from 8.681(1) to 8.689(1) Å (Fe). This observation is noteworthy in light of the fact that the latter bridges consist of a single μ_{1,5}-dca rather than the intra-helix bridges of μ_{1,5}-dca and the longer acenH₂ ligand. In general, the M–ligand and M...M distances are shorter for the iron(II) complex compared to the manganese(II) complex. Consequently, the unit cell dimensions for [Fe(acenH₂)(dca)₂] are about 0.1 Å shorter than those for [Mn(acenH₂)(dca)₂].

In [Fe(acenH₂)(dca)₂] it can be seen that the acenH₂ ligands follow a left-handed screw whilst the dca ligands describe the path of a right-handed screw. Despite this, the helices follow the symmetry rules of the three-fold screw, 3₁. In the structure of [Mn(acenH₂)(dca)₂] the handedness of the helices is reversed and follow a 3₂ screw. An interesting feature of these chiral networks is that they contain only achiral components i.e. there is no intrinsic chirality in the precursors, which may lead to a chiral structure. Additionally, spontaneous chiral resolution of crystals occurred.

Many discrete cluster helical coordination complexes, known as helicates, have been reported.³⁴⁻⁵⁷ Ligands such as benzimidazoles,^{42,58,59} polypyridyls,⁶⁰⁻⁶³ and Schiff-bases,^{35,64,65} many of which possess as part of their backbone the -CH₂- group, which can

twist around two or more metal centres giving rise to double or triple helicate structures. The helicity is induced by the geometrical constraints of the tetrahedral methylene group. For instance, Kruger *et al.* have recently reported some double helicates, $[M^{II}_2L_2] \cdot \text{Solv}$ (where $M^{II} = \text{Co}, \text{Cu}$; $L = \text{bis}(\text{N-salicylidene-4,4'-diaminodiphenyl})\text{methane}$), using a Schiff-base ligand that has a $-\text{Ph}-\text{CH}_2-\text{Ph}-$ bridge moiety.³⁵ Presumably in the $[M^{II}(\text{acenH}_2)(\text{dca})_2]$ structures presented here, the formation of helices is induced, or at least influenced by, the geometrical requirements of the $-\text{CH}_2\text{CH}_2-$ bridge of the acenH_2 ligand as it 'twists' around to bridge two metal centres.

Some examples of infinite helical chain structures include those of $[\text{Mn}^{III}(\text{salpn})(\text{NCS})]_n$ (where $\text{salpnH}_2 = N,N'$ -1,3-propylenebis(salicylideneimine)),⁶⁶ $[\text{Co}^{II}(\text{dca})(\text{H}_2\text{Bilm})_2]\text{Cl}$ (where $\text{H}_2\text{Bilm} = 2,2$ -biimidazole),⁶⁷ and $\text{Ph}_4\text{P}[\text{Co}^{II}(\text{dca})\text{Br}_2]$ (described in Chapter 5) which exist as 2-fold helical chains bridged by NCS^- in the first example and by dca in the other two cases.

Table 4.2 Selected interatomic distances (Å) and angles (°) for [M(acenH₂)(dca)₂], M^{II} = Mn and Fe.

	Mn	Fe		Mn	Fe
M(1)–N(11)	2.172(4)	2.145(5)	M(2)–N(55 ^v)	2.208(5)	2.200(4)
M(1)–N(35 ⁱⁱ)	2.208(4)	2.160(5)	M(2)–O(801)	2.159(3)	2.083(4)
M(1)–N(41)	2.216(4)	2.162(6)	M(2)–O(816 ^{iv})	2.160(3)	2.078(4)
M(1)–N(45 ⁱⁱⁱ)	2.228(4)	2.182(6)	M(3)–N(31)	2.168(4)	2.112(5)
M(1)–O(701)	2.174(3)	2.075(4)	M(3)–N(25)	2.207(4)	2.152(4)
M(1)–O(716 ⁱ)	2.152(3)	2.078(4)	M(3)–N(61)	2.234(4)	2.200(4)
M(2)–N(21)	2.193(4)	2.113(5)	M(3)–N(65 ^{vii})	2.204(4)	2.147(4)
M(2)–N(15)	2.214(4)	2.162(5)	M(3)–O(901)	2.165(4)	2.074(3)
M(2)–N(51)	2.228(5)	2.148(4)	M(3)–O(916 ^{vi})	2.159(4)	2.092(3)
M···M across $\mu_{1,5}$ -dca bridges in <i>ab</i> -plane			Mn	Fe	
		M(1)···M(2)	8.7495(9)	8.684(1)	
		M(2)···M(3)	8.7489(9)	8.689(1)	
		M(3)···M(1 ⁱⁱ)	8.7508(9)	8.681(1)	
M···M across acenH ₂ and $\mu_{1,5}$ -dca bridges parallel to <i>c</i> -axis			Mn	Fe	
		M(1)···M(1 ⁱ)	8.4176(4)	8.3511(6)	
		M(2)···M(2 ^{iv})	8.4111(5)	8.3565(5)	
		M(3)···M(3 ^{vi})	8.4124(5)	8.3601(5)	
	Mn	Fe		Mn	Fe
N(11)–M(1)–N(41)	91.6(2)	94.7(2)	N(21)–M(2)–N(51)	90.9(2)	92.1(2)
N(41)–M(1)–N(35 ⁱⁱ)	88.0(2)	88.0(2)	N(51)–M(2)–N(15)	88.0(2)	89.2(2)
N(35 ⁱⁱ)–M(1)–N(45 ⁱⁱⁱ)	87.5(2)	88.3(2)	N(15)–M(2)–N(55 ^v)	87.7(2)	86.1(2)
N(11)–M(1)–N(45 ⁱⁱⁱ)	93.0(2)	89.9(2)	N(55 ^v)–M(2)–N(21)	93.5(2)	92.6(2)
N(11)–M(1)–N(35 ⁱⁱ)	179.3(2)	178.3(2)	N(21)–M(2)–N(15)	178.7(2)	178.4(2)
N(41)–M(1)–N(45 ⁱⁱⁱ)	175.4(2)	175.2(2)	N(51)–M(2)–N(55 ^v)	175.2(2)	175.3(2)
O(701)–M(1)–O(716 ⁱ)	172.9(1)	174.8(2)	O(801)–M(2)–O(816 ^{iv})	173.8(1)	173.0(2)

O(701)–M(1)–N(11)	92.9(2)	92.4(2)	O(801)–M(2)–N(21)	93.5(2)	91.9(2)
O(701)–M(1)–N(41)	94.5(1)	92.6(2)	O(801)–M(2)–N(51)	90.3(2)	94.4(2)
O(701)–M(1)–N(35 ⁱⁱ)	87.7(1)	87.4(2)	O(801)–M(2)–N(15)	87.1(2)	87.1(2)
O(701)–M(1)–N(45 ⁱⁱⁱ)	86.3(1)	88.5(2)	O(801)–M(2)–N(55 ^v)	87.3(2)	86.1(2)
O(716 ⁱ)–M(1)–N(11)	93.3(1)	92.8(2)	O(816 ^{iv})–M(2)–N(21)	92.5(2)	93.7(2)
O(716 ⁱ)–M(1)–N(41)	89.0(1)	87.7(2)	O(816 ^{iv})–M(2)–N(51)	87.9(2)	89.6(2)
O(716 ⁱ)–M(1)–N(35 ⁱⁱ)	86.2(1)	87.4(2)	O(816 ^{iv})–M(2)–N(15)	86.9(2)	87.2(2)
O(716 ⁱ)–M(1)–N(45 ⁱⁱⁱ)	89.8(1)	90.8(2)	O(816 ^{iv})–M(2)–N(55 ^v)	94.0(2)	89.5(2)
O(901)–M(3)–O(916 ^{vi})	172.7(1)	173.5(1)	O(916 ^{vi})–M(3)–N(31)	92.3(2)	91.8(2)
O(901)–M(3)–N(31)	94.5(2)	93.5(2)	O(916 ^{vi})–M(3)–N(61)	86.8(2)	86.6(2)
O(901)–M(3)–N(61)	90.1(2)	89.4(2)	O(916 ^{vi})–M(3)–N(25)	86.9(2)	87.2(2)
O(901)–M(3)–N(25)	86.3(2)	87.4(2)	O(916 ^{vi})–M(3)–N(65 ^{vii})	93.8(2)	94.2(2)
O(901)–M(3)–N(65 ^{vii})	88.9(2)	89.4(2)			

Hydrogen bonding

N(707)···O(701)	2.626(5)	2.607(6)	N(810)···O(816)	2.605(5)	2.623(6)
N(710)···O(716)	2.626(5)	2.625(6)	N(907)···O(901)	2.629(5)	2.616(6)
N(807)···O(801)	2.625(5)	2.631(5)	N(910)···O(916)	2.635(5)	2.617(6)
H(707)···O(701)	1.92	1.92	H(810)···O(816)	1.91	1.92
H(710)···O(716)	1.93	1.91	H(907)···O(901)	1.92	1.93
H(807)···O(801)	1.91	1.93	H(910)···O(916)	1.94	1.91

N(707)–H(707)···O(701)	136.2	134.0	N(810)–H(810)···O(816)	134.8	135.4
N(710)–H(710)···O(716)	135.0	137.4	N(907)–H(907)···O(901)	136.2	133.8
N(807)–H(807)···O(801)	136.9	134.9	N(910)–H(910)···O(916)	135.1	136.4

Symmetry transformations:

For Mn: (i) $-x+y+1, -x+2, z+1/3$; (ii) $x+1, y+2, z$; (iii) $-y+2, x, y+1, z-1/3$; (iv) $-x+y+1, -x+1, z+1/3$; (v) $-y+1, x-y, z-1/3$; (vi) $-x+y+1, -x, z+1/3$; (vii) $-y, x-y-1, z-1/3$.

For Fe: (i) $-x+y-1, -x+1, z-1/3$; (ii) $x-1, y+1, z$; (iii) $-y+1, x-y+2, z+1/3$; (iv) $-x+y, -x+1, z-1/3$; (v) $-y+1, x-y+1, z+1/3$; (vi) $-x+y+1, -x+1, z-1/3$; (vii) $-y+1, x-y, z+1/3$.

4.3.2 $[M(\text{actchH}_2)(\text{dca})_2]$, $M^{\text{II}} = \text{Mn}$ and Fe

The manganese(II) and iron(II) complexes are isomorphous, crystallizing in the chiral orthorhombic space group $P2_12_12_1$. The crystals were found to show racemic twinning. The formula $[M(\text{actchH}_2)(\text{dca})_2]$ is intended to include the presence of racemic twinning, however, the structures presented here are of the twin component with the *R,R*-actchH₂ ligand. The asymmetric unit consists of a single formula unit (Figure 4.8). Crystal data for the complexes $[M(\text{actchH}_2)(\text{dca})_2]$, $M^{\text{II}} = \text{Mn}$ and Fe , are summarised in Table 4.3 and selected interatomic distances and angles are listed in Table 4.4 (see page 189).

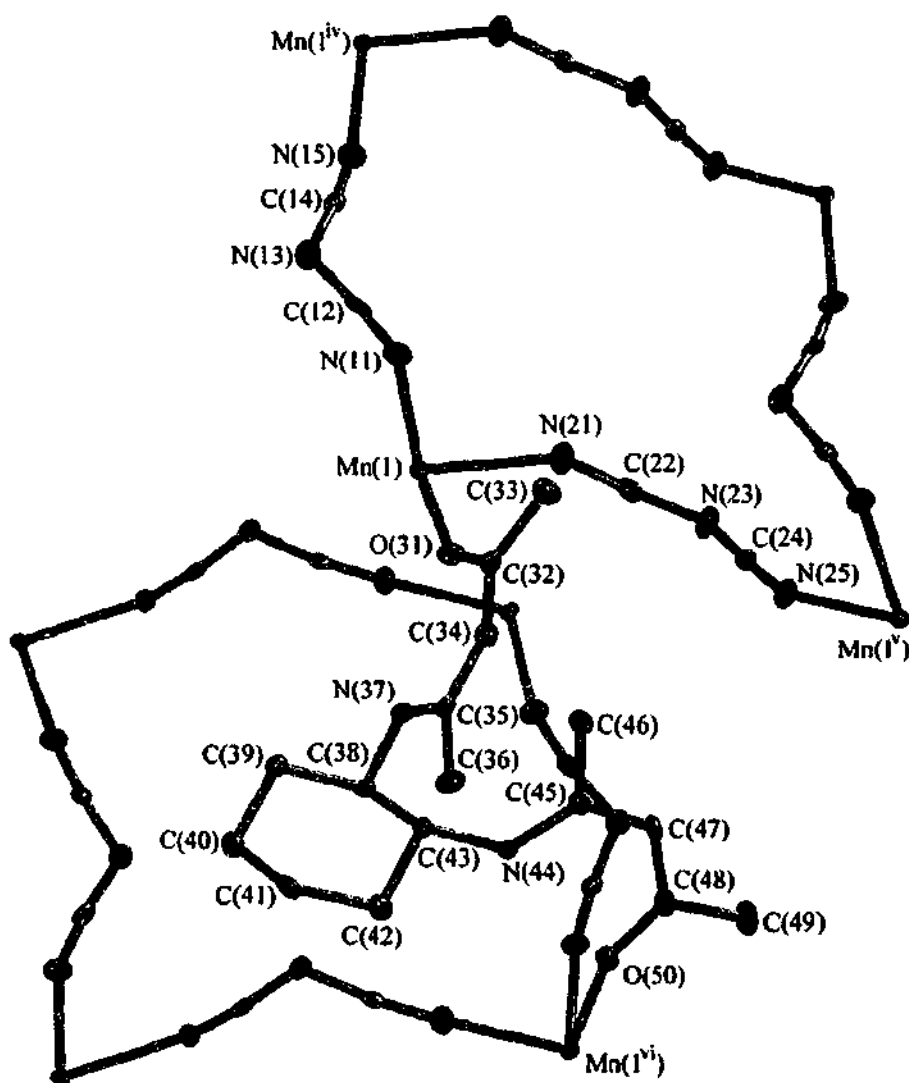


Figure 4.8 Atom labelling diagram for $[\text{Mn}(\text{actchH}_2)(\text{dca})_2]$ (thermal ellipsoids shown at 50 % probability, hydrogen atoms are omitted for clarity). $[\text{Fe}(\text{actchH}_2)(\text{dca})_2]$ is isomorphous.

Table 4.3 Crystal data for $[M(\text{actchH}_2)(\text{dca})_2]$, $M^{\text{II}} = \text{Mn}$ and Fe .

Complex	Mn	Fe
Formula	$\text{C}_{20}\text{H}_{26}\text{MnN}_8\text{O}_2$	$\text{C}_{20}\text{H}_{26}\text{FeN}_8\text{O}_2$
M	465.43	466.34
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
$a/\text{\AA}$	8.7852(1)	8.7312(2)
$b/\text{\AA}$	15.8152(2)	15.7724(3)
$c/\text{\AA}$	16.0912(2)	16.0549(4)
$U/\text{\AA}^3$	2235.71(5)	2206.39(9)
Z	4	4
T/K	123(2)	123(2)
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	0.624	0.718
Crystal dimensions/mm	$0.13 \times 0.13 \times 0.1$	$0.13 \times 0.13 \times 0.1$
Index ranges	$-11 \leq h \leq 11,$ $-20 \leq k \leq 21,$ $-21 \leq l \leq 21$	$-11 \leq h \leq 11,$ $-18 \leq k \leq 20,$ $-20 \leq l \leq 21$
Completeness to $2\theta = 55^\circ / \%$	99.8	99.8
Data collected	37306	19983
Unique data (R_{int})	5531 (0.1010)	5441 (0.0676)
Observed reflections [$I > 2\sigma(I)$]	4462	4387
Parameters	285	285
Final R_1, wR_2 [$I > 2\sigma(I)$] ^(a)	0.0522, 0.0664	0.0539, 0.0693
(all data)	0.0786, 0.0704	0.0781, 0.0732
Goodness of fit, S	1.066	1.099

$$^{(a)} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$$

The structures consist of (4,4) square grid sheets of octahedral M^{II} centres connected by $\mu_{1,5}$ -dca ligands in the ab -plane. The sheets are linked in the c -axis direction

by the actchH₂ ligand bridging through the both the carbonyl oxygen atoms in a bis-monodentate fashion, thus forming a 3D network. The *R,R*-actchH₂ links parallel to the *c*-axis form left-handed 2-fold helices, one of which is shown in Figure 4.9, whereas the other twin component, with *S,S*-actchH₂ ligands, has right-handed 2-fold helices. The cyclohexyl moieties of the actchH₂ ligands are parallel to the *ab*-plane. The sheets are corrugated, with all the troughs parallel, and running in the *a*-axis direction (Figure 4.10). The troughs of one sheet are above and below the troughs of the two adjacent sheets in the *c*-axis direction, and hence likewise for the crests. Within the corrugated sheets the metal centres are in two sets of parallel planes. In Figure 4.10 it can be seen that within each M_{*n*} plane, the equatorial dca N₄ coordination sets of each metal centre are inclined in the opposite direction with respect to the other M_{*n*} plane. The direction is reversed in the adjacent M(dca)₂ sheets. The actchH₂ ligands link the sheets trough-to-trough and crest-to-crest such that adjacent sheets are offset to each other and the M centre in an adjacent sheet is almost directly below the centre of the square grid of the sheet above (Figure 4.11). Thus, the stacking of the square-grid sheets is of the infinite *AB* type (Figure 4.12).

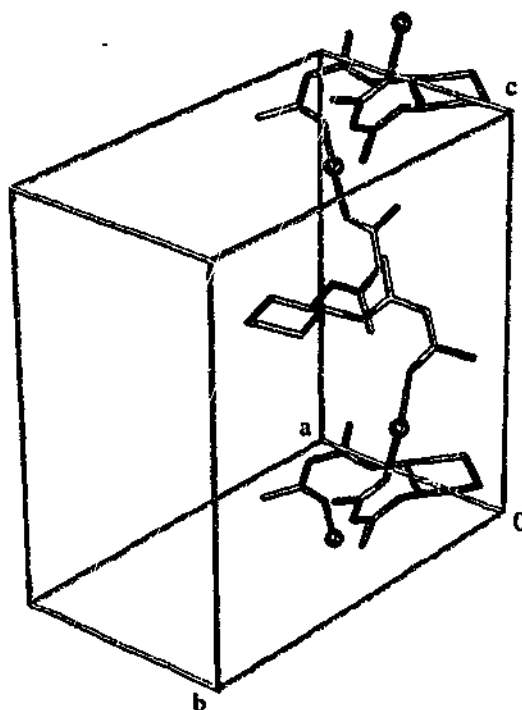


Figure 4.9 A single $\{[M(\mu\text{-actchH}_2)]^{2+}\}_n$ helix in the structure of $[M(\text{actchH}_2)(\text{dca})_2]$.

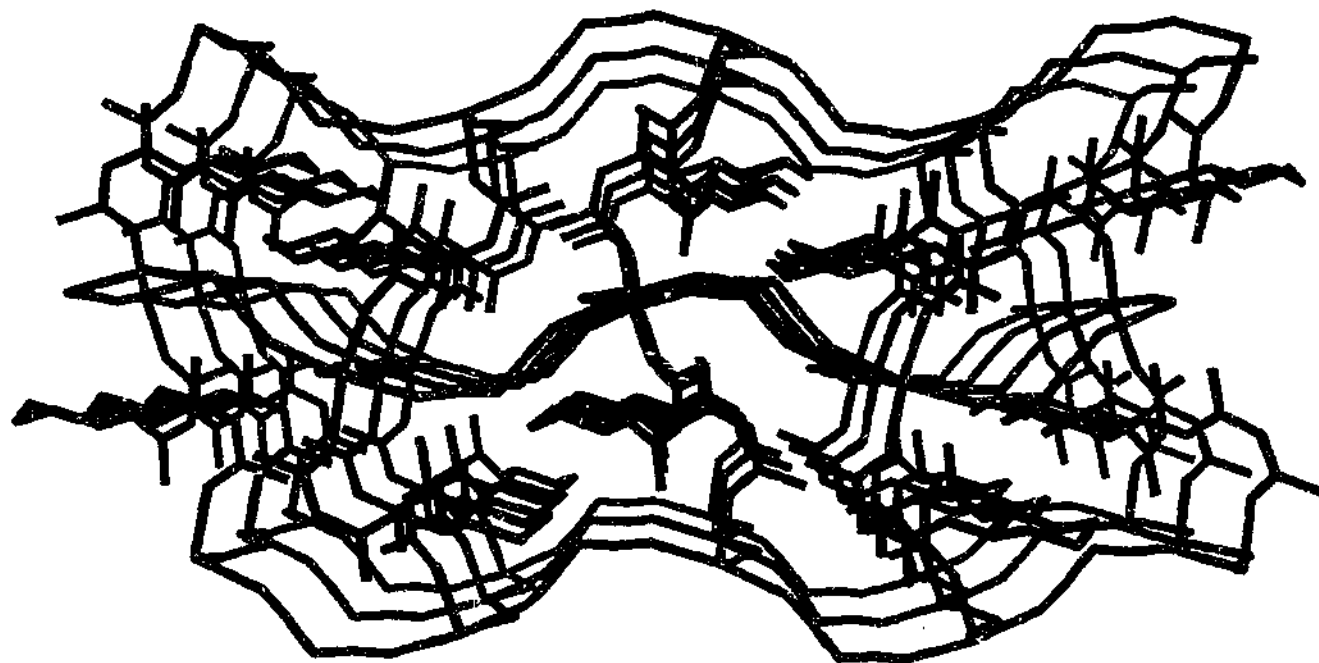


Figure 4.10 The structure of $[M(\text{actchH}_2)(\text{dca})_2]$ viewed parallel to the a -axis direction, where actchH_2 ligands are in purple and the 2D square grid sheets of $[M(\text{dca})_2]$ are shown in red.

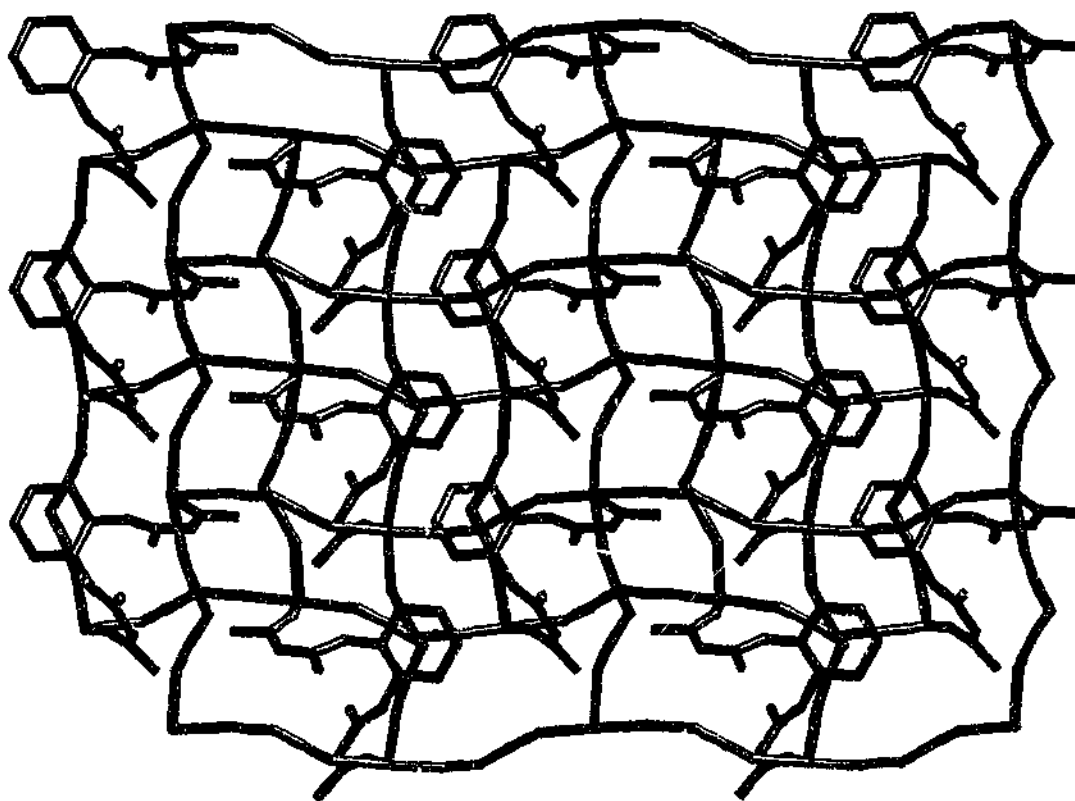


Figure 4.11 A view of $[M(\text{actchH}_2)(\text{dca})_2]$ down the c -axis direction showing two 2D square grid (4,4) sheets of $[M(\text{dca})_2]$ with the bridging actchH_2 ligands (the upper sheet is shown in red, the lower in purple and the actchH_2 ligands in green).

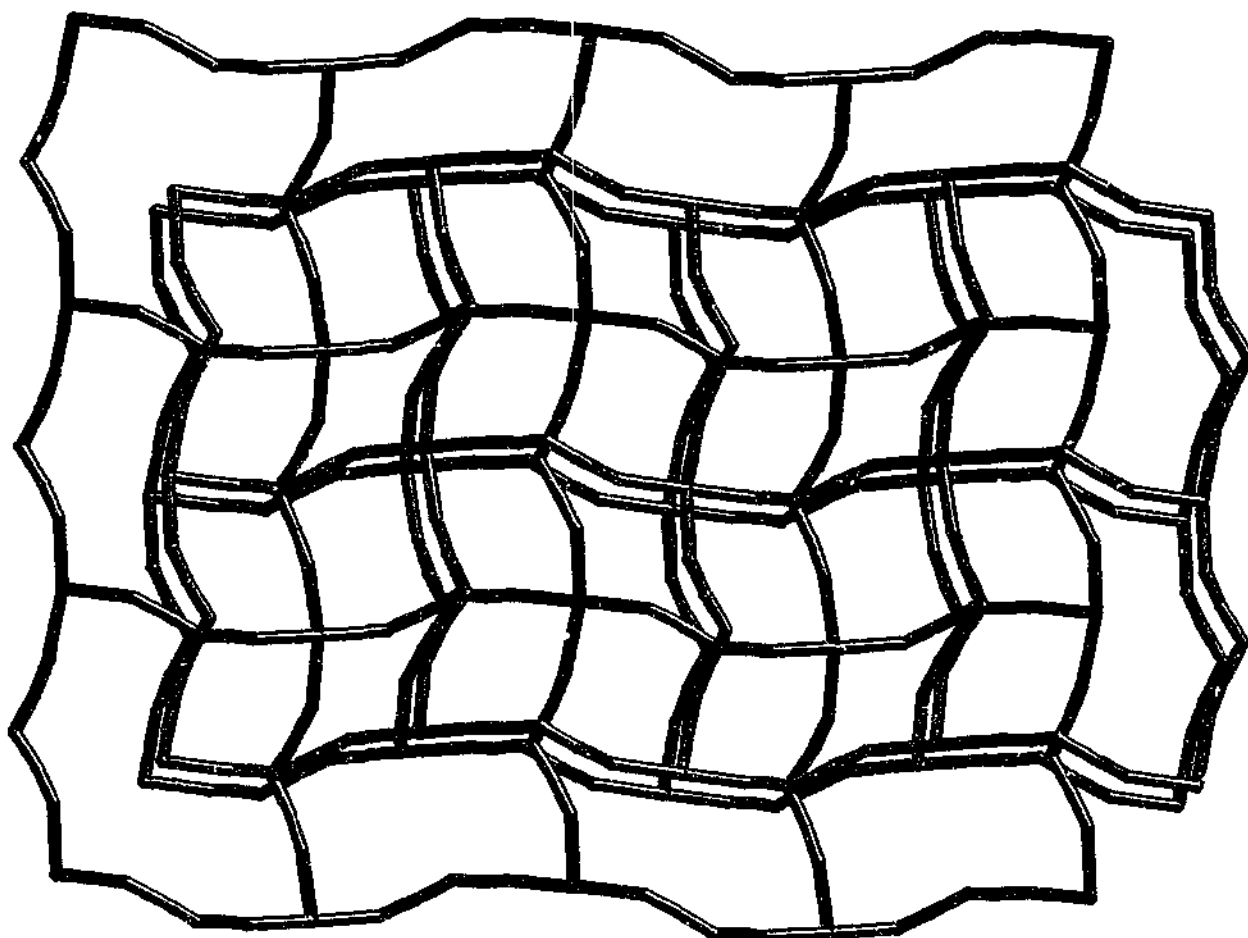


Figure 4.12 Three 2D square grid (4,4) sheets of composition $[M(dca)_2]$ in the structure of $[M(actchH_2)(dca)_2]$ viewed slightly off the c -axis direction showing the AB stacking (upper sheet is red, middle sheet is purple and lower sheet is green, $actchH_2$ ligands are omitted for clarity).

The network formed thus contains 6-connecting nodes (the metal ions). The most common topology for a 6-connected network is that related to α -polonium (Figure 4.13(b)), which has the Schläfli symbol $4^{12}.6^3$.⁶⁸ Examples include the series $[M(dca)_2L]$ (where L = pyrazine or 4,4'-bipyridine), reported by Jensen *et al.*^{1,6} However in the case of $[M(actchH_2)(dca)_2]$, the $actchH_2$ links between the off-set $[M(dca)_2]$ sheets result in an unusual overall 3D structure. The links 'zig-zag', so that between any two layers, the $actchH_2$ ligands are oriented in the same direction parallel to the a -axis, whereas their orientations alternate along the b -axis. This can be seen in a schematic representation of

the connectivity of the network shown in Figure 4.13(a), where the actchH_2 and dca ligands have been reduced to single connections. A similar situation has been observed for the structure of $\text{Cd}(\text{CN})_2\text{pyz}$, reported by Abrahams and Robson *et al.*,⁶⁹ in which corrugated $[\text{Cd}(\text{CN})_2]$ sheets are linked by pyrazine bridges in a 'criss-cross' pattern. However, in that structure the pyrazine orientation alternates in both the a - and b -axis directions, in a criss-cross fashion as shown in Figure 4.13(c). The present structures are the first examples of a new 6-connected 3D network topology, which has the Schläfli symbol $4^8.5^4.6^3$.

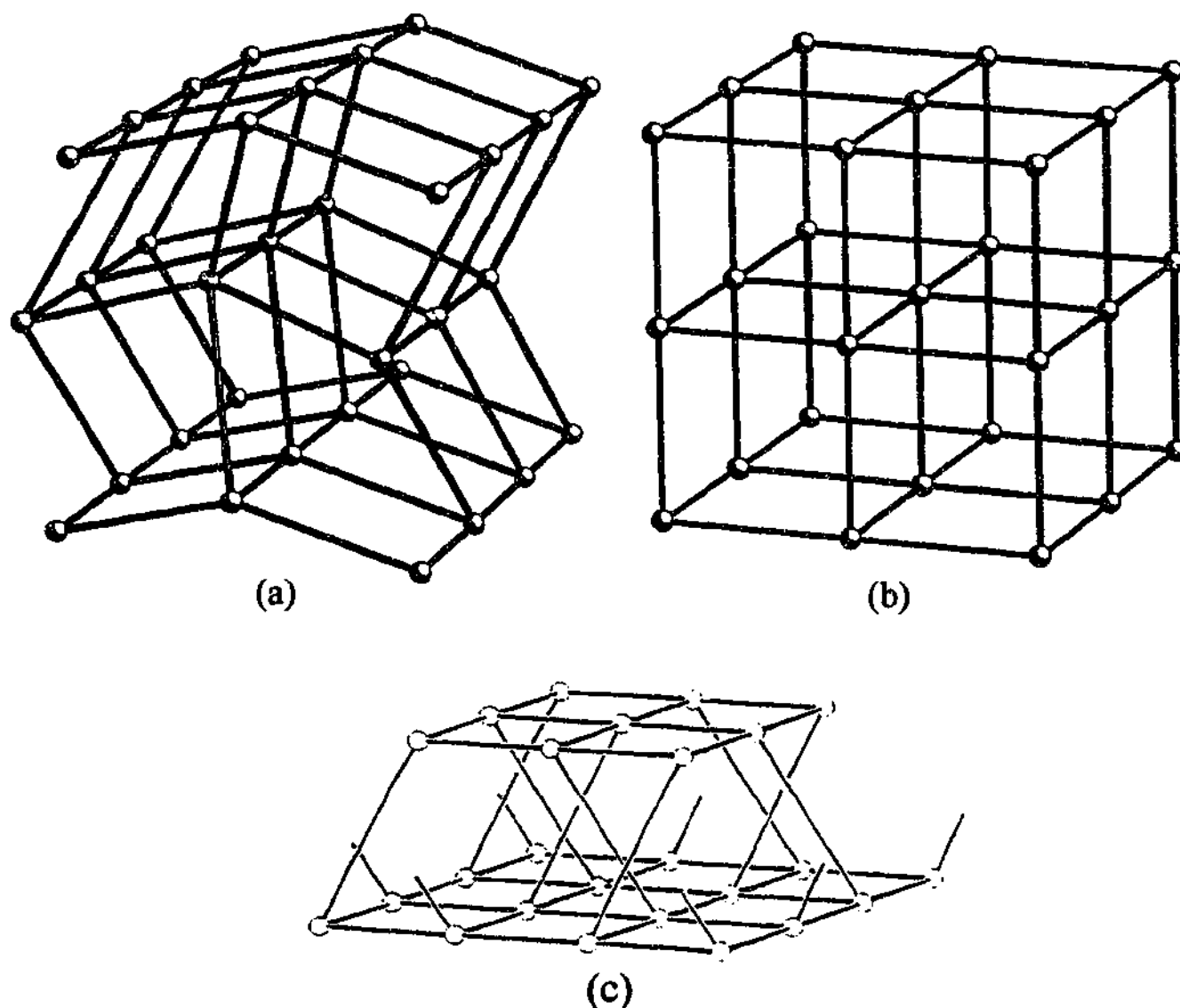


Figure 4.13 Schematic representation of the connectivity in (a) $[\text{M}(\text{actchH}_2)(\text{dca})_2]$ network (2D square grid sheets are coloured as in Figure 4.12), (b) the α -polonium-related net, and (c) $\text{Cd}(\text{CN})_2\text{pyz}$ (reproduced from reference 69).

The local coordination environment of each metal atom is distorted octahedral. The equatorial coordination plane consists of four nitrile nitrogens from the two unique bridging dicyanamide ligands ($M-N_{dca} = 2.208(2) - 2.248(2) \text{ \AA}$ (Mn), and $2.155(2) - 2.194(2) \text{ \AA}$ (Fe)). The axial coordination sites are filled by the carbonyl oxygen atoms of the bridging actchH₂, ($M-O = 2.171(2) \text{ and } 2.169(2) \text{ \AA}$ (Mn), $2.095(2) \text{ and } 2.083(2) \text{ \AA}$ (Fe)). $M \cdots M$ distances within the sheets across the $\mu_{1,5}$ -dca ligands in the *a*-axis direction are equal to the unit cell length *a* ($8.7852(1) \text{ \AA}$ (Mn) and $8.7312(2) \text{ \AA}$ (Fe)), whereas, in the *b*-axis direction, the $M \cdots M$ distances are shorter – $8.3416(2) \text{ \AA}$ (Mn) and $8.2965(3) \text{ \AA}$ (Fe). The $M \cdots M$ distances directly across the actchH₂ ligand are $10.2008(4) \text{ \AA}$ (Mn) and $10.0826(4) \text{ \AA}$ (Fe). The shortest inter-sheet $M \cdots M$ distances are $9.1342(3) \text{ \AA}$ (Mn) and $9.1342(3) \text{ \AA}$ (Fe), and are not *via* direct actchH₂ links.

As with the $[M^{II}(\text{acenH}_2)(\text{dca})_2]$ frameworks, intra-molecular hydrogen bonding between the amine N–H and the coordinating carbonyl oxygen of the actchH₂ ligand forms a pseudo six membered ring (Figure 4.14), thus presumably stabilising the bis-monodentate bridging mode *via* the oxygen atoms. The crystal structure of the racemic free ligand, ($\pm$)-actchH₂, was only recently reported by McCann *et al.*²² As with acenH₂ (*vide supra*), this molecule exists in the solid state in the keto-amine form shown in Scheme 4.1, with intra-ligand bonds between the respective amine NH and carbonyl oxygen. In the same paper the authors report the structure of $[\text{Co}^{II}((\pm)\text{-actchH}_2)\text{Cl}_2]_n$, a 1D coordination polymer consisting of 2-fold helical chains of tetrahedral Co^{II} centres linked by bridging actchH₂ ligands, in the same manner observed here, and terminal Cl[–] ligands. The left- and right-handed 2-fold helices, which contain bridging *R,R*- and *S,S*-actchH₂ ligands respectively, are symmetry related, hence the overall structure is centrosymmetric. The helices are very similar to those observed here, the chief difference being the tetrahedral

Co^{II} geometry. Intra-ligand hydrogen bonding between the amine hydrogen atoms and the carbonyl oxygens is also observed in [Co^{II}((±)-actchH₂)Cl₂]_n. To the best of the candidate's knowledge the actchH₂ bridging mode had not been reported at the time of the present syntheses and characterisations.

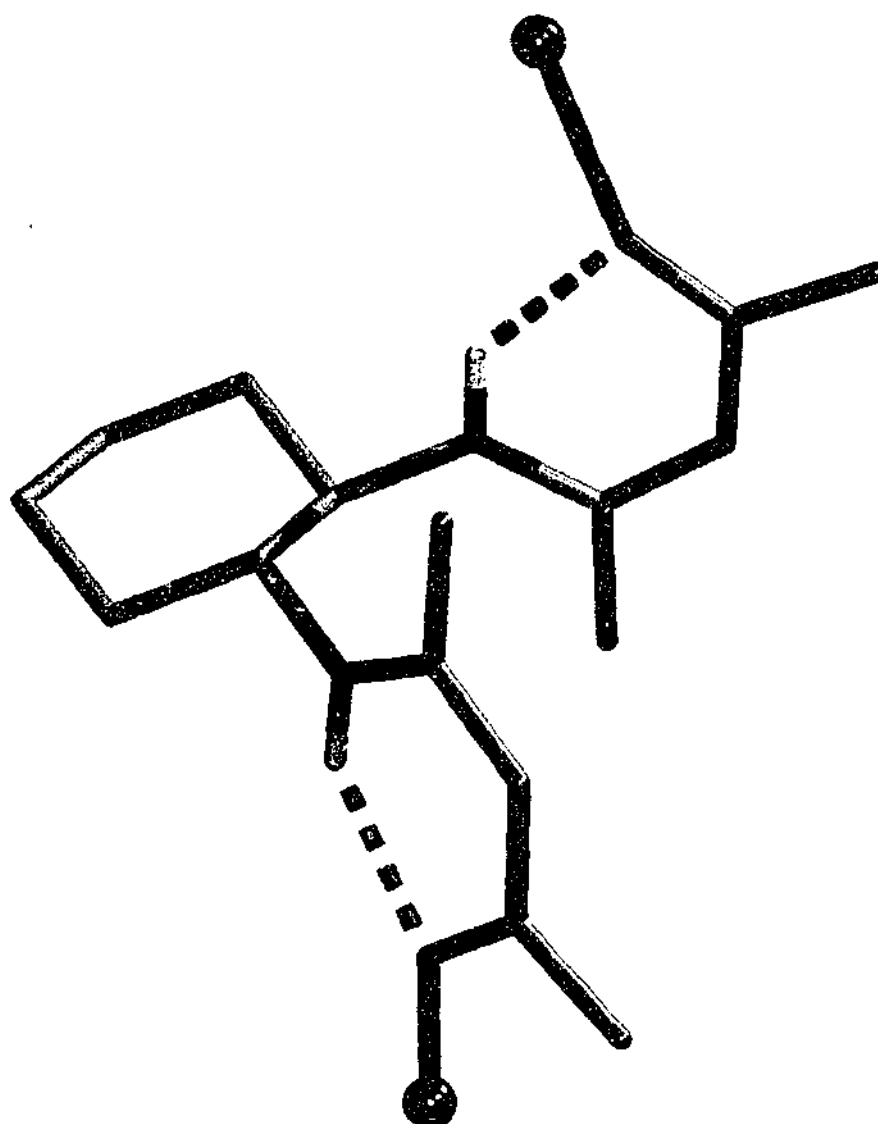


Figure 4.14 A {M(μ-actchH₂)M} moiety showing the presence of intra-ligand hydrogen bonding (dashed green bonds). Hydrogen atoms attached to carbons are omitted for clarity.

Table 4.4 Selected interatomic distances (Å) and angles (°) for $[M(\text{actchH}_2)(\text{dca})_2]$, $M^{\text{II}} = \text{Mn}$ and Fe .

	Mn	Fe		Mn	Fe
M(1)–N(11)	2.208(2)	2.155(2)	M(1)–N(25 ⁱⁱ)	2.248(2)	2.188(2)
M(1)–N(15 ⁱⁱⁱ)	2.248(2)	2.194(2)	M(1)–O(31)	2.171(2)	2.095(2)
M(1)–N(21)	2.219(2)	2.179(2)	M(1)–O(50 ⁱ)	2.169(2)	2.083(2)
M···M across $\mu_{1,5}$ -dca bridges				Mn	Fe
In the <i>a</i> -direction: M(1)···M(1 ^{iv})				8.7852(1)	8.7132(2)
In the <i>b</i> -direction: M(1)···M(1 ^v)				8.3416(2)	8.2965(3)
M···M across μ -actchH ₂			M(1)···M(1 ^{vi})	10.2008(4)	10.0826(4)
	Mn	Fe		Mn	Fe
N(11)–M(1)–N(21)	98.25(8)	97.93(8)	N(15 ⁱⁱⁱ)–M(1)–N(25 ⁱⁱ)	83.12(8)	85.19(8)
N(21)–M(1)–N(15 ⁱⁱⁱ)	95.21(8)	92.61(8)	N(25 ⁱⁱ)–M(1)–N(11)	83.82(8)	84.65(8)
O(31)–M(1)–N(11)	97.25(7)	95.86(8)	O(50 ⁱ)–M(1)–N(11)	94.74(7)	92.93(8)
O(31)–M(1)–N(21)	85.68(7)	85.72(7)	O(50 ⁱ)–M(1)–N(21)	82.25(6)	83.14(7)
O(31)–M(1)–N(15 ⁱⁱⁱ)	85.35(7)	86.41(8)	O(50 ⁱ)–M(1)–N(15 ⁱⁱⁱ)	85.43(7)	86.79(8)
O(31)–M(1)–N(25 ⁱⁱ)	85.38(7)	84.89(7)	O(50 ⁱ)–M(1)–N(25 ⁱⁱ)	106.36(7)	105.95(7)
O(31)–M(1)–O(50 ⁱ)	164.07(6)	166.66(7)			
Hydrogen bonding					
N(37)···O(31)	2.649(2)	2.630(3)	N(44)···O(50)	2.717(2)	2.728(3)
H(37)···O(31)	1.96	1.93	H(44)···O(50)	2.04	2.05
N(37)–H(37)···O(31)	134.1	134.8	N(44)–H(44)···O(50)	133.5	133.5

Symmetry transformations: (i) $-x+3/2, -y, z-1/2$; (ii) $-x+1, y+1/2, -z+1/2$; (iii) $x+1, y, z$; (iv) $x-1, y, z$; (v) $-x+1, y-1/2, -z+1/2$; (vi) $-x+3/2, -y, z+1/2$.

4.3.3 $[\text{Mn}^{\text{II}}(\text{acenH}_2)_2(\text{dcnm})_2]$

The mononuclear complex, shown in Figure 4.15, crystallises in the triclinic space group $P\bar{1}$. Crystal data for *trans*- $[\text{Mn}(\text{acenH}_2)_2(\text{dcnm})_2]$ are summarised in Table 4.5 and selected interatomic distances and angles are listed in Table 4.6 (see page 193). The manganese(II) centre lies on an inversion centre and is coordinated in a distorted octahedral environment by four carbonyl oxygens ($\text{Mn}(1)\text{--O}(1) = 2.160(1)$ and $\text{Mn}(1)\text{--O}(16) = 2.210(1)$ Å) from two acenH₂ ligands in the equatorial plane and by two end-O-dcnm coordinated ligands ($\text{Mn}(1)\text{--O}(21) = 2.157(1)$ Å) in the axial positions.

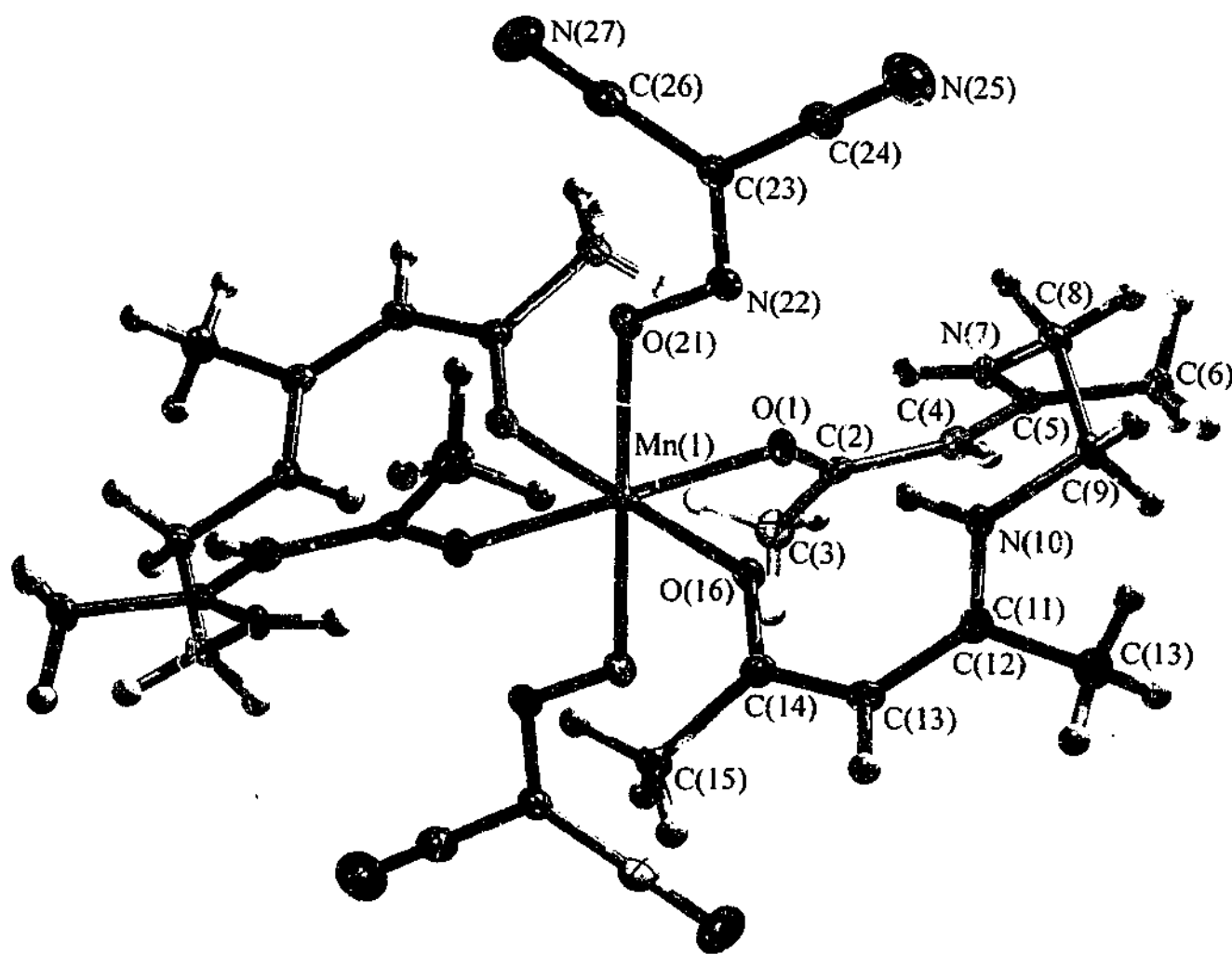


Figure 4.15 The crystal structure of *trans*- $[\text{Mn}(\text{acenH}_2)_2(\text{dcnm})_2]$ with atom labelling scheme (thermal ellipsoids shown at 50 % probability).

Table 4.5 Crystal data for *trans*-[Mn(acenH₂)₂(dcnm)₂].

Complex	<i>trans</i> -[Mn(acenH ₂) ₂ (dcnm) ₂]
Formula	C ₃₀ H ₄₀ MnN ₁₀ O ₆
<i>M</i>	691.66
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> /Å	8.9181(3)
<i>b</i> /Å	10.2670(4)
<i>c</i> /Å	10.8182(2)
α /°	67.269(2)
β /°	88.995(2)
γ /°	71.401(1)
<i>U</i> /Å ³	859.53(5)
<i>Z</i>	1
<i>T</i> /K	123(2)
μ (Mo-K α)/mm ⁻¹	0.440
Crystal dimensions/mm	0.09 × 0.05 × 0.04
Index ranges	-11 ≤ <i>h</i> ≤ 11, -13 ≤ <i>k</i> ≤ 13, -12 ≤ <i>l</i> ≤ 14
Completeness to 2 θ = 55° / %	96.3
Data collected	11926
Unique data (<i>R</i> _{int})	4042 (0.0376)
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	3056
Parameters	218
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] ^(a)	0.0418, 0.0752
(all data)	0.0680, 0.0823
Goodness of fit, <i>S</i>	1.048

^(a) $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$

The acenH₂ coordinates in a bidentate chelation mode involving the oxygen donor atoms exclusively, resulting in a 14 membered chelate ring. This unusual chelating mode has also been recently observed by Junk and Smith in four isostructural lanthanide coordination polymers (*vide supra*),²⁹ and in a uranyl complex with salpnH₂ (*N,N'*-1,3-propylenebis(salicylideneimine)).⁷⁰ The complex presented here is the first such example in a first row transition metal complex. Of the various possible donor atom configurations possible, the O₆ donor set is favoured.

Again, intra-ligand hydrogen bonding, shown in Figure 4.16, occurs in the acenH₂ ligand involving the amine N-H groups and the coordinated carbonyl oxygens with average distances - H...O = 1.97 Å, N...O = 2.645(2) Å.

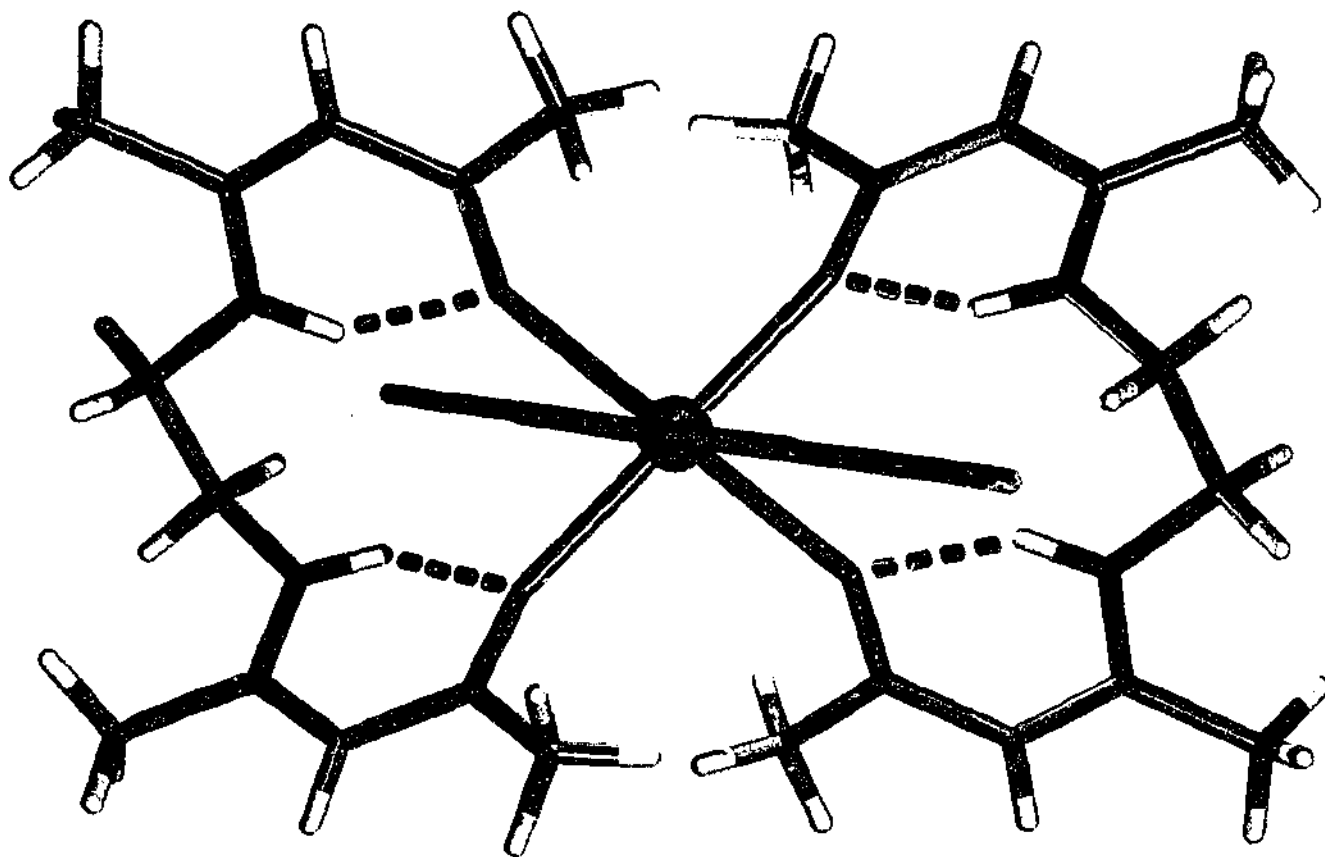


Figure 4.16 The structure of *trans*-[Mn(acenH₂)₂(dcnm)₂] viewed parallel to the axial coordination bonds showing the intra-ligand hydrogen bonding (dashed green bonds) in acenH₂.

A number of mononuclear complexes with end-*O*-dcnm ligands have been reported.⁷¹⁻⁷⁴ For example, *trans*-[Ni(dcnm)₂(pz)₄] (where pz = pyrazole), has four pyrazole groups in the equatorial plane and two *trans* coordinated end-*O*-dcnm ligands, with Ni–O = 2.085(2) Å.

Table 4.6 Selected interatomic distances (Å) and angles (°) for *trans*-[Mn(acenH₂)₂(dcnm)₂].

Mn(1)–O(1)	2.160(1)	Mn(1)–O(21)	2.157(1)
Mn(1)–O(16)	2.210(1)		
O(21)–Mn(1)–O(1)	87.90(4)	O(21)–Mn(1)–O(16)	92.13(4)
O(21)–Mn(1)–O(1 ⁱ)	92.10(4)	O(21)–Mn(1)–O(16 ⁱ)	87.87(4)
O(1)–Mn(1)–O(16)	85.09(4)	O(1 ⁱ)–Mn(1)–O(16)	94.91(4)
Hydrogen bonding			
N(10)···O(16)	2.665(2)	N(7)···O(1)	2.625(2)
H(10)···O(16)	1.99	H(7)···O(1)	1.94
N(10)–H(1)···O(16)	132.9	N(7)–H(7)···O(1)	133.3

Symmetry transformation: (i) $-x, -y, -z+1$.

4.4 Magnetism of [M(L)(dca)₂] Complexes; M^{II} = Mn and Fe; L = acenH₂ and actchH₂

The magnetic data for all four compounds are, as in the [M^{III}(Schiff-base)(dca)]_n series (see Chapter 3), indicative of very weak antiferromagnetic coupling combined with spin-orbit coupling and zero-field splitting effects. There is consequently no long-range

order. Thus the χ/T data are Curie-Weiss like and the μ_{eff}/T plots (Figure 4.17 to Figure 4.20, see pages 195 to 196) show that μ_{eff} is essentially independent of temperature in the range 300–50 K, and then decrease rapidly down to 2 K. The 300 K value of μ_{eff} for the Fe^{II} compounds ($\sim 5.3 \mu_{\text{B}}$) are bigger than $\mu_{\text{spin-only}}$ (d^6) because of orbital degeneracy and spin-orbit effects perturbing the (parent) $^5\text{T}_{2g}$ states. However, the constant value of μ_{eff} , above 50 K, is indicative of a large splitting of the $^5\text{T}_{2g}$ state by the low-symmetry ligand-field around the Fe^{II} centres.⁷⁵ Perusal of the Figgis-type calculation for $^5\text{T}_{2g}$ Fe^{II} monomers^{75–78} show that plots such as Figure 4.18 can be fitted to a monomer model using the spin-orbit constant $\lambda = \text{ca. } -100 \text{ cm}^{-1}$ and Δ (the splitting energy $^5\text{E}_g$, $^5\text{B}_{2g}$ from $^5\text{T}_{2g}$) of *ca.* 10,000 cm^{-1} . The rapid decrease in μ_{eff} below 50 K is then either due to zero-field splitting of the $^5\text{E}_g$ or $^5\text{B}_{2g}$ states (into $M_S \pm 2, \pm 1, 0$ levels) and/or due to weak antiferromagnetic coupling. Indeed, good fits are obtained using Heisenberg 3D or 2D models for $S = 2$ (Fe^{II}) or $S = 5/2$ (Mn^{II}), respectively, in which spin-orbit coupling effects are subsumed in the g value and zero-field splitting is neglected. The best-fit parameters are given in Table 4.7.

Table 4.7 Best-fit parameters for the $[\text{M}^{\text{II}}(\text{L})(\text{dca})_2]$ compounds.

Compound	g	J / cm^{-1}
$[\text{Mn}(\text{acenH}_2)(\text{dca})_2]$	1.91	-0.05
$[\text{Fe}(\text{acenH}_2)(\text{dca})_2]$	2.04	-0.007
$[\text{Mn}(\text{actchH}_2)(\text{dca})_2]$	1.95	-0.07
$[\text{Fe}(\text{actchH}_2)(\text{dca})_2]$	2.15	-0.04

Whatever the limitations of the models employed, it is clear that the very weak coupling reflects the poor superexchange properties of the $\mu_{1,5}$ -dca bridge and the large $\text{M}\cdots\text{M}$ separations. The acenH₂ and actchH₂ links play no part in coupling.

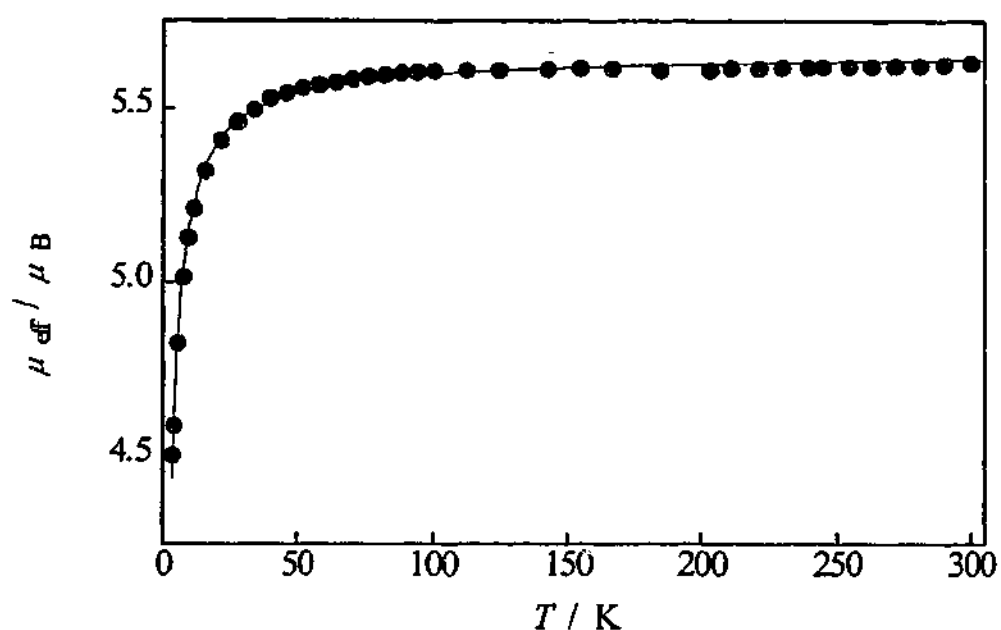


Figure 4.17 Plot of magnetic moment, μ_{eff} , versus temperature, T , for $[\text{Mn}(\text{acenH}_2)(\text{dca})_2]$.

The solid line is the calculated line of best-fit using a $S = 5/2$ Heisenberg model (see text).

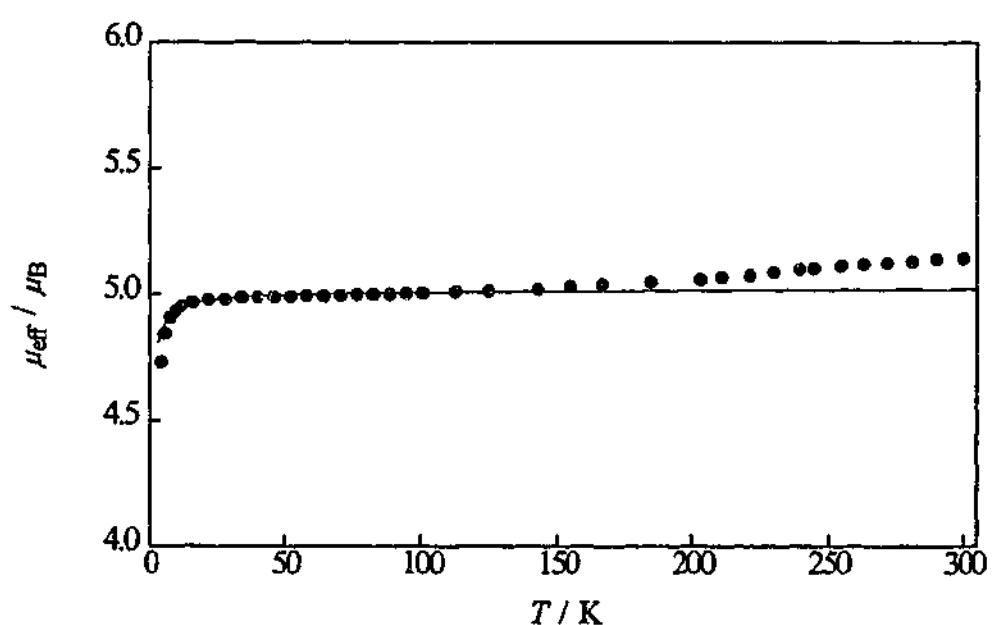


Figure 4.18 Plot of magnetic moment, μ_{eff} , versus temperature, T , for $[\text{Fe}(\text{acenH}_2)(\text{dca})_2]$.

The solid line is the calculated line of best-fit using a 3D model for $S = 2$ (see text).

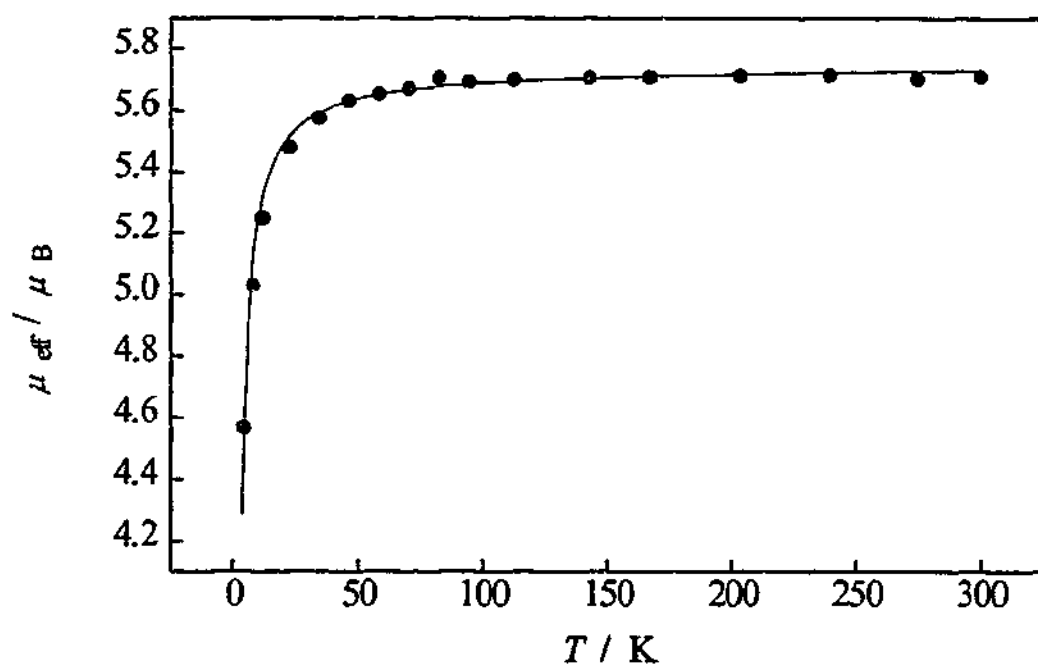


Figure 4.19 Plot of magnetic moment, μ_{eff} , versus temperature, T , for $[\text{Mn}(\text{actchH}_2)(\text{dca})_2]$.

The solid line is the calculated line of best-fit using a $S = 5/2$ Heisenberg model (see text).

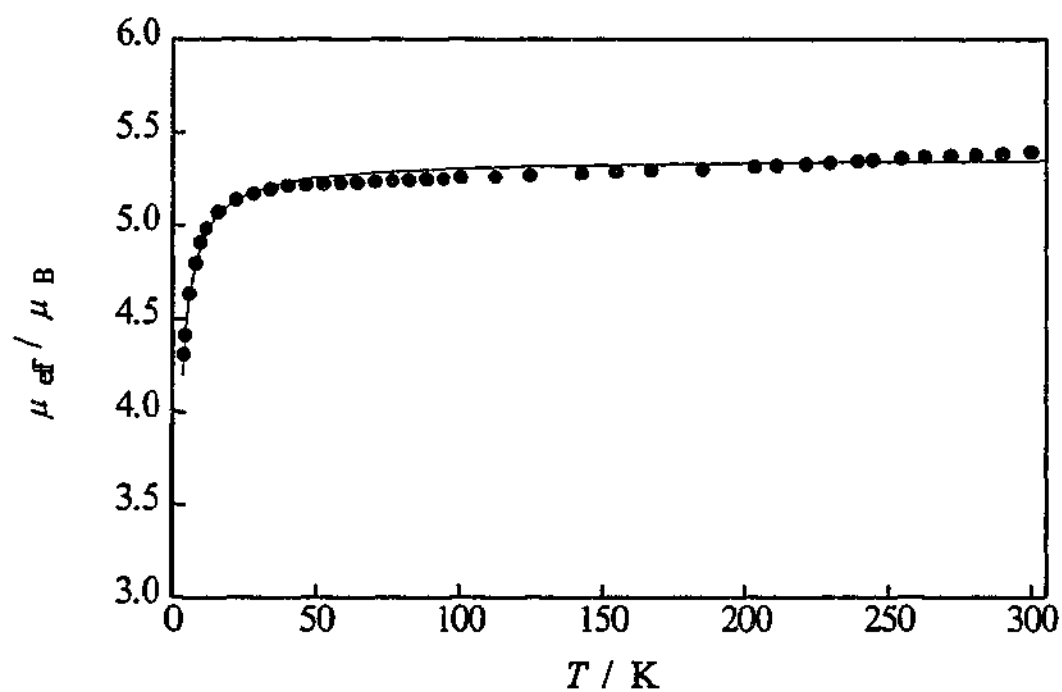


Figure 4.20 Plot of magnetic moment, μ_{eff} , versus temperature, T , for $[\text{Fe}(\text{actchH}_2)(\text{dca})_2]$.

The solid line is the calculated line of best-fit using a 3D model for $S = 2$, as described in the text.

4.5 Conclusions

The coordination polymers $[M(\text{acenH}_2)(\text{dca})_2]$ and $[M(\text{actchH}_2)(\text{dca})_2]$ ($M^{\text{II}} = \text{Mn}$ and Fe) were investigated and found to display interesting chiral 3D network structures. The $[M(\text{acenH}_2)(\text{dca})_2]$ complexes consist of 3-fold helical $[M(\text{acenH}_2)(\text{dca})]^+$ motifs that are cross-linked by $\mu_{1,5}$ -dca ligands. Until very recently, the coordination mode of acenH₂ displayed here (bridging *via* the oxygen donor atoms) was unprecedented. It was reported for the first time in four lanthanide coordination polymers.²⁹ Nevertheless, the complexes presented here are the first transition metal based examples. These networks exhibit the unusual 'dense' 7⁵9 (chiral) topology, which was only observed in a real example for the first time in 1998 in a 3-fold interpenetrated Cu^{II} coordination polymer with the linear bridging ligand 1,2-bis(4-pyridyl)ethyne.²⁸ Thus, the complexes presented here are the first single networks to possess this topology. Interestingly, the precursors or synthons for these chiral networks do not possess any intrinsic chirality. It is perhaps the 'twist' in the bridging mode of acenH₂, which forms helices that result in a chiral network. Additionally, spontaneous resolution of enantiomers in single crystals is observed.

The $[M(\text{actchH}_2)(\text{dca})_2]$ complexes consist of $[M(\text{dca})_2]$ square-grid (4,4) sheets that are linked by two actchH₂ ligands in the third dimension to form the overall 3D network. Unlike the previous complexes, the actchH₂ ligands are intrinsically chiral. A racemic mixture of *R,R*- and *S,S*-actchH₂ was used, resulting in crystals exhibiting racemic twinning. The twin component described here contained the *R,R*-actchH₂ enantiomer. The $\{[M(\text{R,R-actchH}_2)]^{2+}\}_n$ motifs are left-handed 2-fold helices, and right-handed for the twin component with *S,S*-actchH₂ ligands. The actchH₂ ligands bridge in a similar manner to the acenH₂ ligands, *via* the oxygen donor atoms only. At the time of synthesis and characterisation, these complexes were the first examples for any metal to contain such bridging actchH₂. Recently, however, a 1D linear tetrahedral cobalt(II) coordination

polymer was reported with the same actchH₂ bridging mode.²² Additionally, these networks display an unprecedented topology with the Schläfli symbol 4⁸.5⁴.6³.

Interestingly, the acenH₂ and actchH₂ ligands did not deprotonate or the divalent metals oxidise to M^{III} on formation of the networks, which is unusual for Schiff-base ligands.

Variable temperature magnetic susceptibility measurements (2-300 K; $H = 1$ T) show that these complexes display very weak antiferromagnetic coupling, most probably due to the long Schiff-base and $\mu_{1,5}$ -dca linking pathways. No long-range magnetic order for these 3D network compounds was observed under these conditions.

Future work in this area, using different acetylacetone derived Schiff-base ligands, may prove fruitful. In particular, enantiopure chiral Schiff-base ligands in combination with dca may lead to interesting materials that may have interesting structures and potentially useful non-linear optical properties. For instance, as well as further studies with resolved actchH₂ and derivatives thereof, less bulky chiral Schiff-bases such as *R*- and *S*-acpnH₂ (where acpnH₂ = *N,N'*-1,2-propylenebis(acetylacetoneimine)) may lead to network topologies similar to that observed for the [M(acenH₂)(dca)₂] series here.

4.6 Experimental

4.6.1 Synthesis of acenH₂ and (±)-actchH₂

The Schiff-base ligands, acenH₂ and (±)-actchH₂, were prepared from the condensation reaction of acetylacetone and the appropriate diamine; ethylenediamine and (±)-*trans*-1,2-diaminocyclohexane respectively in a 2:1 molar ratio.⁷⁹

acenH₂: IR (Nujol, cm⁻¹): 3134 w, 3084 w, 1574 s, 1520 s, 1454 s, 1354 s, 1287 s, 1220 s, 1202 s, 1144 m, 1087 s, 1022 m, 980 m, 940 m, 929 w, 853 s, 791 vw, 759 m, 739 s, 652 vw, 642 m.

($\pm$)-actchH₂: IR (Nujol, cm⁻¹): 3070vw, 1600s, 1512s, 1447s, 1358s, 1304s, 1262s, 1242s, 1198m, 1150s, 1124s, 1087m, 1024s, 998s, 961m, 932m, 890m, 816s, 766m, 750s, 742s, 658m, 648m, 634w.

4.6.2 Synthesis of Ag(dcnm) and Me₄N(dcnm)

Ag(dcnm) was synthesized by Dr. Stuart Batten according to the literature.⁸⁰ Me₄N(dcnm) was synthesised by adding a solution of Me₄NBr (4.929 g, 32.0 mmol) in a solvent mixture of 100 mL acetonitrile and 40 mL methanol to a stirred suspension of Ag(dcnm) (6.059 g, 30.0 mmol) in 50 mL dichloromethane. AgBr was removed by filtration through Celite on a large sinter. The solvent was evaporated from the filtrate by rotary evaporation and the resulting yellow oil recrystallised by vapour diffusion of diethyl ether into a solution in methanol (Yield 5.08 g, 95%). IR (Nujol, cm⁻¹): 3438mbr, 2212s, 1654m, 1583w, 1487s, 1418m, 1273s, 1233s, 1169m, 951s, 879vw, 832vw, 779m, 669m, 580m.

4.6.3 Synthesis of [Mn(acenH₂)(dca)₂]

A methanolic solution (5 mL) of Na(dca) (0.178 g, 2.0 mmol) and acenH₂ (0.448 g, 2.0 mmol) was added with stirring to a mixture of Mn(OAc)₂·4H₂O (0.490 g, 2.0 mmol) in methanol (10 mL). After about 10 minutes a colourless precipitate began to form. Stirring was continued for 30 minutes, before the mixture was filtered and the precipitate washed three times with small amounts of methanol. (Yield 0.21 g, 46 %, based on Na(dca)). Large colourless hexagonal crystals suitable for X-ray diffraction were obtained from a more dilute, but analogous, reaction. IR (Nujol, cm⁻¹): 3613w, 3579w, 3082m, 2395w, 2310s, 2291s, 2237s, 2169sbr, 1592sbr, 1556s, 1537s, 1505s, 1434s, 1360s, 1294sbr, 1209m, 1130s, 1078vw, 1017s, 992m, 950s, 928w, 894vw, 848vw, 796m, 759s,

660m, 628w. Anal. (%), Found: C, 46.7; H, 4.8; N, 27.3. Calc. for $C_{16}H_{20}MnN_8O_2$: C, 46.7; H, 4.9; N, 27.2.

4.6.4 Synthesis of $[Fe(acenH_2)(dca)_2]$

A methanolic solution (5 mL) of Na(dca) (0.178 g, 2.0 mmol) and acenH₂ (0.336 g, 1.5 mmol) was added to a methanolic solution (5 mL) of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.363 g, 1.0 mmol) in air, resulting in an instant colour change to an orange solution. After less than one week the solution was a dark brown/black with many pale yellow hexagonal crystals present. The crystals were collected and washed briefly with methanol and dried in air. (Yield 0.317 g, 77 %). IR (Nujol, cm^{-1}): 3615vw, 3575vw, 3080w, 2306s, 2284s, 2239s, 2188s, 2172s, 1598s, 1548s, 1436s, 1346s, 1297s, 1211w, 1132w, 1018m, 954m, 924vw, 798w, 760m. Anal. (%), Found: C, 46.1; H, 5.0; N, 26.9. Calc. for $C_{16}H_{20}FeN_8O_2$: C, 46.6; H, 4.9; N, 27.2.

A crystal suitable for X-ray diffraction was obtained from an analogous reaction using $Fe(BF_4)_2 \cdot 6H_2O$ instead of the perchlorate salt. The unit cell of a crystal from the above reaction was measured and found to be identical to the cell of the refined crystal structure.

4.6.5 Synthesis of $[Mn(actchH_2)(dca)_2]$

A methanolic solution (20 mL) of Na(dca) (0.178 g, 2.0 mmol) and ($\pm$)-actchH₂ (0.278 g, 1.0 mmol) was added to a methanolic solution (20 mL) of $Mn(NO_3)_2 \cdot 4H_2O$ (0.251 g, 1.0 mmol). The resulting colourless solution was left to stand for several days, after which time a colourless crystalline precipitate formed. A single crystal suitable for X-ray diffraction was chosen from this precipitate. The solid was later collected and washed with methanol (Yield 0.081 g, 17 %). IR (Nujol, cm^{-1}): 3585vw, 3200vw, 3073vw, 2295s, 2235s, 2171s, 1594s, 1557s, 1369m, 1322m, 1263w, 1213vw, 1150w, 1124w, 1086vw,

1006vw, 948w, 923vw, 888vw, 822w, 803vw, 767m. Anal. (%), Found: C, 51.4; H, 5.6; N, 24.2. Calc. for $C_{20}H_{26}MnN_8O_2$: C, 51.6; H, 5.6; N, 24.1.

4.6.6 Synthesis of $[Fe(actchH_2)(dca)_2]$

A methanolic solution (20 mL) of Na(dca) (0.178 g, 2.0 mmol) and ($\pm$)-actchH₂ (0.336 g, 1.5 mmol) was added to a methanolic solution (20 mL) of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.363 g, 1.0 mmol) in air, resulting in an instant colour change to an orange solution. After approximately three weeks many yellow crystals were present in a deep orange-red solution. These crystals were collected, washed briefly with methanol and dried in air. (Yield 90 mg, 19 %). The sample was kept under N₂ to prevent oxidation, which occurs over a period of weeks. IR (Nujol, cm⁻¹): 2290m, 2234w, 2172s, 1593m, 1567m, 1366s, 1322m, 1260w, 1150w, 1124w, 1026w, 950w, 827vw, 769w. Anal. (%), Found: C, 51.3; H, 5.9; N, 24.4. Calc. for $C_{20}H_{26}FeN_8O_2$: C, 51.5; H, 5.6; N, 24.0.

A crystal suitable for X-ray diffraction was obtained from an analogous reaction using $Fe(BF_4)_2 \cdot 6H_2O$ instead of the perchlorate salt. The unit cell of a crystal from the above reaction was measured and found to be identical to the cell of the refined crystal structure.

4.6.7 Synthesis of *trans*- $[Mn(acenH_2)_2(dcnm)_2]$

A methanolic solution (5 mL) of acenH₂ (0.224 g, 1.0 mmol) and Me₄N(dcnm) (0.168 g, 1.0 mmol) was filtered into a methanolic solution (10 mL) of $Mn(OAc)_2 \cdot 4H_2O$ (0.245, 1.0 mmol) resulting in a dark yellow/orange solution. The solution was left to slowly evaporate. After several weeks there was a dark brown residue in the bottom of the vessel and a few small orange crystal present on the side of the vessel. One of these was chosen for single crystal structural analysis.

4.6.8 X-Ray Crystallography

Data were collected using a Nonius KappaCCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å), using ϕ and ω rotations with 1° frames. Integration was carried out by the program DENZO-SMN,⁸¹ and data were corrected for Lorentz polarisation effects and for absorption using the program SCALEPACK.⁸¹ Solutions were obtained by direct methods (SHELXS 97)⁸² followed by successive Fourier difference methods, and refined by full matrix least squares on F_{obs}^2 (SHELXL 97)⁸² with the aid of the graphical interface program X-SEED.⁸³ All non-hydrogen atoms were refined anisotropically except where otherwise stated. Hydrogen atoms were included at calculated positions with U values 1.5 or 1.2 times the U_{eq} of the adjoining carbon and nitrogen atoms respectively.

For $[\text{Mn}(\text{acenH}_2)(\text{dca})_2]$, the central nitrogen atoms of the cross-linking dca ligands and one of the nitrile carbons of one of the cross-linking dca ligands were found to be disordered over two positions. The nitrogens and carbon were modelled as two atoms each, which were refined isotropically and anisotropically respectively. Individual contributions of the two disordered positions were allowed to refine as free variables, but summing in each case to unity (N(130)/N(131) 0.46/0.54, C(120)/C(121) 0.49/0.51, N(230)/N(231) 0.67/0.33, and N(330)/N(331) 0.32/0.68). Face-indexed numerical absorption corrections were applied to the data for $[\text{Mn}(\text{acenH}_2)(\text{dca})_2]$ and *trans*- $[\text{Mn}(\text{acenH}_2)_2(\text{dcnm})_2]$ using the XPREP program.⁸⁴ Flack parameters²⁶ for $[\text{M}(\text{acenH}_2)(\text{dca})_2]$, $M^{\text{II}} = \text{Mn}$ and Fe, were 0.05(2) and 0.03(2) respectively, indicating the correct absolute structures were assigned. For the racemically twinned complexes $[\text{M}(\text{actchH}_2)(\text{dca})_2]$, $M^{\text{II}} = \text{Mn}$ and Fe, the contributions of the refined structures were 0.54(1) for each.

The CO groups of acenH₂ and (±)-actchH₂ were assigned as carbonyls on the basis of bond lengths, where average C–O = 1.27 Å. The C–NH groups were also assigned as such on the basis of bond lengths, where average C–N = 1.33 Å. Additionally, peaks of electron density were located near the amine nitrogens of the Schiff-base ligands. These were assigned as hydrogens but refined unsatisfactory and therefore were subsequently included at calculated positions.

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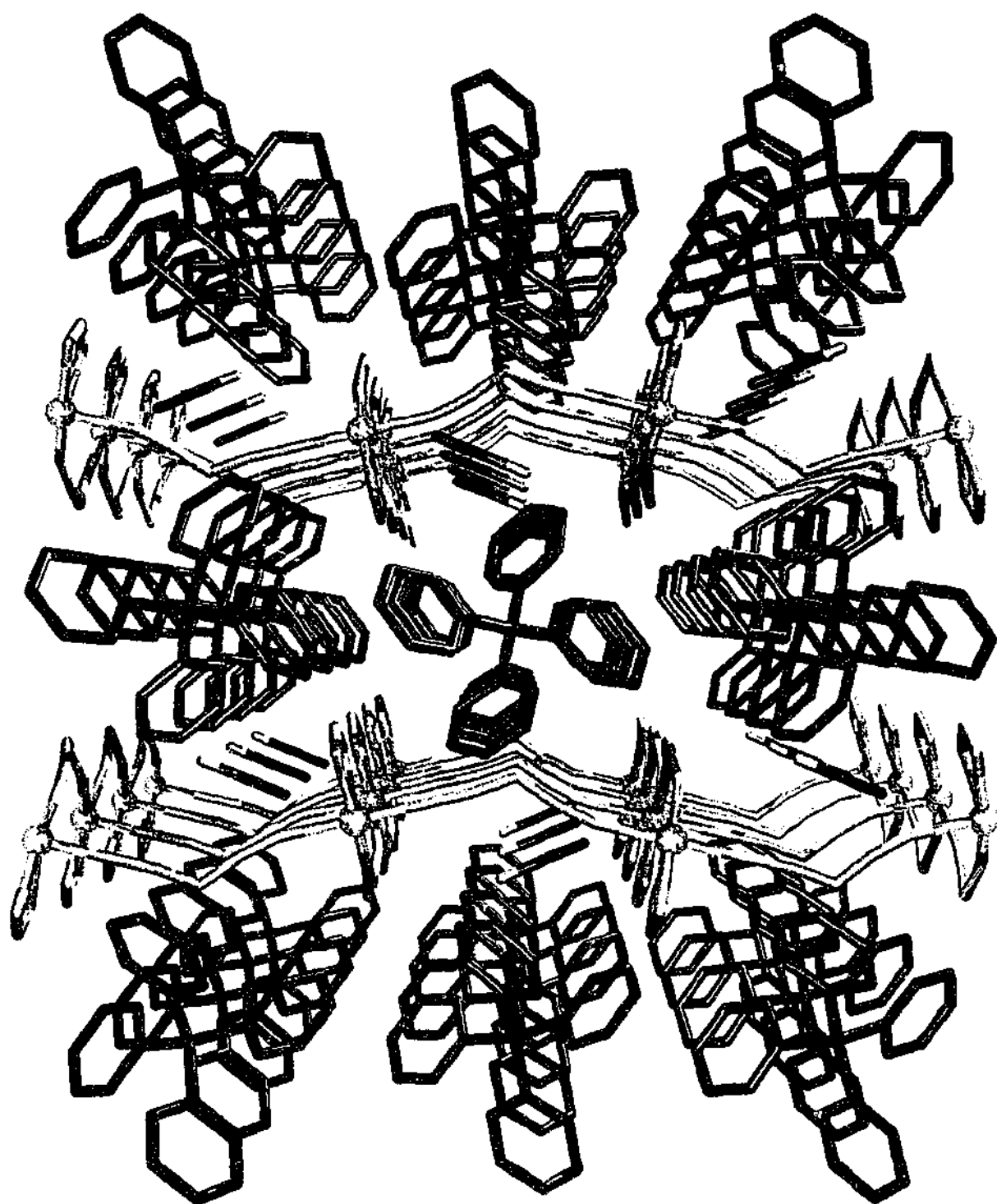
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**CHAPTER 5: ANIONIC MIXED-LIGAND
CHIRAL POLYMERIC COMPLEXES
CONTAINING DICYANAMIDE**

5.1 Introduction

Research into coordination polymers containing dicyanamide has undergone rapid growth since the discovery by Murray and co-workers, and other groups, of long-range magnetic ordering in the binary rutile-like octahedral complexes, α -[M(dca)₂], M^{II} = Cr, Mn, Fe, Co, Ni or Cu.¹⁻⁵ A polymorph with tetrahedral metal centres, the β -form, β -[M(dca)₂], M^{II} = Co, Zn, Co/Zn was also reported.⁶ The Co^{II} complex displays long-range magnetic order. Since then, modifications have been introduced to dicyanamide networks by the use of various bridging and terminal (monodentate and chelating) co-ligands, resulting in a wide variety of new and interesting topologies. The physical properties (magnetic, electrical, porosity etc.) have been investigated.^{3,7-25}

For example, through the use of neutral N-heterocyclic bridging ligands such as 4,4'-bipyridine,¹⁹ and pyrazine^{15,26} interpenetrated α -Po networks, 2D square grid (4,4) sheets or other topologies can be formed. Monodentate terminal co-ligands such as pyridine, DMF, pyridazine,¹⁸ 4-benzoylpyridine²⁷ or 2-pyrrolidone²⁸ typically lead to linear chains with double $\mu_{1,5}$ -dca bridges and *trans* co-ligands.³ Protic terminal ligands such as MeOH,^{3,11} EtOH³ and H₂O,^{3,29} where multiple hydrogen bonding interactions can occur, lead to fascinating networks. This is well illustrated by [Mn(dca)₂(H₂O)₂]·H₂O³ and [Mn(dca)₂(H₂O)].²⁹ In the structure of the former complex, linear chains of [Mn(dca)₂(H₂O)₂] lie in the channels formed by 2D (4,4) sheets of the same composition stacked parallel. The intercalated water molecules participate in complicated 2D hydrogen bonding networks between the chains and sheets. The monohydrate complex, [Mn(dca)₂(H₂O)], which is discussed in Chapter 2, has a 3D self-penetrated network structure that can be related to the rutile networks of α -[M(dca)₂] and the interpenetrated [M(tcm)₂].

In the field of molecule-based magnets the highest T_c values have been predominantly obtained with the short bridging ligand cyanide.³⁰⁻³⁴ It was reasoned that another short, potentially bridging ligand, such as nitrite (NO_2^-), might provide high temperature molecule-based magnets. The aim of the present work was to study the structures and magnetism of new mixed ligand dicyanamide network complexes with the nitrite ligand.

The nitrite ligand has long been of interest in coordination chemistry because of its ability to function as an ambidentate ligand. An extensive review by Hitchman and Rowbottom³⁵ in 1982 covers the various observed coordination modes of the nitrite ion with numerous examples, many of which contain bridging nitrite ligands. Such an example is $[\text{Ni}(\text{en})_2(\text{NO}_2)]\text{X}$, $\text{X} = \text{ClO}_4^-$,^{36,37} I_3^- ,³⁷ or BF_4^- ,³⁸ where NO_2^- bridges each Ni^{II} centre *via* one oxygen and the central nitrogen to form linear polymeric chains. A number of possible coordination modes of the nitrite ion are shown in Figure 5.1. Of those shown, eight modes are bridging. The shortest bridge is one atom long and the longest is the full three atoms of the nitrite ion. The chelating and bridging mode X was observed by Kahn *et al.* in a nickel(II) dinuclear complex, $[\text{Ni}(\text{en})_2(\text{NO}_2)]_2(\text{BPh}_4)_2$.³⁹ Kahn and co-workers also measured strong intrachain magnetic coupling (albeit antiferromagnetic) in the polymeric complex $[\text{Ni}(\text{en})_2(\text{NO}_2)]\text{ClO}_4$.³⁷ The magnetic properties of this complex, also known as NENP in the physics community, have been the subject of intense investigation, as it exhibits what is known as Haldane gap behaviour.⁴⁰⁻⁴⁵

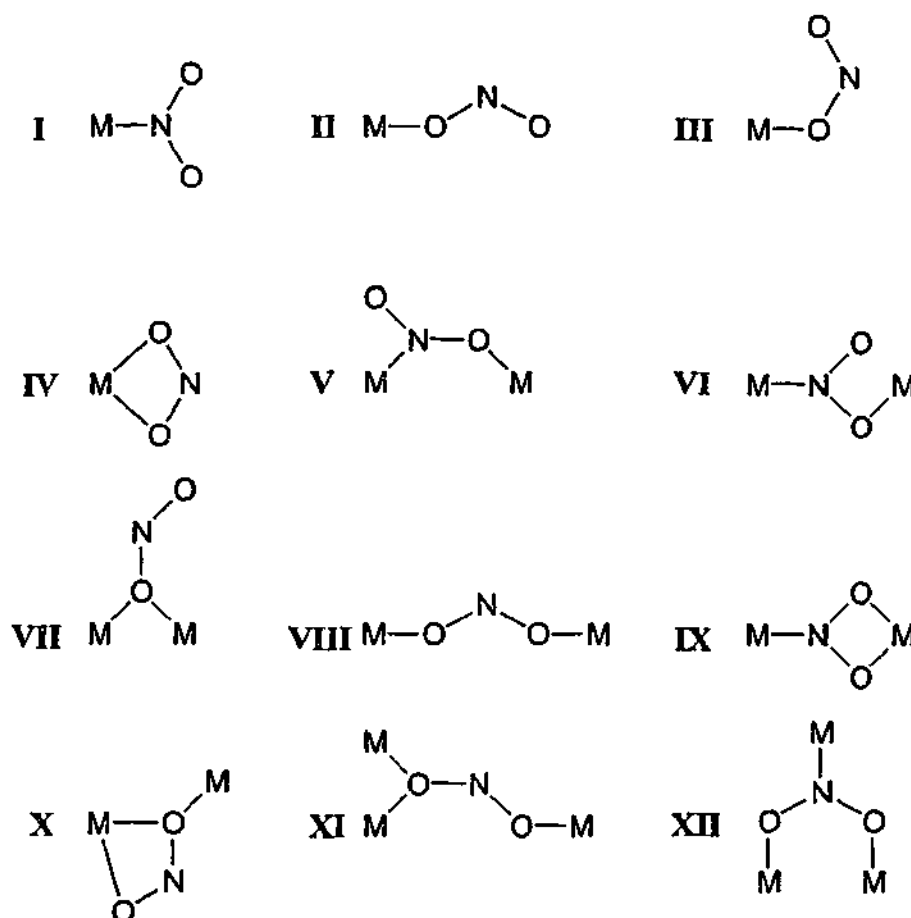


Figure 5.1 A number of possible nitrite coordination modes.³⁵

As both dicyanamide and nitrite are anionic ligands, it was likely that their mixed ligand complexes would be anionic. Indeed, two isostructural anionic dca/ NO_2^- complexes were synthesized, $\text{Ph}_4\text{P}[\text{M}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$, $\text{M}^{\text{II}} = \text{Co}$ and Ni . In addition, a third anionic complex was obtained, $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$. The crystal structures and magnetic properties are presented in this chapter.

Anionic coordination polymers of the type $[\text{M}(\text{dca})_3]^-$, $[\text{M}(\text{dca})_4]^{2-}$,^{46,47} and the mixed ligand complexes, $[\text{M}(\text{dca})_2(\text{NCS})_2]^{2-}$,⁴⁷⁻⁴⁹ were first reported by Köhler *et al.* but without any crystallographic or magnetic characterisation. The results presented in this chapter form part of a wider investigation by Murray, Batten and co-workers of anionic dicyanamide network complexes.⁵⁰ Recently Murray *et al.* found that the network topology is dependent on the choice of counter-cation – the anionic networks are in fact cation

templated.^{51,52} The structures of $\text{Ph}_4\text{E}[\text{M}^{\text{II}}(\text{dca})_3]$, where $\text{E} = \text{As}$ or P , $\text{M}^{\text{II}} = \text{Mn}, \text{Fe}, \text{Co}$ or Ni , consist of 2D square grid (4,4) sheets of $[\text{M}(\text{dca})_3]^-$ with columns of cations separating the 2D layers (Figure 5.2).⁵² The use of coordinating solvents also resulted in the formation of solvated anionic networks with very different topologies. The structures of $(\text{Ph}_4\text{E})_2[\text{M}^{\text{II}}_2(\text{dca})_6(\text{H}_2\text{O})] \cdot \text{H}_2\text{O} \cdot x\text{MeOH}$, $x = 0.5$ or 1 ; $\text{M}^{\text{II}} = \text{Co}, \text{Ni}$; $\text{E} = \text{P}, \text{As}$, consist of layers of 1D ladders that are linked by hydrogen bonding ($\text{dca} \cdots \text{H}_2\text{O}$) to form 2D (4,4) sheets (Figure 5.3).⁵²

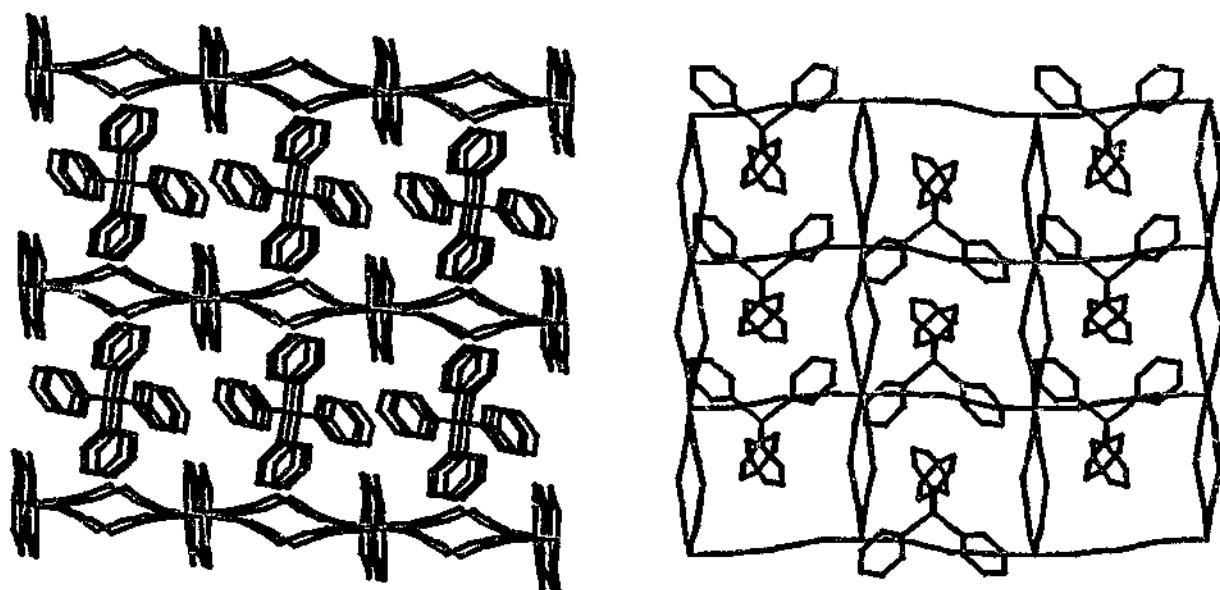


Figure 5.2 (Left) the alternating 2D (4,4) sheets of $[\text{M}(\text{dca})_3]^-$ separated by layers of Ph_4E^+ cations and (Right) a view of a single sheet showing orientation of cations, in the structure of $\text{Ph}_4\text{P}[\text{M}^{\text{II}}(\text{dca})_3]$.

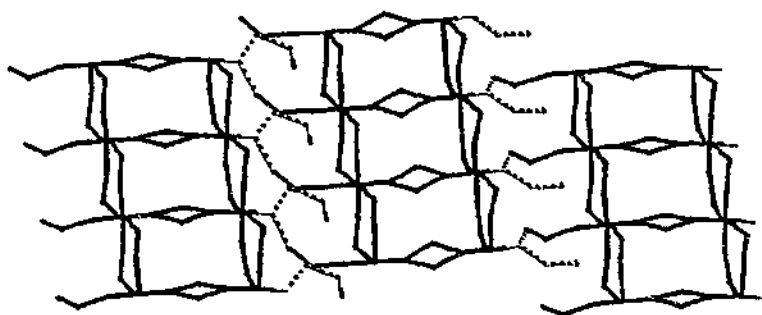


Figure 5.3 Three ladder motifs hydrogen bonded to form overall 2D (4,4) sheets in the structure of $(\text{Ph}_4\text{E})_2[\text{M}^{\text{II}}_2(\text{dca})_6(\text{H}_2\text{O})] \cdot \text{H}_2\text{O} \cdot x\text{MeOH}$.

The structures of $\text{MePh}_3\text{P}[\text{M}^{\text{II}}(\text{dca})_3]$, where $\text{M}^{\text{II}} = \text{Mn}, \text{Fe}, \text{Co}$ and Ni , consist of a 3D network of $[\text{M}(\text{dca})_3]^-$ with cavities within the network that are occupied by pairs of cations (Figure 5.4). Alternatively, the structures of $(\text{PrPh}_3\text{P})_2[\text{M}^{\text{II}}(\text{dca})_4]$ (where $\text{M}^{\text{II}} = \text{Co}$ and Ni) consist of linear chains of $[\text{M}(\text{dca})_4]^{2-}$ containing octahedral M^{II} centres linked by double $\mu_{1,5}$ -dca bridges (Figure 5.5). The nitrile nitrogen atoms from two *trans* terminal monodentate dca ligands occupy the two remaining coordination sites.⁵³

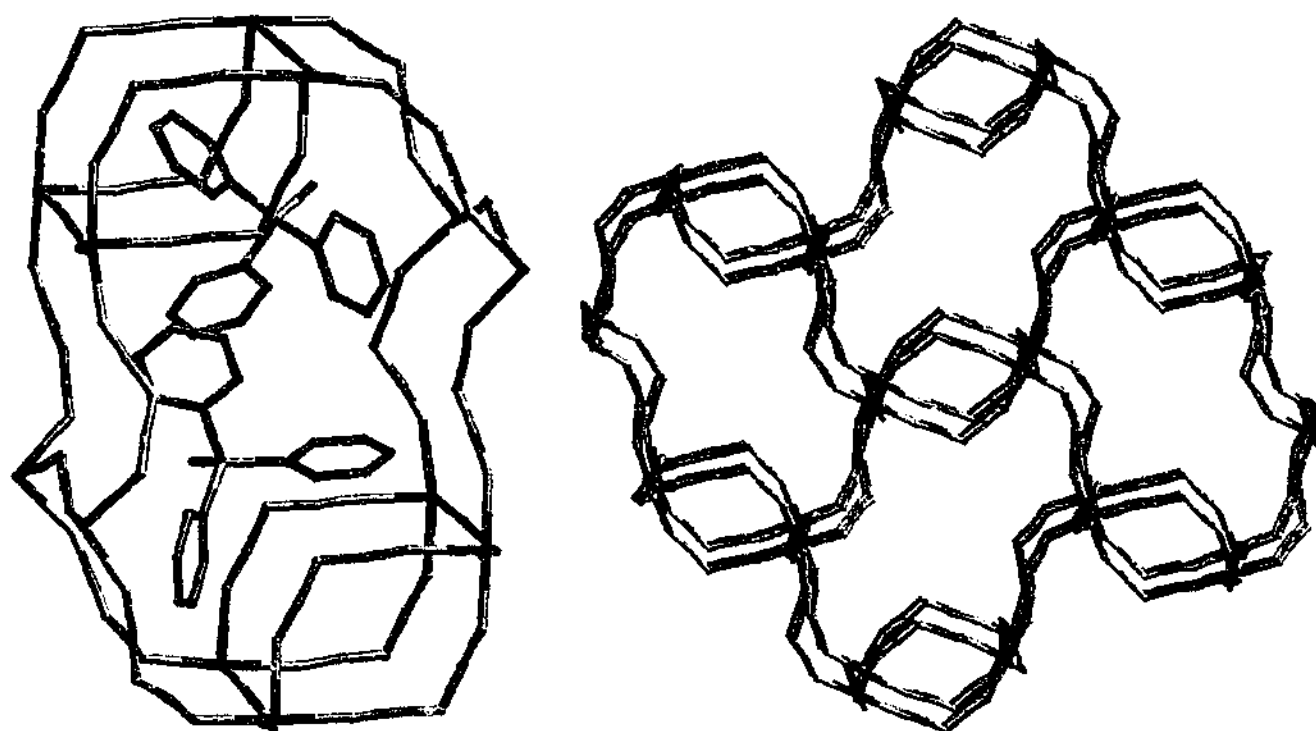


Figure 5.4 (Left) Two Ph_3MeP^+ cations in a cavity and (Right) the anionic $[\text{M}^{\text{II}}(\text{dca})_3]^-$ network, in the structure of $\text{MePh}_3\text{P}[\text{M}^{\text{II}}(\text{dca})_3]$.

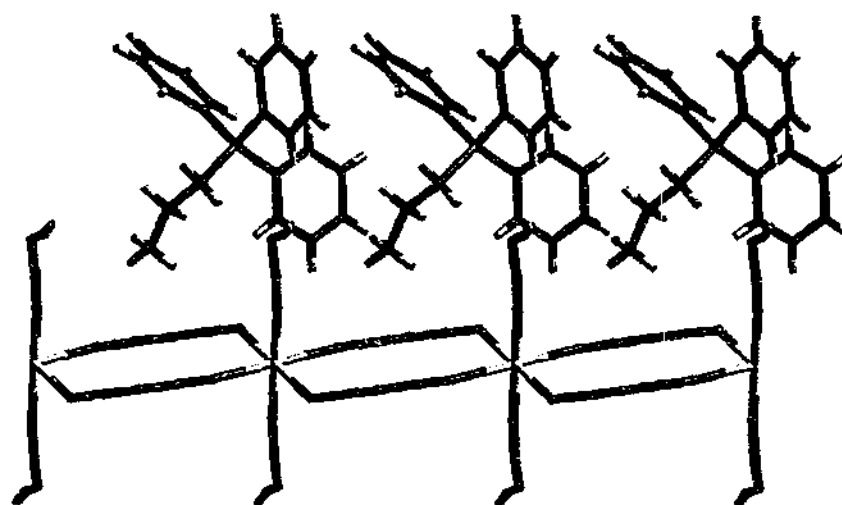


Figure 5.5 The linear chain structure of $(\text{PrPh}_3\text{P})_2[\text{M}^{\text{II}}(\text{dca})_4]$.

Murray, Batten and co-workers have also investigated the inclusion of paramagnetic cations within anionic dca networks.⁵⁴ The structures of $[\text{M}(\text{bipy})_3][\text{M}'(\text{dca})_3]_2$, where $\text{M} = \text{Fe}, \text{Ni}$; $\text{bipy} = 2,2'$ -bipyridine and $\text{M}' = \text{Mn}, \text{Fe}$, consist of 2D (6,3) networks of $[\text{M}'(\text{dca})_3]^-$ with $[\text{M}(\text{bipy})_3]^{2+}$ cations sitting in the hexagonal windows of the sheets (Figure 5.6). These types of “hybrid” networks may have potential spin-crossover and/or long-range order properties.⁵⁴

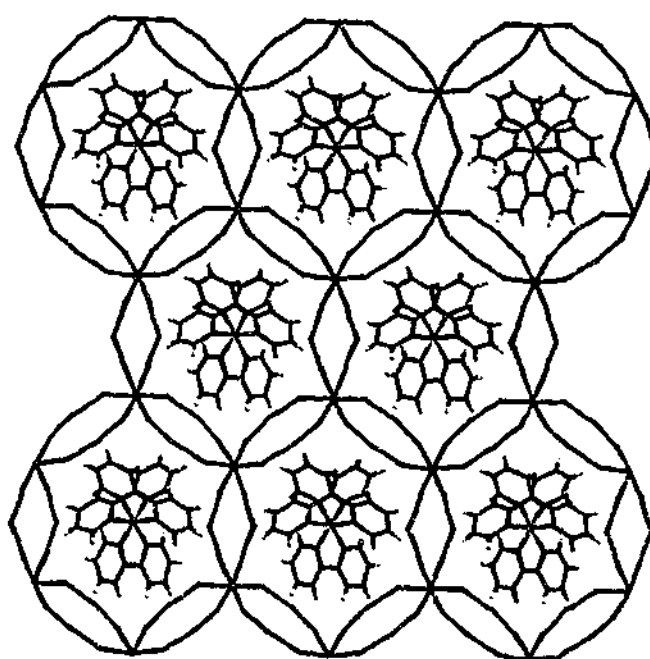


Figure 5.6 The hexagonal (6,3) sheet structure of $[\text{M}(\text{bipy})_3][\text{M}'(\text{dca})_3]_2$.

In general, the $\text{Ph}_4\text{E}[\text{M}^{\text{II}}(\text{dca})_3]$ series of compounds display weak antiferromagnetic coupling, with one exception. The compounds $\text{Ph}_4\text{E}[\text{Ni}(\text{dca})_3]$, where E = As or P, both appear to display long-range order of the spin-canted antiferromagnetic type below a T_N of 20 K. Extensive magnetic measurements were performed to show that the magnetic ordering was not due to possible traces of $\alpha\text{-}[\text{Ni}(\text{dca})_2]$, which displays long-range ferromagnetic order with a T_c close to 20 K.^{51,52}

A number of groups have reported a number of Cu^{I} mixed ligand anionic dicyanamide compounds that display interesting electric and magnetic properties, using the organic radical cation bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF). The compounds, $\kappa\text{-(BEDT-TTF)}_2\text{Cu}(\text{dca})\text{X}$, X = Br, Cl are isomorphous, with the chloride and bromide materials being superconductors ($T_c = 12.5, 11.6$ K, respectively).⁵⁵⁻⁵⁹ The cyanide/dca coordination polymers, $\kappa\text{-(BEDT-TTF)}_2[\text{Cu}_2(\text{CN})(\text{dca})]$ and $\theta\text{-(BEDT-TTF)}_2\text{Cu}(\text{dca})_2(\text{CN})$ display superconductivity ($T_c = 11.2$ K) and 2D Heisenberg antiferromagnetic behaviour (below *ca.* 220 K) respectively.⁶⁰⁻⁶²

5.2 Synthesis and Characterisation

5.2.1 $\text{Ph}_4\text{P}[\text{M}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$, $\text{M}^{\text{II}} = \text{Co}$ and Ni

Reaction of a solution of $\text{M}^{\text{II}}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{M}^{\text{II}} = \text{Co}$ or Ni , in acetonitrile with a solution of $\text{Ph}_4\text{P}(\text{dca})$, Ph_4PBr , and NaNO_2 in an acetonitrile/water solvent mixture in a molar ratio of 1:2:2:1 yielded purple needle/rod-like crystals, and green clusters of rod-like crystals, for the cobalt and nickel products respectively.

The infrared spectra of the products showed absorbances at 2180 (Co) and 2187 (Ni) cm^{-1} due to $\nu_s(\text{C}\equiv\text{N})$ of dicyanamide, and 1587 cm^{-1} (Co and Ni) due to $\nu(\text{C}=\text{C})$ of Ph_4P^+ . The $\nu_s(\text{C}\equiv\text{N})$ value is consistent with the $\mu_{1,5}\text{-dca}$ bridging mode. Comparison with

the infrared spectrum of $\text{Ph}_4\text{As}[\text{Co}(\text{dca})_3]$ (provided by P. van der Werff, School of Chemistry, Monash University) shows that the absorbances at 1204 (Co) and 1212 (Ni) cm^{-1} are due to $\nu_{\text{as}}(\text{NO})$ of NO_2^- , which are decreased in energy, upon coordination, compared to the free-ion value of 1260 cm^{-1} .³⁵ The elemental analyses of the Co and Ni products were consistent with the formulae obtained from the crystal structures (*vide infra*). The powder X-ray diffractograms of the Co and Ni samples match those calculated from the crystal structures with the exception of two peaks in each case ($2\theta = 11.64^\circ$ and 14.66° (Co); 11.20° and 18.19° (Ni)). These peaks could not be indexed to $\alpha\text{-}[\text{M}(\text{dca})_2]$, $\text{Ph}_4\text{P}[\text{M}(\text{dca})_3]$ or $(\text{Ph}_4\text{P})_2[\text{M}(\text{dca})_4]$. The diffractograms were also compared with that of $\text{Ph}_4\text{As}(\text{dca})$ (provided by P. van der Werff), which is believed to possess the same structure as $\text{Ph}_4\text{P}(\text{dca})$. The unidentified peaks in the diffractograms of the Co and Ni samples did not correspond to any peaks in the $\text{Ph}_4\text{As}(\text{dca})$ diffractogram. Hence, the samples contain as yet unidentified impurities.

The crystal of $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_2)]\cdot\text{MeCN}$ used for X-ray crystallographic analysis was chosen from crystals grown from a reaction of a solution of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in acetonitrile with a solution of Ph_4PBr , $\text{Na}(\text{dca})$ and NaNO_2 in an acetonitrile/ethanol solvent mixture in a molar ratio of 1:3:2:1. Colourless crystals co-crystallized with the Co^{II} product, which were probably NaNO_2 or $\text{Na}(\text{dca})$ due to their low solubilities in the solvent mixture used.

Independently, Batten and Harris synthesised the nitrate analogue of the above complex, $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_3)]\cdot\text{MeCN}$, by a reaction similar to that here but with the omission of NO_2^- . This complex is isostructural with the nitrite complex, and has very similar unit cell parameters.⁶³

5.2.2 $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$

$\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$ was initially obtained as a second product in a reaction that was intended to synthesise $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$. A pure sample was subsequently obtained independently by reaction of a solution of $(\text{Et}_4\text{N})_2\text{CoBr}_4$ in acetonitrile with an acetonitrile solution of $\text{Ph}_4\text{P}(\text{dca})$ in a 1:1 molar ratio. Slow evaporation of the solution yielded well-formed dark blue crystals of $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$ in moderate yield. The infrared spectrum showed absorbances at 2184 and 1586 cm^{-1} due to $\nu_s(\text{C}\equiv\text{N})$ of dicyanamide and $\nu(\text{C}=\text{C})$ of Ph_4P^+ respectively. The former value is indicative of bidentate dicyanamide bridging through both nitrile nitrogen atoms. Elemental analysis was consistent with the above formula. The powder X-ray diffractogram matched that calculated from the single crystal data.

5.3 Crystal Structures

5.3.1 $\text{Ph}_4\text{P}[\text{M}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$, $\text{M}^{\text{II}} = \text{Co}$ and Ni

Crystallographic data are summarised in Table 5.1 (see page 221). Table 5.2 contains selected interatomic distances and angles (see page 227). The compounds $\text{Ph}_4\text{P}[\text{M}^{\text{II}}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$ are isomorphous, crystallising in the chiral orthorhombic space group $P2_12_12_1$. The refinement of the structure of the nickel complex was poor compared to that of the cobalt complex. Thus, although the crystallographic data and distances and angles for the nickel complex are included here, only the structure of the cobalt complex is described. The atom labelling scheme for $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$ is shown in Figure 5.7. The structure was refined as a racemic twin with approximately equal twin component contributions. The asymmetric unit contains one formula unit. Each Co^{II} atom is coordinated in a highly distorted octahedral environment by two dca nitrile nitrogens ($\text{Co}(1)-\text{N}(41) = 2.099(5)$ Å and $\text{Co}(1)-\text{N}(45^i) = 2.087(5)$ Å) in the axial

positions, and two dca nitrile nitrogens ($\text{Co-N} = 2.077(5), 2.097(5) \text{ \AA}$) and two oxygens ($\text{Co-O} = 2.138(5), 2.164(5) \text{ \AA}$) of the chelating nitrite (*O,O'*-nitrito, mode IV shown in Figure 5.1, see page 213) ligand in the equatorial plane. The coordination environment of the equatorial plane deviates significantly from a regular square due to the chelating nitrite, which subtends an acute angle of $\text{O}(51)\text{--Co}(1)\text{--O}(53) = 58.4(2)^\circ$. The nitrite bond angle, $\text{O}(51)\text{--N}(52)\text{--O}(53) = 112.2(5)^\circ$, is decreased on chelation by $\sim 2^\circ$ from the 'free ion' value of $114.9(5)^\circ$ in the structure of NaNO_2 .^{64,65} To the best of the candidate's knowledge there has been only one other structurally characterised Co^{II} complex containing chelating nitrite ligands, $[\text{Co}(\text{L})(\text{NO}_2)_2]$, where $\text{L} = (-)\text{-sparteine}$.⁶⁶ The highly distorted octahedral mononuclear complex has two chelating nitrite ligands that are less symmetrically chelated compared to the present structure ($\text{Co-O} = 2.057 - 2.338 \text{ \AA}$, $\text{O-N-O} = 107.0^\circ$ and 110.1° , $\text{O-Co-O} = 54.2^\circ$ and 56.4°) where the sparteine ligand is also bidentate chelating.

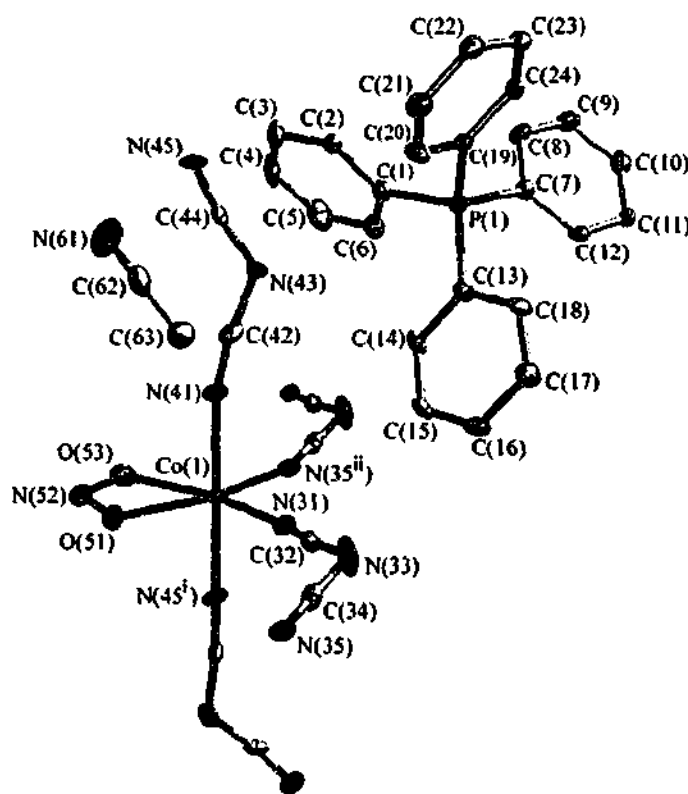


Figure 5.7 The crystal structure of $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$ with the atom labelling scheme (thermal ellipsoids are shown at 50 % probability, hydrogen atoms are omitted for clarity).

Table 5.1 Crystal data for $\text{Ph}_4\text{P}[\text{M}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$, $\text{M}^{\text{II}} = \text{Co}$, Ni and $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$.

Compound	$\text{Ph}_4\text{P}[\text{M}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$		$\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$
	Co	Ni	
Formula	$\text{C}_{30}\text{H}_{23}\text{CoN}_8\text{O}_2\text{P}$	$\text{C}_{30}\text{H}_{23}\text{NiN}_8\text{O}_2\text{P}$	$\text{C}_{26}\text{H}_{20}\text{Br}_2\text{CoN}_3\text{P}$
M	617.46	617.24	624.17
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
$a/\text{\AA}$	7.4914(1)	7.4519(2)	7.3136(1)
$b/\text{\AA}$	16.9427(6)	16.8131(5)	12.3136(2)
$c/\text{\AA}$	22.6970(7)	22.7773(9)	27.8730(7)
$U/\text{\AA}^3$	2880.8(1)		2510.15(8)
Z	4	4	4
$\rho_{\text{calc}} / \text{g cm}^{-3}$	1.424	1.437	1.652
T/K	123(2)	123(2)	123(2)
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	0.694	0.779	3.950
Crystal dimensions	$0.63 \times 0.15 \times 0.15$	$0.5 \times 0.1 \times 0.1$	$0.25 \times 0.15 \times 0.15$
θ range/°	2.16 – 30.05	2.16 – 28.29	1.81 – 28.28
Index ranges	$-10 \leq h \leq 6,$ $-22 \leq k \leq 22,$ $-29 \leq l \leq 29$	$-9 \leq h \leq 7,$ $-18 \leq k \leq 22,$ $-28 \leq l \leq 30$	$-9 \leq h \leq 6,$ $-16 \leq k \leq 15,$ $-37 \leq l \leq 36$
Completeness to $2\theta = 55^\circ / \%$	99.9	99.2	99.3
$T_{\text{min}}, T_{\text{max}}$	0.7733, 0.9174		
Data collected	32974	18267	19022
Unique data (R_{int})	7549 (0.0743)	6776 (0.1624)	6094 (0.1004)
Observed reflections [$I > 2\sigma(I)$]	5512	3798	3543
Parameters	380	381	299
Final R_1, wR_2 [$I > 2\sigma(I)$] ^(a)	0.0868, 0.1815	0.1106, 0.1237	0.0880, 0.2371
(all data)	0.1313, 0.1964	0.2062, 0.1445	0.1563, 0.2712
Goodness of fit, S	1.128	1.043	1.040
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}} / \text{e \AA}^{-3}$	-0.801, 2.004	-0.720, 1.080	-1.785, 1.795

^(a) $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$

Each Co^{II} atom is connected to four others in the ab -plane by two crystallographically unique dca ligands coordinating *via* the nitrile nitrogens in the bidentate $\mu_{1,5}$ mode. This gives square-grid 2D (4,4) sheets, one of which is shown in Figure 5.8. In this figure it can be seen that the chelating nitrite ligands are all oriented in one direction parallel to the a -axis direction, and alternate in direction parallel to the b -axis direction. The overall structure consists of anionic (4,4) square-grid sheets of $[\text{Co}(\text{dca})_2(\text{NO}_2)]^-$ that alternate with layers of the Ph_4P^+ cations, with intercalated acetonitrile molecules also present (Figure 5.9). The anionic sheets are similar to those in the $\text{Ph}_4\text{E}[\text{M}(\text{dca})_3]$ series of compounds (*vide supra*), except in those cases, half of the links within the sheets are double dca bridges ($\text{M}(\mu\text{-dca})_2\text{M}$, see Figure 5.2).

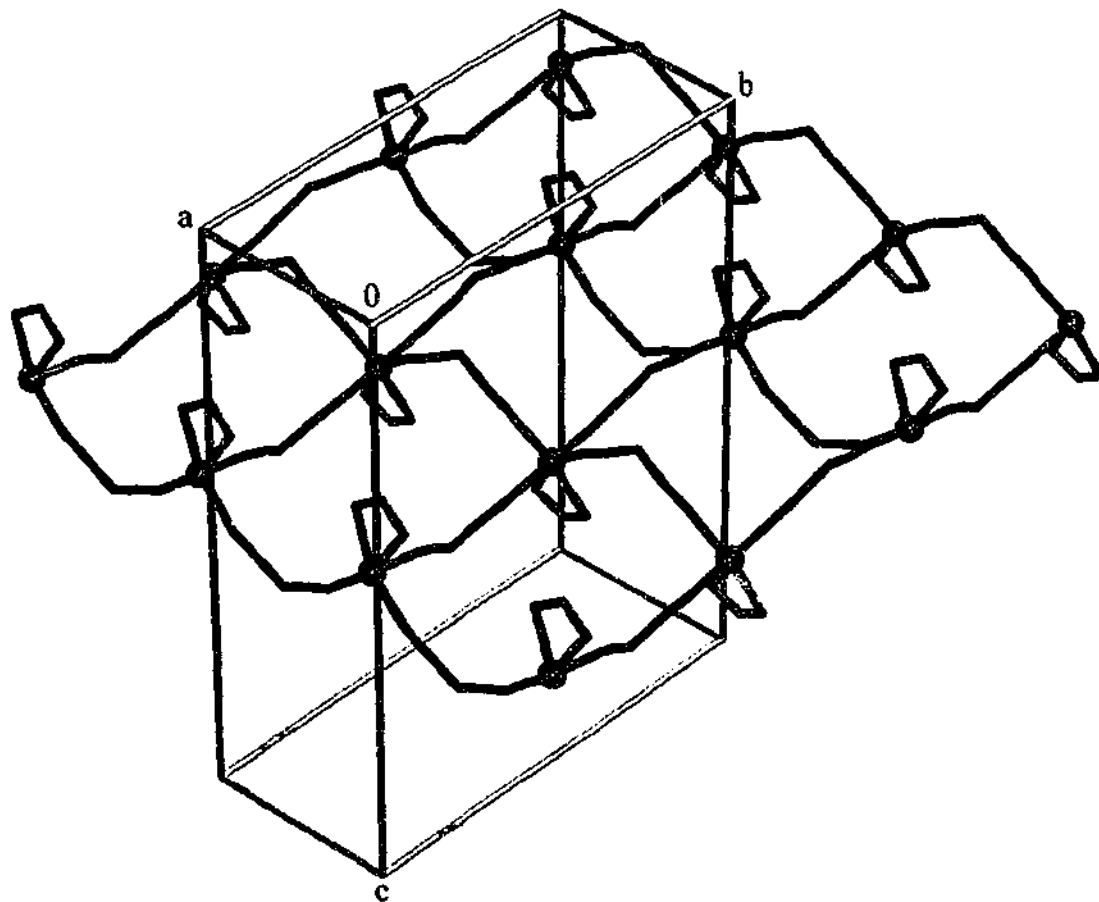


Figure 5.8 A 2D square-grid anionic sheet of $[\text{Co}(\text{dca})_2(\text{NO}_2)]^-$ in the structure of $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$ (red spheres represent Co^{II} ions, dca ligands are shown in blue and nitrite ligands in green).

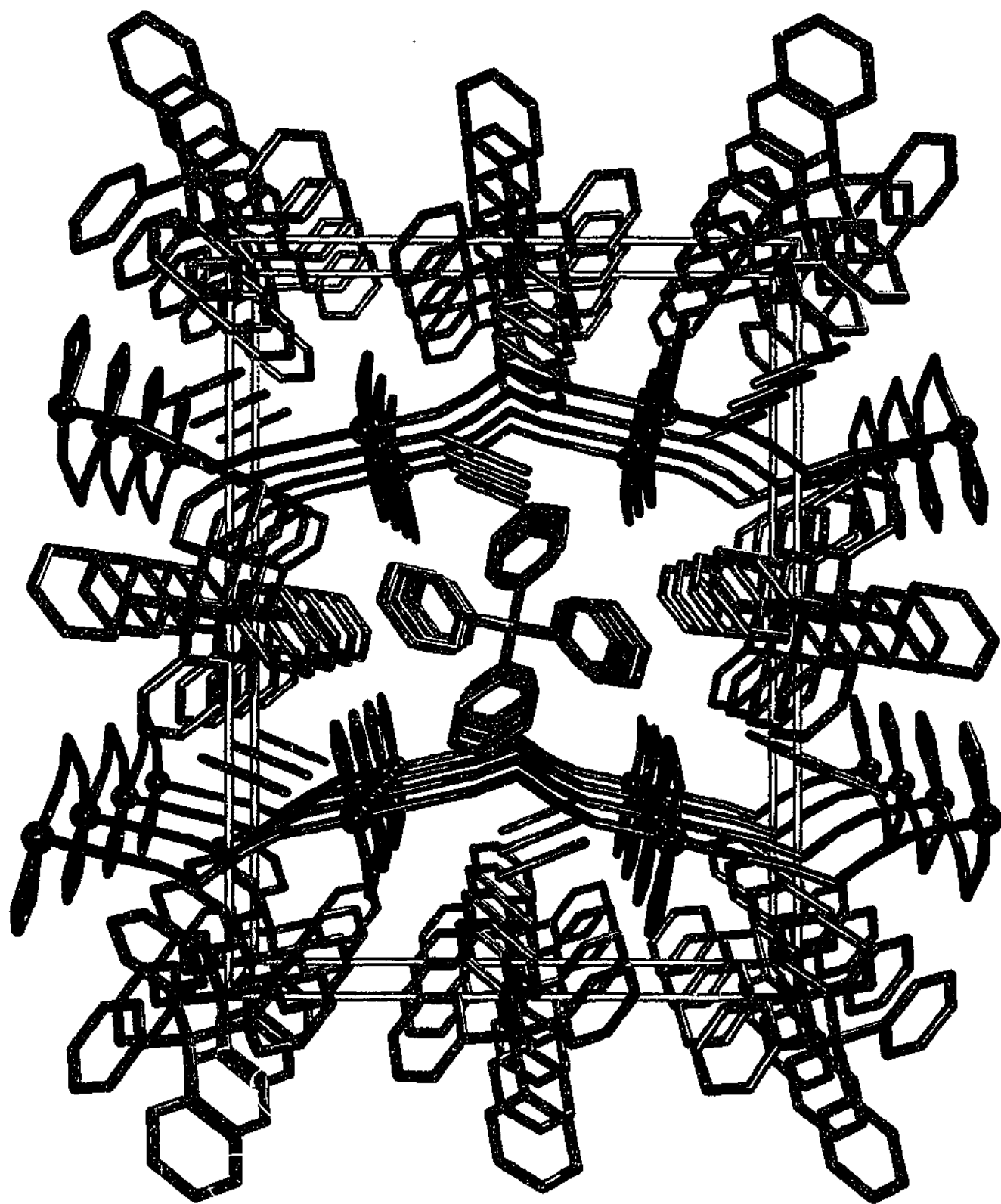


Figure 5.9 Packing diagram of $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$ viewed parallel to the *a*-axis direction. The purple spheres represent Co^{II} ions, dca and nitrite ligands are shown in blue, Ph_4P^+ ions in red, and lattice acetonitrile molecules are in blue (nitrogen) and green (carbons).

The sheets pack parallel to the c -axis direction such that adjacent sheets are offset $\frac{1}{2}$ of the unit cell length a with respect to each other (Figure 5.10). The resulting packing is of the infinite AB type. In Figure 5.11 it can be seen that the cations do not lie directly below (or above) the centres of the $[\text{Co}_4(\text{dca})_4(\text{NO}_2)_4]$ squares, but are slightly offset in the a -axis direction. Each cation layer is oriented antiparallel to its neighbouring cation layers.

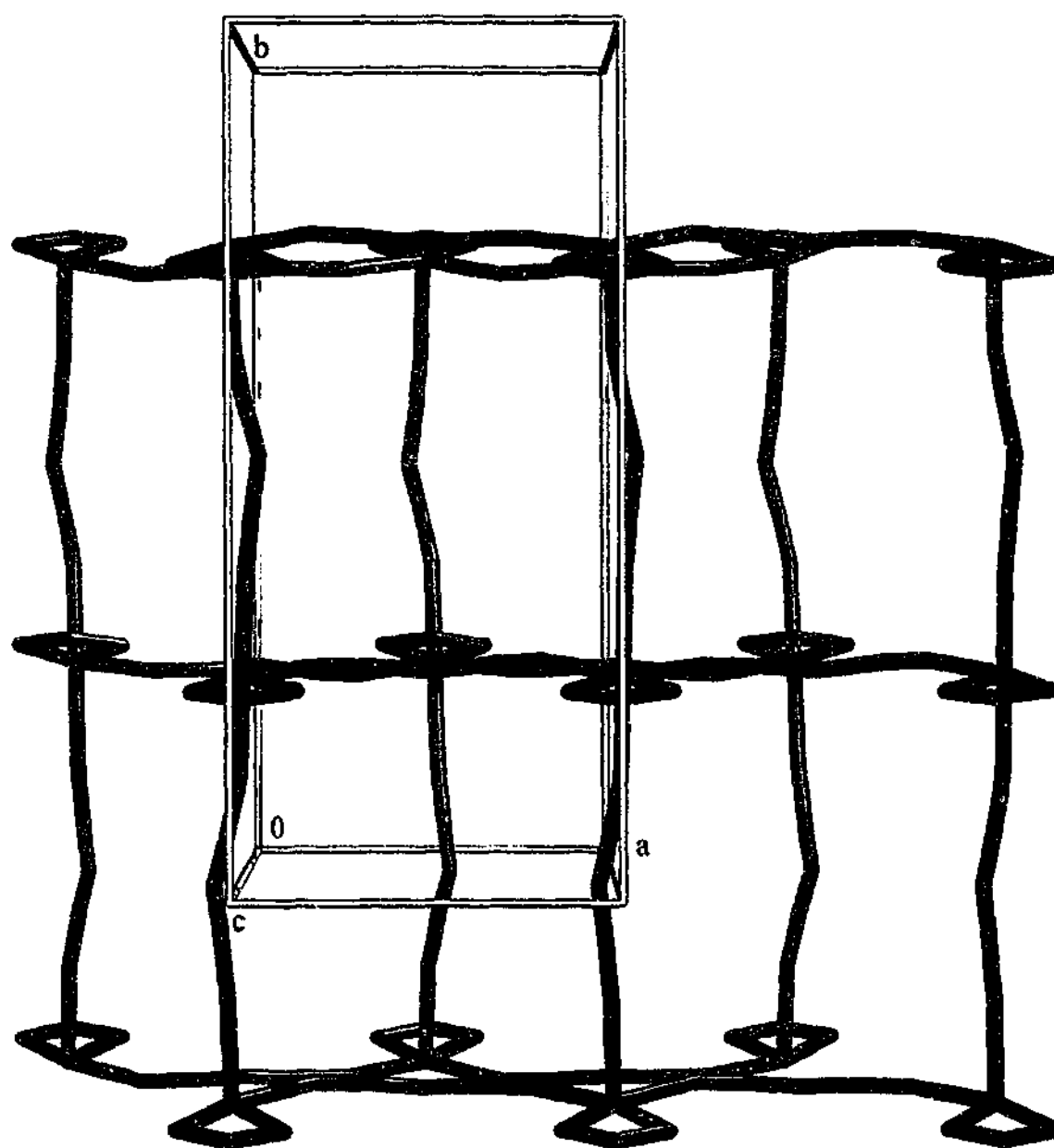


Figure 5.10 Two square-grid sheets of $[\text{Co}(\text{dca})_2(\text{NO}_2)]^-$, viewed parallel to the c -axis direction (the upper sheet is shown in blue and lower in red).

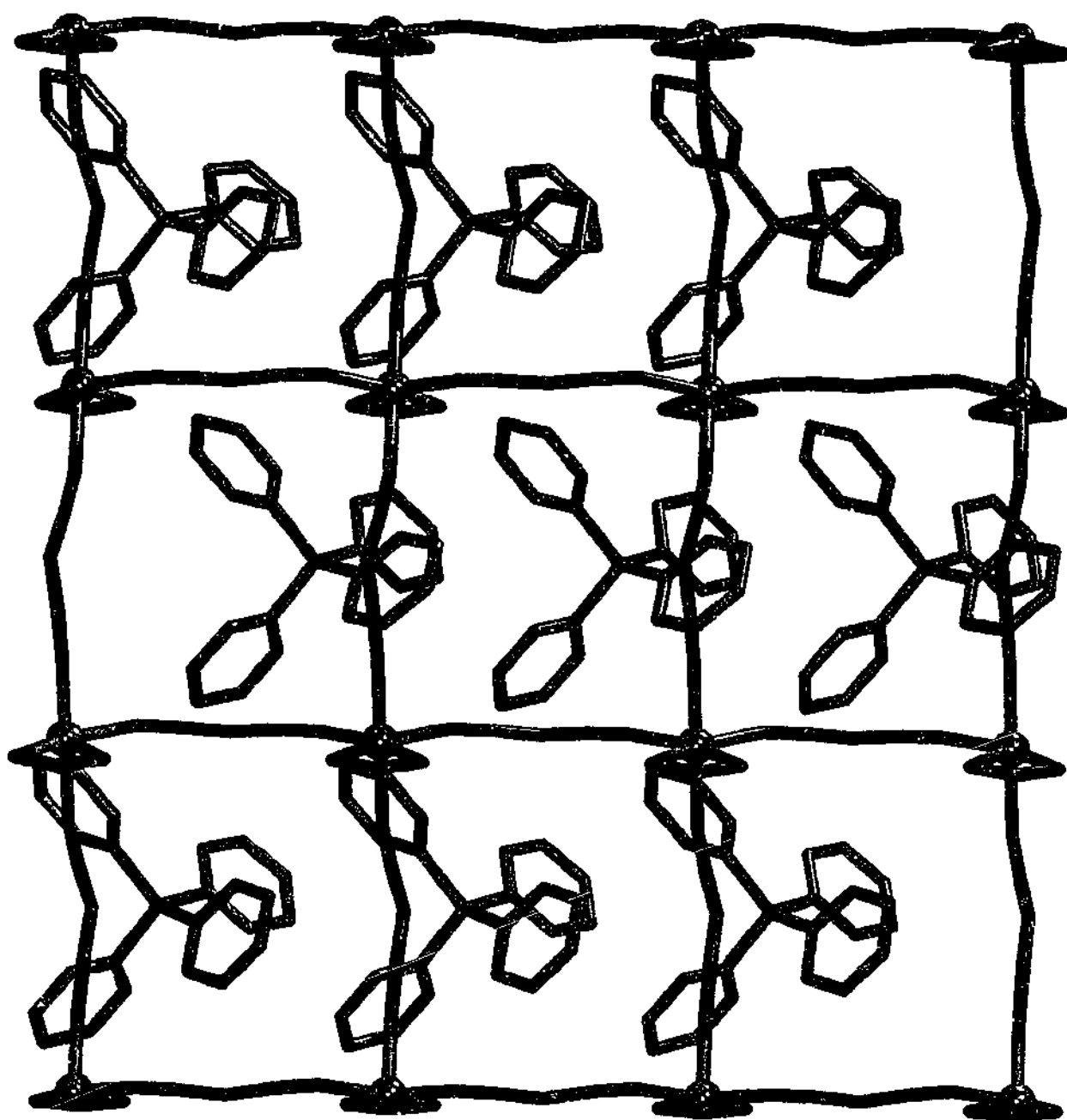


Figure 5.11 One square-grid sheet of $[\text{Co}(\text{dca})_2(\text{NO}_2)]^-$, viewed parallel to the c -axis direction, showing the positions of the Ph_4P^+ cations (green) with respect to the sheet.

The intra-sheet $\text{Co}\cdots\text{Co}$ distance across the dca ligand parallel to the a -axis direction is equal to the unit cell length a (7.4914(1) Å), whereas that across the dca ligand parallel to the b -axis direction is 8.4914(3) Å, approximately half the unit cell length b (the Co centres are not collinear in this direction). The sheets are well separated with the shortest inter-sheet $\text{Co}\cdots\text{Co}$ distance being 12.463(1) Å.

The Ph_4P^+ cations layers are involved in multiple phenyl embraces, as described by Dance and co-workers.⁶⁷ Each of the cations is engaged in 'orthogonal four-fold phenyl embraces' (O4PE) with its neighbours involving four separate edge-to-face $\text{C-H}\cdots\pi$ interactions. These interactions create 'linear infinite chains of translational four-fold phenyl embraces' (LIT4PE) in the *a*-axis direction ($\text{P}\cdots\text{P}$ distance is equal to the unit cell length *a*, 7.4914(1) Å, $\text{CH}\cdots\text{centroid}$ = 3.085, 3.256, 3.373 and 3.625 Å). These chains are cross-linked in *b*-axis direction by further edge-to-face $\text{C-H}\cdots\pi$ interactions ($\text{P}\cdots\text{P}$ = 9.313 Å and $\text{CH}\cdots\text{centroid}$ = 3.228 Å) to form 2D sheets (Figure 5.12).

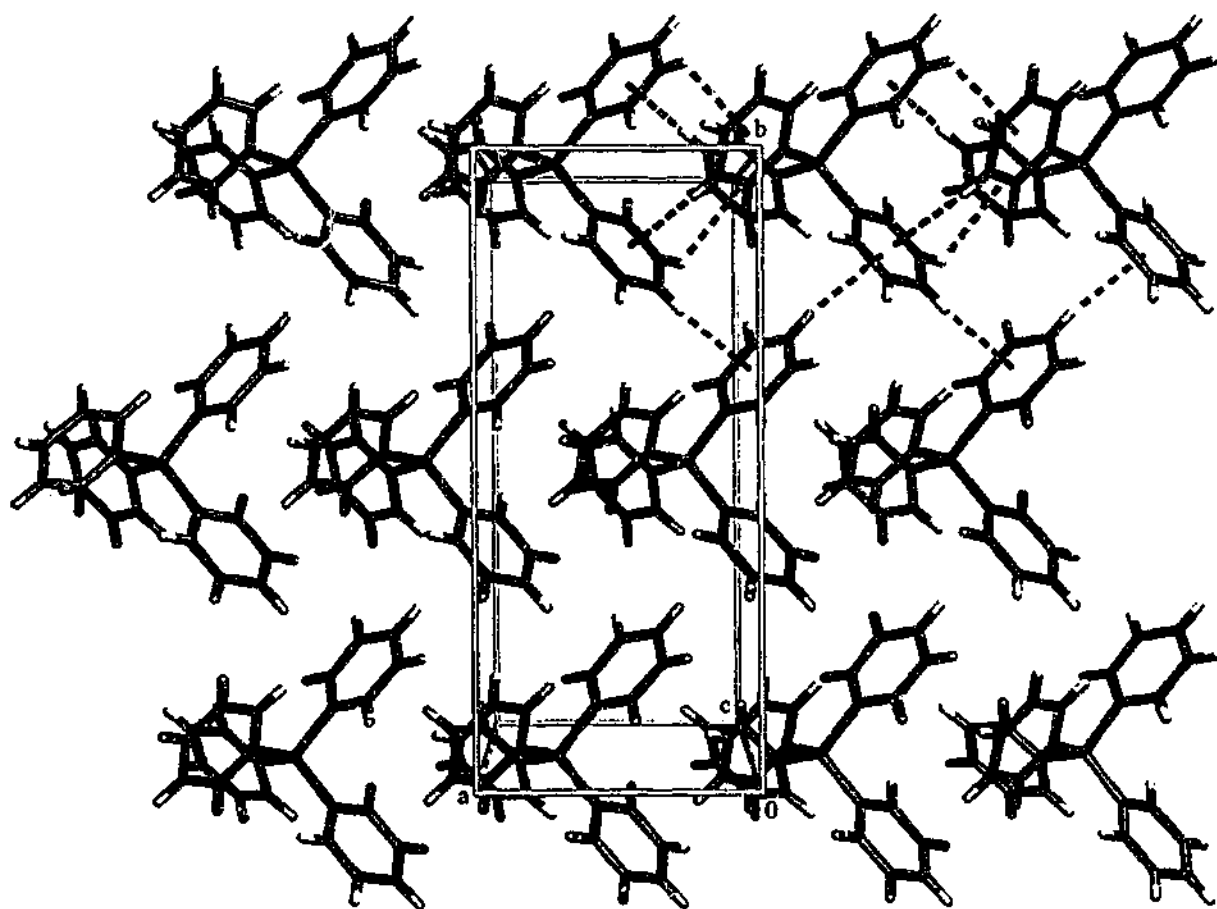


Figure 5.12 Three columns in a single layer of Ph_4P^+ cations in the structure of $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_2)]\cdot\text{MeCN}$ showing edge-to-face $\text{CH}\cdots\pi$ interactions. Some LIT4PE interactions are shown as dashed purple and cross-linking $\text{CH}\cdots\pi$ interactions shown in dashed orange.

The cations in the structure of the $\text{Ph}_4\text{E}[\text{M}(\text{dca})_3]$ series are also involved in LIT4PE interactions (Figure 5.2). However, the chains are cross-linked by 'off-set-face-to-face' phenyl $\pi\cdots\pi$ interactions to form 2D sheets.⁵¹ This difference in the type of cross-linking interaction is due to the orientation of the cation chains in the $\text{Ph}_4\text{E}[\text{M}(\text{dca})_3]$ series. Within each layer, the chains of cations are oriented antiparallel with respect to each other. However, in the present compound, $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_2)]\cdot\text{MeCN}$, the cation chains are oriented parallel to each other.

Table 5.2 Selected interatomic distances (Å) and angles (°) for $\text{Ph}_4\text{P}[\text{M}^{\text{II}}(\text{dca})_2(\text{NO}_2)]\cdot\text{MeCN}$, $\text{M}^{\text{II}} = \text{Co}$ and Ni .

	Co		Ni			Co		Ni	
M(1)–N(31)	2.077(5)	2.037(5)	M(1)–N(35 ⁱⁱ)	2.097(5)	2.044(5)				
M(1)–N(41)	2.099(5)	2.062(5)	M(1)–N(45 ⁱ)	2.087(5)	2.053(6)				
M(1)–O(51)	2.138(5)	2.102(4)	M(1)–O(53)	2.164(5)	2.126(4)				
N(31)–M(1)–N(35 ⁱⁱ)	99.8(2)	100.8(2)	N(41)–M(1)–N(45 ⁱ)	179.1(2)	178.6(2)				
N(31)–M(1)–N(41)	89.2(2)	90.0(2)	N(31)–M(1)–N(45 ⁱ)	91.5(2)	91.2(2)				
N(35 ⁱⁱ)–M(1)–N(41)	89.2(2)	89.1(2)	N(35 ⁱⁱ)–M(1)–N(45 ⁱ)	91.2(2)	91.3(2)				
O(51)–M(1)–O(53)	58.4(2)	59.5(2)	O(51)–M(1)–N(31)	100.8(2)	100.1(2)				
O(51)–M(1)–N(41)	91.5(2)	90.9(2)	O(51)–M(1)–N(35 ⁱⁱ)	159.4(2)	159.1(2)				
O(53)–M(1)–N(41)	89.2(2)	89.0(2)	O(53)–M(1)–N(35 ⁱⁱ)	101.1(2)	99.6(2)				
O(53)–M(1)–N(45 ⁱ)	89.9(2)	88.3(2)	O(53)–M(1)–N(31)	159.1(2)	159.6(2)				

Symmetry transformations: (i) $1-x, y-1/2, 1/2-z$; (ii) $x+1, y, z$.

5.3.2 $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$

Crystallographic data are summarised in Table 5.1 (see page 221). Table 5.3 contains selected interatomic distances and angles (see page 233). The compound $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$ crystallizes in the chiral orthorhombic space group $P2_12_12_1$. While the crystal chosen for X-ray crystallographic analysis was homochiral, the individual components are achiral, and it is thus expected that the bulk sample is a racemic mixture of chirally pure crystals. The structure consists of linear 1D 2-fold helical anionic chains of $[\text{Co}(\text{dca})\text{Br}_2]^-$ and associated Ph_4P^+ cations (Figure 5.13). The coordination environment of each cobalt(II) atom is distorted tetrahedral, consisting of two nitrile nitrogens of two symmetry related $\mu_{1,5}$ -dca ligands ($\text{Co}(1)-\text{N}(1) = 2.001(8) \text{ \AA}$, $\text{Co}(1)-\text{N}(5^i) = 2.02(1) \text{ \AA}$) and two terminal bromide ions ($\text{Co}(1)-\text{Br}(1) = 2.403(2) \text{ \AA}$, and the significantly shorter $\text{Co}(1)-\text{Br}(2) = 2.315(2) \text{ \AA}$). As a comparison, the mononuclear tetrahedral complexes, $[\text{Co}(2,4\text{-Me}_2\text{Py})_2\text{Br}_2]^{68}$ and $[\text{Co}(2\text{-BrPy})_2\text{Br}_2]^{69}$ where $2,4\text{-Me}_2\text{Py} = 2,3\text{-dimethylpyridine}$; $2\text{-BrPy} = 2\text{-bromopyridine}$, have average bond lengths of $\text{Co}-\text{N} = 2.045, 2.050 \text{ \AA}$ and $\text{Co}-\text{Br} = 2.394, 2.3986 \text{ \AA}$ respectively.

The amide nitrogen of the dca ligand was found to be disordered over two positions ($\text{N}(3\text{A})$ and $\text{N}(3\text{B})$). The chains, which are left handed helices, run parallel to the b -axis direction (Figure 5.14). The helical chains and cations pack in layers parallel to the ab -plane, such that in the c -axis direction layers of chains alternate with cation layers (Figure 5.15).

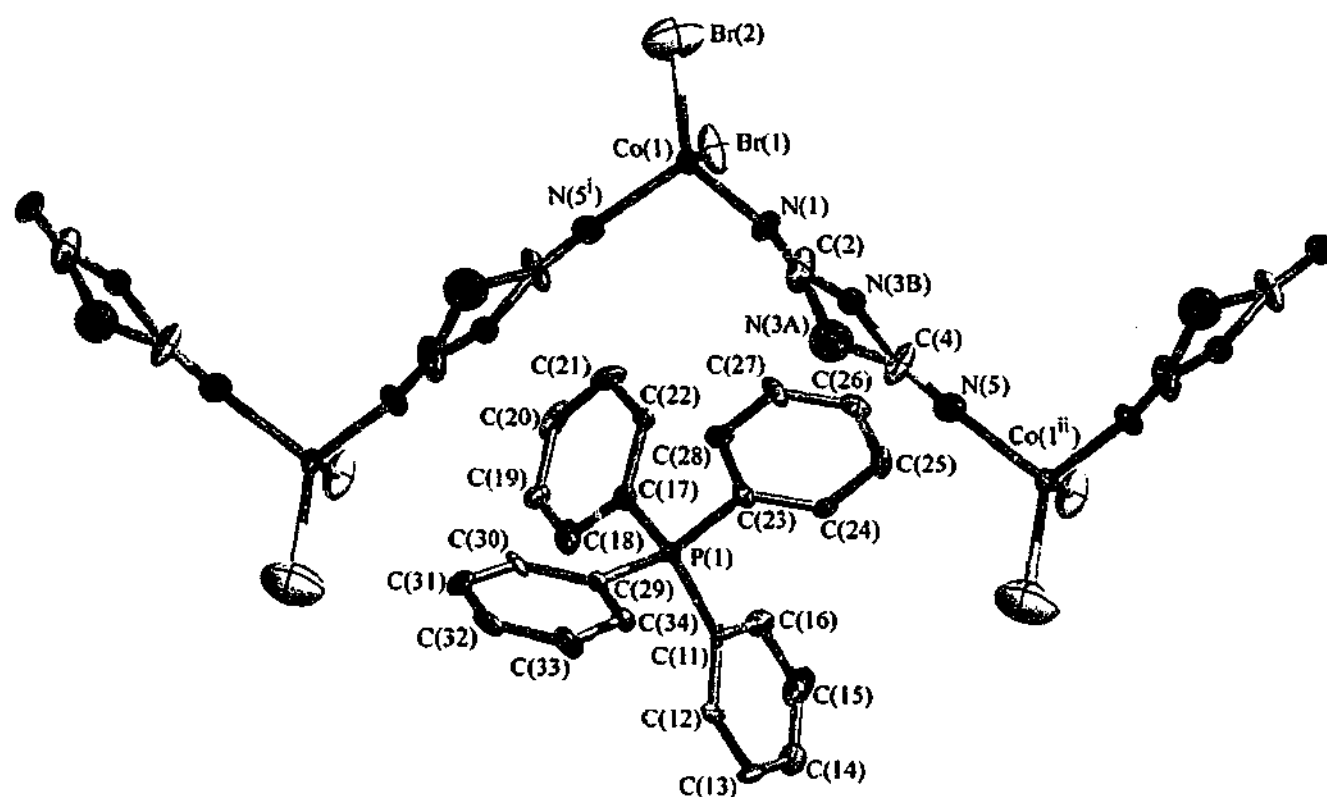


Figure 5.13 The crystal structure of $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$ with atom labelling scheme, also showing the disordered dca amide nitrogen (thermal ellipsoids shown at 50 % probability, hydrogen atoms are omitted for clarity).

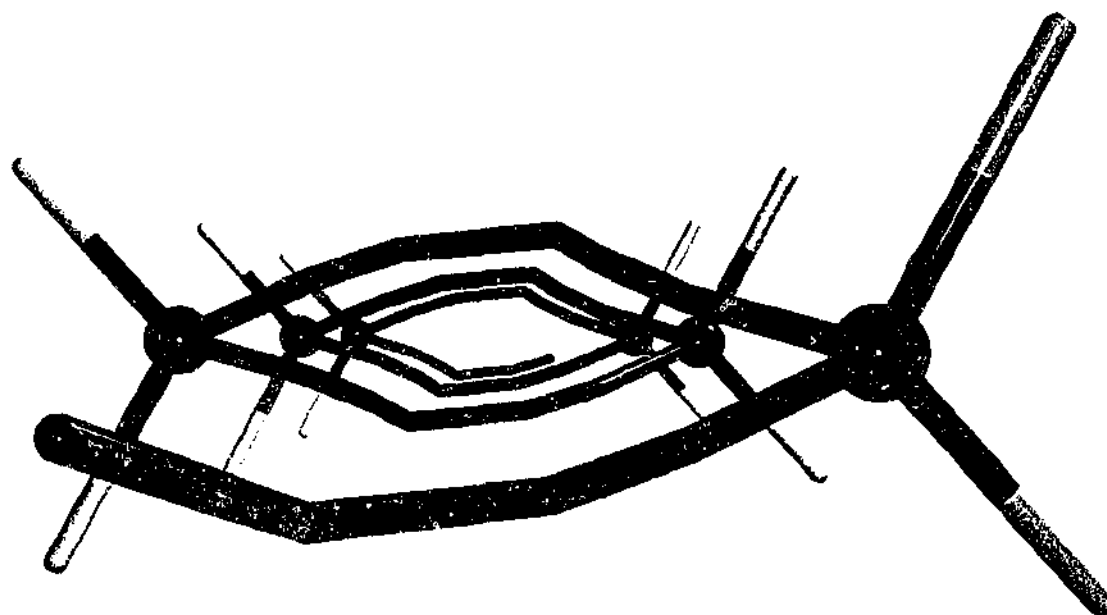


Figure 5.14 View along the *b*-axis direction showing the left-handed helical $[\text{Co}(\text{dca})\text{Br}_2]^-$ chains in the structure of $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$ (only one of the dca amide nitrogen positions is shown for clarity).

Recently Miller and co workers reported a helical cationic dicyanamide complex, $[\text{Co}(\text{dca})_2(\text{H}_2\text{Bilm})_2]\text{Cl}$, where $\text{H}_2\text{Bilm} = 2,2'$ -biimidazole.⁷⁰ The structure of this complex consists of octahedral Co^{II} centres with a N_6 coordination environment containing two imidazole nitrogens of two H_2Bilm ligands in the equatorial plane and two nitrile nitrogens of two $\mu_{1,5}$ -dca ligands. Thus infinite (2-fold) helical chains are formed.

The shortest $\text{Co}\cdots\text{Co}$ distance is found between chains in the layers in the *ab*-plane and is equal to the *a*-axis unit cell length, 7.3136(1) Å. The intra-chain $\text{Co}\cdots\text{Co}$ distance is significantly longer, at 8.333(2) Å. The layers of chains are quite well separated - the shortest $\text{Co}\cdots\text{Co}$ distance between layers is 11.708(2) Å.

Once again, the layers of Ph_4P^+ cations are involved in multiple phenyl embraces. Each cation is engaged in 'orthogonal four-fold phenyl embraces' (O4PE) with its neighbours parallel to the *a*-axis direction (perpendicular to the direction of the anionic chains). Thus, 'linear infinite chains of translational four-fold phenyl embraces' (LIT4PE) in this direction are created ($\text{P}\cdots\text{P}$ is equal to the unit cell length *a*, 7.3136(1) Å, $\text{CH}\cdots\text{centroid} = 3.089, 3.293, 3.420$ and 3.432 Å). These chains are cross-linked by further $\text{CH}\cdots\pi$ interactions to form corrugated 2D sheets of cations in the *ab*-plane (Figure 5.16), with two different inter-chain separations ($\text{P}\cdots\text{P} = 8.905(4)$ Å and $\text{CH}\cdots\text{centroid} = 2.983$ Å; $\text{P}\cdots\text{P} = 9.376(4)$ Å and $\text{CH}\cdots\text{centroid} = 3.293$ Å). There are also a number of weak supramolecular interactions between the cations and the anionic chains. The most significant of these are $\text{H}\cdots\text{N}$ contacts with the disordered dca amide nitrogen of 2.751 Å ($\text{C}-\text{H}\cdots\text{N} = 144.5^\circ$) and 2.805 Å (135.9°); and $\text{C}-\text{H}\cdots\text{Br}$ contacts of 2.957 Å ($\text{C}-\text{H}\cdots\text{Br} = 129.6^\circ$) and 3.005 Å (136.2°).

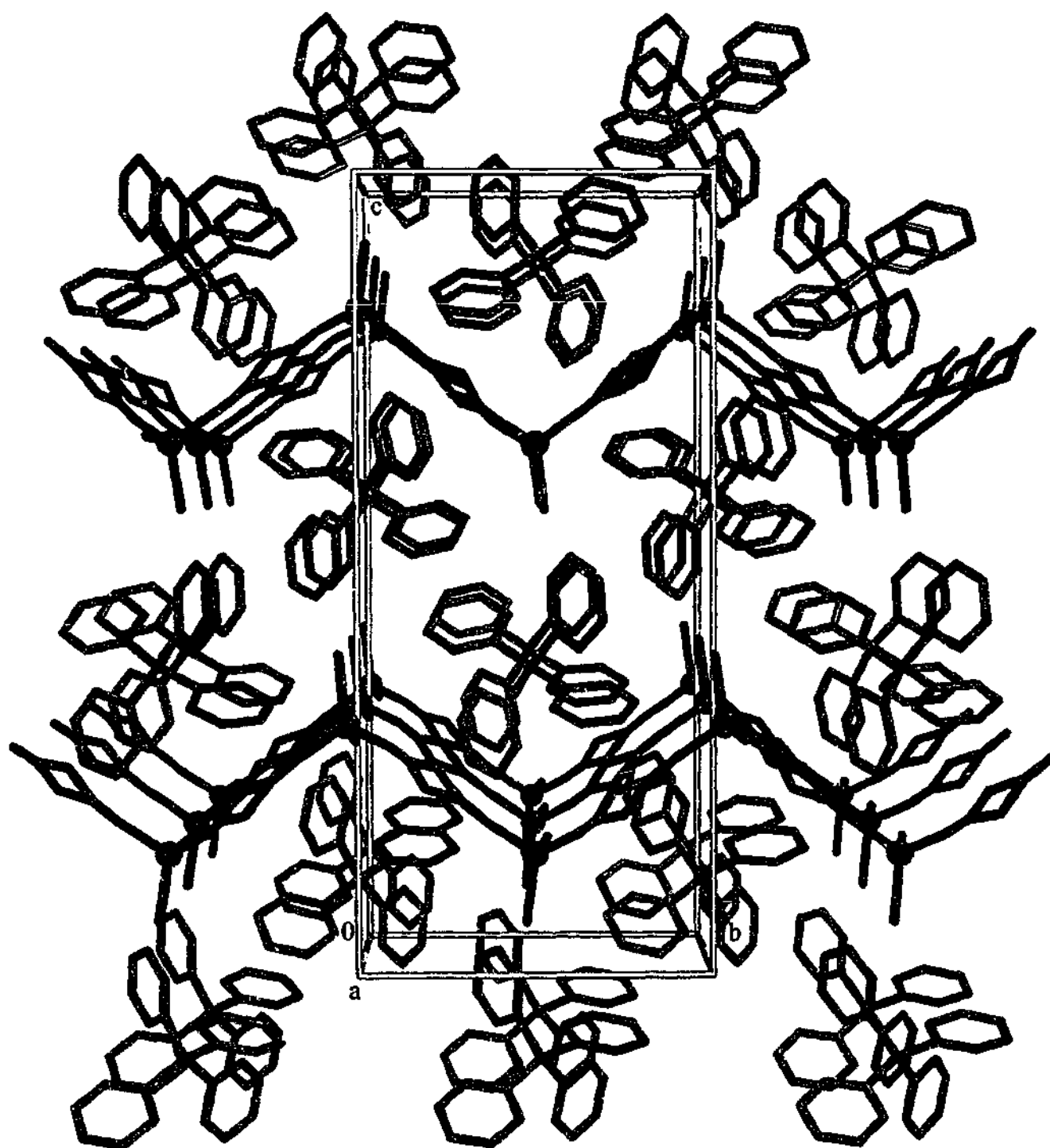


Figure 5.15 Packing diagram of $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$ viewed parallel to the a -axis showing the alternating layers of $[\text{Co}(\text{dca})\text{Br}_2]^-$ chains (blue) and Ph_4P^+ cations (red).

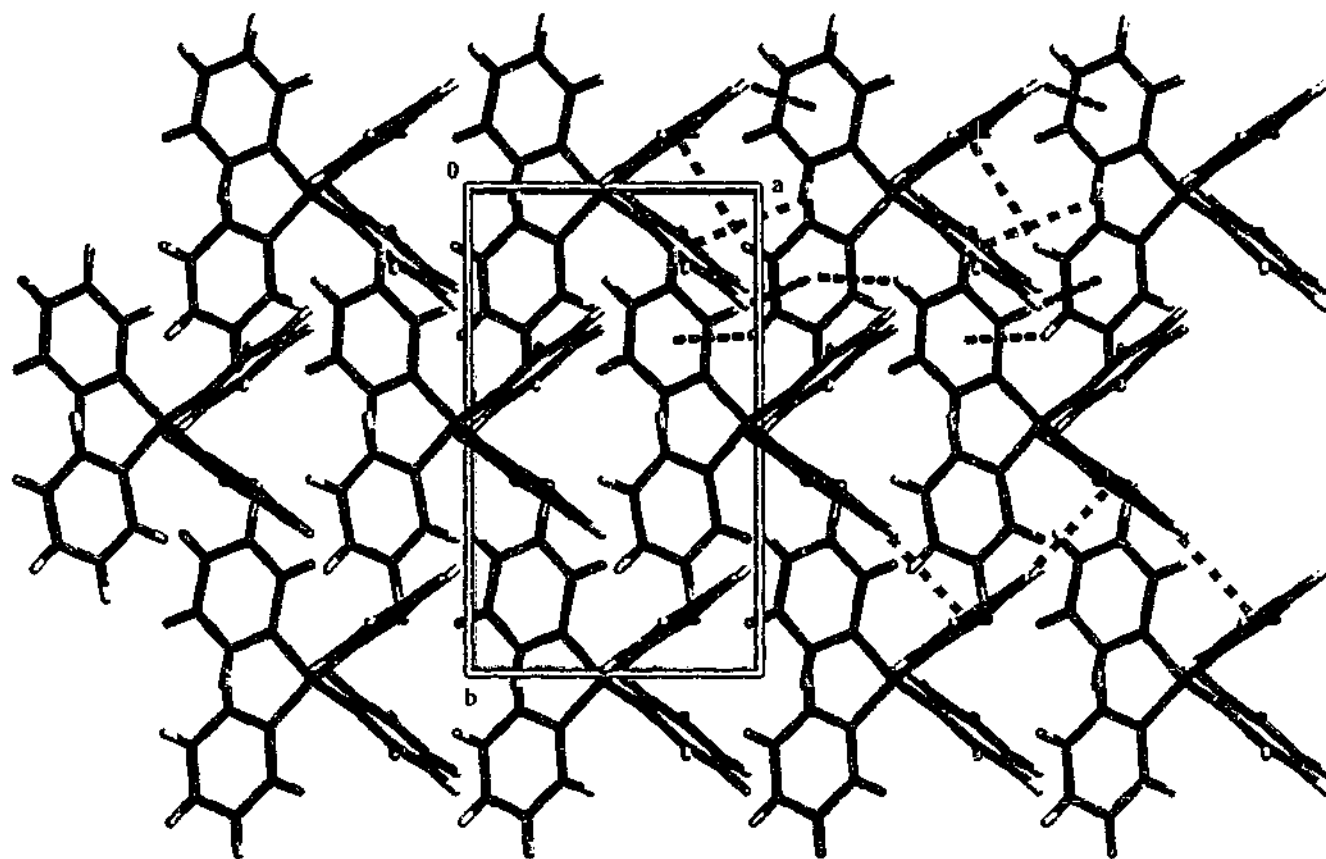


Figure 5.16 Three columns in a single corrugated sheet of Ph_4P^+ cations in the structure of $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$ showing edge-to-face $\text{CH}\cdots\pi$ interactions. Some of the LIT4PE interactions are shown as dashed purple. The two different cross-linking $\text{CH}\cdots\pi$ are shown in dashed red and dashed light blue. The corrugated nature of the sheets can also be seen clearly in Figure 5.15.

$\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$ is the first air-stable structurally characterised tetrahedral cobalt complex containing dca ligands. The binary complex, $\beta\text{-}[\text{Co}(\text{dca})_2]$, which consists of tetrahedral Co^{II} atoms bridged by $\mu_{1,5}$ -dca ligands into 2D square grid (4,4) sheets, undergoes a phase transition in air to form the octahedral rutile-like phase, $\alpha\text{-}[\text{Co}(\text{dca})_2]$. $\beta\text{-}[\text{Co}(\text{dca})_2]$ is a spin-canted antiferromagnet below a T_{N} of 9 K.⁶ This structural isomer of the rutile-like phase, first reported by Köhler *et al.*⁷ but without detailed magnetism or structural data, was studied as part of the candidate's Honours degree and published by

Jensen *et al.* with accompanying magnetic data and the crystal structure of the isostructural complexes, β -[Zn(dca)₂] and the doped β -[Co/Zn(dca)₂].⁶

Table 5.3 Selected interatomic distances (Å) and angles (°) for Ph₄P[Co(dca)Br₂].

Co(1)–N(1)	2.001(8)	Co(1)–N(5 ⁱ)	2.02(1)
Co(1)–Br(1)	2.403(2)	Co(1)–Br(2)	2.315(2)
N(1)–Co(1)–N(5 ⁱ)	102.4(4)	Br(1)–Co(1)–Br(2)	111.27(8)
N(1)–Co(1)–Br(1)	114.4(3)	N(5 ⁱ)–Co(1)–Br(1)	103.5(2)
N(1)–Co(1)–Br(2)	109.9(3)	N(5 ⁱ)–Co(1)–Br(2)	115.1(3)

Symmetry transformation: (i) $-x, y-1/2, -z+3/2$.

5.4 Magnetism

5.4.1 Ph₄P[M(dca)₂(NO₂)]·MeCN, M^{II} = Co and Ni

The temperature dependence of μ_{eff} , per Ni, for Ph₄P[Ni(dca)₂(NO₂)]·MeCN is shown in Figure 5.17. The sample had to be dispersed in a Nujol mull to prevent orientation of crystallites and consequent anomalies in the data such as a maximum in μ_{eff} at ~ 20 K. These orientation effects are not common in octahedral nickel(II) samples but more so in Mn^{III}, Co^{II} or Fe^{II} systems whose T ground states display large magnetic anisotropy (i.e. $\mu_{\parallel} \neq \mu_{\perp}$).⁷¹ The observed data are typical of octahedral Ni^{II} compounds, μ_{eff} at 300 K being $3.2 \mu_{\text{B}}$ because of spin-orbit coupling to the ³A_{2g} single-ion ground states. The gradual, small decrease in μ_{eff} , between 300 - 20 K, is indicative of very weak antiferromagnetic coupling occurring. The rapid decrease down to $2.39 \mu_{\text{B}}$, below 20 K, is due to this weak coupling combined with zero-field splitting effects. The data were fitted

to a $S = 1$ Heisenberg chain model with best-fit parameter values of $g = 2.23$ and $J = -0.18$ cm^{-1} . Zero-field splitting was assumed to be zero. The very small value of J is typical of $\mu_{1,5}$ -dca bridging. Interestingly, this complex shows only traces of a long-range ordered material in low fields (~ 5 Oe), at 21 K, compared to cases of $\text{Ph}_4\text{E}[\text{Ni}(\text{dca})_3]$ (where E = P or As) for which great efforts were made to distinguish intrinsic magnetic order from that due to traces of α - $[\text{Ni}(\text{dca})_2]$. The presence of long-range order would appear to be due to traces of α - $[\text{Ni}(\text{dca})_2]$ in the present sample.

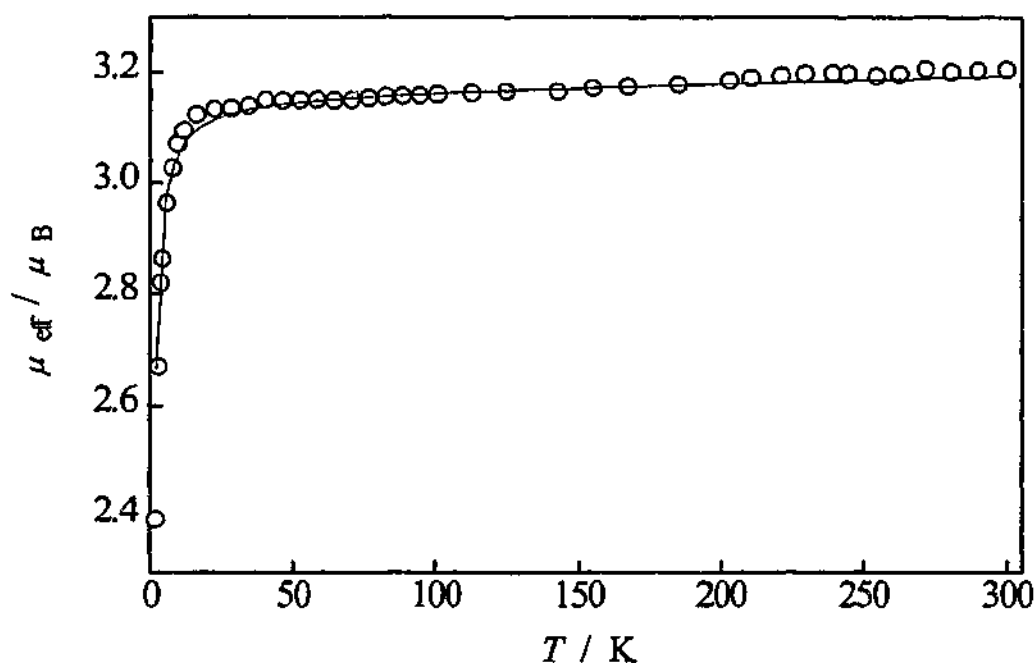


Figure 5.17 Plot of magnetic moment, μ_{eff} , versus temperature, T , for $\text{Ph}_4\text{P}[\text{Ni}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$ (dispersed as a Nujol mull), applied field, $H = 1$ T. The solid line is the best-fit curve to a $S = 1$ Heisenberg chain model (see text).

The Co^{II} analogue, $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$ also presented some magnetic anomalies in very low applied fields. In a 'normal' field of 1 T (Figure 5.18) the μ_{eff} versus T plot is typical of those displayed by octahedral Co^{II} species. The decrease in μ_{eff} from $4.95 \mu_{\text{B}}$ at 300 K, first gradually then more rapidly, to reach an inflection at $4.05 \mu_{\text{B}}$ at 5 K

and a value of $3.55 \mu_B$ at 2 K, is due to an orbitally degenerate $^4T_{1g}$ state being split by low-symmetry ligand-fields and spin-orbit coupling. The plot is very similar to that of $\text{Ph}_4\text{As}[\text{Co}(\text{dca})_3]$.⁵¹

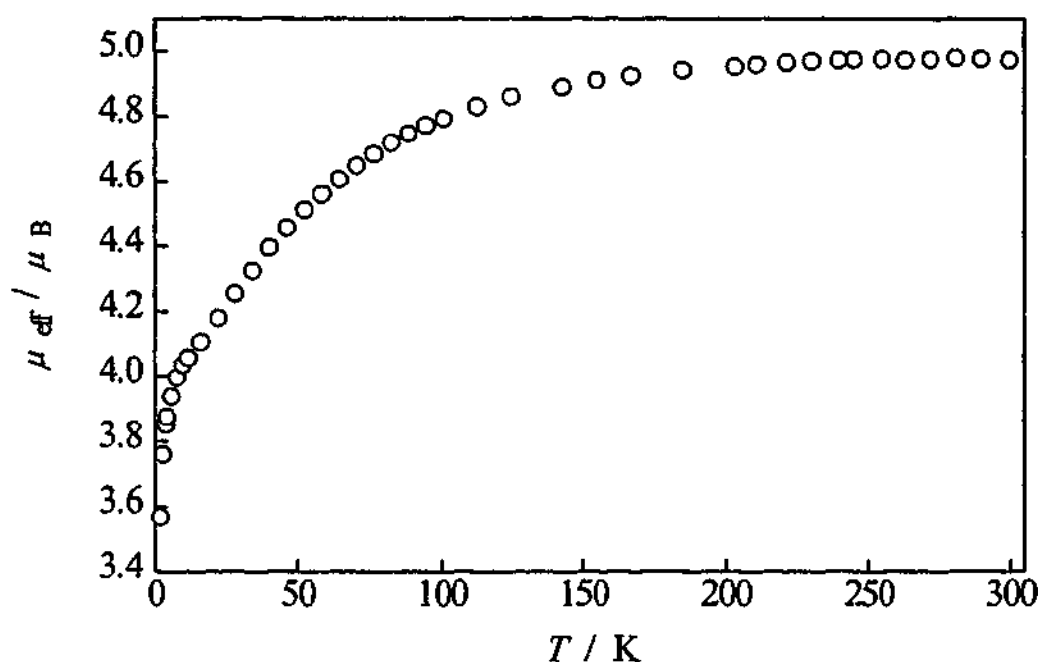


Figure 5.18 Plot of magnetic moment, μ_{eff} , versus temperature, T , for $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$ in an applied field of $H = 1 \text{ T}$.

In low fields (Figure 5.19) there is a sharp increase in μ_{eff} at $\approx 9.0 \text{ K}$ which is tentatively assigned to traces of $\alpha\text{-}[\text{Co}(\text{dca})_2]$.¹ However, the M / H hysteresis plot, measured at 2 K, (Figure 5.20) shows very small coercive field (60 Oe) and remnant magnetisation ($0.01 N\beta$) values and a shape typical of antiferromagnetic coupling (canted antiferromagnet) rather than a ferromagnetic increase at $H \approx 0$. 'Spiking' with 1 % $\alpha\text{-}[\text{Co}(\text{dca})_2]$ (Figure 5.21) gave a more conventional ferromagnetic increase¹ in M superimposed on the plot of the neat sample. As in the case of $\text{Ph}_4\text{As}[\text{Ni}(\text{dca})_3]$,⁵¹ it is hard to be definitive on the origin of this 9 K transition. A somewhat similar situation was reported for $\text{Co}(\text{dca})_2(\text{pyrimidine}) \cdot \text{EtOH}$.⁷²

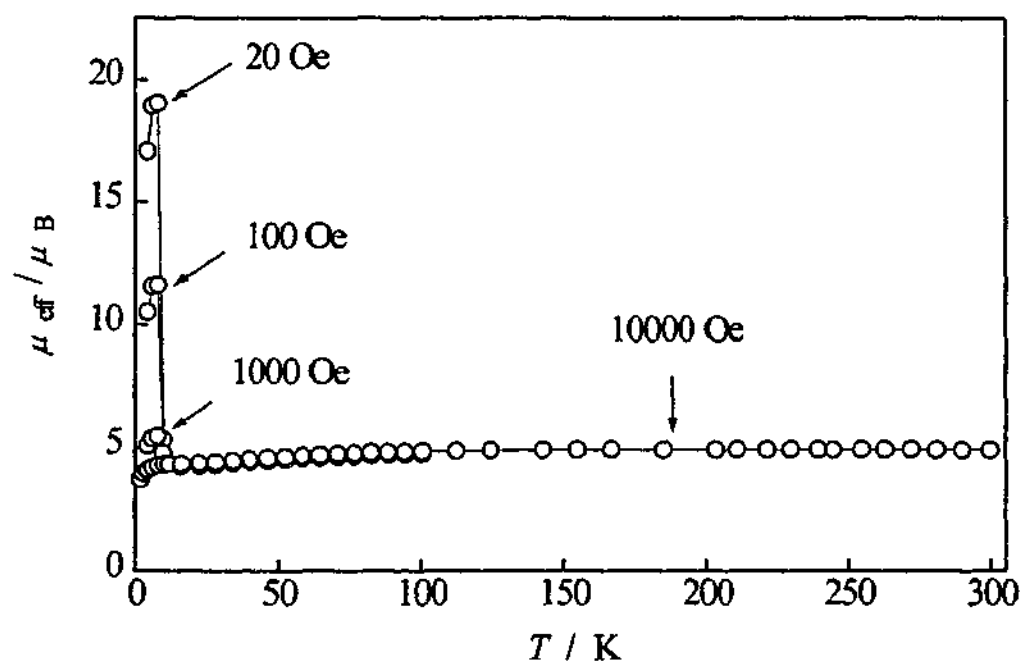


Figure 5.19 Plots of magnetic moment, μ_{eff} , versus temperature, T , for $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$ in applied fields of 10000 Oe, 1000 Oe, 100 Oe and 20 Oe. The solid line is not a fitted curve.

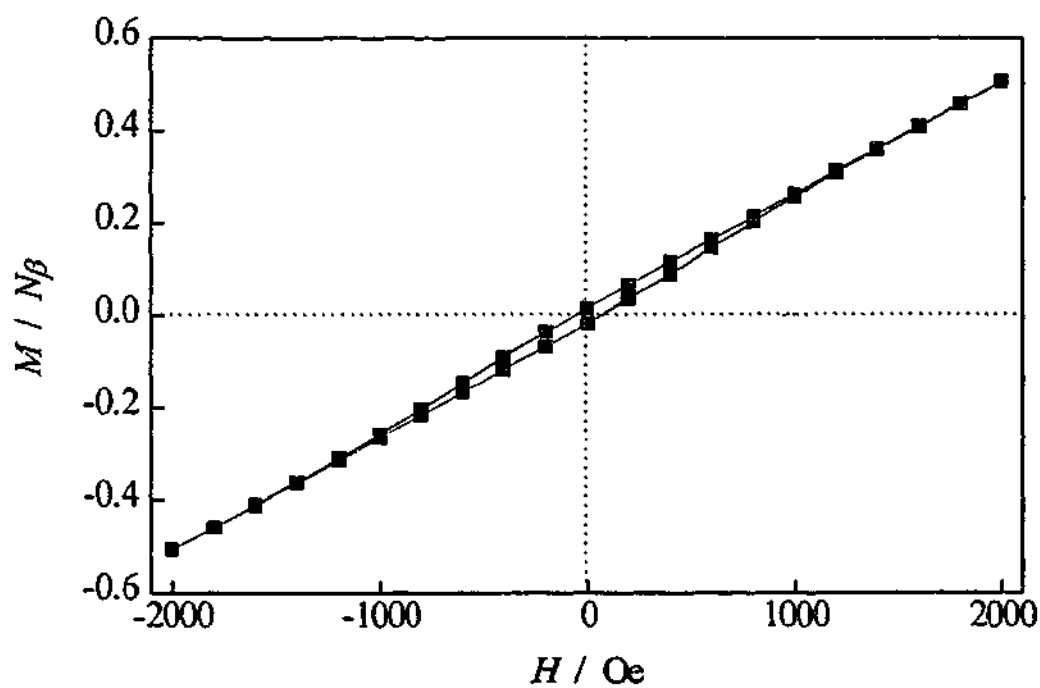


Figure 5.20 Hysteresis plot of M versus H for $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$.

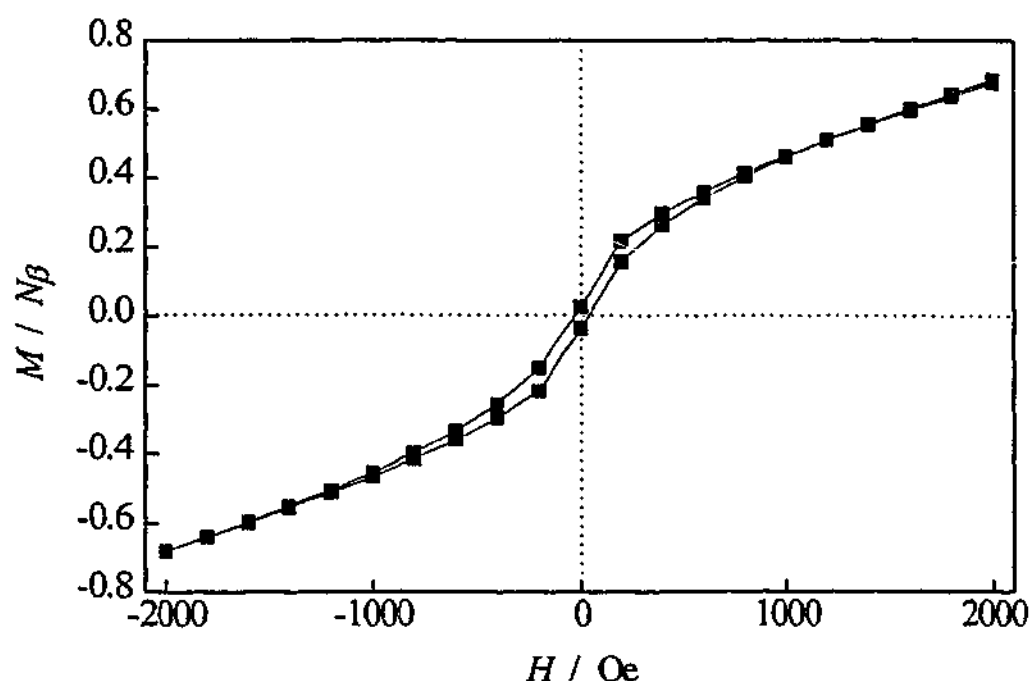


Figure 5.21 Hysteresis plot of M versus H for $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN} + 1\% \alpha\text{-}[\text{Co}(\text{dca})_2]$.

5.4.2 $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$

The magnetic moment *versus* temperature plot, shown in Figure 5.22, is typical of the behaviour of high-spin tetrahedral Co^{II} systems having $^4\text{A}_2$ ground states. The magnetic moment at 300 K of $4.5 \mu_{\text{B}}$ is raised from the spin-only value ($3.87 \mu_{\text{B}}$) because of spin-orbit coupling (spin-orbit constant λ negative; $\sim -170 \text{ cm}^{-1}$) and ligand-field splitting ($10 Dq$; $\sim 3500 \text{ cm}^{-1}$) effects combined with a second order Zeeman (temperature independent paramagnetism) term, as follows (Equation 5.1 and Equation 5.2).⁷³

$$\chi(\text{cm}^3 \text{mol}^{-1}) = \frac{15N\beta^2}{3kT} \left(1 - \frac{4\lambda}{10Dq} \right)^2 + \frac{8N\beta^2}{10Dq} \quad \text{Equation 5.1}$$

$$\mu(\mu_{\text{B}}) = \sqrt{15} \left(1 - \frac{4\lambda}{10Dq} \right) \quad \text{Equation 5.2}$$

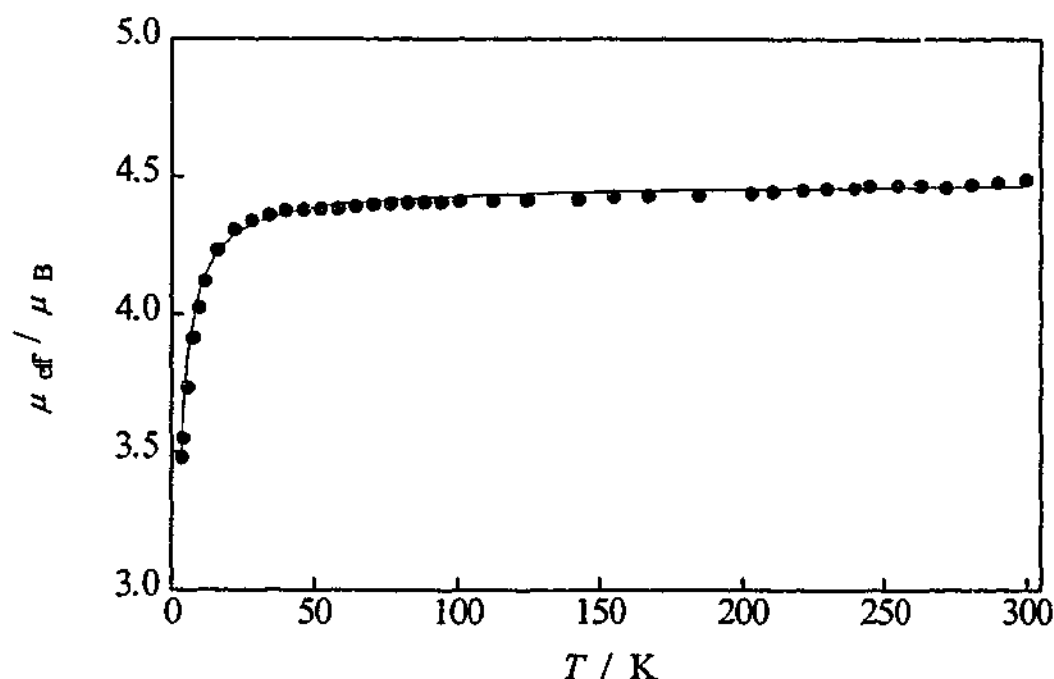


Figure 5.22 Plot of magnetic moment, μ_{eff} , versus temperature, T , for $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$. The solid line indicates the best-fit to the data (see text).

Curie-Weiss behaviour should therefore be obeyed (see Figure 1.1, page 7) and this is what is observed with $\theta = -0.35$ K, there being a sharp decrease in μ_{eff} only below 50 K. This decrease could be due to a combination of zero-field splitting (z.f.s.) of the single-ion $^4\text{A}_2$ state and very weak antiferromagnetic coupling. If it is assumed that z.f.s. is negligible, fitting to an $S = 3/2$ Fisher chain model⁷⁴ yields $g = 2.3$ and $J = -0.25$ cm⁻¹. The increase in the effective g value from 2.0 essentially allows for the spin-orbit coupling effect in the same way as shown above in the equation for μ . Further detailed magnetisation isotherms and calculation of susceptibilities using the thermodynamic equation for χ (involving the field, H)⁷⁵ would be required to separate D and J contributions. Suffice it to say that exchange coupling *via* the $\mu_{1,5}$ -dca bridges in this chain complex is, as usual, very weak.

5.5 Conclusion

The compounds $\text{Ph}_4\text{P}[\text{M}(\text{dca})_2(\text{NO}_2)]\cdot\text{MeCN}$, where $\text{M}^{\text{II}} = \text{Co}$ and Ni , possess interesting structures, which consist of alternating layers of anionic $[\text{M}(\text{dca})_2(\text{NO}_2)]^-$ 2D square grid (4,4) sheets and Ph_4P^+ cations. The anionic $[\text{M}(\text{dca})_2(\text{NO}_2)]^-$ sheets have chelating nitrite ligands. The overall structures are similar to those of the $\text{Ph}_4\text{E}[\text{M}(\text{dca})_3]$ ($\text{E} = \text{As}$ or P ; $\text{M}^{\text{II}} = \text{Mn}, \text{Fe}, \text{Co}$ or Ni) series, with the exception that in the latter cases half of the links in the (4,4) sheets are double $\mu_{1,5}$ -dca bridges (Figure 5.2, see page 214). Similarly, several weak $\text{CH}\cdots\pi$ and $\pi\cdots\pi$ interactions are present within the layers of Ph_4P^+ cations. Additionally, these examples are the first structurally characterised coordination polymers to contain both the dca and NO_2^- ligands.

The compound $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$ possesses a chiral structure, which consists of linear anionic 1D helical chains of $[\text{Co}(\text{dca})\text{Br}_2]^-$ that pack in layers, which in turn alternate with layers of Ph_4P^+ cations. It is the first air-stable tetrahedral cobalt(II) dca network complex.

The magnetic properties of the $\text{Ph}_4\text{P}[\text{M}(\text{dca})_2(\text{NO}_2)]\cdot\text{MeCN}$, $\text{M}^{\text{II}} = \text{Co}$ and Ni , complexes are indicative of very weak antiferromagnetic exchange coupling occurring *via* $\mu_{1,5}$ -dca bridges. Traces of α - $[\text{M}(\text{dca})_2]$ are thought to be responsible for long-range ordering effects observed in low fields but this is not definitive in the Co^{II} case.

$\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$ displays very weak intra-chain antiferromagnetic coupling with no magnetic order.

5.6 Experimental

5.6.1 Synthesis of $\text{Ph}_4\text{P(dca)}$

Typical preparation: an aqueous solution (30 mL) of Na(dca) (2.03 g, 23 mmol) was added to a hot aqueous solution (140 mL) of Ph_4PBr (9.82 g, 23 mmol). The white precipitate of $\text{Ph}_4\text{P(dca)}$ formed immediately. The mixture was left to cool in ice and the precipitate was collected by filtration and recrystallised from acetone (Yield 6.92 g, 74 %). IR (Nujol, cm^{-1}): 3485w, 3061w, 2227s, 2188m, 2130s, 1584m, 1482m, 1438s, 1306s, 1188vw, 1162w, 1106s, 1027vw, 996m, 932vw, 901w, 862w, 760m, 753m, 724m, 692m.

5.6.2 Synthesis of $\text{Ph}_4\text{P}[\text{Co(dca)}_2(\text{NO}_2)] \cdot \text{MeCN}$

A solution of $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.146 g, 0.5 mmol) in 5 mL of acetonitrile was added to a solution of $\text{Ph}_4\text{P(dca)}$ (0.203 g, 0.5 mmol), Ph_4PBr (0.210 g, 0.5 mmol) and NaNO_2 (0.017 g, 0.25 mmol) in a mixture of 20 mL of acetonitrile and ~1 mL of water. The resulting bright blue solution was left to stand. After one day the blue colour of the solution had weakened and several large clusters of needle/rod-like purple crystals had formed. The mother liquor was decanted and the crystals were washed with acetonitrile (3 $\times$ 5 mL) then collected by filtration (Yield 0.19 g, 60 %). IR (Nujol, cm^{-1}): 2308s, 2255s, 2180s, 1828vw, 1587w, 1484s, 1456s, 1436s, 1352s, 1309w, 1204m, 1178m, 1160m, 1026w, 996m, 944vw, 924vw, 850w, 808vw, 756m, 750m, 724s, 689s, 648w, 616w. Anal. (%): Found: C, 57.5; H, 3.6; N, 18.2. Calc. for $\text{C}_{30}\text{H}_{23}\text{CoN}_8\text{O}_2\text{P}$: C, 57.7; H, 3.7; N, 18.0. XRD: The diffractogram of the bulk product matches that calculated from the crystal structure, with the exception of two peaks ($2\theta = 11.64^\circ$ and 14.66°) that could not be indexed to either the title compound or $\alpha\text{-}[\text{Co(dca)}_2]$, $\text{Ph}_4\text{P}[\text{Co(dca)}_3]$ or $(\text{Ph}_4\text{P})_2[\text{Co(dca)}_4]$.

Crystals suitable for X-ray diffraction analysis were grown from the following reaction. A solution of $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.146 g, 0.5 mmol) in 5 mL of acetonitrile was

added to a solution of Ph_4PBr (0.630 g, 1.5 mmol), Na(dca) (0.089 g, 1.0 mmol) and NaNO_2 (0.035 g, 0.5 mmol) in a mixture of 15 mL of acetonitrile and 10 mL of ethanol. The resulting bright blue solution was left to stand. After one day the blue colour of the solution had weakened and several large clusters of rod-like purple/pink crystals had formed. In addition many small colourless crystals had formed, some of which were embedded within the aforementioned clusters. A rod-like crystal suitable for X-ray diffraction analysis was cut from one of the clusters. An infrared spectrum was measured of a portion of one cluster. IR (Nujol, cm^{-1}): 3624vw, 3558vw, 3093vw, 3068vw, 2309s, 2254s, 2180s, 1906vw, 1825vw, 1778vw, 1587m, 1496m, 1484m, 1439s, 1352s, 1315vw, 1293vw, 1204m, 1177m, 1160m, 1111s, 1026w, 996m, 923w, 852w, 751m, 725s, 690s, 648vw, 616vw.

5.6.3 Synthesis of $\text{Ph}_4\text{P}[\text{Ni(dca)}_2(\text{NO}_2)]\cdot\text{MeCN}$

A solution of Ph_4PBr (0.230 g, 0.55 mmol) and NaNO_2 (0.017 g, 0.25 mmol) in acetonitrile (10 mL) and water (1 mL) to an acetonitrile solution (10 mL) of $\text{Ni(NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.073 g, 0.25 mmol). This was left to stand for a minute then an acetonitrile solution (10 mL) of $\text{Ph}_4\text{P(dca)}$ (0.203 g, 0.50 mmol) was added. After a few minutes a small amount of fine pale green precipitate had formed in the pale green solution. After one day several clusters of light green crystals had formed. The comparatively small amount of fine precipitate was removed from these crystals by successive washings with acetonitrile. The crystals were collected by filtration (Yield 70 mg, 44 %). IR (Nujol, cm^{-1}): 3632vw, 3604vw, 3114vw, 2309s, 2261s, 2187s, 1654vw, 1587w, 1485m, 1438s, 1352s, 1316w, 1280w, 1212s, 1180w, 1162w, 1111s, 1026w, 996m, 920vw, 860w, 806vw, 757m, 751m, 724s, 689s, 642vw. Anal. (%): Found: C, 58.0; H, 3.8; N, 18.3. Calc. for $\text{C}_{30}\text{H}_{23}\text{NiN}_8\text{O}_2\text{P}$: C, 58.4; H, 3.8; N, 18.2. XRD: The diffractogram of the bulk product matches that calculated from the crystal structure, with

the exception of two peaks ($2\theta = 11.20^\circ$ and 18.19°) that could not be indexed to either the title compound or α -[Ni(dca)₂], Ph₄P[Ni(dca)₃] or (Ph₄P)₂[Ni(dca)₄].

5.6.4 Synthesis of Ph₄P[Co(dca)Br₂]

A solution of (Et₄N)₂CoBr₄ (0.640 g, 1.0 mmol) in acetonitrile (10 mL) was added to a solution of Ph₄Pdca (0.406 g, 1.0 mmol) in acetonitrile (10 mL). A colour change occurred instantly to a darker blue colour than the original cobalt solution. The solution was left to slowly evaporate. After approximately two weeks the solution had reduced to about 1 mL. Several large clusters of deep blue rod-like crystals had formed. These were collected, quickly washed with acetonitrile and dried in air (Yield 0.21 g, 33%). IR (Nujol, cm⁻¹): 2263m, 2218s, 2184s, 1586w, 1483m, 1496s, 1413m, 1313w, 1187vw, 1166vw, 1109s, 1028vw, 996m, 937vw, 928vw, 850vw, 763m, 752m, 723s, 690s. Anal. (%): Found: C, 50.2; H, 3.3; N, 6.8. Calc. for C₂₆H₂₀Br₂CoN₃P: C, 50.0; H, 3.2; N, 6.7. XRD: The diffractogram of the bulk product matches that calculated from the crystal structure.

A single blue rectangular crystal for an X-ray diffraction experiment was chosen from a reaction that produced Ph₄P[Co(dca)₂(NO₂)]·MeCN as the major product. This reaction was conducted as follows. A solution of Co(NO₃)₂·6H₂O (0.146 g, 0.5 mmol) in *n*-PrOH (10 mL) was added to a solution of Ph₄PBr (0.630 g, 1.5 mmol), Na(dca) (0.089 g, 1.0 mmol) and NaNO₂ (0.035 g, 0.5 mmol) in a solvent mixture comprising 35 mL *n*-PrOH, 5 mL EtOH and 3 mL MeCN. Immediately on addition the resultant solution became deep blue in colour. After about three hours several clusters of purple-pink crystals of Ph₄P[Co(dca)₂(NO₂)]·MeCN had formed. After several more hours additional small clusters of fine blue rod-like crystals had formed. The crystal employed in crystallographic studies was cut from one of these clusters.

5.6.5 X-Ray Crystallography

Data were collected using a Nonius KappaCCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Integration was carried out by the program DENZO-SMN,⁷⁶ and data were corrected for Lorentz polarisation effects and for absorption using the program SCALEPACK.⁷⁶ Solutions were obtained by direct methods (SHELXS 97)⁷⁷ followed by successive Fourier difference methods, and refined by full matrix least squares on F_{obs}^2 (SHELXL 97)⁷⁷ with the aid of the graphical interface program X-SEED.⁷⁸ All non-hydrogen atoms were refined anisotropically (unless otherwise stated). Phenyl hydrogen atoms were assigned to calculated positions with isotropic thermal parameters fixed at 1.2 times U_{eq} of the adjoining carbon atom.

The crystal of $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_2)]\cdot\text{MeCN}$ was face indexed and numerical absorption corrections were applied using the XPREP program.⁷⁹ The structure of $\text{Ph}_4\text{P}[\text{Co}(\text{dca})_2(\text{NO}_2)]\cdot\text{MeCN}$ was refined as a racemic twin with a BASF⁸⁰ (twin component) parameter that refined freely to 0.49. There was a residual electron peak of $0.89 \text{ e } \text{\AA}^{-3}$, at 1.05 Å from the nitrite nitrogen, indicating the presence of very little NO_3^- (but perhaps some). Thus, the crystal analysed and therefore the bulk sample may be doped with a very small amount of nitrate. It can be noted that the unit cell length c is approximately 0.4 Å longer for the nitrate complex, which corresponds to the direction of the uncoordinated nitrate oxygen.

The structure refinement for $\text{Ph}_4\text{P}[\text{Ni}(\text{dca})_2(\text{NO}_2)]\cdot\text{MeCN}$ was of a lesser quality than that of the Co structure. The thermal parameters of the dca ligands were less than ideal, consequently C(34) was refined isotropically to prevent it becoming non-positive definite. Like the Co structure, there was the presence of racemic twinning, but the twin component refined to 0.73. Similarly, there was a residual electron peak of $1.05 \text{ e } \text{\AA}^{-3}$ at 1.12 Å from the nitrite nitrogen, indicating perhaps a small amount of nitrate doping.

For $\text{Ph}_4\text{P}[\text{Co}(\text{dca})\text{Br}_2]$ no numerical absorption corrections were applied. The central amide nitrogen of the dicyanamide ligand was found to be disordered over two positions, modelled as two atoms with site occupancies fixed at 0.5 each, and refined isotropically. The absolute structure was assigned on the basis of the Flack parameter^{80,81} of 0.08(3).

5.6.6 Magnetic Measurements

The instrumentation (Quantum Design MPMS 5) DC magnetisation protocols have been described previously.³ Crystals of $\text{Ph}_4\text{P}[\text{Ni}(\text{dca})_2(\text{NO}_2)] \cdot \text{MeCN}$ were dispersed in a Nujol mull to prevent orientation effects. Dr. B. Moubaraki kindly carried out these magnetic studies.

5.6.7 Powder X-Ray Diffraction

Powder X-ray diffraction data were collected by Mr. Rod Mackie (School of Physics and Materials Engineering, Monash University, Clayton) on a Scintag Automated Powder Diffractometer using a $\text{Cu-K}\alpha$ monochromatic radiation source ($\lambda = 154.059 \text{ pm}$), a solid state Ge detector, 2 mm divergence slit and a 3 mm receiving slit at room temperature. The programs Crystal Diffract⁸² and Unit Cell⁸³ were used by Dr. Stuart Batten (School of Chemistry, Monash University, Clayton) to confirm that the single crystals were representative of the bulk samples.

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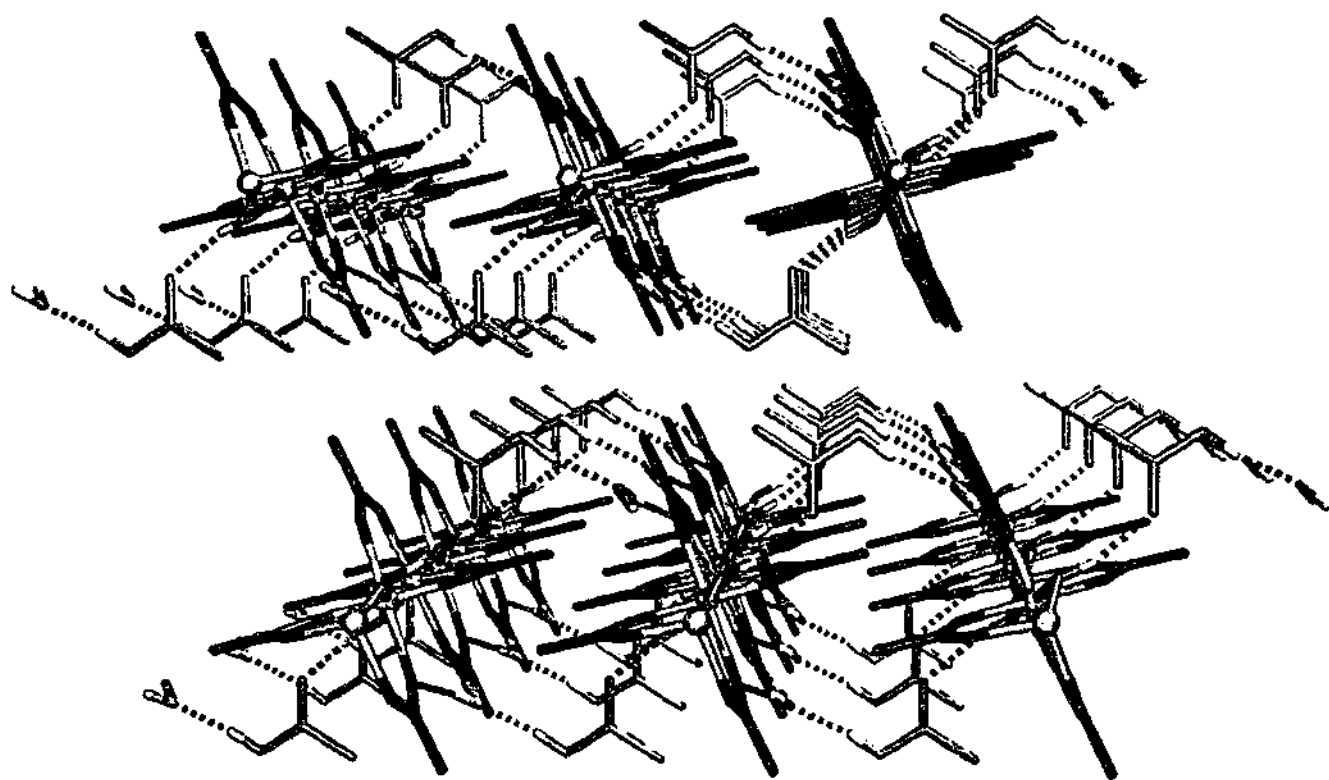
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**CHAPTER 6: SYNTHESIS, STRUCTURE AND
MAGNETISM OF
 $\{(\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2)\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ AND THE
FACILITATION OF LONG-RANGE MAGNETIC
ORDER THROUGH HYDROGEN BONDING**

6.1 Introduction

Studies of covalent ligand bridging in extended network coordination polymers and how this influences magnetic coupling and long-range order have increased enormously in recent years. The bridging groups CN^- , $\text{C}_2\text{O}_4^{2-}$, RCO_2^- ¹⁻⁶ and poly-cyano ligands such as $\text{N}(\text{CN})_2^-$ ⁷⁻⁹ have received most attention. Less well studied, however, is magnetic order occurring *via* hydrogen bonding pathways, but this is a growing field within supramolecular magnetochemistry and a number of examples have been discovered recently.¹⁰⁻¹³ Generally, the J values and T_c (or T_N) values in such systems are very low with the ordering temperatures less than 10 K. However, a T_c value of 23 K was observed members of the Murray group at Monash in a heterobimetallic Ni_3Fe_2 cluster system in which well ordered hydrogen bonded $(\text{H}_2\text{O})_7$ arrays join the clusters.¹⁴

Described in this chapter is a new polymeric carboxylate-bridged complex, $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$, which displays long-range antiferromagnetic order ($T_N = 6.1$ K) facilitated by hydrogen bonding, together with a field induced metamagnetic transition. In contrast, the desolvated material, $[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]_n$, does not order magnetically. The solvated complex was discovered during attempts to link Mn_3 and Mn_4 carboxylate cluster complexes with pseudohalide and pseudochalcogenide ligands, in this case dicyanonitrosomethanide ($\text{ONC}(\text{CN})_2^-$, dcnm), to form extended networks of clusters. The dcnm group was not contained in the product. Similar work, described in Chapter 6, with dicyanamide (dca, $\text{N}(\text{CN})_2^-$) recently led to the simultaneous discovery of a large manganese(III/IV) carboxylate-alkoxo cluster, $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_{16}(\text{MeOH})_3(\text{H}_2\text{O})_3]\cdot 6\text{H}_2\text{O}$, which is a new example of a single molecule magnet (SMM), and a linear chain Mn^{III} complex $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$.¹⁵ Again, the $\text{N}(\text{CN})_2^-$ ligand was not present in these products.

During the writing of this thesis, and while a paper presenting these results was in press, the preparation, structure and magnetism of $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ was reported by Christou *et al.*¹⁶ However, the reported magnetic studies were not as detailed as those presented here.

6.2 Synthesis and Characterisation of

$\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$

Reaction of $n\text{-Bu}_4\text{NMnO}_4$ with a solution of $\text{Mn}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ ($\sim 1:5$ molar ratio) in acetonitrile/ethanol/glacial acetic acid gave a dark brown solution. After several months of slow evaporation the solution had become colourless and red-orange needles of $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ were formed. Interestingly, Christou and co-workers¹⁶ synthesised $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ by reaction of KMnO_4 with $\text{Mn}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ in methanol/acetic acid, obtaining a product with no $\mu\text{-OMe}^-$ groups, which might be expected given the reaction conditions. In Chapter 8, $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$ is described, which is synthesised from a methanol/acetic acid mixture using reagents similar to those used by Christou and co-workers to synthesise the complex presented here.

The infrared spectrum of the red-orange crystals shows $\nu(\text{OH})$ at 3326 cm^{-1} . This peak is relatively sharp due to the presence of hydrogen bonding of both the $\mu\text{-OH}^-$ and the lattice water. An absorption at 1700 cm^{-1} is probably due to the $\delta(\text{HOH})$ vibration of the lattice water, while a strong absorption at 1538 cm^{-1} is due to the $\nu(\text{C=O})$ vibrations of the bridging acetates and lattice acetic acid. The first synthetic method, described in the experimental section, employed dcnm as it was actually aimed at incorporating the pseudochalcogenide bridging ligand. It gave crystals within one week. TGA studies showed the acetic acid and water molecules can be removed to yield $[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]_n$.

OAc)₂]_n. The microanalyses of two samples were consistent with a formulation of {[Mn(μ-OH)(μ-OAc)₂]·HOAc·H₂O}_n.

6.3 Crystal Structure of {[Mn(μ-OH)(μ-OAc)₂]·HOAc·H₂O}_n

Crystallographic data for {[Mn(μ-OH)(μ-OAc)₂]·HOAc·H₂O}_n are summarised in Table 6.1. Table 6.2 contains selected interatomic distances and angles (see page 259). The compound {[Mn(μ-OH)(μ-OAc)₂]·HOAc·H₂O}_n crystallizes in the monoclinic space group *P*2₁/*m*. The asymmetric unit contains half a manganese(III) ion, two half acetates, one half hydroxide, acetic acid and water. The metal lies on an inversion centre whereas all other groups lie on the same mirror plane (excluding the oxygens and two of the hydrogen atoms of the acetates, and the water hydrogen). As seen in Figure 6.1, the crystal structure consists of chains of manganese(III) ions bridged by single μ-OH⁻ and double μ-OAc⁻ bridges. These chains run parallel to the *b*-axis direction. A network of hydrogen bonding exists between each adjacent chain in the *ab*-plane that involves the μ-OH⁻, the lattice acetic acid and water molecules. This results in hydrogen bonded sheets (Figure 6.2) that stack parallel to the *c*-axis direction. The coordination environment of each Mn^{III} atom is Jahn-Teller elongated as expected for a near-octahedral d⁴ ion. The equatorial plane contains the shortest coordination bond, which is to the μ-OH⁻ oxygen (Mn(1)–O(8) = 1.8993(8) Å), and also contains one of the μ-OAc⁻ ligand oxygen atoms (Mn(1)–O(5) = 1.939(1) Å). The remaining two equatorial sites are filled by the two symmetry equivalents of these atoms. The other μ-OAc⁻ ligand oxygen atom and its symmetry equivalent occupy the elongated axial sites (Mn(1)–O(2) = 2.179(1) Å). The intra-chain Mn···Mn distance, 3.3824(2) Å, is equal to half the unit cell length *b*. Similarly, the shortest inter-chain Mn···Mn distance within the hydrogen bonded sheets, 7.9134(2) Å, is equal to the unit cell length *a*. The lattice acetic acid molecule was assigned as such rather than a free acetate

ion for a number of reasons. The manganese ion was assigned as Mn^{III} from coordination bond distance and Jahn-Teller distortion considerations and thus charge balance is obtained by the $\mu\text{-OH}^-$ and the two $\mu\text{-OAc}^-$ bridging ligands. Also, the colour (red) of the product is consistent with Mn^{III} . One of the C–O bond distances ($\text{C}(10)\text{--O}(9) = 1.191(4) \text{ \AA}$) of the acetic acid molecule is consistent with a carbonyl bond and the other ($\text{C}(10)\text{--O}(12) = 1.316(4) \text{ \AA}$) is likewise consistent with a single C–O bond. Finally, a proton was found on O(12) in the direction of the lattice water, O(13), further indicating it to be a molecule of acetic acid.

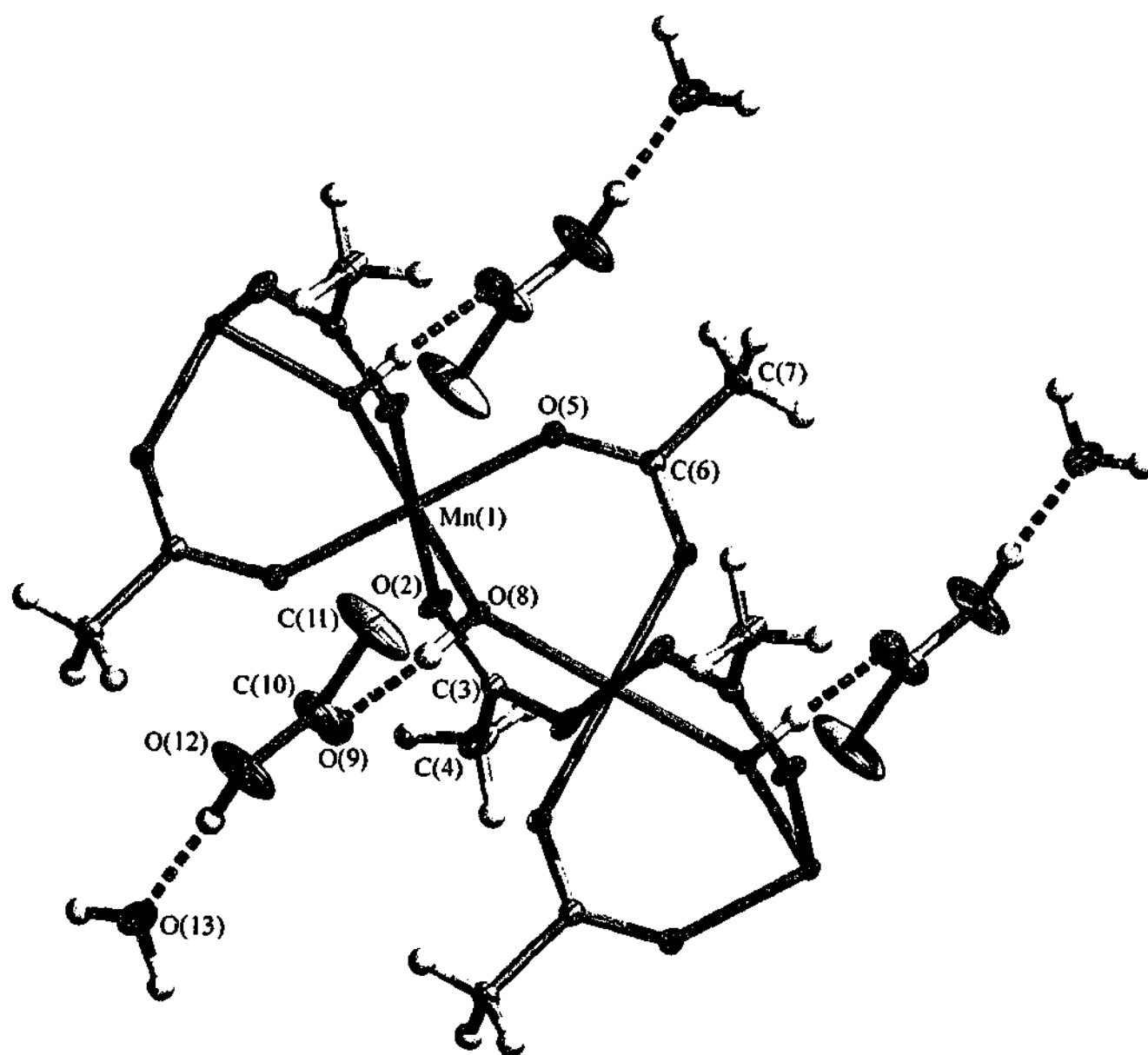


Figure 6.1 Crystal structure of $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ with atom labelling scheme (thermal ellipsoids shown at 50 % probability).

Table 6.1 Crystal data for $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$

Compound	$\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$
Formula	$\text{C}_6\text{H}_{13}\text{MnO}_8$
M	268.10
Crystal system	Monoclinic
Space group	$P2_1/m$
$a/\text{\AA}$	7.9134(2)
$b/\text{\AA}$	6.7648(2)
$c/\text{\AA}$	10.8644(3)
$\beta/^\circ$	106.90(1)
$U/\text{\AA}^3$	556.48(3)
Z	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.600
T/K	123(2)
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	1.207
Crystal dimensions/mm	$0.22 \times 0.03 \times 0.03$
θ range / $^\circ$	2.69 – 28.28
Index ranges	$-10 \leq h \leq 9,$ $-9 \leq k \leq 7,$ $-14 \leq l \leq 14$
Completeness to $2\theta = 55^\circ / \%$	99.8
$T_{\text{min}}, T_{\text{max}}$	0.7730, 0.9705
Data collected	4528
Unique data (R_{int})	1482 (0.0437)
Observed reflections [$I > 2\sigma(I)$]	1224
Parameters	109
Final R_1, wR_2 [$I > 2\sigma(I)$] ^(a)	0.0329, 0.0835
(all data)	0.0433, 0.0883
Goodness of fit, S	1.081
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}} / \text{e \AA}^{-3}$	-0.472, 0.554

^(a) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

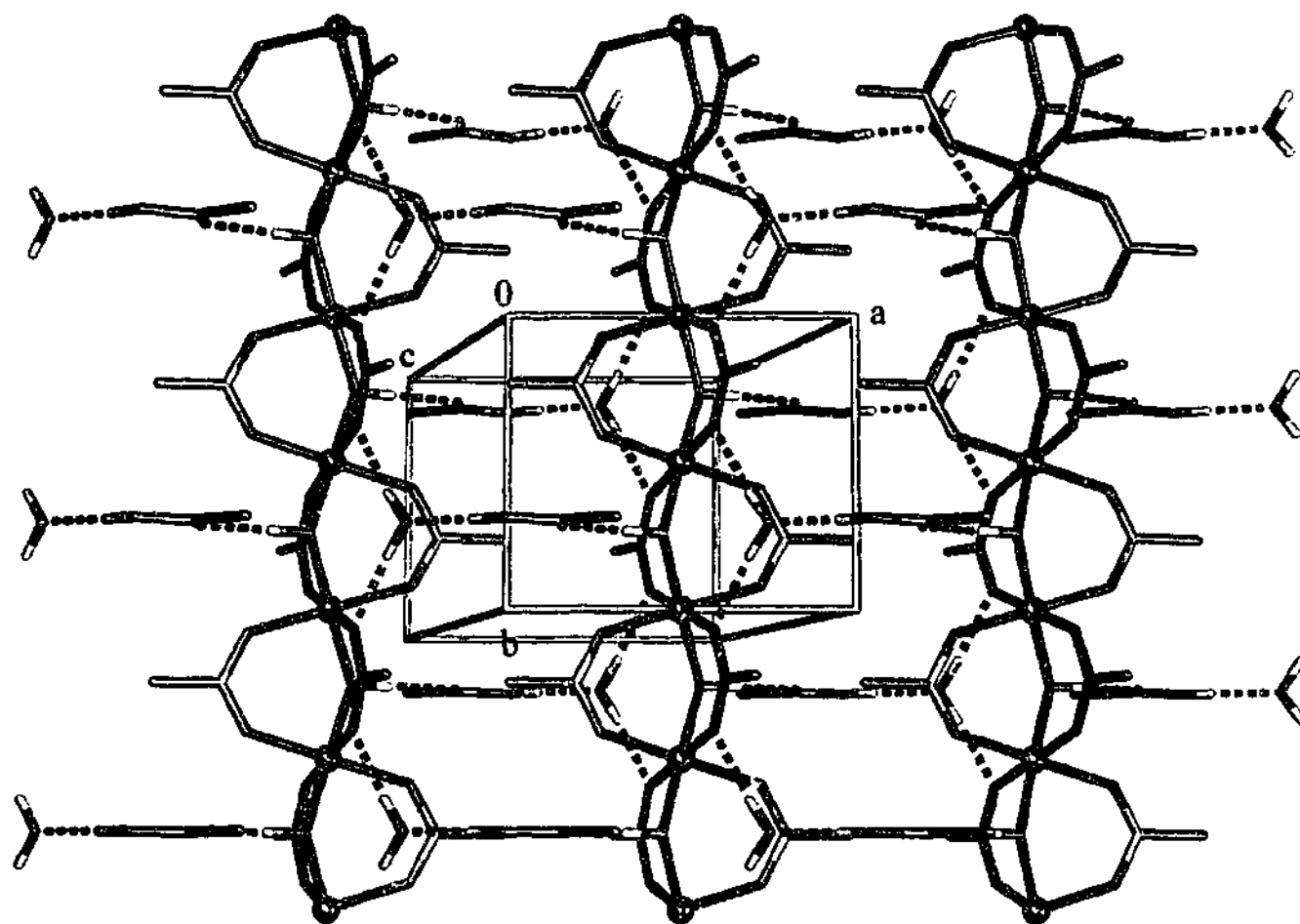


Figure 6.2 View of $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ slightly off the ab -plane showing a single hydrogen bonded sheet (acetate hydrogen atoms are omitted for clarity).

The hydrogen bonding network between chains occurs *via* the following pathway. The $\mu\text{-OH}^-$ hydrogen bonds to the carbonyl oxygen atom of the lattice acetic acid molecule ($\text{O}(8)\cdots\text{O}(9) = 2.691(3) \text{ \AA}$). The acetic acid then hydrogen bonds to the lattice water ($\text{O}(12)\cdots\text{O}(13) = 2.550(3) \text{ \AA}$) which is in turn hydrogen bonded to two acetate oxygen atoms on two $\mu\text{-OAc}^-$ ligands on the adjacent chain ($\text{O}(13)\cdots\text{O}(2^{\text{iii}}) = 2.759(2) \text{ \AA}$). The shortest inter-sheet $\text{Mn}\cdots\text{Mn}$ distance, $10.8644(3) \text{ \AA}$, is equal to the unit cell length c . Figure 6.3 shows two such hydrogen bonded sheets.

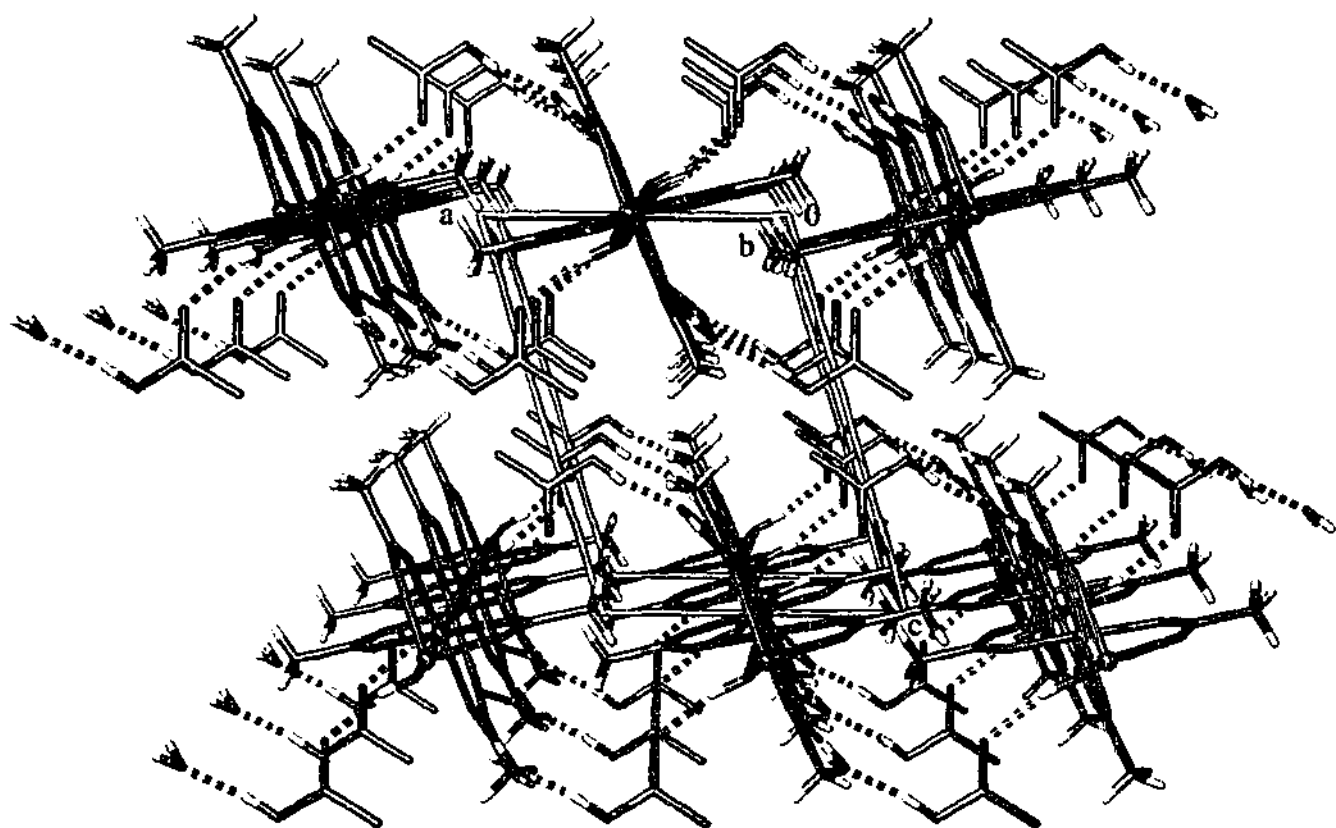


Figure 6.3 Packing diagram of $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ viewed along the b -axis, showing covalent chains hydrogen bonding to form sheets.

Table 6.2 Selected interatomic distances (Å) and angles (°).

Mn(1)–O(2)	2.179(1)	Mn(1)–O(8)	1.8993(8)
Mn(1)–O(5)	1.939(1)	Mn(1)···Mn(1 ⁱⁱ)	3.3824(2)
O(2)–Mn(1)–O(5)	91.54(6)	O(2)–Mn(1)–O(5 ⁱ)	88.46(6)
O(2)–Mn(1)–O(8)	92.69(6)	O(2)–Mn(1)–O(8 ⁱ)	87.31(6)
O(5)–Mn(1)–O(8)	92.16(6)	O(5)–Mn(1)–O(8 ⁱ)	87.84(6)
Hydrogen bonding			
O(8)–H(8)	0.89(2)	O(12)–H(12)	0.90(2)
H(8)···O(9)	1.82(2)	H(12)···O(13)	1.66(2)
O(8)···O(9)	2.691(3)	O(12)···O(13)	2.550(3)
O(13)–H(13)	0.92(2)	O(13)···O(2 ⁱⁱⁱ)	2.759(2)
H(13)···O(2 ⁱⁱⁱ)	1.85(2)		
O(8)–H(8)···O(9)	166(4)	O(12)–H(12)···O(13)	170(8)
O(13)–H(13)···O(2 ⁱⁱⁱ)	171(3)		

Symmetry transformations: (i): $-x+1, -y, -z$; (ii): $1-x, 1/2+y, -z$; (iii): $-x+2, -y, -z$

6.4 Magnetism of $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$

Two samples were investigated and gave identical results. In a field of 1 T the magnetic moment of $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ decreases gradually from $4.7 \mu_{\text{B}}$ ($\chi T = 2.76 \text{ cm}^3\text{mol}^{-1}\text{K}$) at 300 K to $2.9 \mu_{\text{B}}$ ($\chi T = 1.05 \text{ cm}^3\text{mol}^{-1}\text{K}$) at ~ 12 K, then increases to yield a sharp maximum at ~ 8 K of $3.5 \mu_{\text{B}}$ ($\chi T = 1.53 \text{ cm}^3\text{mol}^{-1}\text{K}$) before decreasing to reach $1.9 \mu_{\text{B}}$ at 2 K ($\chi T = 0.45 \text{ cm}^3\text{mol}^{-1}\text{K}$) (Figure 6.4). The 12–300 K region shows a corresponding Curie-Weiss behaviour with $\theta = -27$ K and $C = 2.8 \text{ cm}^3\text{mol}^{-1}\text{K}$. This is indicative of intra-chain antiferromagnetic coupling. When the sample is desolvated by heating at 80°C *in vacuo*, the sharp transition at 12 K disappears and the moments decrease more quickly than in the parent solvate, from $4.6 \mu_{\text{B}}$ ($\chi T = 2.65 \text{ cm}^3\text{mol}^{-1}\text{K}$) at 300 K to $1.25 \mu_{\text{B}}$ ($\chi T = 0.195 \text{ cm}^3\text{mol}^{-1}\text{K}$) at 2 K. The corresponding χ_{Mn} values show Curie-Weiss behaviour, without a maximum, which indicates very weak coupling and/or monomer impurity being present which shows a maximum in χ_{Mn} . These differences in behaviour show that intra-chain antiferromagnetic coupling persists in the desolvated species and that a magnetic phase transition to an ordered state below ~ 12 K occurs in $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$. It is likely that the hydrogen bonded pathways between the chains are responsible for long-range order but this can not be proven unambiguously.

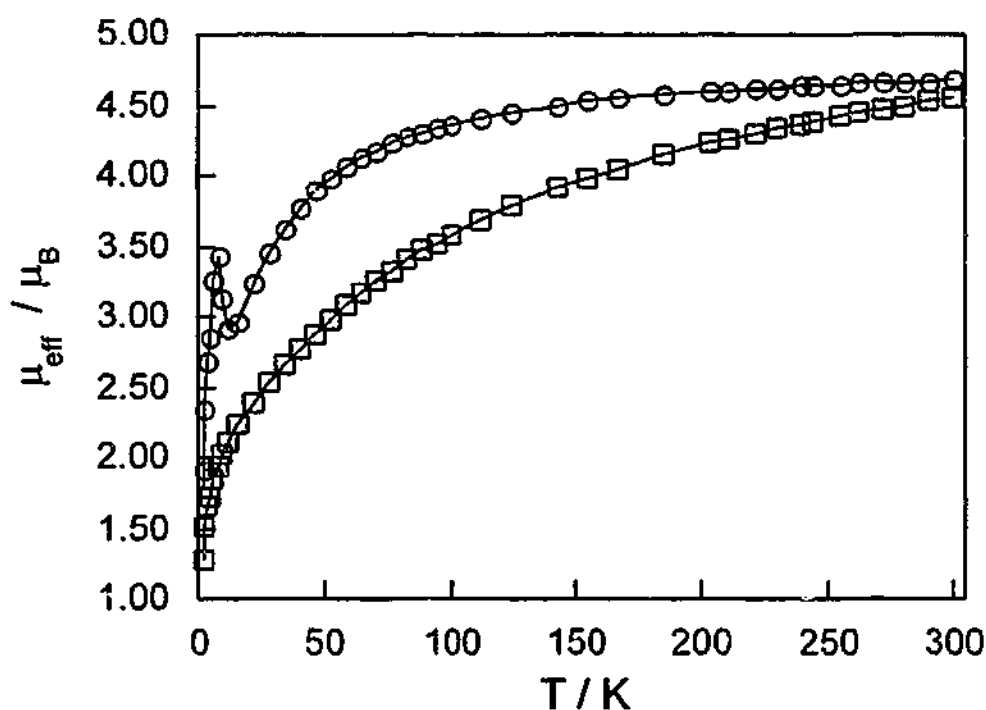


Figure 6.4 Plots of effective magnetic moment, μ_{Mn} , versus temperature in a field of 1 T for $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ (○) and the desolvated species, $[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]_n$ (□) (in these and other magnetic plots in this chapter, the solid lines are not calculated fits).

A range of magnetic measurements was employed to probe the nature of the long-range order in $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$. First, the use of lower fields in the DC susceptibility measurements (20, 100, 400, 800 Oe) confirmed the sharp maximum in χ_{Mn} at 6.0 K in these fields, with χ_{max} moving only a little to lower temperature and increasing only a little in value when applied fields of 20 to 800 Oe were progressively used (Figure 6.5). The T_N value of 6.1 K was confirmed from plots of $d(\chi T)/dT$ versus T . The shape of the sharp maxima in χ_{Mn} is indicative of long-range antiferromagnetic order occurring although extrapolation of the χ_{Mn} values to 0 K, below χ_{max} , in a field of 20 Oe, is close to 1/6 of the value at χ_{max} (T_N) rather than the $2/3(\chi_{\text{max}})$ expected for a two sublattice collinear-antiferromagnet. Kurmoo has observed similar ratio values in Co^{II}

carboxylate materials.¹⁷ It is possible that orientation of crystallites is occurring giving $\chi_{||}$ like behaviour, a phenomenon not unknown in anisotropic Mn^{III} species.¹⁸ Use of a 1500 Oe field showed no maximum but a saturation in χ_{Mn} below ~ 4 K. The 3000 Oe field data behaved likewise, but the saturation χ value was lower than in the 1500 Oe field and lower again in the 1 T field. This field dependent behaviour in the 20-1500 Oe region is indicative of either spin-flop behaviour observed in weakly coupled antiferromagnets^{12,19-21} or, more likely, of metamagnetic behaviour in which a ferromagnetic phase is induced by increasing the applied field. In the present case the high temperature region (10-300 K) displays antiferromagnetic coupling and thus, if metamagnetism occurs, a ferromagnetic phase must be of the weak ferromagnet / canted-spin antiferromagnet type. The decrease observed in the saturation value of χ , at temperatures below 6 K, as H is increased from 1500 Oe to 3000 Oe and 10,000 Oe is a result of the canted-spin antiferromagnetism that will align spins opposite to the field. Indeed, this can be seen in the magnetization isotherms shown in Figure 6.6 which, at 2, 3 and 4 K, show sigmoidal M vs. H behaviour typical of metamagnetism (critical field ≈ 1000 Oe), while at higher fields e.g. 3000, 10,000 Oe the χ (from M/H) values at 2-5 K are lower than at 1500 Oe because of the spin-canting. The M values increase slowly, and almost linearly, between 1 and 5 T (below T_N), reaching $0.79 N\beta$ at $H = 5$ T (not shown in Figure 6.6 for clarity), a value well below the $S = 2$ value of $4 N\beta$. Presumably an enormous field would be required to reach saturation and a ferromagnetic phase. This contrasts with the rapid change from antiferromagnetic to canted-spin phase in small, increasing fields. Recent examples of somewhat similar but not identical field induced antiferromagnetic to canted-spin antiferromagnetic or to ferromagnetic transitions have been given by Kurmoo *et al.*¹⁷ and by Mallah *et al.*²² for a 2D Co^{II} -pyromellitate and a 2D $\text{Cr}^{\text{III}}\text{Ni}^{\text{II}}$ cyano-bridged system, respectively.

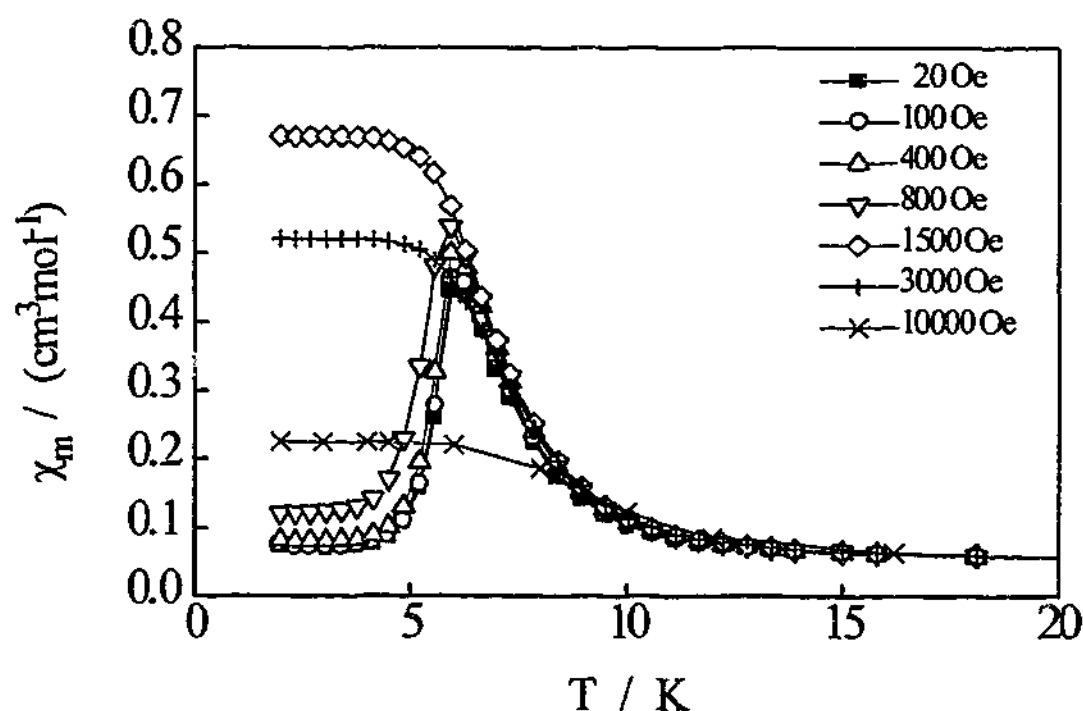


Figure 6.5 Temperature dependence of the DC magnetic susceptibilities for $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ in applied fields of 20 (■), 100 (○), 400 (△), 800 (▽), 1500 (◇), 3000 (+) and 10,000 (×) Oe.

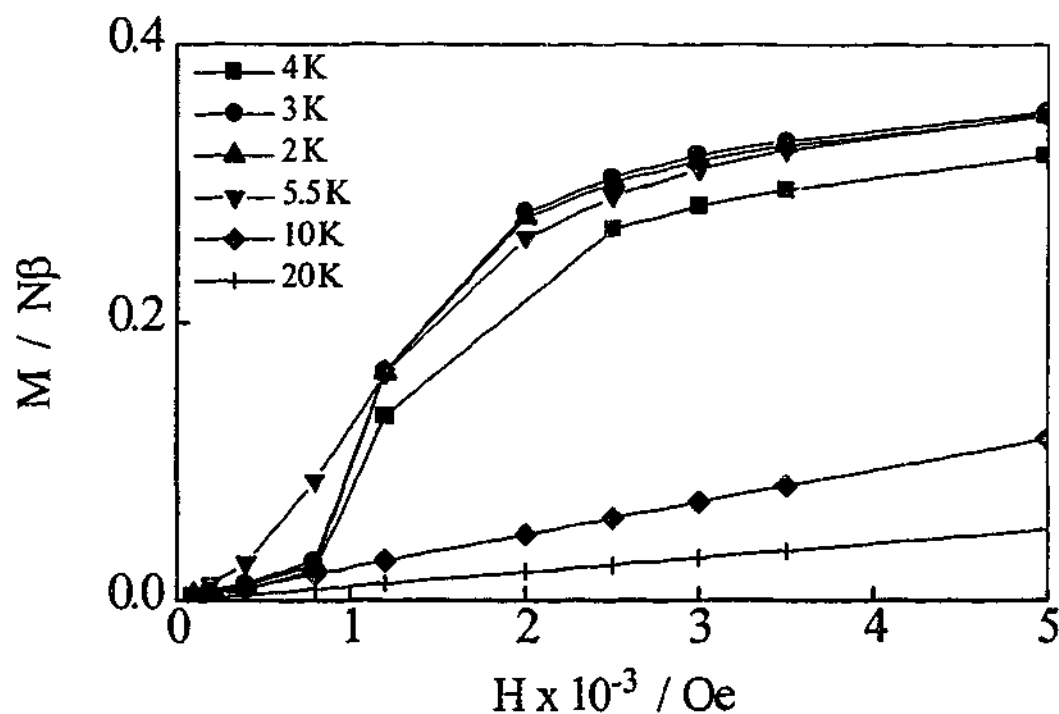


Figure 6.6 Isothermal magnetization of $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ at 2 (▲), 3 (●), 4 (■), 5.5 (▼), 10 (◆), 20 (+) K. Note that at 2 K the M values have a close to linear dependence on H up to 5 T and do not saturate (see text).

The present compound shows essentially no hysteresis in M , at 2 K, in the ± 2000 Oe DC sweep (Figure 6.7), the sigmoidal behaviour being clearly evident. The in-phase AC susceptibility component, χ' , measured using a field of 10 Oe and frequency of 100 Hz, shows a sharp maximum at 6.2 K and a shoulder at 3.9 K, while the out-of-phase component χ'' shows zero at 6.2 K but, surprisingly, a sharp maximum at 2.3 K (Figure 6.8). These data also support antiferromagnetic order occurring below 6.2 K, the transition at 2.3 K probably being due to the spin-canting. Further work is required to confirm the latter.

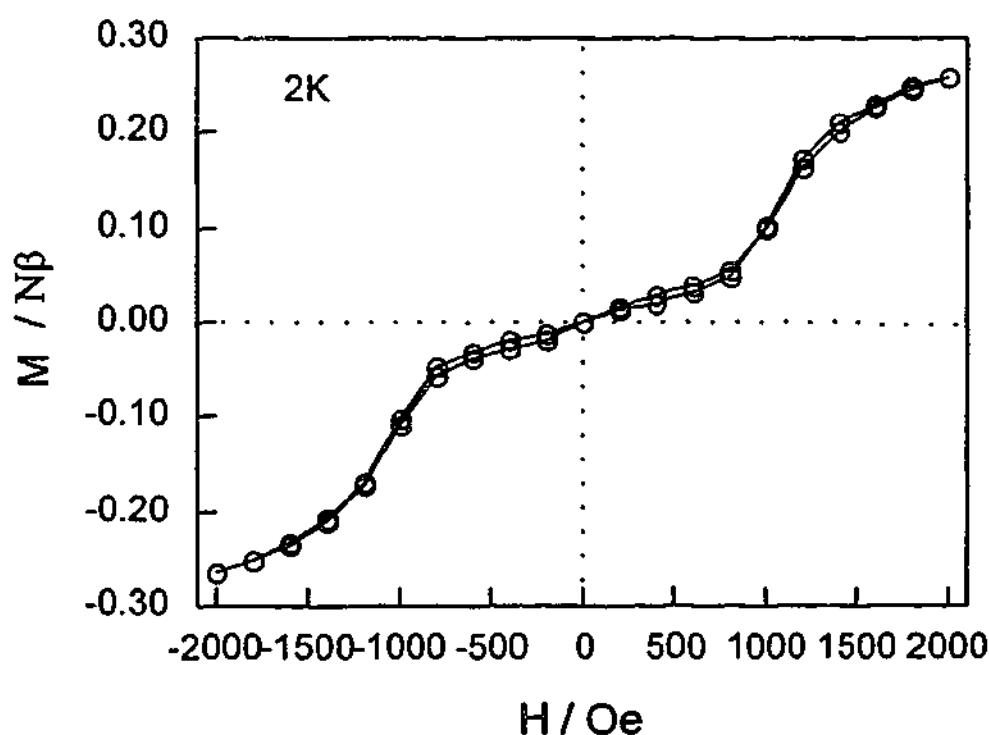


Figure 6.7 Isothermal magnetization of $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ at 2 K in the field ranges of ± 2000 Oe.

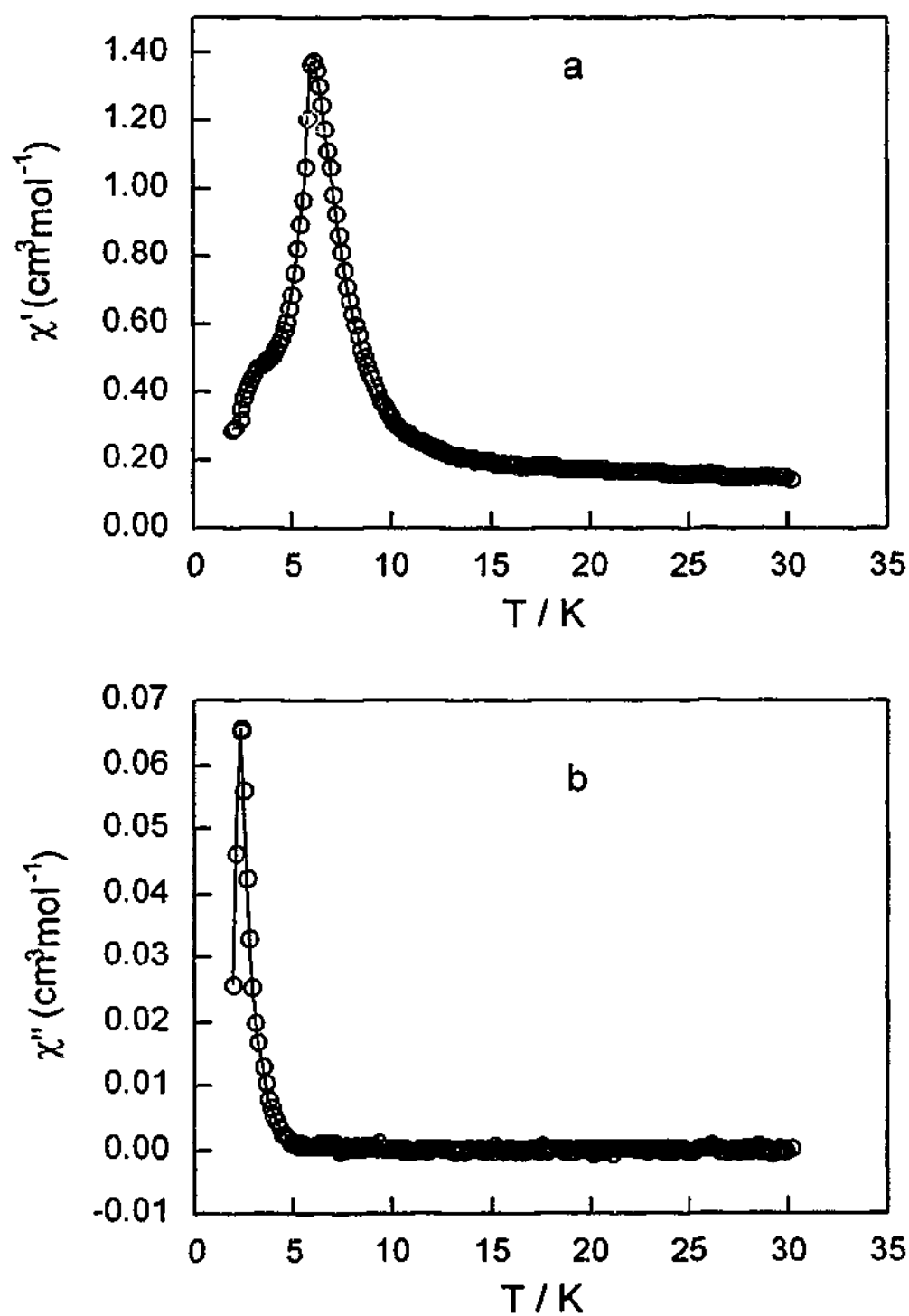


Figure 6.8 (a) Temperature dependence of the AC in-phase magnetic susceptibility, χ' , in a field of 10 Oe and frequency of 100 Hz, and (b) temperature dependence of the AC out-of-phase component, χ'' .

Measurement of the field-cooled magnetization (*FCM*; $H = 10$ Oe) and the zero-field cooled magnetization (*ZFCM*) show identical behaviour at temperatures 4–25 K with a sharp maximum at 6.1 K and the cusp-like decrease in M , below T_N (Figure 6.9). The lack of any bifurcation of the *FCM* and *ZFCM* plots is indicative of being in an antiferromagnetic phase in this 10 Oe field. Canted-spin antiferromagnets or ferromagnets would show bifurcation at T_c and would show hysteresis.

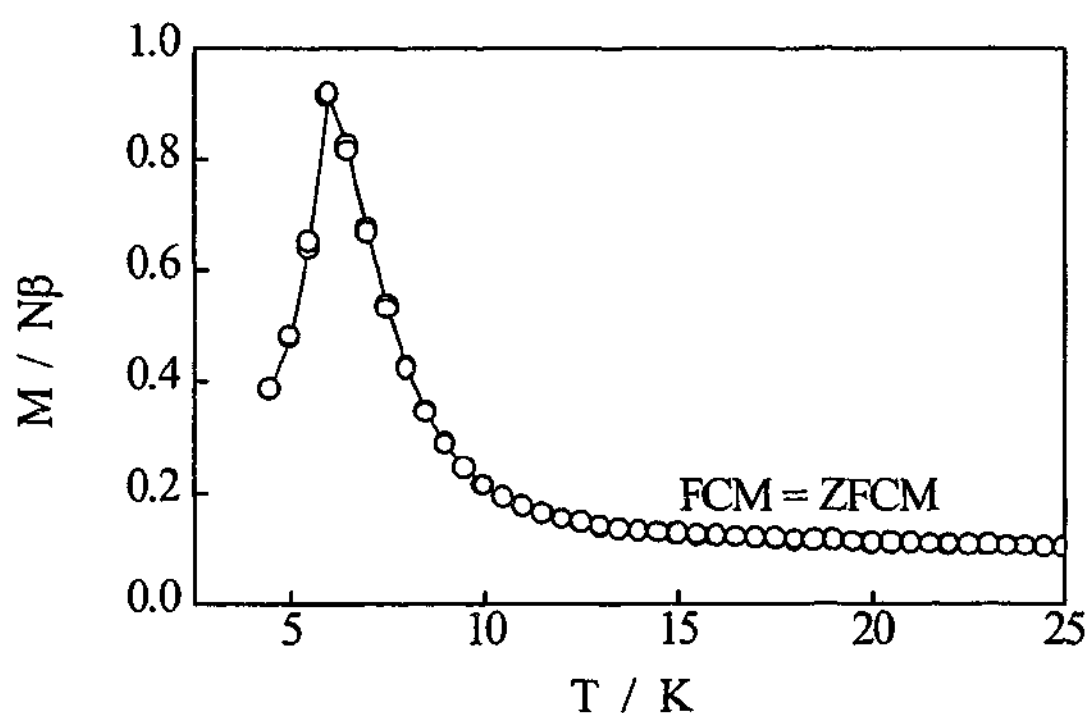


Figure 6.9 Temperature dependence (4–25 K) of the *FCM* and *ZFCM* for $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$.

6.5 Conclusions

A new solvated linear chain manganese(III) complex, $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$, has been isolated. The chains, similar to those observed in a complex also reported by the candidate, $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$ (see Chapter 8) are

composed of octahedral Mn^{III} atoms linked by single methoxide bridges and double acetate bridges. The chains are linked *via* hydrogen bonding pathways through the solvated acetic acid and water molecules, to form 2D sheets.

Detailed magnetic measurements on this material have revealed fascinating magnetic properties. The magnetic data for the layered structure in $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ are compatible with the occurrence of weak antiferromagnetic coupling along the Mn^{III} chains mediated by the two $\mu\text{-OAc}^-$ and one $\mu\text{-OH}^-$ bridges, as often is the case in similarly tri-bridged dinuclear Mn^{III} complexes.²³ Long-range antiferromagnetic order occurs below a T_N of 6.1 K probably involving hydrogen bonded $(\text{Mn}-\text{OH}\cdots\text{HO}_2\text{CCH}_3\cdots\text{OH}_2\cdots\text{O}_2\text{CCH}_3-\text{Mn})$ pathways between the chains. An unusual phase transition from antiferromagnetic to canted-spin antiferromagnetic (weak ferromagnetic) occurs as the field is raised from 0 to *ca.* 1000 Oe, the spin-canting originating from chain-chain interactions containing anisotropic Mn^{III} centres. Removal of the solvate molecules removes the 3D magnetic order. The similar Mn^{III} carboxylate chain, $[\text{Mn}(\mu\text{-OMe})(\text{OAc})_2]_n$, having bridging methoxide groups instead of hydroxide moieties and no acetic acid or water solvent molecules, displays no long-range order. The fact that it possesses no hydrogen bonding pathways and displays no magnetic long-range order would seem to support the conclusion that the magnetic order observed here is indeed facilitated by the hydrogen bonding network.

There are other recent examples of hydrogen bonded networks having ordering temperatures of similar magnitude to that observed here.¹⁰⁻¹³ In one such example, a $\{\text{Ni}^{\text{II}}\text{alcohol-nitroxyl radical}\}$ heterospin system, a field induced antiferromagnetic to canted-spin antiferromagnetic phase was observed, similar to that observed here.¹¹

6.6 Experimental

6.6.1 Synthesis of $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$

An ethanolic solution (10 mL) of $\text{Me}_4\text{N}(\text{dcm})$ (0.195 g, 1.16 mmol) was added with stirring to a solution of $\text{Mn}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (0.284 g, 1.16 mmol) in 10 mL acetonitrile, 20 mL ethanol and 7 mL glacial acetic acid. Solid $n\text{-Bu}_4\text{NMnO}_4$ (0.076 g, 0.210 mmol) was then added in small portions. At this time the solution was a dark red/brown colour. The solution was stirred for about three hours, after which a small amount of the solution was placed in a Petrie dish to evaporate, the remainder covered and left to stand. After one day many red-orange crystals had formed. These were collected by filtration, washed with ethanol and dried with ether and placed in a sealed vessel (under nitrogen) to prevent desolvation that occurred in air over a period of days. (Yield ~90 mg, 21 % based on total available Mn). IR (Nujol mull, cm^{-1}): 3336sbr, 2601vw, 2040vw, 1776vw, 1699s, 1505s, 1455s, 1277s, 1148m, 1039m, 963vw, 888w, 676w. Anal. (%) Found: C, 26.8; H, 4.7; N, 0.0. Calc. for $\text{C}_6\text{H}_{13}\text{MnO}_8$: C, 26.9; H, 4.9; N, 0.0.

After about one week many red-orange crystals rod-like crystals were present in the remaining solution. A suitable crystal was chosen for a single-crystal X-ray diffraction experiment.

It was subsequently found that $\text{Me}_4\text{N}(\text{dcm})$ was not necessary for the successful synthesis of $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$. Thus, solid $n\text{-Bu}_4\text{NMnO}_4$ (0.076 g, 0.210 mmol) was added in small portions with stirring to a solution of $\text{Mn}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (0.284 g, 1.16 mmol) in 10 mL acetonitrile, 20 mL ethanol and 7 mL glacial acetic acid. The resultant dark black-brown solution was left to stand to slowly evaporate. After several months the solution (now colourless) had almost evaporated to dryness and a solid was present consisting of red-orange needles. About half of this solid was collected by

filtration, washed quickly with ethanol, dried with ether, then placed in a sealed vessel (under nitrogen). (Yield 0.076 g, 21 % based on total available Mn). The remainder of the solid was left in the mother liquor. IR (Nujol mull, cm^{-1}): 3326sbr, 1700s, 1538s, 1438s, 1278m, 1150m, 1038m, 888w. Anal. (%) Found: C, 27.0; H, 4.8; N, 0.0. Calc. for $\text{C}_6\text{H}_{13}\text{MnO}_8$: C, 26.9; H, 4.9; N, 0.0.

6.6.2 X-Ray Crystallography

Data were collected on a dichroic yellow-red rod-like crystal using a Nonius KappaCCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Integration was carried out by the program DENZO-SMN,²⁴ and data were corrected for Lorentz polarisation effects and for absorption using the program SCALEPACK.²⁴ Further face-indexed numerical absorption corrections were applied using the program XPREP. Solutions were obtained by direct methods (SHELXS 97)²⁵ followed by successive Fourier difference methods, and refined by full matrix least squares on F_{obs}^2 (SHELXL 97)²⁵ with the aid of the graphical interface program X-SEED.²⁶ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the chain, the oxygen bound acetic acid hydrogen atom and the water hydrogen atom were located and refined isotropically and their bond lengths were restrained using the DFIX instruction to be 0.96(2) and 0.90(2) Å for the carbon and oxygen bound hydrogens respectively. The methyl hydrogen atoms of the acetic acid were not included due to the large thermal motion of the methyl carbon (refinements of such hydrogen atoms presented extremely large U_{iso} values) and their relative unimportance with respect to the hydrogen bonding interactions.

6.6.3 Magnetic Measurements

The instrumentation (Quantum Design MPMS 5 and PPMS (AC)), DC magnetisation and AC susceptibility protocols have been described previously.⁷ Care was taken to see that $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ did not partially desolvate in the sample chamber and it was found that use of a gelatine capsule to contain the sample was adequate. Dr. B. Moubaraki kindly carried out these magnetic studies.

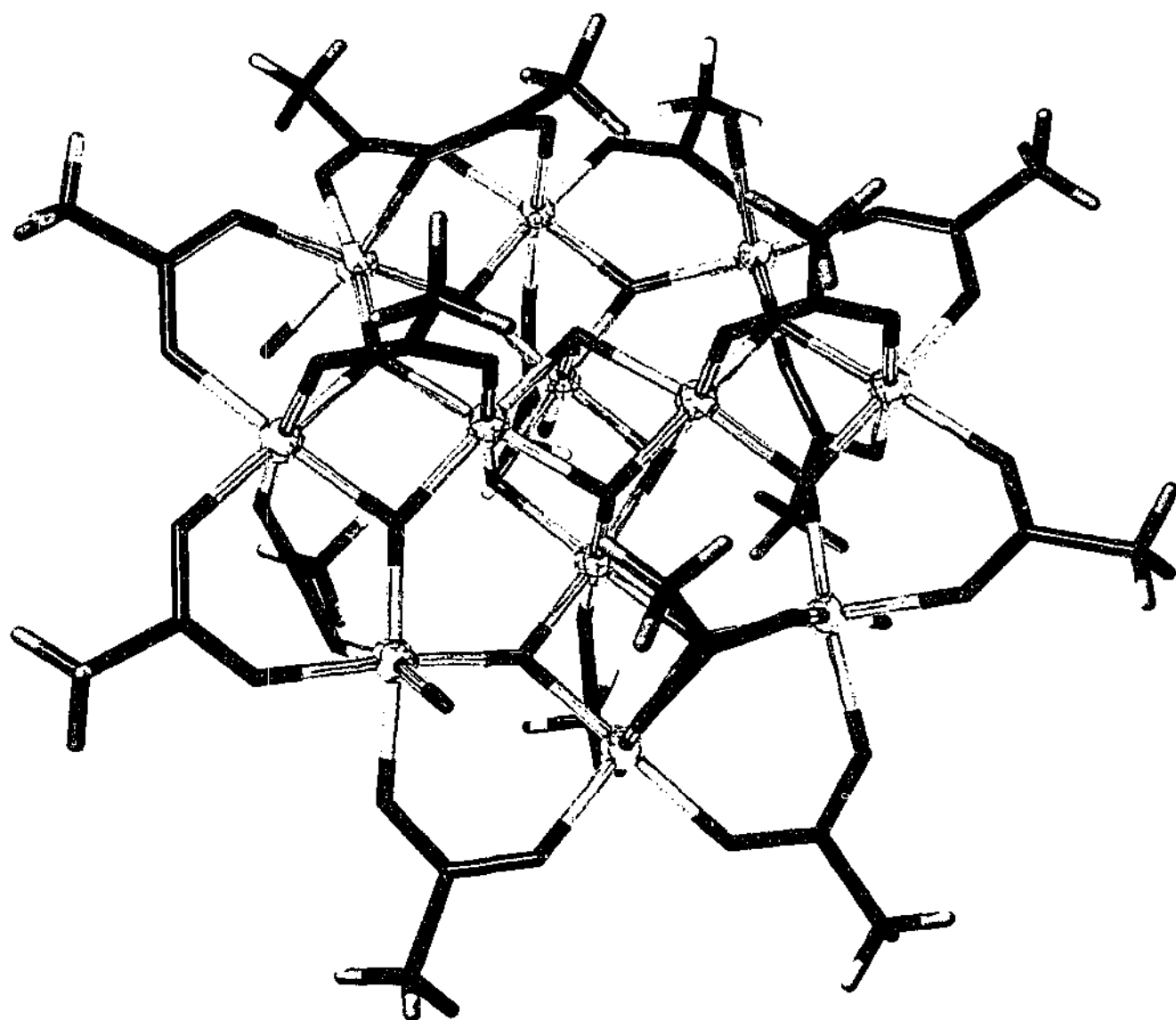
6.6.4 Thermogravimetric Analyses

Thermal degradation studies were performed on a Simultaneous Thermal Analyzer (Rheometric Scientific, STA 1500), which was calibrated using a four point melt series (indium, tin, lead, and zinc). Experiments were performed in aluminium pans. Three freshly prepared samples of $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ were used. Two experiments were performed under a N_2 flow, between 25-400°C with heating rates of 2 and 10°C per minute. One experiment was performed under a flow of dried air, between 25-150°C with a heating rate of 0.5°C per minute. A mass loss of 27-28 % occurred up to 80°C, the calculated value of loss of $\text{HOAc}\cdot\text{H}_2\text{O}$ being 29.1 %.

6.7 References

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**CHAPTER 7: A REVIEW OF POLYNUCLEAR
MANGANESE CLUSTER COMPLEXES WITH AN
EMPHASIS ON SINGLE MOLECULE MAGNETS**

This chapter is the second of two introductions, the first of which, Chapter 1, is a general introduction to molecule-based magnets. It introduces the closely related field of single-molecule magnetism, with a review of manganese cluster complexes. It is noted that much of the literature refers to large multinuclear (or oligonuclear) complexes as 'cage complexes', whereas other authors use the term 'cluster'. Both terms are used interchangeably in this thesis, although 'cluster' is used more often.

7.1 Background

A great deal of current research into Mn cluster chemistry focuses on two main topics of interest. Firstly, in the bioinorganic arena many model complexes have been made to replicate the properties and function of manganese containing proteins and enzymes, including, significantly, the water oxidation complex (WOC) in the Photosystem II (PSII) of green plants and cyanobacteria, which is responsible for the catalysis of the light driven oxidation of H_2O to O_2 .¹⁻⁹ Despite the absence of definitive structural details,¹⁰ it has been established that the active site of the protein contains a Mn_4 aggregate (possibly a tetranuclear cluster, or a trinuclear cluster located near a single Mn ion, or a pair of dinuclear complexes) bridged by O^{2-} or OH^- and ligated by O- and/or N-donor atoms from amino acid side chains (aspartate and/or glutamate carboxylate, tyrosine phenoxide, histidine imidazole). Detailed spectroscopic, EXAFS, XANES and crystallographic studies have been made to probe the $\text{Mn}_4(\text{Ca})$ μ -oxo cluster in the redox states S_0 to S_4 .^{8,11-14} Secondly, in the field of nanomagnetic materials, some large high-spin manganese carboxylate clusters display magnetic properties previously only associated with nano-sized particles of magnetic metal oxides, that is, they can be magnetized and as such have been termed single-molecule magnets (SMMs). They also display unusual quantum mechanical effects in their single-crystal magnetisation hysteresis plots.

In 1980 the structure of a dodecanuclear manganese complex, $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{HOAc} \cdot 4\text{H}_2\text{O}$ (' Mn_{12} -acetate', Figure 7.1) was determined by Lis.¹⁵ In 1993, Christou *et al.*¹⁶ and Gatteschi *et al.*¹⁷ discovered that Mn_{12} -acetate functions as a single magnetic domain with slow relaxation of magnetisation (of several months) at temperatures below its blocking temperature (T_B) of 4 K.¹⁶ There has since been considerable interest in the magnetic properties of Mn_{12} -acetate, which has an unusually high $S = 10$ ground state brought about by the antiparallel coupling of 8 Mn^{III} (total $S = 32/2$) and 4 Mn^{IV} (total $S = 12/2$).¹⁸⁻³¹ In 1996, it was reported that Mn_{12} -acetate displays quantum tunnelling of magnetization hysteresis and this led to the possibility of use in quantum computing.³²⁻³⁵

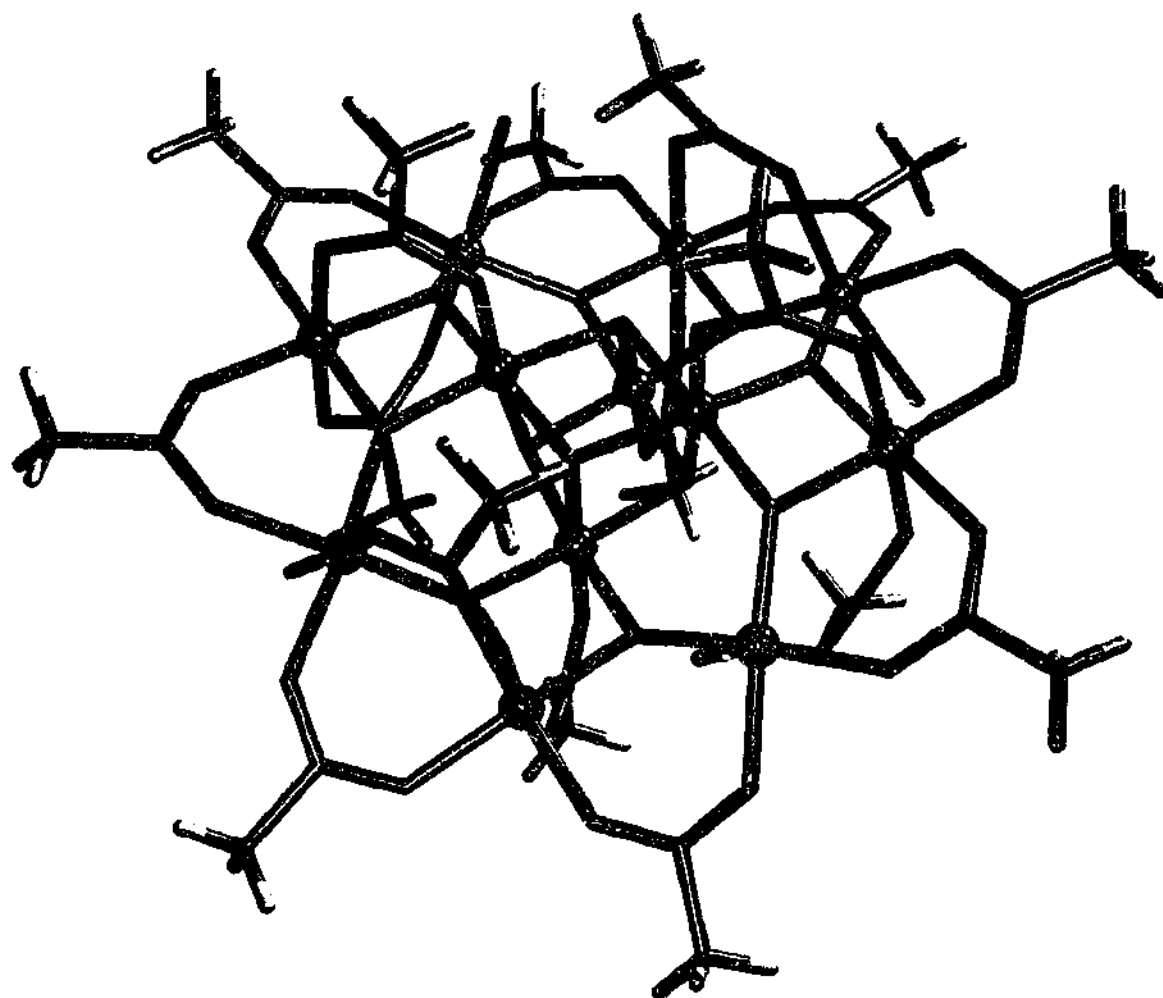


Figure 7.1 The crystal structure of Mn_{12} -acetate (spheres represent Mn atoms, lattice waters and acetic acid are omitted for clarity).

Classical nanomagnets are prepared by fragmentation of macroscopic ferromagnetic multi-domain particles, whereas SMMs are prepared by solution methods from smaller precursors.³⁶ This has been referred to as an 'upscale' approach, i.e. a ground up approach rather than the 'downscale' or fragmentation synthetic procedure.^{37,38} As such SMMs are single domains with a single particle size, not a distribution of sizes. SMMs, like infinite network molecule-based magnets, are amenable to chemical modifications by slight alteration or complete change of the molecular precursors. SMMs can be soluble in a range of solvents, meaning thin films can be prepared.³⁶ Additionally, SMMs have the potential to be high-density memory devices or components in quantum computers.^{36,39,40} SMMs also present the opportunity for chemists and physicists to co-operate towards bridging the gap between the classical and quantum theories of magnetism.³⁶ The major disadvantage SMMs possess is the extremely low temperatures at which they undergo slow magnetisation relaxation.

Briefly, before discussing these species in more detail below, to date the family of SMMs includes many manganese carboxylate clusters of nuclearities Mn_4 ,⁴¹ Mn_9 ,^{42,43} Mn_{10} ,⁴⁴⁻⁴⁷ Mn_{12} ,^{26,48-51} Mn_{18} ⁵² and the largest to date, Mn_{30} .⁵³ Very recently a $\text{Mn}^{\text{III}}_{26}$ cage complex has been reported to show preliminary evidence of SMM behaviour.⁵⁴ Other nuclearities such as Mn_3 , Mn_6 ,^{55,56} Mn_7 ,⁵⁷ Mn_8 ,^{43,58,59} Mn_{11} ,⁶⁰ Mn_{13} ,⁶¹ Mn_{14} ,⁶² $\text{Ba}_8\text{Na}_2\text{ClMn}_{16}$,^{63,64} Mn_{19} -oxo-alkoxide,⁶⁵ and Mn_{21} ⁶⁶ do not display SMM behaviour, even though some have high-spin ground states, one of the prerequisites for being an SMM. The best and most well studied class of SMMs are the Mn_{12} -acetate variations, $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_x]^{n-}$ ($n = 0, 1, 2$; $x = 3, 4$) and their derivatives, which include mixed carboxylates, and partial non-carboxylate substituted species.^{17,37,38,67-70}

A comparatively small number of SMMs that do not contain manganese have also been reported. These include Fe_4 ,⁷¹ Fe_8 ,⁷²⁻⁷⁶ Fe_{10} ,^{77,78} Fe_{19} ,⁷⁹ and V_4 ^{80,81} complexes. Very recently Ni_{12} ,⁸²⁻⁸⁴ Ni_{21} ,⁸⁵ Co_4 ,⁸⁶ and Ni_4 ⁸⁷ clusters have been reported to display SMM behaviour in the millikelvin temperature range. The SMM family is not limited to oxo-based species, and now includes a few examples of cyano-bridged clusters (*vide infra*).⁸⁸

The chief research goals in the field of SMMs are to discover new species with ever-higher ground state spin values, S , and larger negative values of axial zero-field splitting parameter, D . The latter usually requires non-symmetrical cluster geometries. By synthesising larger metal clusters of higher nuclearity and low symmetry, it is thought these goals, and obtaining higher blocking temperatures, can be achieved.

7.2 The Origin of Single Molecule Magnetism, and the Occurrence of Quantum Phenomena

What follows here is a superficial treatment of what is an enormously complex subject that requires a level of understanding of quantum physics beyond the scope of this thesis. The candidate endeavours here to introduce some basic concepts to give the reader, who is not already familiar with this relatively new and multidisciplinary field, a background for the results presented in the following two chapters. The interested reader is directed to some excellent recent review articles on this field by Christou and Hendrickson *et al.*,^{18,38,89,90} and Gatteschi *et al.*,^{37,91-94} some more in-depth than others.

Single molecule magnets (SMMs) are so named because at temperatures below a blocking temperature, T_B , each molecule can be magnetized and behaves as a single magnetic domain. Below this T_B the thermal energy is not sufficient to allow free rotation of the spin (the value of T_B depends on the experimental technique).^{75,95} When a sample of an SMM is exposed to a large external magnetic field all of the molecules have their spins

aligned with the external field. When the field is cycled to zero, the rate of magnetization relaxation is very slow. For example, if a molecule of Mn_{12} -acetate is magnetised at 2 K by an applied field, after two months kept at that temperature, the magnetisation is still *ca.* 40 % of the saturation value.⁹⁶

The aforementioned archetypal SMM, $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{HOAc} \cdot 4\text{H}_2\text{O}$, Mn_{12} -acetate, consists of a central $[\text{Mn}^{\text{IV}}_4\text{O}_4]^{8+}$ cubane unit connected to an outer ring of $[\text{Mn}^{\text{III}}_8\text{O}_8]^{8+}$. AC magnetic susceptibility and high-frequency electron paramagnetic resonance (HFEP) measurements indicate that it has a ground state spin of $S = 10$. The large ground state is a result of ferrimagnetism, the antiferromagnetic coupling of the four central Mn^{IV} ions ($S = 3/2$) and the eight perimeter Mn^{III} ions ($S = 2$) (Figure 7.2).³⁸ An axial zero-field splitting is present, largely due to the single ion magnetic anisotropy of the eight Mn^{III} ions, leading to a splitting of the $S = 10$ ground state into 21 levels, each characterised by a spin projection quantum number M_S , where $-S \leq M_S \leq S$. Each level has an energy given by $E(M_S) = M_S^2 D$, where D is the axial zero-field splitting parameter, which for Mn_{12} -acetate is *ca.* -0.46 cm^{-1} .³⁶ The negative sign of D leads to a potential energy barrier between the “spin-up” ($M_S = -10$) and the “spin-down” ($M_S = 10$) orientations of the individual Mn_{12} molecules. Thus, the inversion of the spin of an individual molecule requires energy to overcome the barrier potential (Figure 7.3). If the barrier height is appreciable the molecule can be “trapped” on one side of the double potential energy well. Thus the SMM is magnetised in one direction. The barrier height energy is given by $\Delta E = E(M_S = 0) - E(M_S = \pm 10) = S^2 |D|$.³⁸

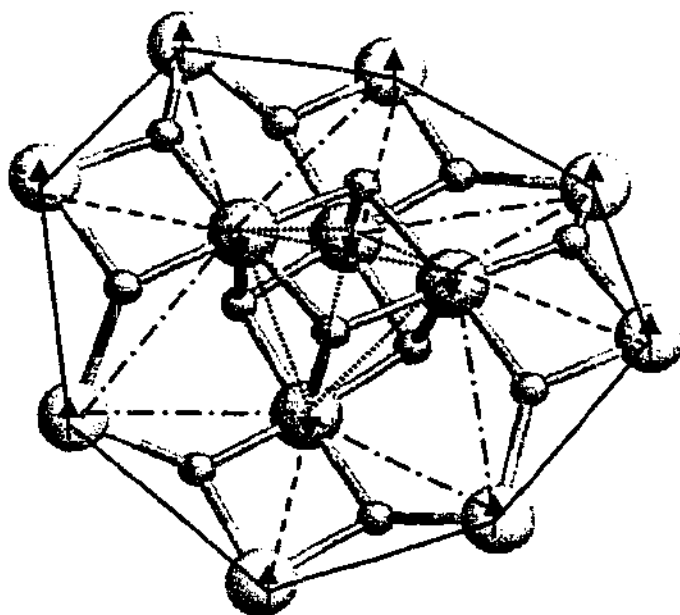


Figure 7.2 A schematic diagram showing ferrimagnetic interactions between central cubane Mn^{IV} ions and perimeter Mn^{III} ions in the core of Mn_{12} -acetate (smaller spheres represent $\mu_3\text{-O}^{2-}$ ions). The ferromagnetic interactions in the Mn^{III}_8 perimeter (continuous line) and Mn^{IV}_4 cubane (dotted line) and antiferromagnetic interactions between perimeter and cubane (dot-dashed line) are shown. Reproduced from reference 99.

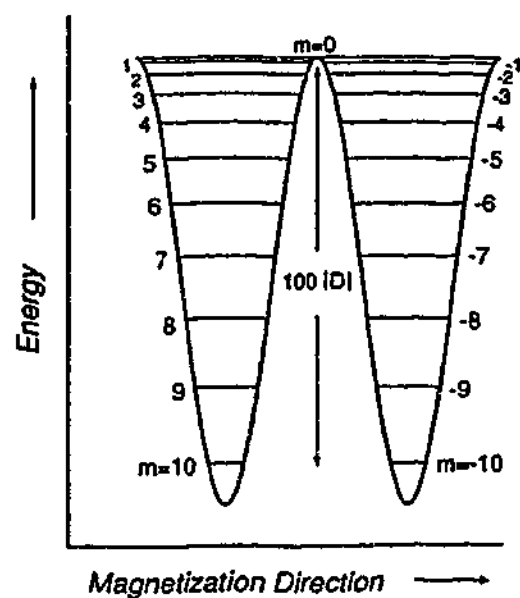


Figure 7.3 Plot of the potential energy vs. magnetisation direction for an SMM (Mn_{12} -acetate) with an $S = 10$ ground state, in zero external magnetic field. There is an axial zero field splitting, $D < 0$ (reproduced from reference 36).

In addition to high spin ground state values, 'easy axis' type (meaning the magnetisation is preferentially oriented in a single direction) magnetic anisotropy is an essential feature of SMMs.⁹⁹ In the case of Mn_{12} -acetate and other Mn based SMMs, it is the Jahn-Teller distortions in the crystal field of the Mn^{III} ions, together with spin-orbit interactions that give rise to the single-ion anisotropies. It follows that structural anisotropy is also required to give overall magnetoanisotropy. For example, a Mn^{III}_6 complex⁵⁵ (*vide infra*) with an $S = 12$ ground state has a highly symmetrical arrangement of the Mn^{III} centres resulting in magnetic isotropy with $D \approx 0$.³⁸

The slow relaxation of magnetisation is a key indicator of SMM behaviour and is usually detected as a frequency dependence of the out-of-phase, χ'' , signal in AC susceptibility measurements (Figure 7.4). A species that possesses a magnetisation relaxation mechanism that is slower than the oscillating applied field cannot stay in phase with this field, and will exhibit a peak in the out-of-phase component of the AC susceptibility.^{49,100} At the temperature at which χ'' goes through a maximum, the relaxation frequency of magnetisation is equal to the operating AC field frequency.⁹¹ The magnetisation relaxation rate is quantified by analysing the frequency dependencies of the χ'' signals. The relaxation times at each temperature are determined and the data least squares fit to the Arrhenius equation (Equation 7.1). From this plot, the height of the barrier to reversal of magnetisation ($\Delta E = S^2 |D|$) and the pre-exponential factor, τ_0 , are determined. Mn_{12} -acetate has a barrier height of $\Delta E = 43 \text{ cm}^{-1}$ (62 K).^{91,100}

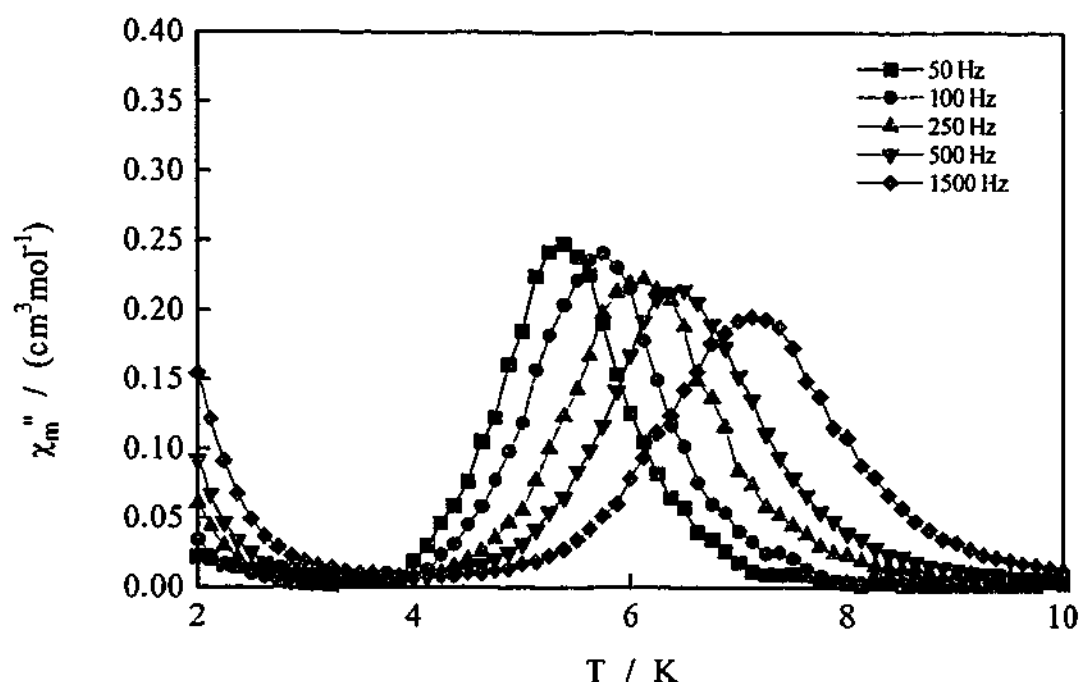


Figure 7.4 Plots of AC χ'' versus temperature at different frequencies for an SMM (taken from Chapter 8).

$$\tau = \tau_0 e^{-\Delta E / kT} \quad \text{Equation 7.1}$$

τ = relaxation time = $1/(2\pi\nu)$ (s),

τ_0 = pre-exponential factor,

ν = AC frequency (Hz) of applied field,

ΔE = activation energy or barrier height of the double potential energy well (cm^{-1}),

k = Boltzmann constant.

SMMs show magnetic hysteresis due to the presence of the potential energy barrier between the “spin-up” and “spin-down” states. When a sample of SMMs is exposed to a large external field, the magnetisation of each molecule is saturated on one side of the double well and is “frozen” due to the barrier potential, and thus only slowly returns to zero magnetisation. A negative field reduces the height of the barrier and “unfreezes” the spins, thus allowing a rapid reversal of magnetisation. Therefore, hysteresis of a purely molecular origin is observed. Therefore, it is in principle possible to store data on a single

bistable molecule.³⁸ The magnetisation hysteresis loop of Mn_{12} -acetate is shown in Figure 7.5.

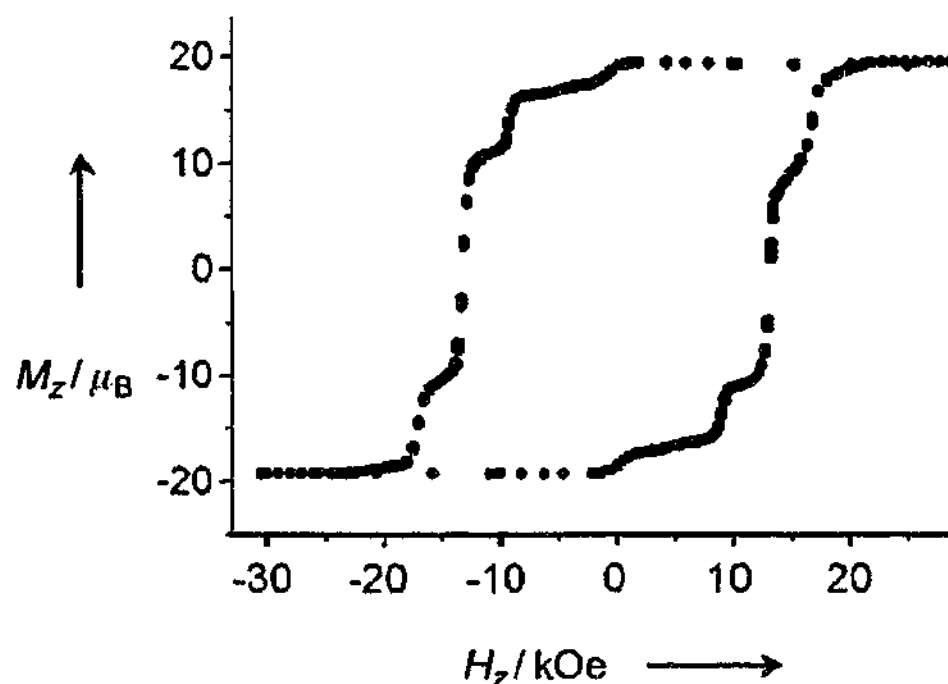


Figure 7.5 Plot of magnetisation vs. applied field hysteresis loop for a single crystal of Mn_{12} -acetate with the field parallel to the tetragonal axis (*c*-axis) at 2.1 K, showing 'stepped' hysteresis (reproduced from reference 91).

It has been shown that the magnetic behaviour exhibited by an SMM is entirely due to individual molecules and, unlike long-range ordered materials, is not the result of cooperative effects throughout the bulk solid. This conclusion is supported by several experiments, such as magnetisation measurements on frozen solutions^{20,23,31} or polymer doped films,¹⁹ which show the same properties as the solid crystalline sample. In addition heat capacity measurements gave no indication of long-range magnetic order, thus ruling out intercluster interactions.^{91,101}

An exciting aspect of these systems is that due to their small size they are able to display quantum effects such as quantum tunnelling of magnetisation. In Figure 7.5 'steps' can be seen in the hysteresis loop. These steps correspond to an increased rate of change in

the magnetisation occurring when there is an energy coincidence of the levels on the opposite sides of the double-well potential. The molecules relax *via* resonant tunnelling through the barrier potential.³⁸ This may be understood by remembering that a quantum object possesses a wave nature. The wavefunction of a quantum particle in a potential well with a *finite* energy barrier has a non-zero value beyond the well. So in the case here, when the energy levels coincide on opposite sides of the *finite* barrier potential the two wavefunctions can mix or superimpose. Therefore there is a non-zero probability that the quantum particle is on both sides of the well, hence it has tunneled through the barrier potential.⁹¹

The observations of quantum phenomena such as quantum tunnelling and quantum coherence in these SMM systems have excited many researchers worldwide. Not only do they bridge the gap between classical and quantum physics, but are potential hardware components in quantum computers, where information is carried in quantum bits or 'qubits' in individual molecules.^{40,91,102-104} The rapid growth of high-speed computing and the need for still faster and smaller magnetic devices for computers has lead to much interest in the field of nano-scale magnetic materials. One of the very difficult challenges is to be able to address individual molecules and read the information stored. The goal of the ultimate miniaturization of information storage to the molecular scale could conceivably lead to massive increases in data storage and processing.

7.3 Examples of Manganese Carboxylate Cluster Complexes and Single Molecule Magnets

What follows is not intended to be a totally exhaustive review of manganese carboxylate cluster chemistry, but rather an exposure to the field with a number of examples described to illustrate the considerable structural variation that has appeared in

the literature to date. Winpenny has recently published a detailed review of high-nuclearity 3d-metal complexes with O- and N-donor ligands.¹⁰⁵ It is clear from what is presented below, the fascinating structural diversity and resultant magnetic properties possible, are seemingly limited only by the inspiration (and perspiration) of the synthetic chemist. Chance also plays a role – for many years the synthesis leading to $\text{Mn}^{\text{III/IV}}_{12}$ -acetate was regarded as a method of making “ Mn^{III} acetate”. The rational design of clusters of particular nuclearities from the given precursors is very difficult - many of those that follow were obtained serendipitously.

7.3.1 Tetranuclear Manganese Carboxylate Complexes

In terms of the field of SMMs, the trinuclear oxo-centred species, $[\text{M}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3]^{x+}$, $x = 0, \text{Mn}^{\text{II}}, 2\text{Mn}^{\text{III}}; x = 1, 3\text{Mn}^{\text{III}}; \text{R} = \text{Me}, \text{Et} \text{ etc.}; \text{L} = \text{py}, \text{H}_2\text{O} \text{ etc.}$ (also other metals, e.g. Cr, V, Fe), are predominantly utilised as starting materials for higher nuclearity complexes.¹⁸ For example, Christou and co-workers have reacted these complexes with chelating ligands such as 2,2'-bipy to yield a number of Mn_4 species.⁷ The chief models for the WOC are tetranuclear manganese complexes, consequently, a great number of examples have appeared in the literature.^{1,4-8,106-108} Several structural types of Mn_4 carboxylate complexes have been reported to date. One of the most frequently observed families is that containing a $[\text{Mn}_4(\mu_3\text{-O})_2]^{x+}$, $x = 6-8$ ($\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_2; \text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_3; \text{Mn}^{\text{III}}_4$), core with a planar or bent butterfly-like arrangement of four manganese ions bridged by two $\mu_3\text{-O}^{2-}$ ions, shown in Figure 7.6, where a line drawn between the two central Mn centres represents the ‘body’ of the butterfly and the two end Mn centres represent the two ‘wingtips’.

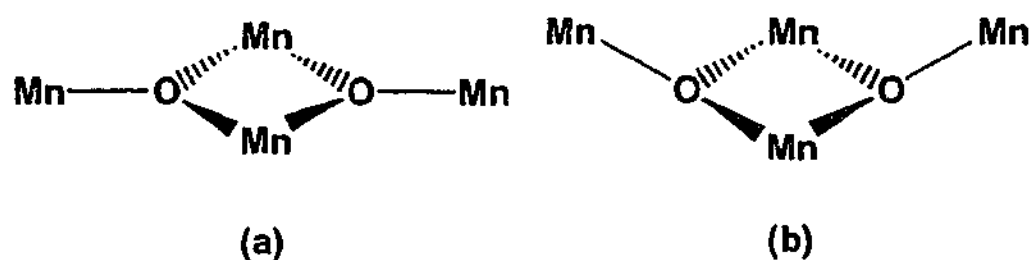


Figure 7.6 Schematic representations of the $[\text{Mn}_4\text{O}_2]$ core with the (a) planar or (b) bent, “butterfly” structure.

Two particular model examples were synthesized by Christou and co-workers, $[\text{Mn}_4\text{O}_2(\text{OAc})_7(\text{bipy})]^{x+}$ ($x = 0$ and 1) and $[\text{Mn}_4\text{O}_2(\text{OAc})_6(\text{bipy})_2]$.⁷ The former two complexes possess the bent butterfly structure (Figure 7.6(b)) with Mn^{II} , 3Mn^{III} (S_0 model) and 4Mn^{III} (S_1 model) respectively. The latter complex has a planar structure (Figure 7.6(a)), with 2Mn^{II} , 2Mn^{III} and is a model for the “superreduced” state, S_{-1} , of the WOC that is apparently not involved in the catalytic cycle.¹⁰⁹ Other $[\text{Mn}_4\text{O}_2]$ type clusters have been reported with peripheral ligation provided, for example, by the anions of picolinic acid (pic^-),⁸ 8-hydroxyquinoline (hqn^-),¹¹⁰ 5-chloro-8-hydroxyquinoline (Cl-hqn^-),¹¹⁰ 2-(hydroxymethyl)pyridine (hmp^-),¹¹⁰ or dibenzoylmethane (dbm^-).^{111,112} These types of complexes generally do not display SMM behaviour. The examples given above have not proven to be useful for the synthesis of higher nuclearity species, presumably due to the chelating ligands blocking further aggregation.¹⁸ However, a related anionic complex $(n\text{-Bu}_4\text{N})[\text{Mn}^{\text{III}}_4\text{O}_2(\text{O}_2\text{CPh})_9(\text{H}_2\text{O})]$,^{59,113} shown in Figure 7.7, contains a $[\text{Mn}_4\text{O}_2]^{8+}$ bent butterfly core with only H_2O and PhCO_2^- peripheral ligands, and it has proven to be an excellent starting material for larger clusters, for example a Mn_8 species.⁵⁹

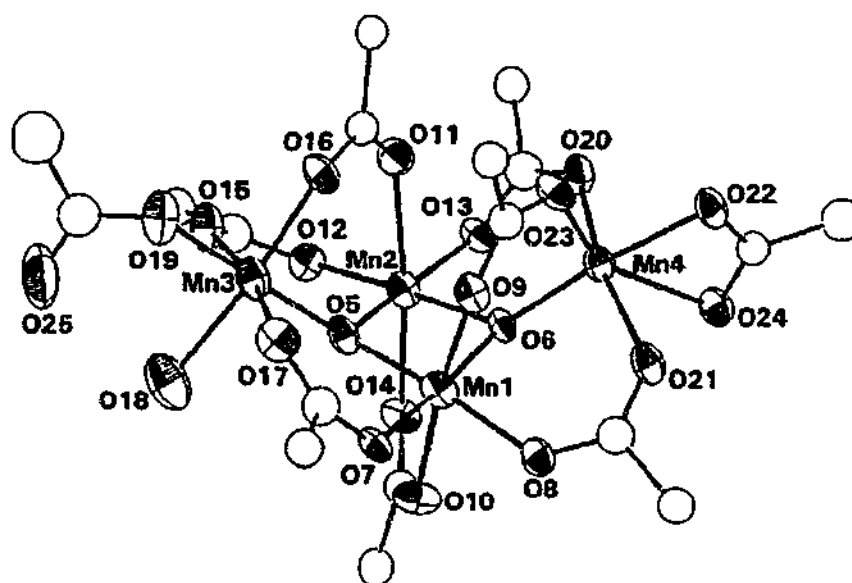


Figure 7.7 The crystal structure of $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_9(\text{H}_2\text{O})]^-$ possessing the bent butterfly core structure (only the *ipso* carbons of the benzoate groups are shown for clarity, reproduced from reference 18).

A related class of Mn_4 clusters has a similar core unit to those above, but two μ_3 -alkoxo groups from nitrogen-oxygen donor chelates replace the two $\mu_3\text{-O}^{2-}$ ions, and four additional μ -alkoxo groups also make up the rhombohedral core (Figure 7.8). This type can be derived from the planar butterfly model by changing the geometry of the planar $\mu_3\text{-O}$ centres to trigonal pyramidal, with one either side of the planar Mn_4 rhombus. By inspection of the resulting core unit, including the four μ -alkoxo groups, it can be seen that it displays the CdI_2 layered structure with Mn centres occupying octahedral sites sandwiched between two layers of hexagonally packed O atoms.

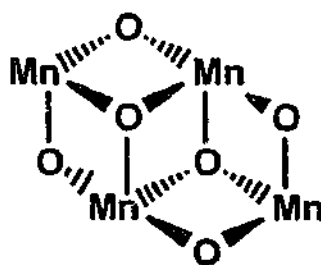


Figure 7.8 A schematic representation of the CdI_2 -like core unit of the second type of Mn_4 cluster, where all bridging oxygen atoms shown are alkoxo groups from nitrogen-oxygen chelates.

This phenomenon of large poly-oxo cluster complexes adopting layered mineral type core structures is not uncommon and is discussed in detail in a review on polynuclear cage complexes by Winpenny⁸⁴ and is mentioned in Chapter 8 in connection with the new hexadecanuclear cluster complex $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_{16}(\text{MeOH})_3(\text{H}_2\text{O})_3] \cdot 6\text{H}_2\text{O}$ synthesised by the candidate. Several examples of this Mn_4 class have been shown to exhibit SMM behaviour.^{114,115} One example, $[\text{Mn}_4(\text{OAc})_2(\text{pdmH})_6](\text{ClO}_4)_2$ (2Mn^{II} , 2Mn^{III}), (where pdmH_2 = pyridine-2,6-dimethanol),¹¹⁶ is shown in Figure 7.9(a). Depending on the type of solvation, the complex possesses either an $S = 8$ (desolvated) or $S = 9$ (hydrated) ground state. The hydrated species has an axial zero-field splitting parameter of $D/k = -0.45$ K and a barrier potential energy, $\Delta E = 36.5$ K (25 cm^{-1}). An example without any carboxylate bridging groups is the cationic SMM $[\text{Mn}_4(\text{hmp})_6\text{Br}_2(\text{H}_2\text{O})_2]\text{Br}_2 \cdot 4\text{H}_2\text{O}$ (Figure 7.9(b)), where hmp^- is the anion of 2-hydroxymethylpyridine and is the only bridging ligand. It has an $S = 9$ ground state with $D/k = -0.498$ K (-0.34 cm^{-1}) and $\Delta E = 15.8$ K (11 cm^{-1}).¹¹⁵

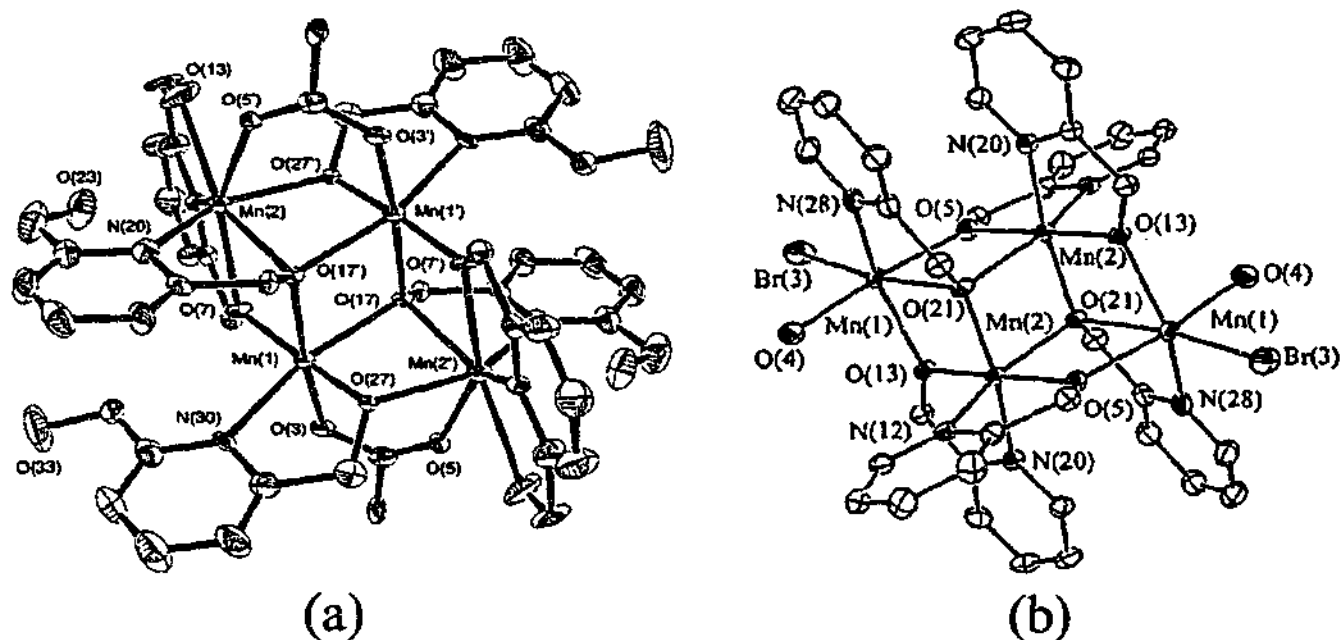


Figure 7.9 The crystal structures of the (a) $[\text{Mn}_4(\text{OAc})_2(\text{pdmH})_6]^{2+}$ and (b) $[\text{Mn}_4(\text{hmp})_6\text{Br}_2(\text{H}_2\text{O})_2]^{2+}$ cations (thermal ellipsoids shown at 50 % probability). Reproduced from references 116 and 115 respectively.

Another major class of Mn_4 SMMs has the distorted cubane core, $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_3(\mu_3\text{-O})_3(\mu_3\text{-X})]^{6+}$, shown in Figure 7.10, where one vertex of the cubane is occupied by an X group (halide, OH , OMe , O_2CR , N_3 or NO_3) and the Mn^{IV} centre resides at the opposite vertex of the cubane.¹⁸ $[\text{Mn}_4\text{O}_3(\text{OAc})_4(\text{dbm})_3]$ (Figure 7.11(a)) has one $\eta^1, \mu_3\text{-OAc}^-$, three $\mu\text{-OAc}^-$ ligands and three chelating dbm^- ligands.^{18,117} The benzoate analogue, $[\text{Mn}_4\text{O}_3(\text{O}_2\text{CPh})_4(\text{dbm})_3]$ (Figure 7.11(b)) is less symmetrical, having an $\eta^2, \mu_3\text{-O}_2\text{CPh}$ group, owing to the larger size and resultant steric hindrance of the benzoate ligand.

Interestingly, this distorted cubane core type can be identified at the centre of Mn_{12} -acetate and related complexes, where $\text{X} = \mu_3\text{-O}^{2-}$ and all Mn centres are Mn^{IV} .

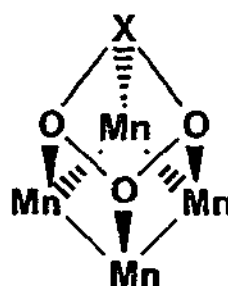


Figure 7.10 Distorted cubane core unit of $[\text{Mn}_4(\mu_3\text{-O})_3(\mu_3\text{-X})]^{6+}$.

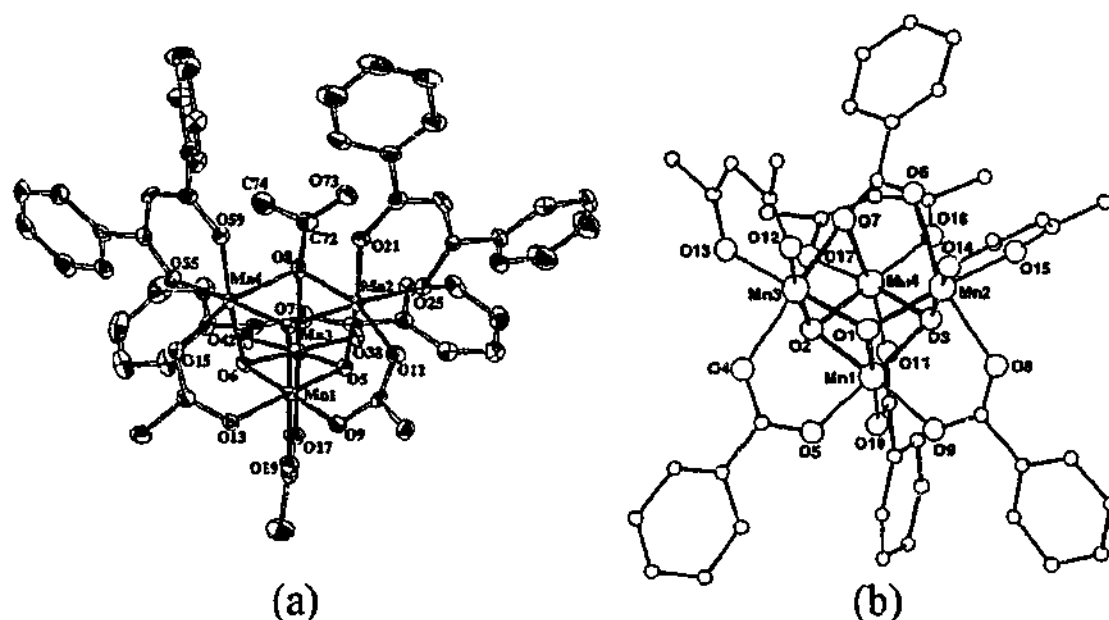


Figure 7.11 The crystal structures of $[\text{Mn}_4\text{O}_3(\text{O}_2\text{CR})_4(\text{dbm})_3]$ $\text{R} = \text{Me}$ (a) and Ph (b), with the central cubanes and surrounding Mn-O bonds highlighted (black). Reproduced from reference 18.

Some examples of Mn_4 clusters with less common structural types are described below. Using a ligand related to hmp^- , Yoo *et al.*¹¹⁵ reported a $\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_2$ complex, $[\text{Mn}_4(6\text{-Me-hmp})_6\text{Cl}_4] \cdot 4\text{H}_2\text{O}$ (6-Me-hmpH = 6-methyl-2-hydroxymethylpyridine), which has four manganese ions arranged in a 'bent chain' (Figure 7.12). A ladder-like $[\text{Mn}_4\text{O}_2]$ core is present in a $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_3$ complex, $[\text{Mn}_4\text{O}_2(\text{OMe})_3(\text{O}_2\text{CPh})_2\text{L}_2(\text{MeOH})](\text{ClO}_4)_2$ (Figure 7.13), where $\text{L} = 1,2\text{-bis}(2,2'\text{-bipyridine-6-yl})\text{ethane}$. This complex is an SMM with an $S = 7/2$ ground state and axial zero-field splitting parameter $D = -0.77 \text{ cm}^{-1}$.¹¹⁸

Ladder-like cores with the same ligand, L, have been observed previously in the Fe^{III} complexes $[\text{Fe}_6\text{O}_4\text{Cl}_4(\text{O}_2\text{CPh})_4\text{L}_2]^{2+}$ and $[\text{Fe}_6\text{O}_6(\text{O}_2\text{CPh})_3(\text{H}_2\text{O})_2\text{L}_2]^{3+}$.^{119,120}

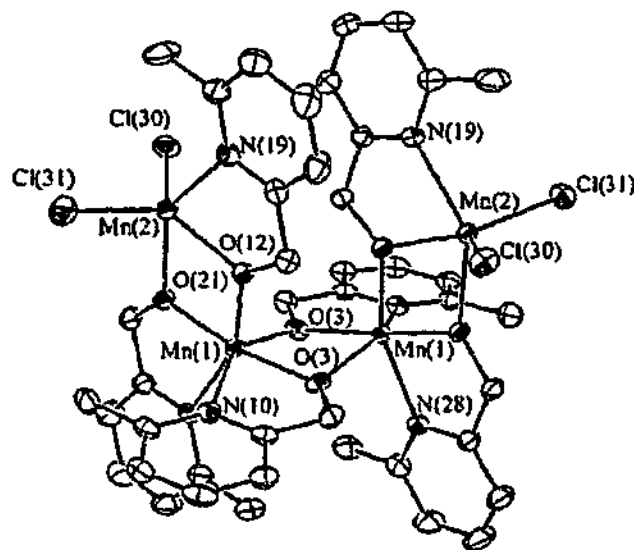


Figure 7.12 The crystal structure of $[\text{Mn}_4(6\text{-Me-hmp})_6\text{Cl}_4]\cdot 4\text{H}_2\text{O}$ (reproduced from reference 115).

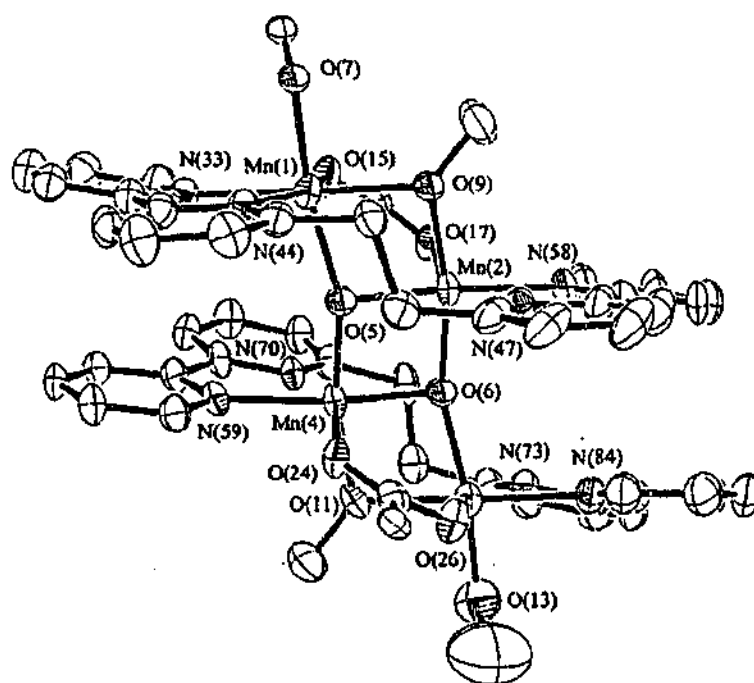


Figure 7.13 The crystal structure of $[\text{Mn}_4\text{O}_2(\text{OMe})_3(\text{O}_2\text{CPh})_2\text{L}_2(\text{MeOH})](\text{ClO}_4)_2$, which possesses the ladder-like $[\text{Mn}_4\text{O}_2]$ core (reproduced from reference 118).

7.3.2 Mn_{12} -acetate, its Derivatives and Related Dodecanuclear Manganese Carboxylate Clusters

As stated above, the first complex characterised to be what was later called a single-molecule magnet (SMM), was $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{HOAc} \cdot 4\text{H}_2\text{O}$ (Mn_{12} -acetate) shown in Figure 7.1. The molecule is roughly planar or disc-like in shape. Its structure consists of a central $[\text{Mn}^{\text{IV}}_4(\mu_3\text{-O})_4]^{8+}$ cubane that is linked to an outer perimeter of 8Mn^{III} centres by 8 $\mu_3\text{-O}^{2-}$ ions and 4 $\mu\text{-OAc}^-$ (above and below the disc plane).⁹¹ Peripheral ligation of these 8Mn^{III} centres consist of 8 $\mu\text{-OAc}^-$ (in the plane of the molecule), 8 $\mu\text{-OAc}^-$ (perpendicular to the plane of the molecule) and 4 terminal H_2O ligands. The H_2O ligands are situated on every second Mn^{III} centre, oriented in an 'up-down-up-down' fashion. If we consider only the $\mu_3\text{-O}^{2-}$ bridges between the perimeter Mn^{III} and cubane Mn^{IV} centres, the Mn^{III} centres fall equally into two classes. We can define the 'type I' Mn^{III} centres as the ones with double $\mu_3\text{-O}^{2-}$ bridges to *single* Mn^{IV} centres, whereas 'type II' Mn^{III} centres are defined as those with single $\mu_3\text{-O}^{2-}$ bridges to *two* Mn^{IV} centres. The arrangement of the four H_2O ligands in Mn_{12} -acetate has been given the notation 1:1:1:1, meaning that there is one H_2O ligand per type II Mn^{III} centre.

Mn_{12} -acetate is prepared by a reaction of $\text{Mn}^{\text{II}}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ with KMnO_4 in 60 % (v/v) acetic acid/water, summarised in Equation 7.2, with typical yields of 80 %.^{18,91}



Today, it remains the most comprehensively studied SMM.⁹¹ Many diverse experimental techniques have been used to probe the physical properties of this species.^{24,91,97,121-128}

Very recently, a low temperature (83 K) crystal structure of Mn_{12} -acetate was determined.^{129,130} The original structural determination by Lis¹⁵ at ambient temperature

was solved in the highly symmetric tetragonal space group $I\bar{4}$, hence the molecule is structurally isotropic. The low temperature study gave evidence for effective symmetry reduction of the Mn_{12} -acetate molecules by structural disorder in the peripheral ligands, induced by hydrogen bonding interactions with the disordered lattice acetic acid molecules (Figure 7.14). Up to six Mn_{12} -acetate isomers are potentially present in the crystal lattice (preserving the crystal tetragonal $I\bar{4}$ symmetry), which differ in the number and arrangement of the hydrogen-bonded acetic acid molecules, four having symmetry lower than tetragonal.^{129,130}

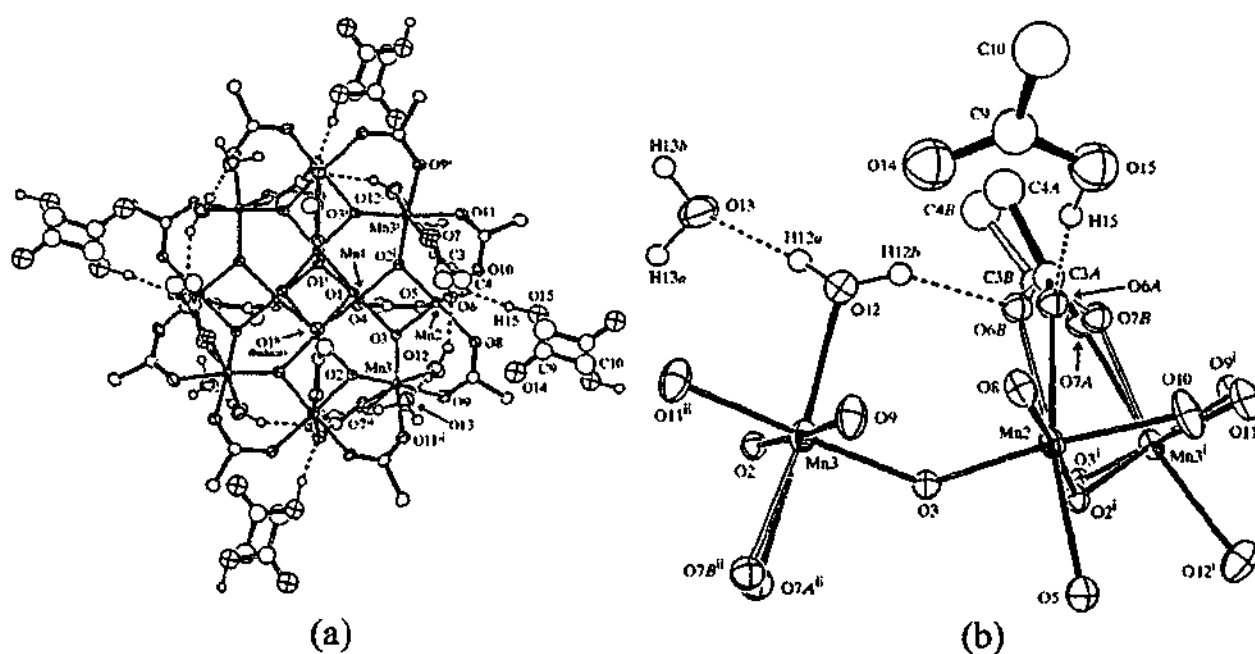


Figure 7.14 (a) The crystal structure of Mn_{12} -acetate with the two positions occupied by the acetic acid molecules shown and hydrogen bonds indicated by dashed lines. (b) The disorder induced in the peripheral acetate ligands by hydrogen bonding interactions with lattice acetic acid, where the two positions are shown (reproduced from reference 129).

In addition to Mn_{12} -acetate, several other carboxylate derivatives with the general formula, $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x] \cdot \text{Solvent}$, have been prepared.⁹¹ Those for which the

structures have been reported are given in Table 7.1. The various carboxylate derivatives are generally obtained by ligand substitution, involving reacting a slurry of Mn_{12} -acetate in a suitable solvent with a large excess of the desired carboxylic acid. The major structural difference is the presence of either three or four H_2O ligands. Examples of the former case, $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CEt})_{16}(\text{H}_2\text{O})_3]$,⁴⁹ and $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CEt})_{16}(\text{H}_2\text{O})_3]\cdot 4\text{H}_2\text{O}$ ¹⁹ (Table 7.1) have three terminal H_2O ligands, resulting in one Mn^{III} centre being five-coordinate. It is believed this is a solid-state effect and that in solution the complexes would have four terminal H_2O ligands.⁹¹ Additionally, differences in the arrangements of the peripheral carboxylate and H_2O ligands have been observed. These are described by the arrangement of the water coordination using the notation given above for Mn_{12} -acetate. For example the *p*-methybenzoate derivatives, $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh-}p\text{-Me})_{16}(\text{H}_2\text{O})_4]\cdot \text{S}$ where $\text{S} = 3\text{H}_2\text{O}$ ($\text{Mn}_{12}\text{-O}_2\text{C-}p\text{-Me-Ph}\cdot 3\text{H}_2\text{O}$) and *p*-Me-PhCO₂H ($\text{Mn}_{12}\text{-O}_2\text{C-}p\text{-Me-Ph}\cdot \text{HO}_2\text{C-}p\text{-Me-Ph}$),^{49,100} are structural isomers with 1:2:1:0 and 1:1:2:0 arrangements of the four terminal H_2O ligands. These structural isomers also exhibit a phenomenon known as Jahn-Teller isomerism (Figure 7.15).^{49,100} While $\text{Mn}_{12}\text{-O}_2\text{C-}p\text{-Me-Ph}\cdot 3\text{H}_2\text{O}$ has all eight Jahn-Teller elongation axes of the perimeter Mn^{III} centres oriented roughly perpendicular to the plane of the molecule, the other isomer ($\text{Mn}_{12}\text{-O}_2\text{C-}p\text{-Me-Ph}\cdot \text{HO}_2\text{C-}p\text{-Me-Ph}$) has an unusual disordered Jahn-Teller elongation axis directed towards a $\mu_3\text{-O}^{2-}$ ion and as such is approximately parallel to the Mn_{12} plane. The AC out-of-phase, χ'' , susceptibility behaviours of these two isomers are shown in Figure 7.16. $\text{Mn}_{12}\text{-O}_2\text{C-}p\text{-Me-Ph}\cdot 3\text{H}_2\text{O}$ exhibits magnetisation relaxation at 4-6 K, whereas $\text{Mn}_{12}\text{-O}_2\text{C-}p\text{-Me-Ph}\cdot \text{HO}_2\text{C-}p\text{-Me-Ph}$ does so at lower temperatures, 2-3 K, which suggests a lower barrier potential to reversal of magnetisation for the latter isomer. As both molecules have identical ground state spin values of $S = 10$, the difference is due to the lesser zero-field splitting parameter, D , in $\text{Mn}_{12}\text{-O}_2\text{C-}p\text{-Me-Ph}\cdot \text{HO}_2\text{C-}p\text{-Me-Ph}$ because it has one of its Jahn-Teller elongation axes

roughly parallel to the plane of the molecule. As the overall magnetic anisotropy is largely due to the vector sum of the individual Mn^{III} single-ion anisotropies, the sum is clearly less for $\text{Mn}_{12}\text{-O}_2\text{C-}p\text{-Me-Ph-HO}_2\text{C-}p\text{-Me-Ph}$.^{49,91} When the 4-6 K and 2-3 K AC χ'' signals are seen simultaneously, both isomers are present in the sample.

Table 7.1 Mn_{12} derivatives, of formula $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_x]\cdot\text{Solvent}$, with reported structures (modified from reference 91).

R	x	Solvent	Water Coordination	Space Group	Ground-State S	Ref
Me	4	2MeCO ₂ H, 4H ₂ O	1:1:1:1	$I\bar{4}$	10	15
Et ^(a)	3	4 H ₂ O	1:1:1 ^(a)	$P\bar{1}$	9	19,49
Et ^(a)	3		1:1:1 ^(a)	$P2_1/c$	9	49
Me, Et	4	2 H ₂ O, 4 EtCO ₂ H	1:1:1:1	$I4m$	10	131
CH ₂ Bu ^f	4	CH ₂ Cl ₂ , MeNO ₂	1:2:1:0	$P\bar{1}$	10	26
Ph	4		2:2:0:0	$P\bar{1}$	10	16,29
Ph	4	2 PhCO ₂ H	2:2:0:0	$Fdd2$	10	132
<i>p</i> -Me-Ph	4	<i>p</i> -Me-PhCO ₂ H	1:2:1:0	$C2/c$	10	49
<i>p</i> -Me-Ph	4	3 H ₂ O	1:1:2:0	$I2/a$	10	49
<i>p</i> -Cl-Ph	4	8 CH ₂ Cl ₂	2:2:0:0	$C2/c$	10	49
<i>m</i> -Cl-Ph ^(b)	3	<i>m</i> -Cl-PhCO ₂ H	1:1:2 ^(b)	$P\bar{1}$	9	133
<i>o</i> -Cl-Ph	4	CH ₂ Cl ₂ , 5 H ₂ O	1:1:2:0	$Pnn2$	10	134
CH ₂ Ph	4		1:2:1:0	$P\bar{1}$	10	26
CH ₂ Cl	4	2 CH ₂ Cl ₂ , 6 H ₂ O	1:1:1:1	$C2/c$	10	135
CH ₂ Br	4	4 CH ₂ Cl ₂	1:1:1:1	$I4_1/a$	10	135
CHCHCH ₃	4	H ₂ O	1:1:1:1	$Ibca$	10	136

^(a) Since there are only three terminal H₂O ligands, one of the Mn^{III} centres is five-coordinate.

^(b) Formula is actually $[\text{Mn}_{12}\text{O}_{12}(\textit{m}\text{-Cl-PhCO}_2)_{15}(\textit{m}\text{-Cl-PhCO}_2\text{H})(\text{H}_2\text{O})_3]\cdot\textit{m}\text{-Cl-PhCO}_2\text{H}$, where the terminal *m*-Cl-PhCO₂H and 3 H₂O ligands are in a 1:1:2:0 arrangement.

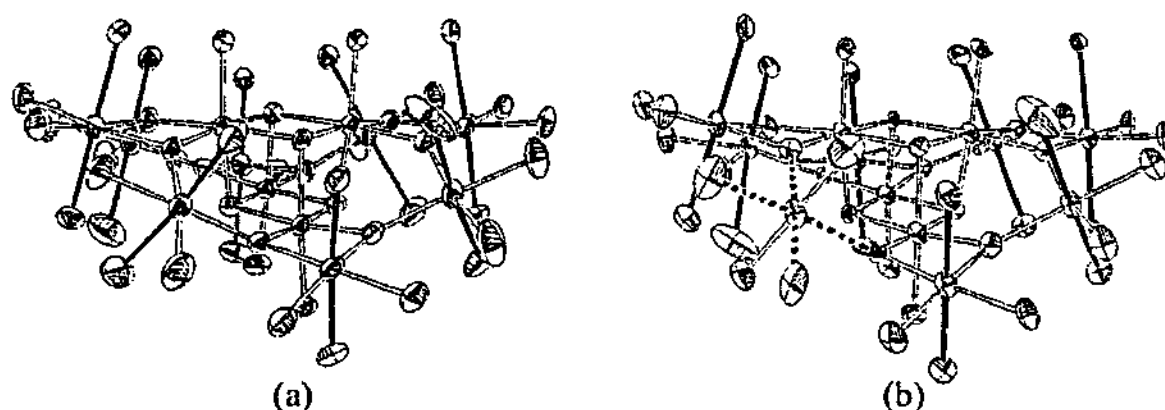


Figure 7.15 Side-on views of the core structures of (a) $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh-}p\text{-Me})_{16}(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ and (b) $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh-}p\text{-Me})_{16}(\text{H}_2\text{O})_4] \cdot (p\text{-Me-PhCO}_2\text{H})$. The coordination geometries around each Mn atom are shown. Each of the eight Mn^{III} centres shows Jahn-Teller (JT) elongation. For (a) these are indicated by solid lines, and for (b) the JT elongation axis, dashed line, pointed at an O^{2-} is unusual. There are two dashed lines because the molecule displays a crystallographic C_2 axis disorder (reproduced from reference 49).

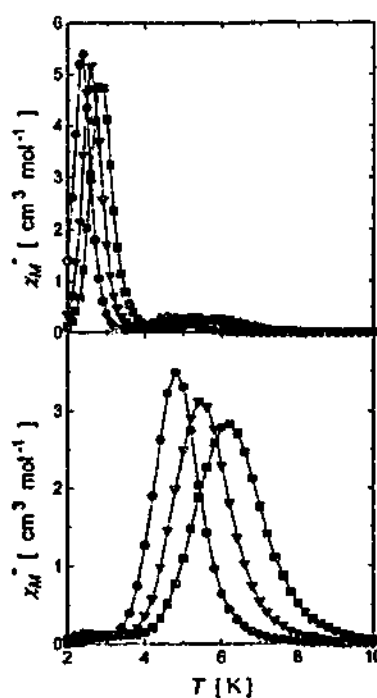


Figure 7.16 Plots of χ'' versus temperature for $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh-}p\text{-Me})_{16}(\text{H}_2\text{O})_4] \cdot (p\text{-Me-PhCO}_2\text{H})$ (upper) and $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh-}p\text{-Me})_{16}(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ (lower) for three different field frequencies (reproduced from reference 49).

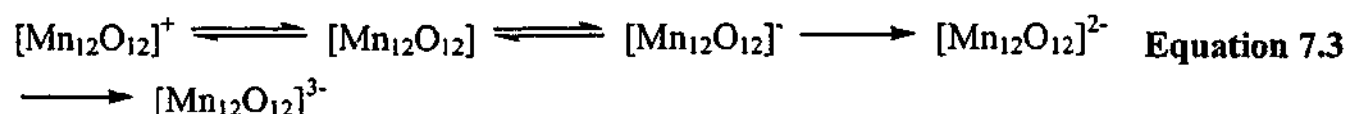
A small number of mixed-carboxylate derivatives have also been prepared, including $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_8(\text{O}_2\text{CR}')_8(\text{H}_2\text{O})_3]\cdot\text{S}$, where $\text{R} = \text{CHCl}_2$, $\text{R}' = \text{CH}_2\text{Bu}'$, $\text{S} = \text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}$ and $\text{R} = \text{CHCl}_2$, $\text{R}' = \text{Et}$, $\text{S} = \text{CH}_2\text{Cl}_2$, by a 1:1 reaction of the corresponding homocarboxylate species.⁶⁸ In these Mn_{12} derivatives site-specific ligand substitution was observed, i.e. the O_2CR groups were found at the axial positions and the $\text{O}_2\text{CR}'$ groups were at the equatorial sites. This was rationalised on the basis of the relative basicities of the different carboxylate groups. It was found the less basic carboxylates would preferentially substitute at the axial Jahn-Teller elongated sites where $\text{Mn}-\text{O}$ bonds were weaker and consequently ligands more easily displaced.

Several Mn_{12} derivatives have been reported with non-carboxylate ligands. Christou *et al.*⁶⁹ prepared the complexes $[\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CR})_{12}(\text{H}_2\text{O})_4]\cdot\text{S}$, where $\text{R} = \text{CH}_2\text{Bu}'$, $\text{S} = \text{MeNO}_2$ and $\text{R} = \text{Ph}$, $\text{S} = 3\text{H}_2\text{O}$, by reacting the corresponding carboxylate derivatives with nitric acid in MeCN. In those complexes the four NO_3^- ligands take the place of four axial $\mu\text{-OAc}^-$ groups. The nitrate derivatives exhibit almost identical magnetic behaviour to their corresponding homocarboxylate clusters. The diphenylphosphinate derivative also reported by Christou *et al.*, $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_8(\text{O}_2\text{PPh}_2)_8(\text{H}_2\text{O})_4]$, was prepared by reacting eight equivalents of $\text{Ph}_2\text{PO}_2\text{H}$ with Mn_{12} -acetate in MeCN.¹³⁷ The eight $\mu\text{-O}_2\text{PPh}_2$ groups replace the acetate groups at four of the axial $\text{Mn}^{\text{III}}\text{--Mn}^{\text{III}}$ and four of the equatorial $\text{Mn}^{\text{III}}\text{--Mn}^{\text{III}}$ sites. In a similar situation to the *p*-methylbenzoate derivatives described above, three Jahn-Teller isomers of this mixed acetate/diphenylphosphinate cluster were observed. Similarly, Kuroda-Sowa *et al.*⁶⁷ recently reported a diphenylphosphate derivative, $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{P}(\text{OPh})_2)_4(\text{O}_2\text{CPh})_{12}(\text{H}_2\text{O})]$, by reacting the benzoate cluster with four equivalents of $(\text{PhO})_2\text{PO}_2\text{H}$ in CH_2Cl_2 . The four $\mu\text{-O}_2\text{P}(\text{OPh})_2$ groups substitute at four axial $\text{Mn}^{\text{III}}\text{--Mn}^{\text{III}}$ positions. The benzoate groups in

the axial $\text{Mn}^{\text{IV}}-\text{Mn}^{\text{III}}$ sites were not substituted, hence site specific ligand replacement or abstraction occurred.

A number of heterometallic analogues have been prepared with essentially the same core structure as Mn_{12} -acetate. These include $[\text{Mn}_8\text{Fe}_4\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4]$,³⁰ and $[\text{Mn}_{11}\text{CrO}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4]$.¹³⁸ The former complex is prepared by reacting $\text{Fe}(\text{OAc})_2$ with KMnO_4 in 60 % aqueous acetic acid. The structure has alternating Mn^{III} and Fe^{III} centres in the perimeter metal sites. The ground state spin, $S = 2$, is much lower than Mn_{12} -acetate, but the axial zero-field splitting parameter is much larger, being $D = -1.8 \text{ cm}^{-1}$. However, the authors did not perform AC susceptibility measurements and did not discuss slow relaxation of magnetisation. The Mn_{11}Cr analogue was obtained by reacting $\text{K}_2\text{Cr}_2\text{O}_7$ with $\text{Mn}(\text{OAc})_2$ in aqueous acetic acid, and was reported to have the Cr^{III} centre occupying 1/4 of one of the two crystallographically independent Mn^{III} atoms. The third crystallographically independent Mn site is Mn^{IV} . A ground state spin of $S = 8$ was found for this analogue.

An interesting feature of Mn_{12} clusters is that they remain intact in solution as shown by ^1H NMR spectroscopic measurements on the acetate, propionate and benzoate derivatives.^{19,49,91,139} The high stability of the Mn_{12} clusters in solution has led to the study of their redox properties. For instance, Mn_{12} -acetate exhibits four redox processes in acetonitrile, which are summarised in Equation 7.3.¹⁶



Consequently, several reduced Mn_{12} species have been reported.^{19,28,50,51,140,141} The first reduction potential is low enough that mild reducing reagents such as iodide have been used to prepare the singly reduced mono-anionic species, $[\text{Mn}_{12}]^-$. For example, the

complexes $(\text{Ph}_4\text{P})[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ (where $\text{R} = \text{Et}, \text{Ph}$),^{19,28,50} were obtained by treating the neutral species with Ph_4PI .⁹¹ The $\text{R} = \text{Et}$ anion has been shown to be trapped valence $\text{Mn}^{\text{IV}}_4\text{Mn}^{\text{III}}_7\text{Mn}^{\text{II}}$,¹⁹ where one of the perimeter Mn^{III} centres is reduced to Mn^{II} . These species have a half-integer ground state of $S = 19/2$, appreciable magnetoanisotropy ($D = -0.62 \text{ cm}^{-1}$) and like the neutral species display slow relaxation of magnetisation. A small number of singly reduced species have been reported with paramagnetic cations, including $[m\text{-MPYNN}][\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{16}(\text{H}_2\text{O})_4]$ (where $m\text{-MPYNN}^+ = m\text{-N-methylpyridinium nitronyl nitroxide}$),¹⁴⁰ and $[\text{Fe}(\text{L})_2][\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{F}_5)_{16}(\text{H}_2\text{O})_4]$, (where $\text{L} = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5$).^{70,142} The former cluster ($S = 19/2$) has enhanced magnetisation relaxation due to presence of the organic radical cation ($S = 1/2$). Unlike the previously mentioned $[\text{Mn}_{12}]^-$ species, the clusters with the metallocene cations have ground states of $S = 21/2$. No significant change was observed in the magnetisation relaxation.^{70,91} Like the non-reduced species, the $[\text{Mn}_{12}]^-$ clusters display magnetic hysteresis with steps, including a step at zero field. The occurrence of zero-field quantum tunnelling was not predicted for non-integer ground state spin species.

By using stronger electron withdrawing carboxylate groups, the electron density on the Mn centres is decreased, and hence the first and second reduction potentials are lowered.⁵¹ Consequently, several $[\text{Mn}_{12}]^{2-}$ species have been obtained using I^- as the reducing agent, as employed for the $[\text{Mn}_{12}]^-$ species (*vide supra*). The addition of two equivalents of Ph_4PI to the corresponding $[\text{Mn}_{12}]^-$ species led to the compounds $(\text{Ph}_4\text{P})_2[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_x]$, where $\text{R} = \text{CHCl}_2$, $x = 3$; $\text{R} = \text{C}_6\text{F}_5$, $x = 4$ and $\text{R} = \text{C}_6\text{H}_3\text{-2,4-(NO}_2)_2$, $x = 4$.⁵¹ These species are trapped valence, $\text{Mn}^{\text{IV}}_4\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}$, where both Mn^{II} centres are located on the Mn_8 perimeter. SMM behaviour is retained with $S = 10$ ground states.

Very recently Boskovic and Christou *et al.*^{48,143} reported a new class of Mn_{12} carboxylate clusters of formula $[\text{Mn}_{12}\text{O}_8\text{X}_4(\text{O}_2\text{CPh})_8\text{L}_6]$, where $\text{X}^- = \text{Cl}$ and $\text{L} = \text{hmp}^-$ (2-(hydroxymethyl)pyridinato) or hep^- (2-(hydroxyethyl)pyridinato); $\text{X}^- = \text{Br}$ and $\text{L} = \text{hep}^-$. These clusters consist of an isomeric $[\text{Mn}^{\text{III}}_{10}\text{Mn}^{\text{II}}_2(\mu_4\text{-O})_4(\mu_3\text{-O})_4(\mu\text{-O})_8(\mu_3\text{-X})_2]$ core but with differing peripheral ligation. The eight μ_4 - and μ_3 -O atoms are O^{2-} ions and the μ -O atoms are provided by the hmp^- or hep^- ligands. The crystal structure of $[\text{Mn}_{12}\text{O}_8\text{Cl}_4(\text{O}_2\text{CPh})_8(\text{hep})_6]$ is shown in Figure 7.17. The Mn^{II} atoms are the 'end' Mn centres (Mn6 and Mn6' in Figure 7.17). For $\text{X}^- = \text{Cl}$ and $\text{L} = \text{hmp}^-$ the complex is an SMM with $S = 6$ or 7, and has out-of-phase, χ'' , signals at higher temperatures than those of the previous Mn_{12} species above. However, for $\text{X}^- = \text{Cl}$ or Br and $\text{L} = \text{hep}^-$, the molecules are low spin with $S = 0$ ground states.

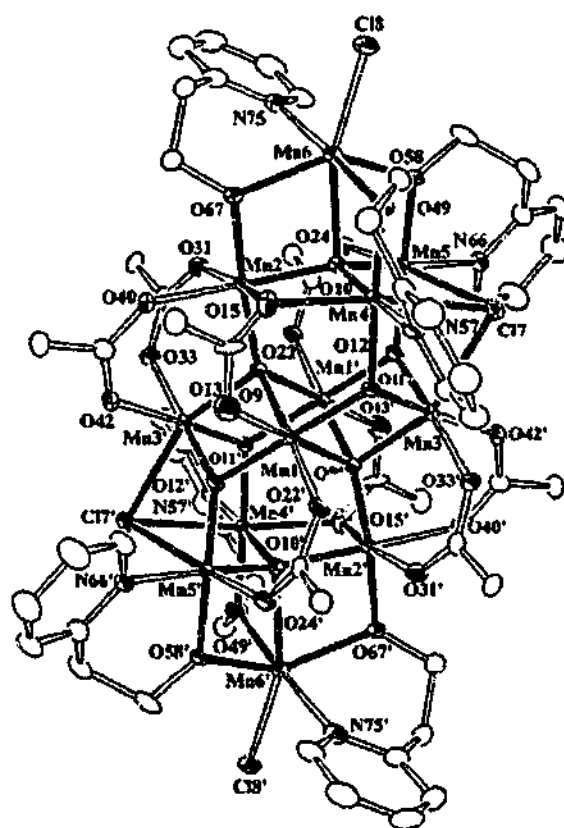


Figure 7.17 The crystal structure of $[\text{Mn}_{12}\text{O}_8\text{Cl}_4(\text{O}_2\text{CPh})_8(\text{hep})_6]$ (thermal ellipsoids shown at 50 % probability) reproduced from reference 48.

7.3.3 Other Manganese Cluster Nuclearities

The most common metal nuclearities for manganese oxo bridged clusters and consequently SMMs are 4 and 12. However, there is a wide range of species with different nuclearities and interesting structures, some of which are SMMs. Presented below are some examples of the following nuclearities known to date, which are (besides Mn_4 and Mn_{12}): Mn_{6-11} , Mn_{13} , Mn_{14} , Mn_{16} , Mn_{18} , Mn_{21} , Mn_{26} and Mn_{30} .

The first hexanuclear Mn cluster was reported by Thornton *et al.* in 1986.¹⁴⁴ $[\text{Mn}_6\text{O}_2(\text{HO}_2\text{CCMe}_3)_4(\text{O}_2\text{CCMe}_3)_{10}]$ ($4\text{Mn}^{\text{II}}, 2\text{Mn}^{\text{III}}$) consists of two MnO_4 tetrahedra sharing an edge with the four other Mn atoms connected to the core unit *via* pivalate bridges. In 1988 Caneschi and Gatteschi *et al.*¹⁴⁵ reported a hexanuclear Mn^{II} wheel-like complex with a ground state spin $S = 12$, $[\text{Mn}(\text{hfac})_2(\text{NITPh})]_6$ (where Hhfac = hexafluoroacetylacetone; NITPh = 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl 3-oxide), shown in Figure 7.18. The spin results from antiferromagnetic exchange between the $S = 5/2$ (Mn^{II}) and $S = 1/2$ (NITPh radical) moieties.¹⁰⁵

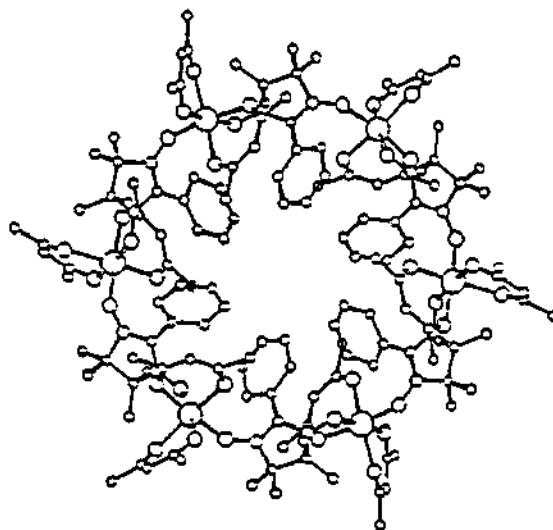


Figure 7.18 The crystal structure of $[\text{Mn}(\text{hfac})_2(\text{NITPh})]_6$ (large spheres represent Mn centres). Reproduced from reference 145.

Recently, Cañada-Vilalta and Christou *et al.*¹⁴⁶ used the dicarboxylate ligand *m*-phenylenedipropionate (mpdp^{2-}), to synthesise, in addition to dinuclear and trinuclear Mn complexes, the hexanuclear cluster $[\text{Mn}_6\text{O}_7(\text{mpdp})_3(2,2'\text{-bipy})_3](\text{ClO}_4) \cdot 3.5\text{MeCN}$, shown in Figure 7.19. The Mn_6 complex was obtained by oxidation of the Mn^{III}_2 species with $(n\text{-Bu}_4\text{N})\text{MnO}_4$ in acetonitrile. The core can be described as being composed of two triangular units, $[\text{Mn}^{\text{IV}}_3(\mu_2\text{-O})_3]^{6+}$ and the oxo-centred $[\text{Mn}^{\text{III}}_3(\mu_3\text{-O})_4]^+$ superimposed with a pseudo- C_3 axis perpendicular to both. This complex possesses an $S = 3/2$ ground state and $D = -0.79\text{ cm}^{-1}$.¹⁴⁶ The authors did not report AC susceptibility data, and did not discuss whether it is an SMM.

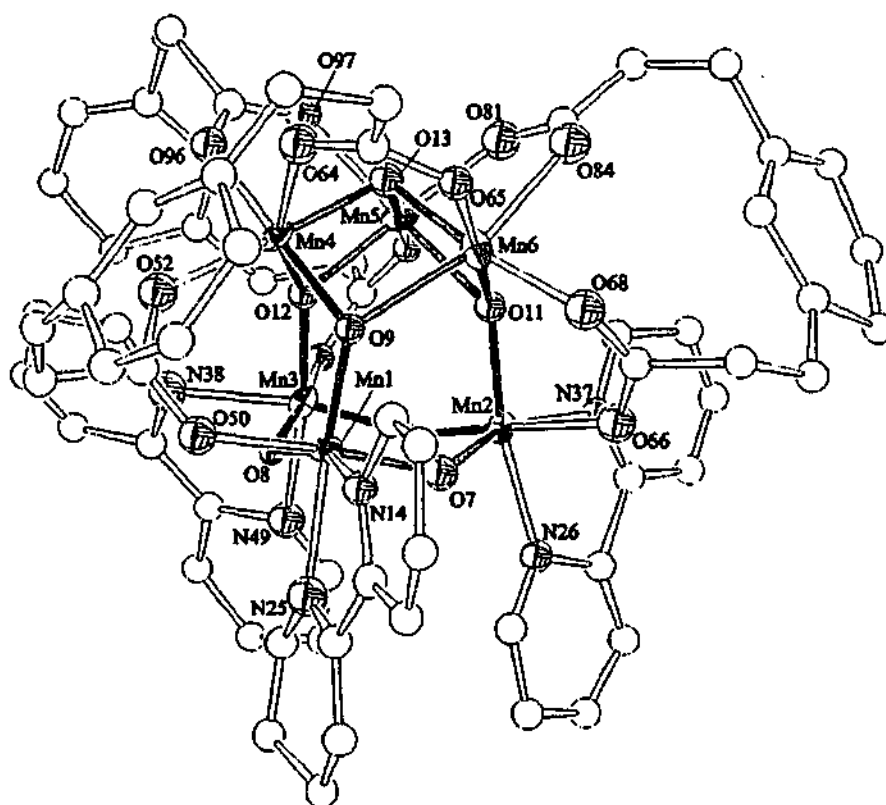


Figure 7.19 Crystal structure (of one of the enantiomeric cations of) $[\text{Mn}_6\text{O}_7(\text{mpdp})_3(2,2'\text{-bipy})_3](\text{ClO}_4) \cdot 3.5\text{MeCN}$ with the $[\text{Mn}^{\text{IV}}_3(\mu_2\text{-O})_3]^{6+}$ (lower) and $[\text{Mn}^{\text{III}}_3(\mu_3\text{-O})_4]^+$ (upper) units are highlighted (reproduced from reference 146).

Examples of another structural family of Mn_6 carboxylate clusters include $[\text{Mn}_6\text{O}_2(\text{O}_2\text{CPh})_{10}(\text{py})_2(\text{MeCN})_2] \cdot 2\text{MeCN}$,¹⁴⁷ $[\text{Mn}_6\text{O}_2(\text{O}_2\text{CPh})_{10}(\text{py})_4] \cdot \text{Et}_2\text{O}$,¹⁴⁷ $[\text{Mn}_6\text{O}_2(\text{O}_2\text{CPh})_{10}(\text{EtOH})_4(\text{H}_2\text{O})] \cdot \text{EtOH}$,¹⁴⁸ $[\text{Mn}_6\text{O}_2(\text{O}_2\text{C}-3,5-(\text{NO}_2)_2\text{Ph})_{10}(\text{py})_2((\text{Me})_2\text{CO})_2] \cdot 2(\text{Me})_2\text{CO} \cdot 2\text{Et}_2\text{O}$ and $[\text{Mn}_6\text{O}_2(\text{O}_2\text{CPh})_{10}(\text{MeCN})_4]$.¹⁴⁹ Each of these complexes contain a $[\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_2(\mu_4\text{-O})_2]^{10+}$ core (Figure 7.20), which consists of two $\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_2(\mu_4\text{-O})$ oxo-centred tetrahedra sharing the $\text{Mn}^{\text{III}}\text{--Mn}^{\text{III}}$ edge.

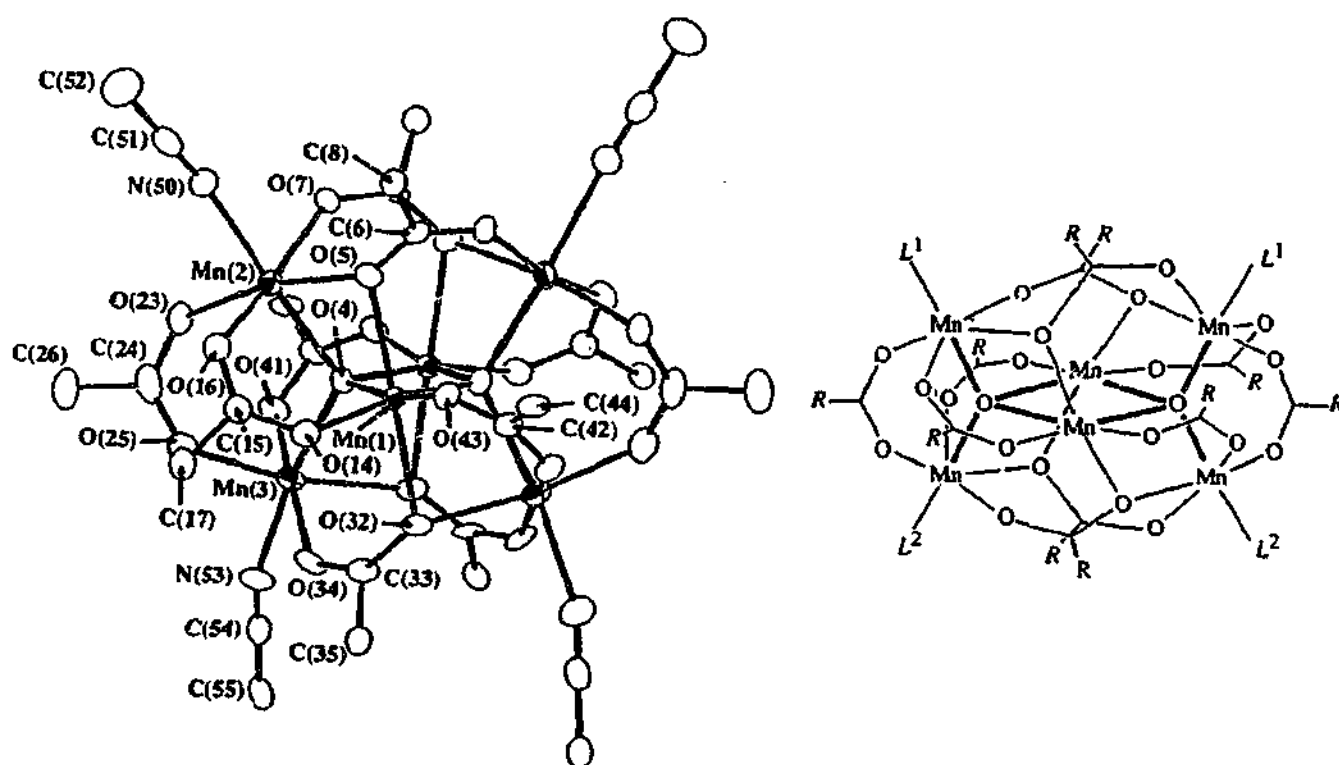


Figure 7.20 The crystal structure of $[\text{Mn}_6\text{O}_2(\text{O}_2\text{CPh})_{10}(\text{MeCN})_4]$ (left) with only the Mn centres shown with octant slices. A schematic of the structure (right), where $\text{R} = \text{Ph}$, $\text{L}^1 = \text{L}^2 = \text{MeCN}$. The $[\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_2(\mu_4\text{-O})_2]^{10+}$ core unit is highlighted. Reproduced from reference 149.

The hexanuclear clusters, $[\text{Mn}_6\text{O}_4\text{X}_4(4,4'\text{-R}_2\text{dbm})_6]$ (where $\text{X} = \text{Cl}^-$, Br^- and $\text{R} = \text{Me}$, Et),^{55,56} are obtained by the slow hydrolysis of the mononuclear species $[\text{Mn}^{\text{III}}(4,4'\text{-R}_2\text{dbm})_2\text{X}]$ in $\text{CH}_2\text{Cl}_2/\text{MeCN}$. The structures, shown in Figure 7.21, contain a $[\text{Mn}^{\text{III}}_6(\mu_3\text{-O})_4]$ core.

$\text{O})_4(\mu_3\text{-X})_4]^{6+}$ core, which consists of a Mn^{III}_6 octahedron whose faces are capped by O^{2-} or Cl^- ions. These complexes have a particularly high $S = 12$ ground state due to being completely ferromagnetic coupled, however as $D \approx 0 \text{ cm}^{-1}$, these molecules do not display SMM behaviour. The lack of an appreciably negative D value is thought to be due to the high symmetry (near T_d) of the complexes, which averages out to zero the individual single-ion anisotropies of the six Jahn-Teller distorted Mn^{III} .⁵⁶

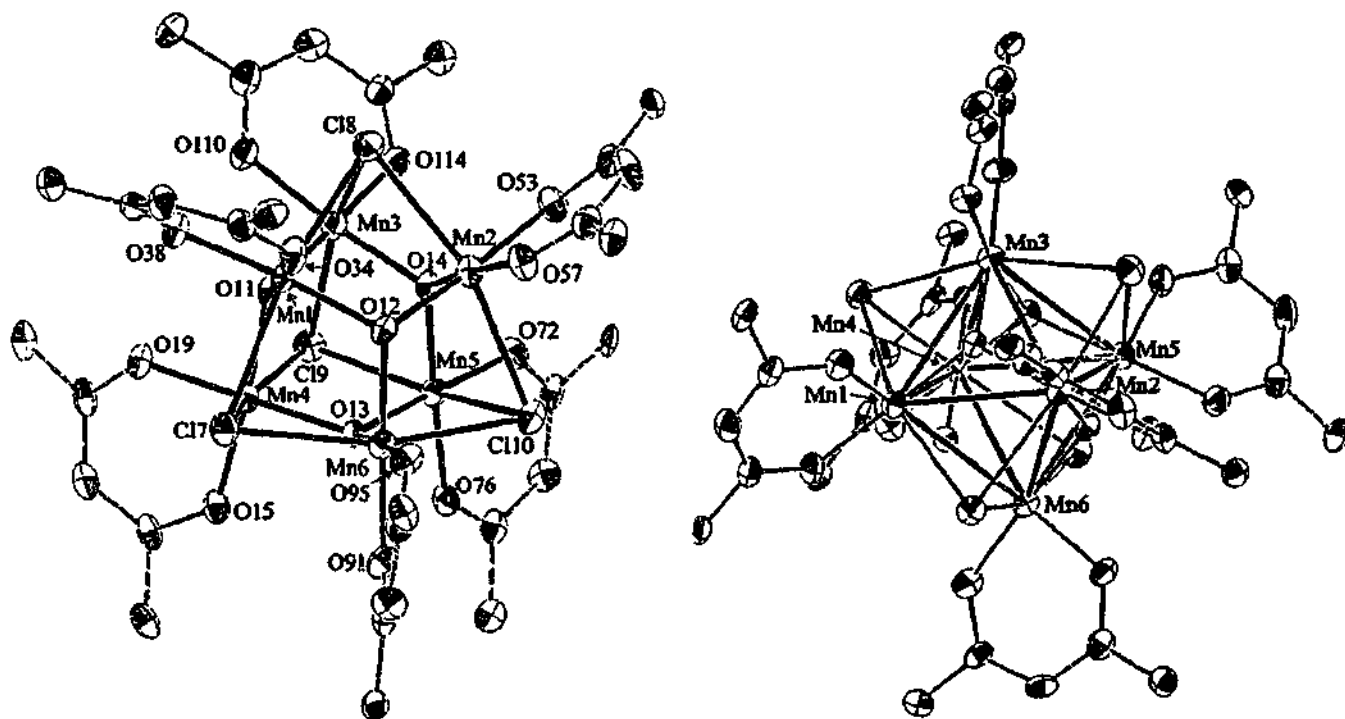


Figure 7.21 Two different representations of the crystal structure of $[\text{Mn}_6\text{O}_4\text{Cl}_4(4,4'\text{-Me}_2\text{dbm})_6]$ (only the *ipso* carbons of the $4,4'\text{-Me}_2\text{dbm}^-$ ligands are shown for clarity). On the left, the near tetrahedron is emphasised by filled bonds. On the right, the Mn-Mn vectors are shown to emphasise the Mn_6 octahedron with O^{2-} and Cl^- ions capping the faces (reproduced from reference 56).

The high ground state value of $S = 12$ has also been observed in the $[\text{Na} \llcorner \text{Mn}^{\text{III}}_6(\text{OMe})_{12}(\text{dbm})_6]^+$ complex.¹⁵⁰ The structure, which is shown in Figure 7.22 is isostructural with the Fe^{III} analogue,^{151,152} and consists of a $[\text{Mn}_6(\text{OMe})_{12}]$ ring with the 12-

metallacrown-6 structure that hosts a Na^+ ion in a trigonally distorted octahedral environment. Interestingly, though not unusually, the Mn/Na/O core adopts the CdI_2 type layered structure.

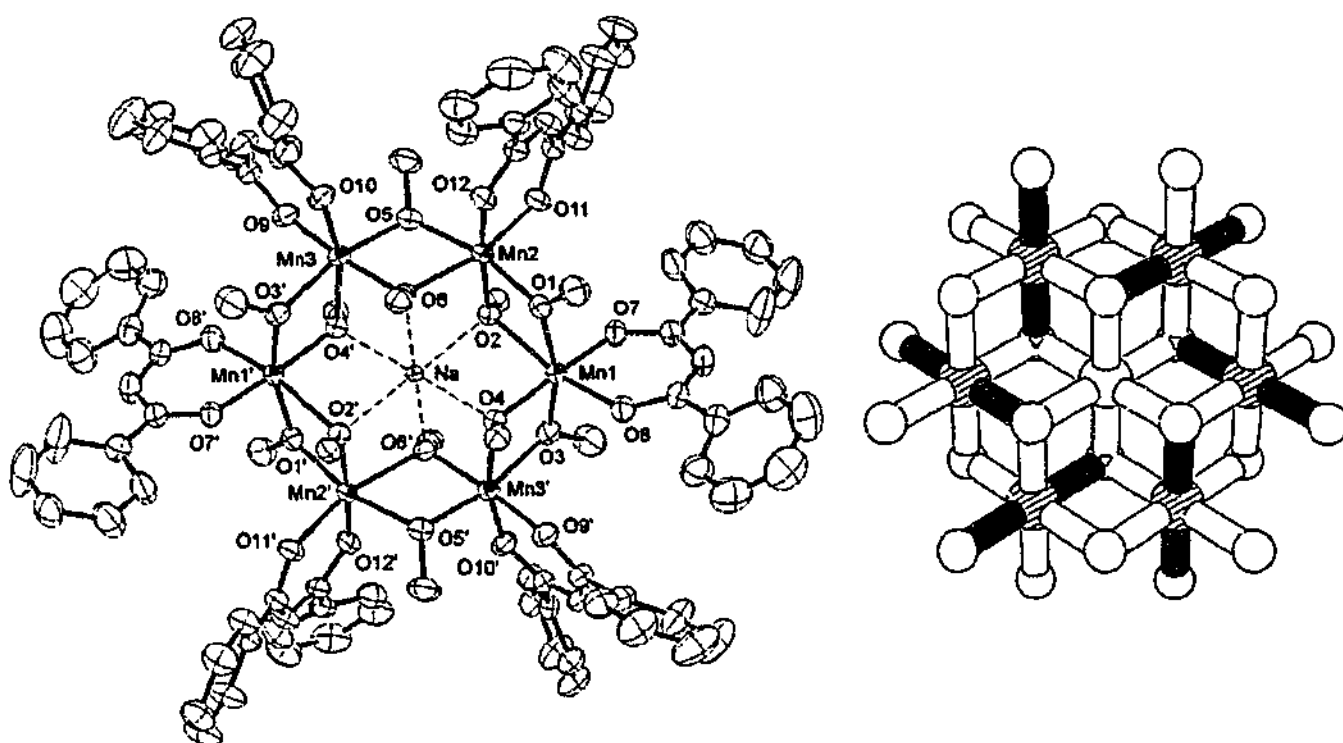


Figure 7.22 The crystal structure of $[\text{NaMn}^{\text{III}}_6(\text{OMe})_{12}(\text{dbm})_6]^+$ (left) and a schematic representation of the CdI_2 type Mn/Na/O core (right), where the Mn^{III} Jahn-Teller elongated bonds are highlighted (black). Reproduced from reference 150.

The Mn_7 compound $(\text{Et}_4\text{N})[\text{Mn}_7(\text{OH})_3\text{Cl}_3(\text{hmp})_9]\text{Cl}(\text{MnCl}_4)$ (4Mn^{II} , 3Mn^{III}), contains a heptanuclear complex that has the same layered CdI_2 core structure of the previous NaMn_6 complex, where the central Na^+ ion is replaced by a Mn^{II} ion.⁵⁷ The crystal structure of the cationic complex is shown in Figure 7.23. In addition to the central Mn(1) being Mn^{II} , Mn(3), Mn(5) and Mn(7) are also Mn^{II} , with the remainder being Mn^{III} . The high ground state value of $S \geq 10$ (10 or 11 from two equally good fits to magnetisation vs. field data) possessed by this complex, which is less than the fully ferromagnetically coupled value of 16, is reported to result from competing exchange

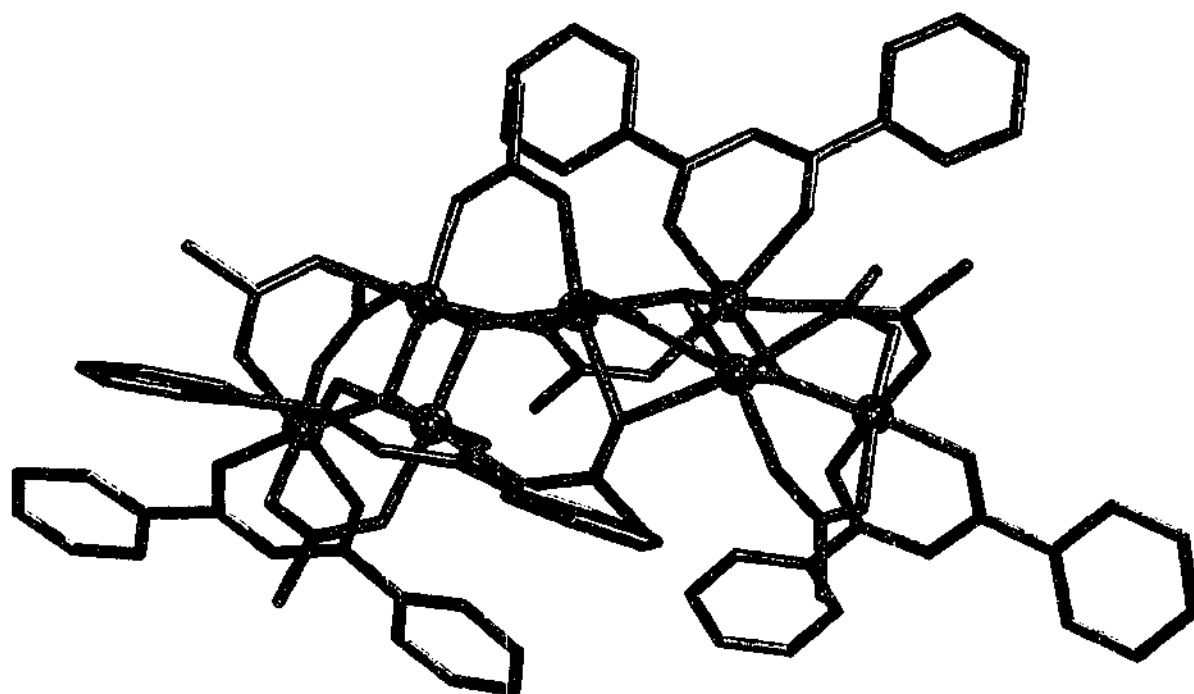


Figure 7.24 The crystal structure of $[\text{Mn}_7\text{O}_4(\text{OAc})_{10}(\text{dbm})_4]^-$. The spheres represent Mn ions. Image rendered from CSD simulated SHELX res file from entry JOTTER.

Many octanuclear manganese clusters have been reported, most of which can be described as having formed by the aggregation of smaller $[\text{Mn}_4\text{O}_2]$ units. $[\text{Mn}^{\text{III}}_8\text{O}_4(\text{OAc})_{12}(\text{pic})_4]$ (where pic^- = picolate), shown in Figure 7.25, is obtained by treatment of $(n\text{-Bu}_4\text{N})[\text{Mn}^{\text{III}}_4\text{O}_2(\text{OAc})_7(\text{pic})_2]$, which has the bent butterfly structure, with Me_3SiCl , leading to selective abstraction of the unique Jahn-Teller labilised 'body' $\mu\text{-OAc}$ and dimerization of the resulting fragment to form the octanuclear species.^{58,154} This octanuclear species can also be obtained by reaction of $[\text{Mn}^{\text{IV}}_2\text{O}_2(\text{pic})_4]$ with $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$.⁵⁸

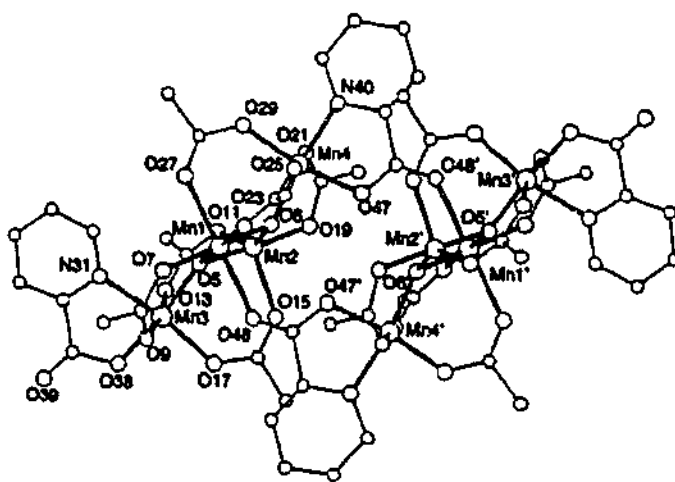


Figure 7.25 The crystal structure of $[\text{Mn}^{\text{III}}_8\text{O}_4(\text{OAc})_{12}(\text{pic})_4]$ with the two $[\text{Mn}_4\text{O}_2]$ butterfly units highlighted (black). Reproduced from reference 154.

Similarly, treatment of $(n\text{-Bu}_4\text{N})[\text{Mn}^{\text{III}}_4\text{O}_2(\text{O}_2\text{CPh})_9(\text{H}_2\text{O})]$ with 2,2-diethylmalonate (Et_2mal) leads to the formation of the mixed-valent $(n\text{-Bu}_4\text{N})[\text{Mn}_8\text{O}_4(\text{O}_2\text{CPh})_{12}(\text{Et}_2\text{mal})_2(\text{H}_2\text{O})_2]$, $(2\text{Mn}^{\text{II}}, 6\text{Mn}^{\text{III}})$.⁵⁹ The structure, shown in Figure 7.26, contains a $[\text{Mn}_8\text{O}_4]^{14+}$ core that consists of two $[\text{Mn}_4\text{O}_2]^{7+}$ ($\text{Mn}^{\text{II}}, 3\text{Mn}^{\text{III}}$) butterfly units linked together *via* two $\mu_4\text{-O}^{2-}$ ions.

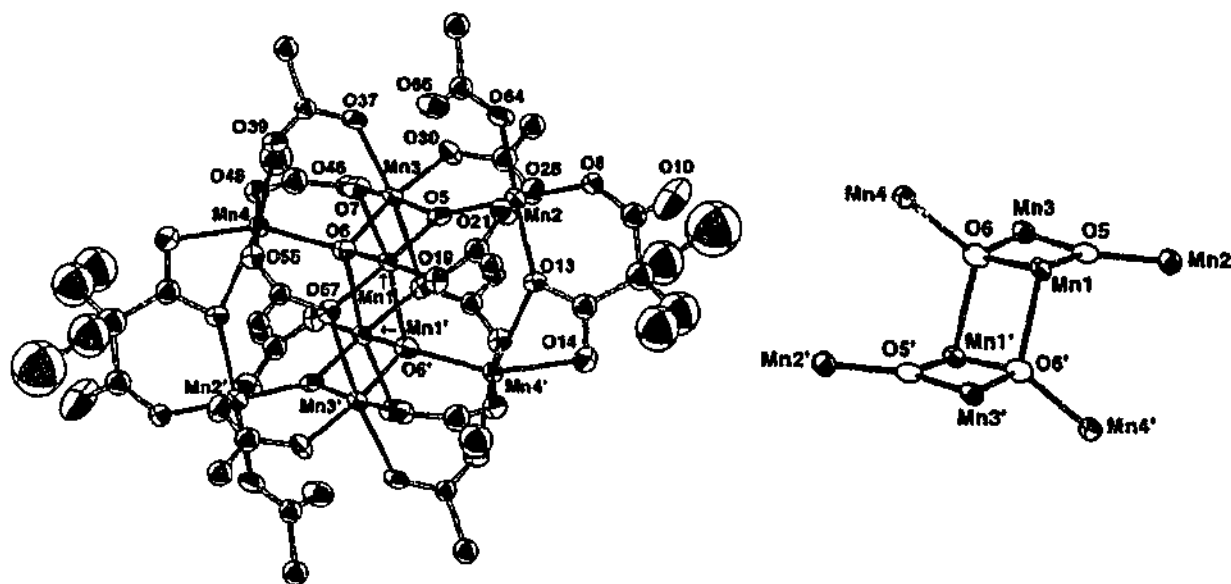


Figure 7.26 The crystal structure of $[\text{Mn}_8\text{O}_4(\text{O}_2\text{CPh})_{12}(\text{Et}_2\text{mal})_2(\text{H}_2\text{O})_2]^{2-}$ (left) and its $[\text{Mn}_8\text{O}_4]^{14+}$ core (right); the Mn^{II} ions are Mn4 and Mn4' (reproduced from reference 59).

Boskovic and Christou *et al.*⁴³ recently reported the octanuclear and nonanuclear Mn complexes, $[\text{Mn}_8\text{O}_2(\text{py})_4(\text{O}_2\text{CEt})_8(\text{L})_2](\text{ClO}_4)_2$ ($6\text{Mn}^{\text{II}}, 2\text{Mn}^{\text{III}}$) and $[\text{Mn}_9(\text{O}_2\text{CEt})_{12}(\text{pdm})(\text{pdmH})_2(\text{L})_2]$ ($7\text{Mn}^{\text{II}}, 2\text{Mn}^{\text{III}}$), which were formed from the reaction of pyridine-2,6-dimethanol (pdmH_2) with the trinuclear species $[\text{Mn}_3\text{O}(\text{O}_2\text{CEt})_6(\text{py})_3](\text{ClO}_4)$ and $[\text{Mn}_3\text{O}(\text{O}_2\text{CEt})_6(\text{py})_3]$ respectively. The pentadentate ligand LH_2 (6-hydroxymethylpyridin-2-yl)-(6-hydroxymethylpyridin-2-ylmethoxy)-methanol), was formed *in situ* from pdmH_2 . The Mn_8 complex (Figure 7.27(a)) contains a $[\text{Mn}^{\text{II}}_6\text{Mn}^{\text{III}}_2(\mu_4\text{-O})_2(\mu_3\text{-O})_4(\mu\text{-O})_4]^{2+}$ core unit that can be described as two distorted cubane units linked together. The Mn_9 complex contains a $[\text{Mn}^{\text{II}}_7\text{Mn}^{\text{III}}_2(\mu_3\text{-O})_6(\mu\text{-O})_6]^{4+}$ core unit, which can likewise be described in terms of two distorted cubanes, but in this case, linked by an additional Mn^{II} centre (Figure 7.27(b)). The Mn_8 cluster has a ground state spin value of $S = 0$, whereas the Mn_9 cluster has an $S = 11/2$ value with $D = -0.11 \text{ cm}^{-1}$ with magnetic hysteresis shown below 0.3 K. Thus, the latter is an SMM.

The family of Mn_8 carboxylate complexes also includes $[\text{Mn}_8\text{O}_6\text{Cl}_6(\text{O}_2\text{CPh})_7(\text{H}_2\text{O})_2]^-$,^{113,155} $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_6(\text{dbm})_2(\text{bpe})]_2$ ($\text{dbmH} =$ dibenzoylmethane, $\text{bpe} = \text{trans-1,2-bis-(4-pyridyl)ethene}$),¹⁵⁶ $[\text{Mn}_8\text{O}_4(\text{O}_2\text{CEt})_{14}(\text{L}_2)_2]^{2+}$ (L_2 is a bis-2,2'-bipyridine ligand),¹⁵⁷ $[\text{Mn}^{\text{II}}_8\text{L}_{12}(\mu_4\text{-O})_2]$ ($\text{LH} =$ 2-amino-3-bromo-5-methylpyridine),¹⁵⁸ the triple helicate $[\text{Mn}_8\text{O}_2(\text{L}^{\text{Pr}})_6]$ ($\text{H}_2\text{L}^{\text{Pr}} =$ 1,1'-(2,6-Bispyridyl)bis-4-methyl-1,3-pentanedione, a pentadentate tritopic ligand),¹⁵⁹ and $[\text{Mn}_8\text{L}_8(\text{HOPr})_4]$ ($\text{H}_2\text{L} =$ diethyl keptinate).¹⁶⁰ These species are not known to display SMM behaviour.

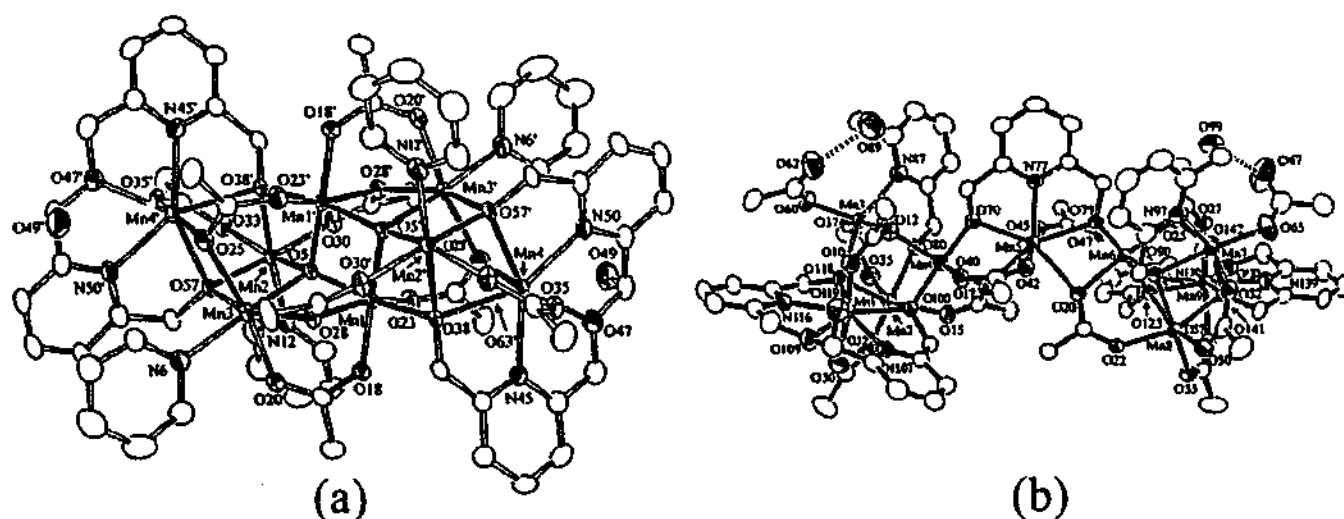


Figure 7.27 The crystal structures of (a) $[\text{Mn}_8\text{O}_2(\text{py})_4(\text{O}_2\text{CEt})_8(\text{L})_2](\text{ClO}_4)_2$ and (b) $[\text{Mn}_9(\text{O}_2\text{CEt})_{12}(\text{pdm})(\text{pdmH})_2(\text{L})_2]$ (right), with the respective core units highlighted (black). Reproduced from reference 43.

Other members of the family of Mn_9 carboxylate complexes include $[\text{Mn}_9\text{O}_4(\text{O}_2\text{CPh})_8(\text{salO})(\text{salOH})_2(\text{py})_2]$ (salOH_2 = salicylic acid, py = pyridine),¹⁶¹ $[\text{Mn}_9\text{M}_2\text{O}_7(\text{O}_2\text{CR})_{15}(\text{X})_2]$ ($\text{M} = \text{Na}^+$, $\text{X} = \text{MeCN}$; $\text{M} = \text{K}^+$, $\text{X} = \text{RCO}_2\text{H}$),^{113,155,162} $[\text{Mn}_9\text{O}_7(\text{O}_2\text{CPh})_{13}(\text{py})_2]$,¹⁶³ and $[\text{Mn}_9\text{O}_7(\text{OAc})_{11}(\text{thme})(\text{py})_3(\text{H}_2\text{O})_2]$ (thmeH_3 = 1,1,1-tris(hydroxymethyl)ethane, 2Mn^{II} , 4Mn^{III} , 3Mn^{IV}).⁴² The last complex, shown in Figure 7.28, formed from the reaction of $[\text{Mn}_3\text{O}(\text{OAc})_6(\text{py})_3]$ with thmeH_3 , has an $S = 17/2$ ground state and frequency dependency of the out-of-phase AC susceptibility signals, and hence is an SMM. It consists of a $[\text{Mn}^{\text{IV}}_3\text{O}]^{10+}$ ring unit held within a larger $[\text{Mn}^{\text{III}}_4\text{Mn}^{\text{II}}_2\text{O}]^{4+}$ ring.

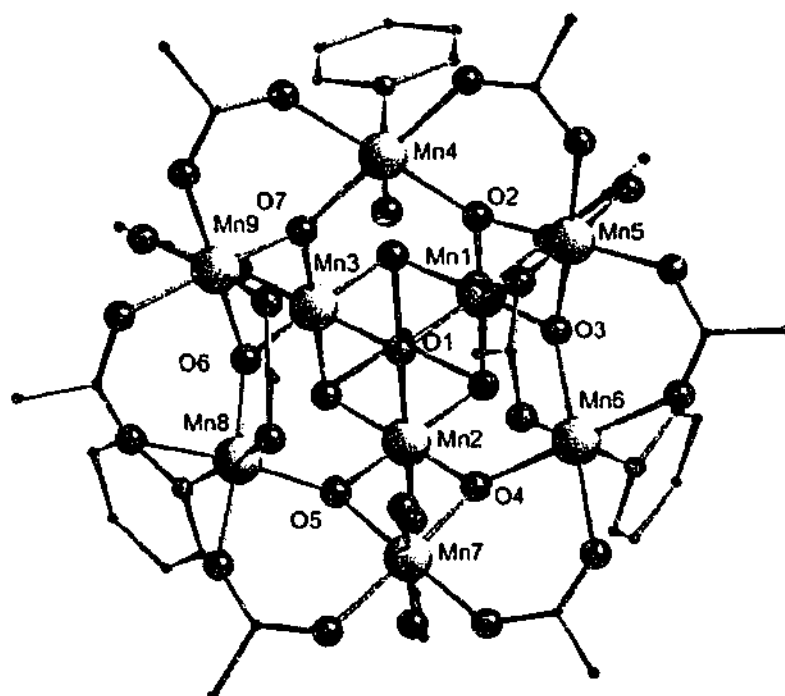
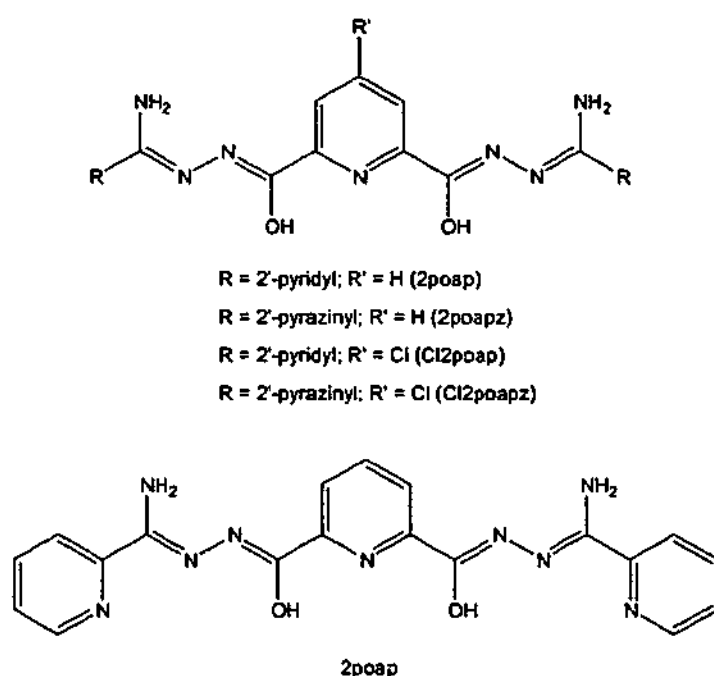


Figure 7.28 The crystal structure of $[\text{Mn}_9\text{O}_7(\text{OAc})_{11}(\text{thme})(\text{py})_3(\text{H}_2\text{O})_2]$ (reproduced from reference 42).

Thompson *et al.*¹⁶⁴⁻¹⁶⁸ have reported a number of novel nonanuclear Mn^{II} 3×3 grid or portcullis-like clusters using tritopic 2poap related ligands (Scheme 7.1). For instance, $[\text{Mn}_9(\text{Cl}_2\text{poap-2H})_6](\text{ClO}_4)_6 \cdot 10\text{H}_2\text{O}$,¹⁶⁸ shown in Figure 7.29, exhibits intra-cluster antiferromagnetic coupling with an $S = 5/2$ ground state. Unlike the majority of the complexes presented in this chapter, these are the products of rational design. This particularly logical approach to designing and making nanoscale cluster complexes, most of which to date show intra-cluster exchange coupling and/or spin-crossover rather than SMM behaviour, is the 'self-assembly' (supramolecular) method of Lehn *et al.*¹⁶⁹⁻¹⁷² and Thompson *et al.*^{173,174} Polytopic ligands are employed which are rigid and able to coordinate two or three (or more) metal ions, which then spontaneously self-assemble into 2×2 (M_4) grids or 3×3 (M_9) grids (*vide supra*).



Scheme 7.1 Tritopic 2poap related ligands and the parent, 2poap.

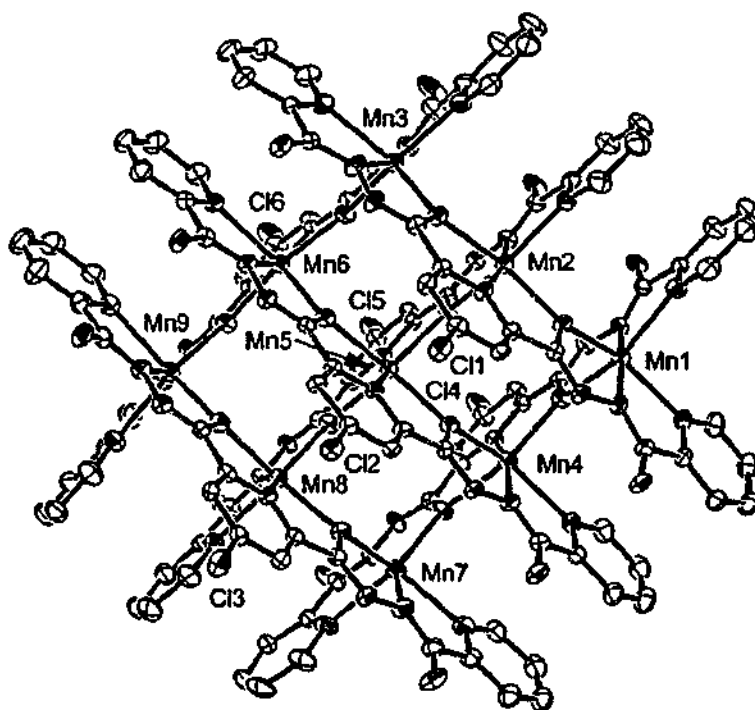


Figure 7.29 The structure of the 3×3 grid cluster $[\text{Mn}_9(\text{Cl2poap-2H})_6]^{6+}$ (reproduced from reference 168).

Several decanuclear Mn clusters have appeared in the literature. These include $[\text{Mn}_{10}\text{O}_4(\text{biphen})_4\text{X}_{12}]^{4-}$ (biphen = 2,2'-biphenoxide, $\text{X} = \text{Cl}^-, \text{Br}^-$),^{44-47,175}

$[\text{Mn}_{10}\text{O}_8(\text{O}_2\text{CPh})_6(\text{chel})_8]$ ($\text{chel} = \text{pic}^-, \text{dbm}^-$),¹⁷⁶ $[\text{Mn}_{10}\text{O}_4(\text{OH})_2(\text{OAc})_8(\text{hmp})_8](\text{ClO}_4)_4$ ($\text{hmpH} = 2\text{-hydroxymethylpyridine}$),¹⁸ $[\text{Mn}_{10}\text{O}_{14}(\text{tren})_6]^{8+}$ ($4\text{Mn}^{\text{III}}, 6\text{Mn}^{\text{IV}}$; $\text{tren} = \text{tris}(2\text{-aminoethyl})\text{amine}$),¹⁷⁷ $[\text{Mn}_{10}\text{O}_2\text{Cl}_8((\text{OCH}_2)_3\text{CMe})_6]^{2-}$ ($2\text{Mn}^{\text{II}}, 8\text{Mn}^{\text{III}}$),¹⁷⁸ and a [30]metallacrown-10 $[\text{Mn}(\text{bzshz})(\text{MeOH})]_{10}$ ($\text{H}_3\text{bzshz} = \text{a pentadentate ligand, } N\text{-phenylsalicylhydrazidine}$).¹⁷⁹ $[\text{Mn}_{10}\text{O}_4(\text{biphen})_4\text{Br}_{12}]^{4-}$ ($4\text{Mn}^{\text{III}}, 6\text{Mn}^{\text{II}}$), shown in Figure 7.30, contains terminal, μ - and $\mu_3\text{-Br}^-$ ions; μ_3 - and $\mu_4\text{-O}^{2-}$ ions; bridging biphen ligands and no carboxylate ligands. The cluster has been characterised as an SMM with an $S = 12$ ground state and negative axial zero-field splitting parameter, $D = -0.037(1) \text{ cm}^{-1}$. It displays slow relaxation of magnetisation below 1 K with a barrier potential to reversal of magnetisation of 7.7 K (5.3 cm^{-1}).⁴⁶

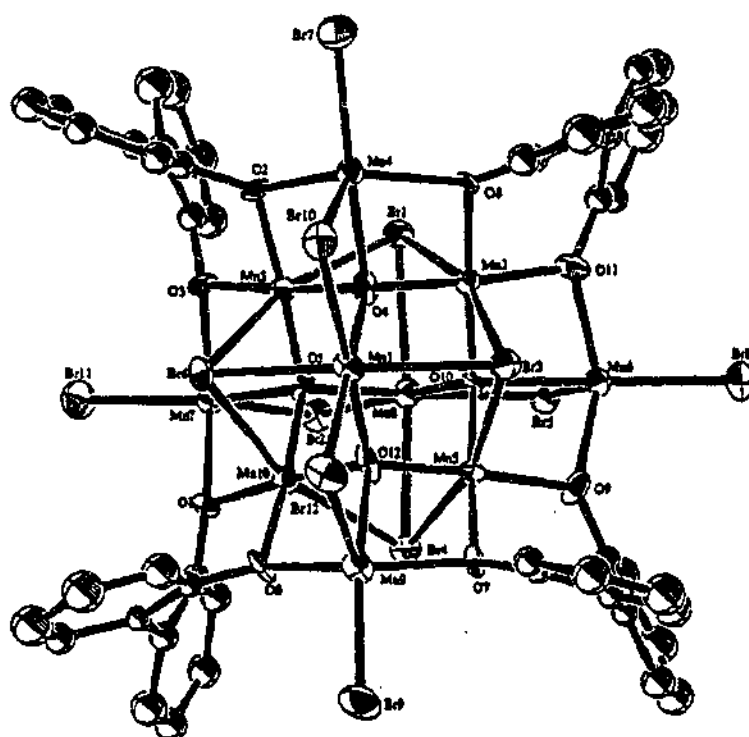


Figure 7.30 The crystal structure of $[\text{Mn}_{10}\text{O}_4(\text{biphen})_4\text{Br}_{12}]^{4-}$ (thermal ellipsoids shown at 50 % probability, hydrogens are omitted for clarity). Reproduced from reference 175.

Further examples of Mn_{10} clusters, $[\text{Mn}_{10}\text{O}_8(\text{O}_2\text{CPh})_6(\text{pic})_8]$ and $[\text{Mn}_{10}\text{O}_8(\text{O}_2\text{CPh})_6(\text{pic})_6(\text{dbm})_2]$, are prepared by reacting $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_6(\text{MeCN})_2(\text{pic})_2]$

with picH or dbmH respectively, in MeCONMe₂ (DMA) and CH₂Cl₂.¹⁷⁶ These two related clusters possess the same [Mn^{III}₁₀(μ₃-O)₆(μ₄-O)₂]¹⁴⁺ core (Figure 7.31), which can be described as a segment of the layered CdI₂ type structure with additional links to six Mn^{III} ions, three above and three below the layered segment. Another example, [Mn₁₀O₄(OH)₂(OAc)₈(hmp)₈](ClO₄)₄ (10Mn^{III}) shown in Figure 7.32, likewise consists of a core related to the layered CdI₂ type structure.

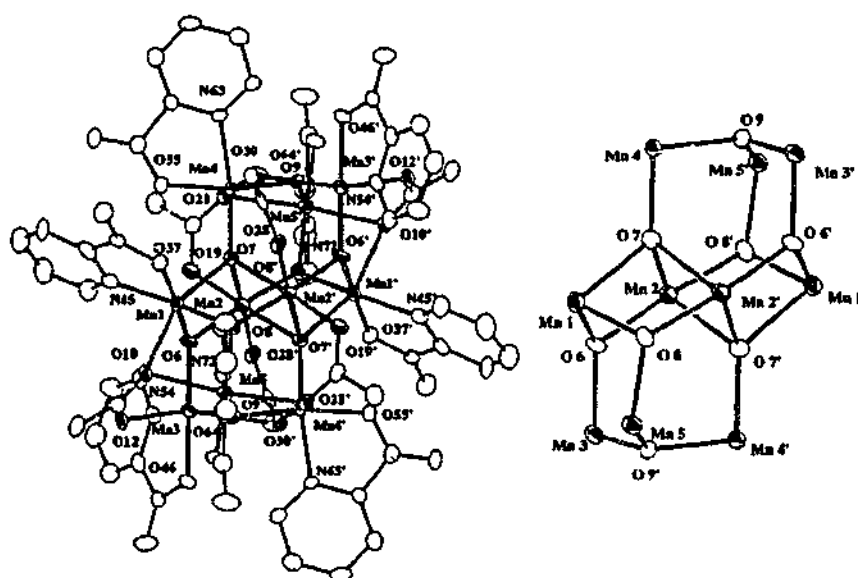


Figure 7.31 The crystal structure of [Mn₁₀O₈(O₂CPh)₆(pic)₈] (left) and the [Mn^{III}₁₀(μ₃-O)₆(μ₄-O)₂]¹⁴⁺ core (right). Reproduced from reference 176.

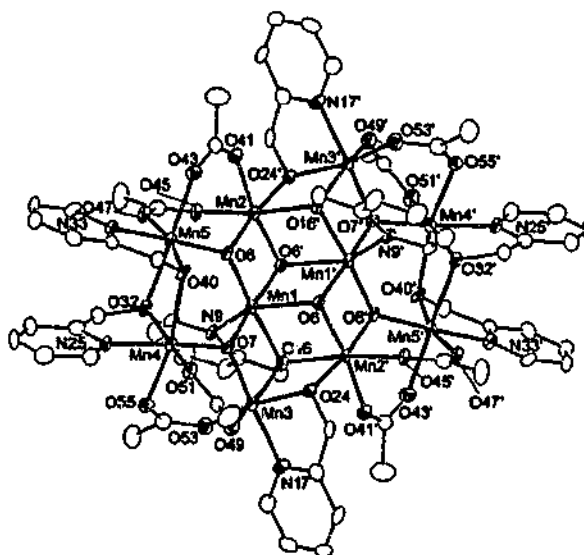


Figure 7.32 The structure of the [Mn₁₀O₄(OH)₂(OAc)₈(hmp)₈]⁴⁺ cation (reproduced from reference 18).

To date, the Mn cluster nuclearities 11, 13 and 14 have only single representatives. In 1991, Christou *et al.*⁶⁰ reported the preparation and structure of $[\text{Mn}_{11}\text{O}_{10}\text{Cl}_2(\text{OAc})_{11}(\text{bipy})_2(\text{MeCN})_2(\text{H}_2\text{O})_2]^{2+}$, shown in Figure 7.33, obtained by treatment of $[\text{Mn}_4\text{O}_2(\text{OAc})_7(\text{bipy})_2](\text{ClO}_4) \cdot 3\text{H}_2\text{O}$ with Me_3SiCl in MeCN. It contains a core that consists of two $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_3(\mu_3\text{-O})_3(\mu_3\text{-Cl})]^{6+}$ distorted cubane units, as seen in the $[\text{Mn}_4\text{O}_3\text{X}]^{6+}$ SMMs (Figure 7.11), bridged by a nearly linear $[\text{Mn}^{\text{III}}_3(\mu_3\text{-O})_4]^+$ moiety. The communication did not include magnetic characterisation. To the best of the candidate's knowledge, the authors have not since published magnetic data for this cluster.

Hendrickson *et al.*⁶¹ reported $[\text{Mn}_{13}\text{O}_8(\text{OEt})_6(\text{O}_2\text{CPh})_{12}]$, shown in Figure 7.34. It contains a novel 'supercubane' $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_6(\mu_5\text{-O})_6(\mu_3\text{-O})_2(\mu_3\text{-OEt})_6]^{12+}$ core, which strongly resembles a segment of an extended cubic metal oxide lattice.⁶¹ Magnetic measurements indicate an $S = 15/2$ ground state for this complex with overall antiferromagnetic coupling.

Recently Winpenny *et al.*⁶² reported the preparation, structure and preliminary magnetic properties of a new tetradecanuclear Mn(II/III) complex, $[\text{Mn}_{14}\text{O}_2(\text{OH})_4(\text{ppo})_{18}(\text{Hppo})_4(\text{NO}_3)_4(\text{MeCN})_4]$ (12Mn^{II} , 2Mn^{III} ; where $\text{ppoH} = 3\text{-phenyl-3-pyrazolin-5-one}$), shown in Figure 7.35. As the molecules are centrosymmetric, the core can be described as two connected Mn_7 fragments. The N/O donor ligands ppo^- and ppoH display three and one distinct coordination modes respectively. This complex exhibits strong antiferromagnetic coupling leading to an $S = 0$ ground state.

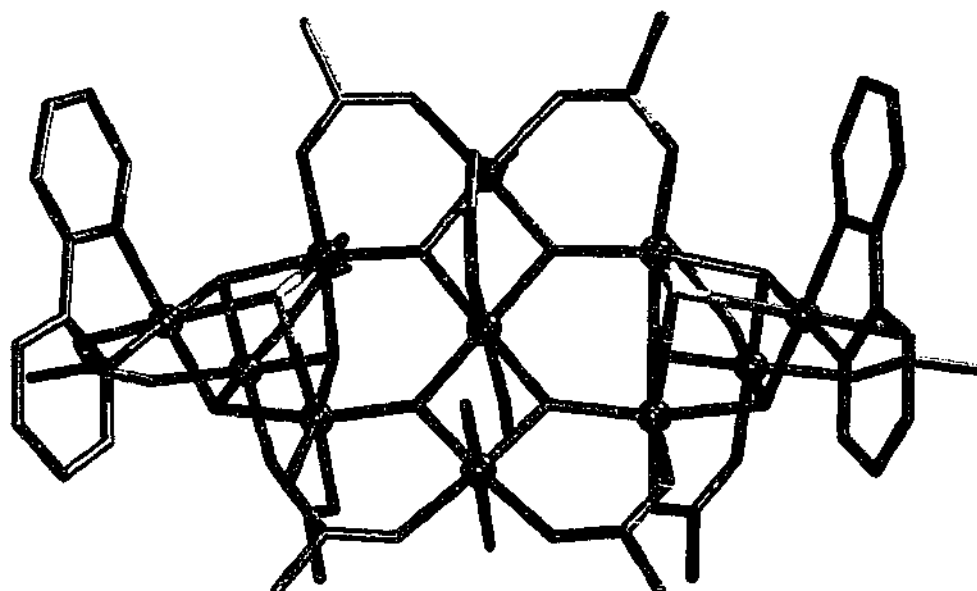


Figure 7.33 The crystal structure of $[\text{Mn}_{11}\text{O}_{10}\text{Cl}_2(\text{OAc})_{11}(\text{bipy})_2(\text{MeCN})_2(\text{H}_2\text{O})_2]^{2+}$. The spheres represent Mn ions. Image rendered from CSD simulated SHELX res file from entry JOFVIJ.

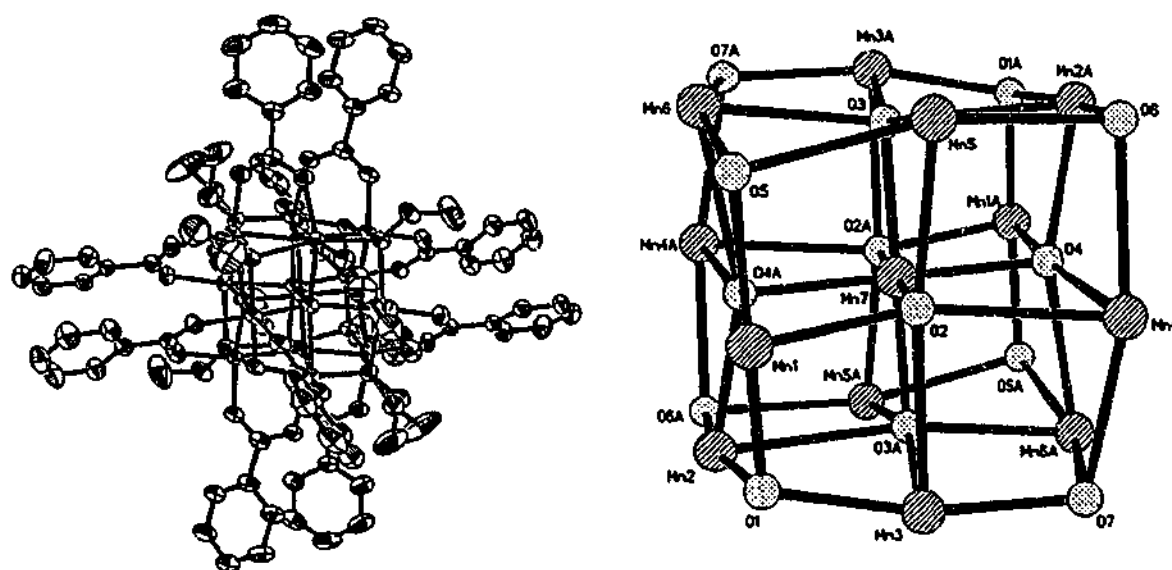


Figure 7.34 The crystal structure of $[\text{Mn}_{13}\text{O}_8(\text{OEt})_6(\text{O}_2\text{CPh})_{12}]$ (left) and the 'supercubane' $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_6(\mu_5\text{-O})_6(\mu_3\text{-O})_2(\mu_3\text{-OEt})_6]^{12+}$ core (right). Reproduced from reference 61.

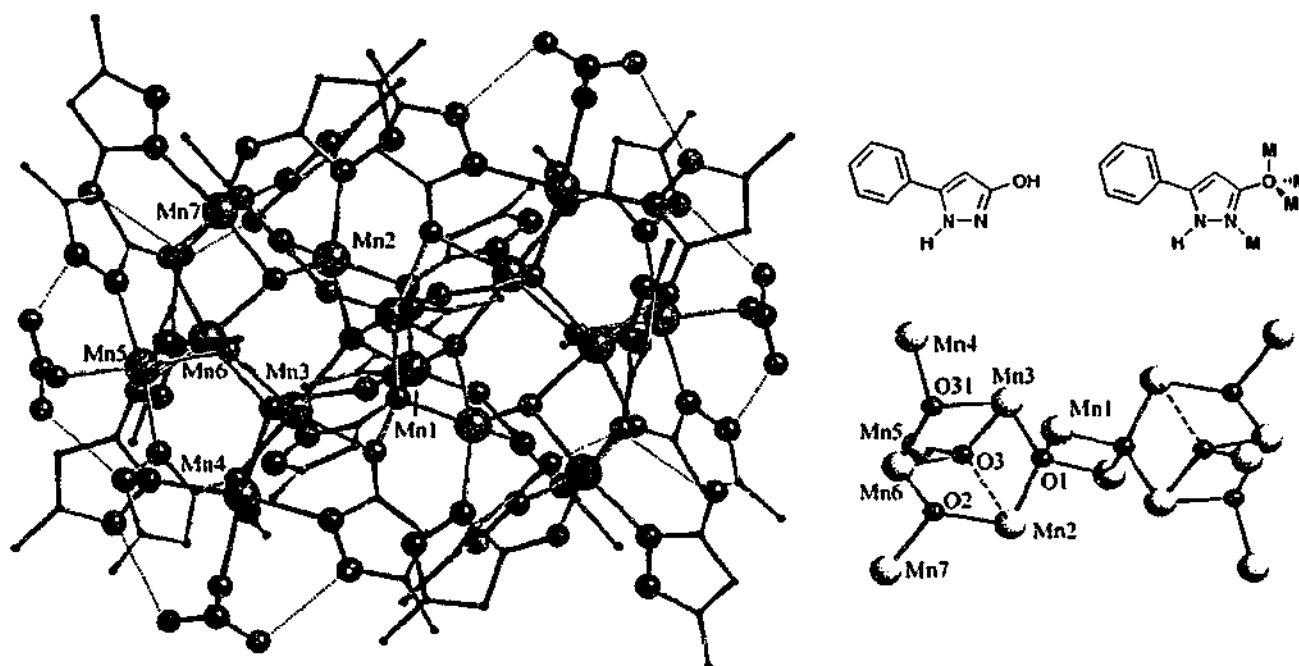


Figure 7.35 The crystal structure of $[\text{Mn}_{14}\text{O}_2(\text{OH})_4(\text{ppo})_{18}(\text{Hppo})_4(\text{NO}_3)_4(\text{MeCN})_4]$ (left) with intramolecular hydrogen bonds shown. Only the *ipso* carbons of the phenyl rings are shown. Mn ions are green, O atoms are red, N atoms are blue and C atoms are grey. On the lower right, the Mn_{14} core with Mn^{III} ions shown in purple and Mn^{II} ions in green. On the upper right, Hppo and ppo shown in its '4.31' coordination mode. Reproduced from reference 62.

The subject of the following chapter is a new hexadecanuclear manganese(III/IV) carboxylate cluster. There have been only two (II/III) Mn_{16} complex previously reported in the literature, $[\text{Ba}_8\text{Na}_2\text{ClMn}_{16}\text{O}_4(\text{OH})_4(\text{CO}_3)_4(\text{H}_2\text{O})_{22}\text{L}_8] \cdot x\text{H}_2\text{O}$ ⁶³ and $[\text{Ba}_8\text{Na}_2\text{ClMn}_{16}(\text{OH})_8(\text{CO}_3)_4\text{L}_8] \cdot 53\text{H}_2\text{O}$ (where $\text{L} = 1,3\text{-diamino-2-hydroxypropane-}N,N,N',N'\text{-tetraacetic acid}$).⁶⁴ The former complex, which appeared in a US patent and is shown in Figure 7.36, contains a core of 4 Ba^{2+} and 2 Na^+ ions surrounding a central Cl^- ion. The core is surrounded by 16 Mn ions.

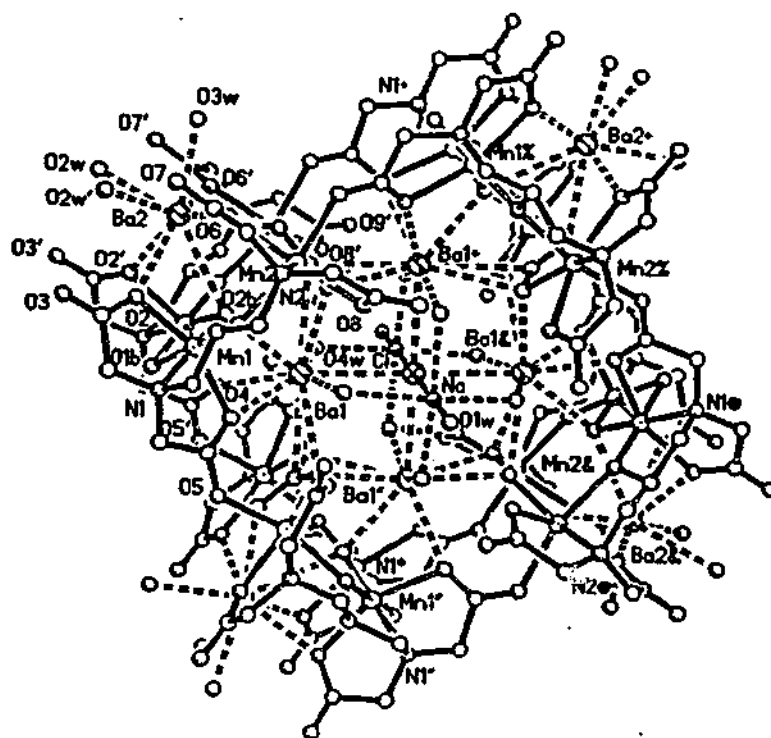


Figure 7.36 The crystal structure of $[\text{Ba}_8\text{Na}_2\text{ClMn}_{16}\text{O}_4(\text{OH})_4(\text{CO}_3)_4(\text{H}_2\text{O})_{22}\text{L}_8]$ where Mn coordination bonds are represented by double lines; Ba coordination bonds are represented by dashed double lines; and Na coordination bonds are represented by dashed solid lines. Reproduced from reference 63.

The next largest known Mn cluster nuclearity is 18. A few octadecanuclear manganese carboxylate clusters have been reported, including $[\text{Mn}_{18}\text{O}_{14}(\text{OMe})_{14}(\text{O}_2\text{CCMe}_3)_8(\text{MeOH})_6]$,¹⁸⁰ $\text{K}_4[\text{Mn}^{\text{III}}_{18}\text{O}_{16}(\text{O}_2\text{CPh})_{22}(\text{phth})_2(\text{H}_2\text{O})_4] \cdot 10\text{MeCN}$ (where $\text{phth}^{2-} = \text{phthalate}$),¹⁸¹ and recently, the SMM $[\text{Mn}_{18}\text{O}_{14}(\text{O}_2\text{CMe})_{18}(\text{hep})_4(\text{hepH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ ($2\text{Mn}^{\text{II}}, 16\text{Mn}^{\text{III}}$; where $\text{hepH} = 2\text{-(hydroxyethyl)pyridine}$)⁵² The first example has an interesting core that closely resembles the MnO 'rock salt' mineral structure, which can be thought of as an extension of the core structure in the Mn_{13} cluster described above (Figure 7.34). The latter two examples are distinctly different structures (the former lies on a crystallographic 2-fold axis whereas the latter lies on an inversion centre), despite the cores possessing some similarities, such as the Mn_4O_6 fragment (Figure 7.37). The $\text{Mn}^{\text{III}}_{18}$ cluster has an $S = 0$ ground state, whereas

the $\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_{16}$ cluster has an $S = 13$ ground state, which is one of the largest spin ground states for molecules of this type. The cation has an axial zero-field splitting parameter $D = -0.13 \text{ cm}^{-1}$ and a barrier potential to reversal of magnetisation of $\Delta E = 14.8 \text{ cm}^{-1}$. Magnetisation hysteresis is observed below 1 K.⁵²

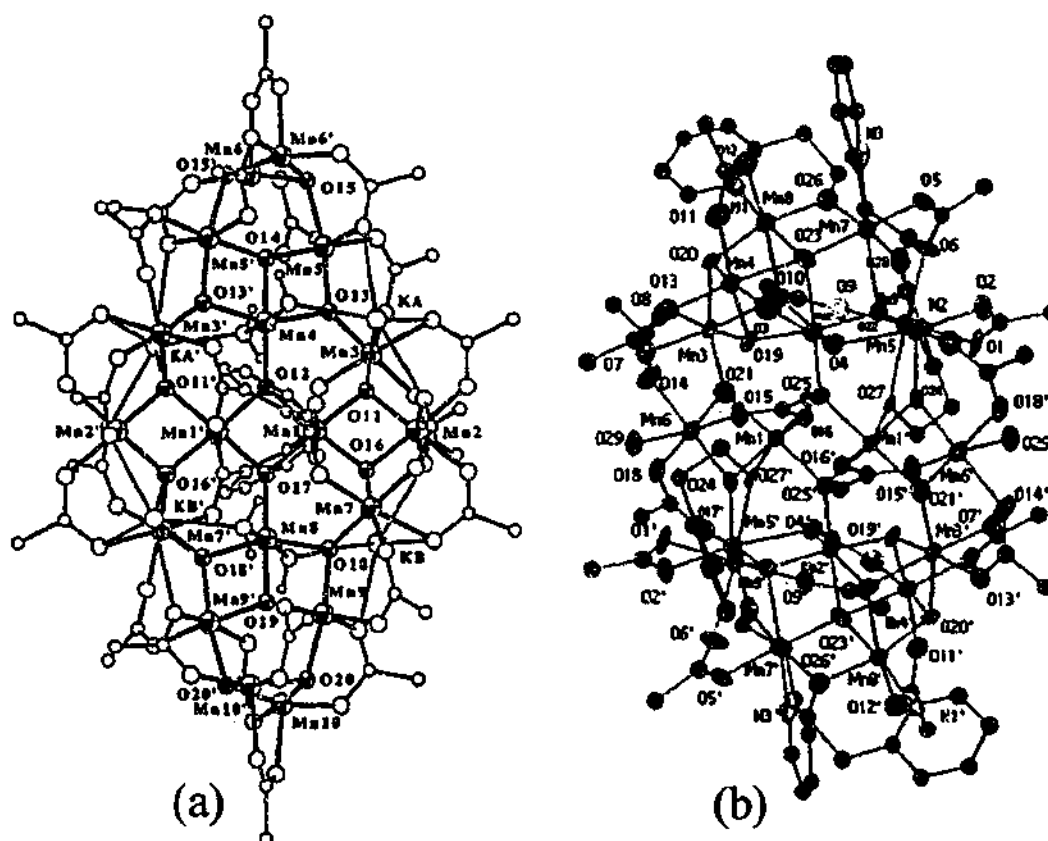


Figure 7.37 The crystal structures of (a) $\text{K}_4[\text{Mn}^{\text{III}}_{18}\text{O}_{16}(\text{O}_2\text{CPh})_{22}(\text{phth})_2(\text{H}_2\text{O})_4]$ (only *ipso* carbon atoms of the phenyl groups shown), and (b) $[\text{Mn}_{18}\text{O}_{14}(\text{O}_2\text{CMe})_{18}(\text{hep})_4(\text{hepH})_2(\text{H}_2\text{O})_2]^{2+}$ (colours: Mn^{II} green; Mn^{III} purple; O red; N blue; C black. Reproduced from references 18 and 52 respectively.

One step up is a novel ‘disc-like’ $\text{Mn}^{\text{II}}_{19}$ oxo-alkoxide cluster, $[\text{Mn}_{19}\text{O}_{12}(\text{moe})_{14}(\text{moeH})_{10}]\cdot\text{moeH}$ (where $\text{moeH} = \text{methoxyethanol}$), reported by Westin *et al.*⁶⁵ as part of their work on metal alkoxide precursors for sol-gel synthesis of ceramics. The Mn/O core of the complex quite clearly resembles a fragment of a layered $\text{Mn}(\text{OH})_2$

mineral (Figure 7.38(a)) and is remarkably similar to the Fe_{19} oxo-hydroxide cluster reported by Powell *et al.* (Figure 7.44).^{79,182} This Mn_{19} complex exhibits antiferromagnetic coupling.

Likewise, Christou *et al.*⁶⁶ reported a 'disk-like' manganese(III/IV) cluster, $[\text{Mn}_{21}\text{O}_{24}(\text{OMe})_8(\text{O}_2\text{CCH}_2\text{Bu}')_{16}(\text{H}_2\text{O})_{10}]$ ($12\text{Mn}^{\text{III}}, 9\text{Mn}^{\text{IV}}$) that contains a $[\text{Mn}_{21}\text{O}_{24}(\text{OMe})_8]^{16+}$ core. This core consists of a planar $[\text{Mn}^{\text{IV}}_9\text{O}_{20}]^{4-}$ sub-unit with the CdI_2 type structure, held within a non-planar $[\text{Mn}^{\text{III}}_{12}\text{O}_{12}]^{12+}$ ring (Figure 7.38(b)).⁶⁶ Fittings to magnetic measurements reveal this complex displays antiferromagnetic coupling with an $S = 13/2$ ground state, however no χ_M'' signals were observed, indicating it is not an SMM.

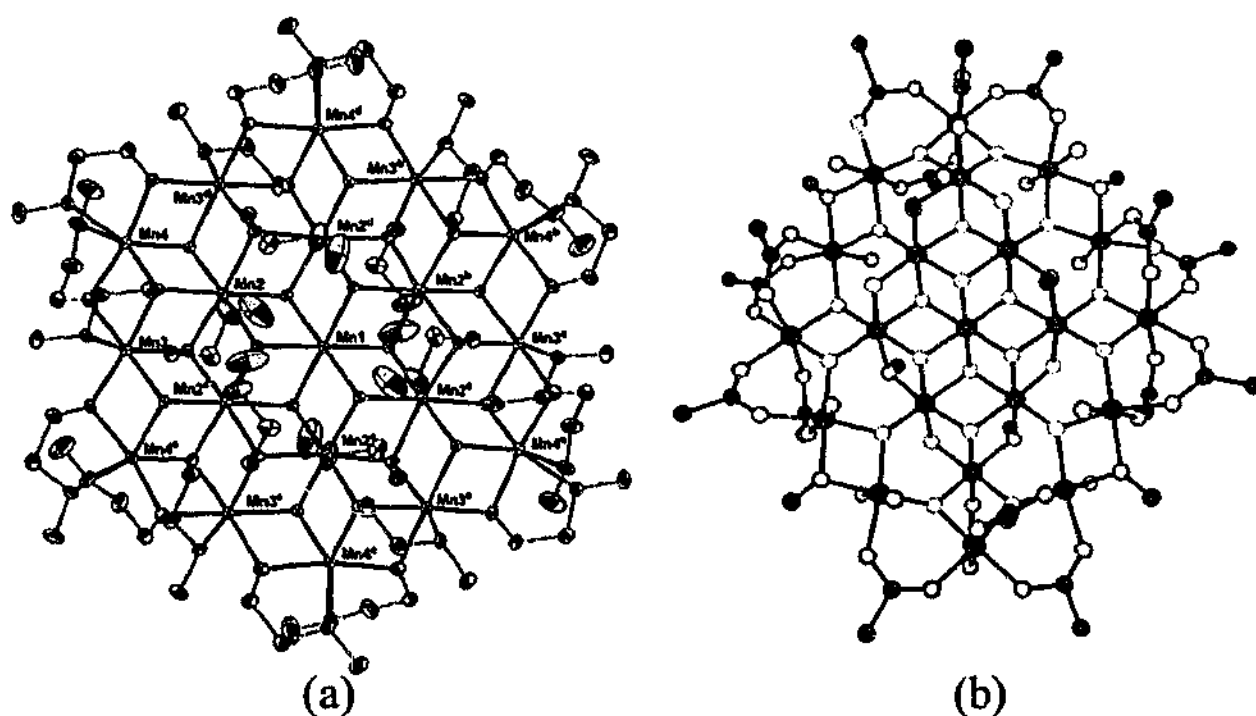


Figure 7.38 The crystal structures of (a) $[\text{Mn}_{19}\text{O}_{12}(\text{moe})_{14}(\text{moeH})_{10}]$ viewed down the crystallographic 3-fold axis, and (b) $[\text{Mn}_{21}\text{O}_{24}(\text{OMe})_8(\text{O}_2\text{CCH}_2\text{Bu}')_{16}(\text{H}_2\text{O})_{10}]$ (colours: Mn^{IV} red; Mn^{III} green; O^{2-} yellow; other types of O atoms off white; C black). Reproduced from references 65 and 66 respectively.

The last two high nuclearity Mn complexes that will be discussed here are $[\text{Mn}_{26}\text{O}_{16}(\text{OH})_{10}(\text{OMe})_6\text{F}_{10}(\text{bta})_{20}(\text{btaH})_2(\text{MeOH})_{13}(\text{H}_2\text{O})]$ (26Mn^{III} , btaH = benzotriazole) recently reported by Brechin and Collison *et al.*⁵⁴ and the largest Mn carboxylate cluster known to date, $[\text{Mn}_{30}\text{O}_{24}(\text{OH})_8(\text{O}_2\text{CCH}_2\text{Bu}')_{32}(\text{H}_2\text{O})_2(\text{MeNO}_2)_4]$ ($3\text{Mn}^{\text{II}}, 26\text{Mn}^{\text{III}}, \text{Mn}^{\text{IV}}$) reported by Hendrickson and Christou *et al.*⁵³

The $[\text{Mn}_{26}]$ complex (Figure 7.39), prepared by reaction of anhydrous MnF_3 with benzotriazole (btaH) in hot MeOH , contains a complex $[\text{Mn}^{\text{III}}_{26}\text{O}_{16}(\text{OH})_{10}(\text{OMe})_6]^{30+}$ core unit. Preliminary magnetic analysis indicates that it exhibits magnetic hysteresis and temperature independent magnetisation relaxation below 1.2 K. Further work by this group is being done to confirm it as a new SMM.⁵⁴

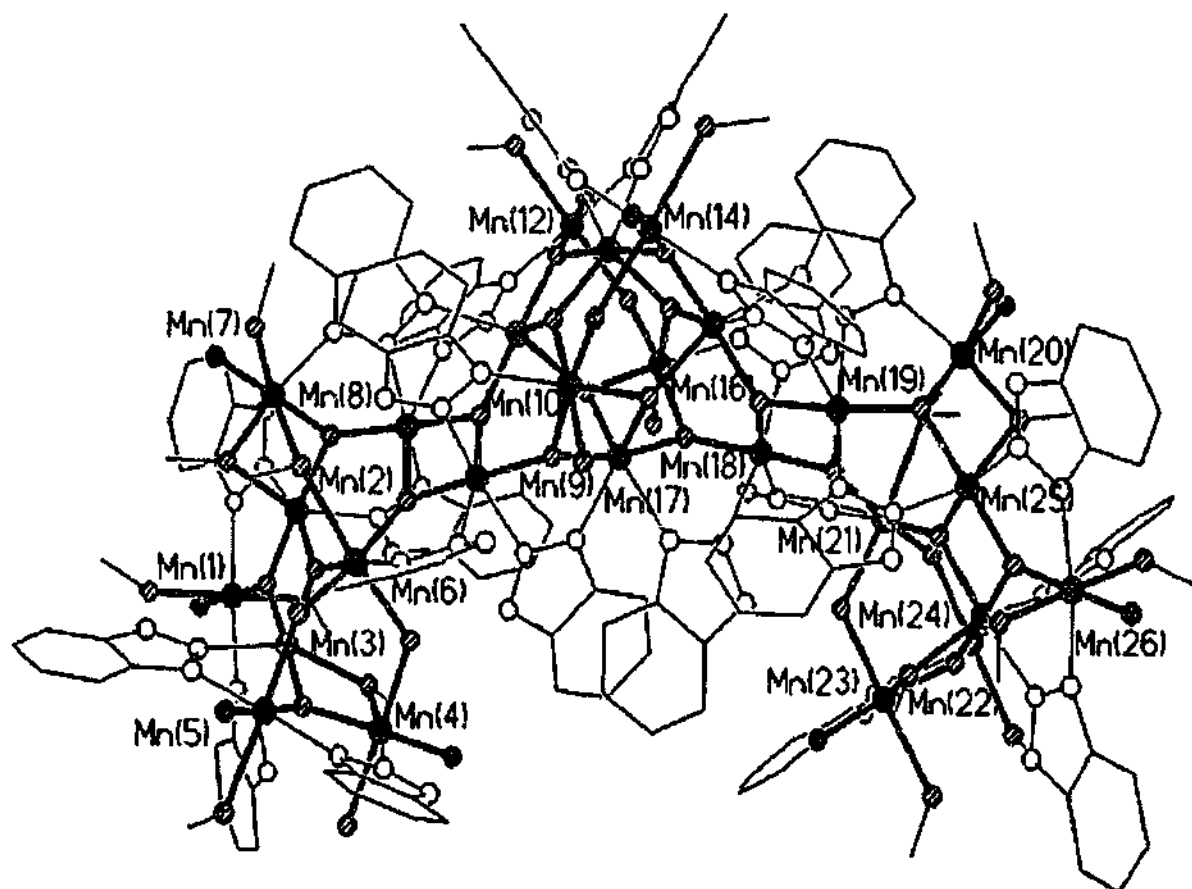


Figure 7.39 The crystal structure of $[\text{Mn}_{26}\text{O}_{16}(\text{OH})_{10}(\text{OMe})_6\text{F}_{10}(\text{bta})_{20}(\text{btaH})_2(\text{MeOH})_{13}(\text{H}_2\text{O})]$ with the $[\text{Mn}^{\text{III}}_{26}\text{O}_{16}(\text{OH})_{10}(\text{OMe})_6]^{30+}$ core unit highlighted (black). Reproduced from reference 54.

The $[\text{Mn}_{30}]$ cluster also possesses a complex structure. Two different representations are shown in Figure 7.40. Briefly, it contains a $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_{26}\text{Mn}^{\text{IV}}\text{O}_{24}(\text{OH})_8]^{32+}$ core, where Mn2, Mn10 and Mn10' are Mn^{II} , Mn1 (approximately at the centre of the molecule) is Mn^{IV} and the rest are Mn^{III} . The complex has an $S = 7$ ground state with $D = -0.79 \text{ cm}^{-1}$, and shows frequency dependent AC χ_M'' signals, indicating it to be an SMM, therefore the largest known to date.

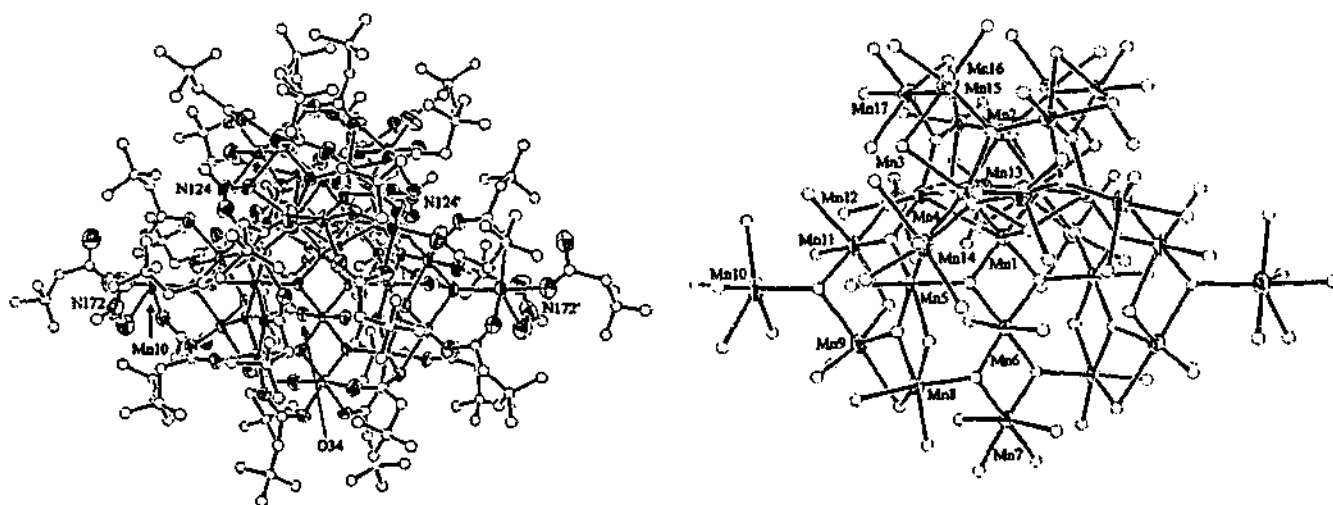


Figure 7.40 Left: the complete crystal structure of $[\text{Mn}_{30}\text{O}_{24}(\text{OH})_8(\text{O}_2\text{CCH}_2\text{Bu}')_{32}-(\text{H}_2\text{O})_2(\text{MeNO}_2)_4]$. Right: the structure with only Mn and O atoms shown. Reproduced from reference 53.

7.4 Other Metal Based SMMs

As stated earlier, the SMMs 'club' is not exclusively the domain of manganese carboxylate complexes, although they contain the majority of its members. A number of iron⁹⁶ and vanadium^{81,183} clusters and cyano-based clusters⁸⁸ have been reported to display SMM behaviour and are discussed here briefly.

The tetranuclear methoxy bridged iron(III) cluster $[\text{Fe}_4(\text{OMe})_6(\text{dpm})_6]$ ($\text{dpmH} = \text{dipivaloylmethane}$),^{71,96} is the smallest Fe cluster to be classed as a SMM. The structure of this complex (Figure 7.41) consists of a central Fe ion linked to three terminal Fe ions by three double $\mu\text{-OMe}$ bridges. Antiferromagnetic coupling between the Fe^{III} ($S = 5/2$) ions in the manner shown in Figure 7.41 leads to non-compensation of the spins and an $S = 5$ ground state.⁹⁶ It is interesting to note, historically, that Martin and Winter *et al.*¹⁸⁴⁻¹⁸⁶ and Blake *et al.*¹⁸⁷⁻¹⁸⁹ studied first row transition metal alkoxide clusters many years ago, although few crystal structures were obtained.

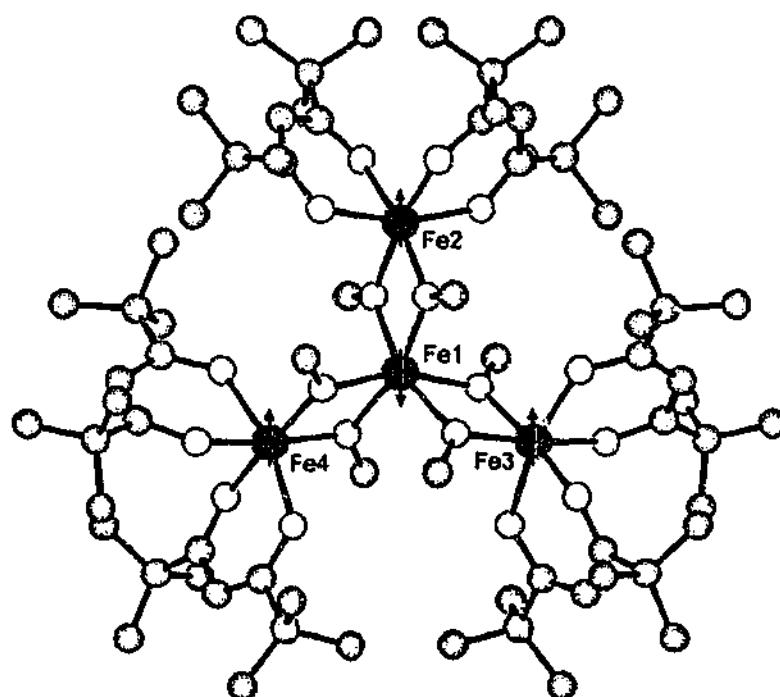


Figure 7.41 The crystal structure of $[\text{Fe}_4(\text{OMe})_6(\text{dpm})_6]$, where the Fe ions are red, oxygen atoms are yellow and carbon atoms are grey. The arrows indicate the spin structure in the ground $S = 5$ state (reproduced from reference 96).

In 1984 Wieghardt *et al.* reported the crystal structure of $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]\text{Br}_8 \cdot 9\text{H}_2\text{O}$ (Fe_8Br),⁷² (where $\text{tacn} = 1,4,7\text{-triazacyclononane}$), which is shown in Figure 7.42. The complex was prepared by the hydrolysis of $[\text{FeCl}_3(\text{tacn})]$ at pH

9 in the presence of Br^- ions. Subsequent magnetic susceptibility measurements showed this complex has an $S = 10$ ground state,¹⁹⁰ and single crystal polarised neutron diffraction experiments have been performed to determine the magnetic spin structure.¹⁹¹ High-frequency/high-field EPR (HFEPR) experiments have been used to analyse the magnetic anisotropy of the complex, yielding a zero-field splitting parameter of $D = -0.205 \text{ cm}^{-1}$ measured on a polycrystalline powder.^{74,75} After Mn_{12} -acetate, Fe_8Br is perhaps the most actively studied SMM to date.^{76,91} Faster magnetisation relaxation and larger transverse anisotropy than Mn_{12} -acetate lead to more pronounced quantum tunnelling. Therefore, Fe_8Br has proved extremely interesting for the experimental observation of quantum size effects.⁷⁶

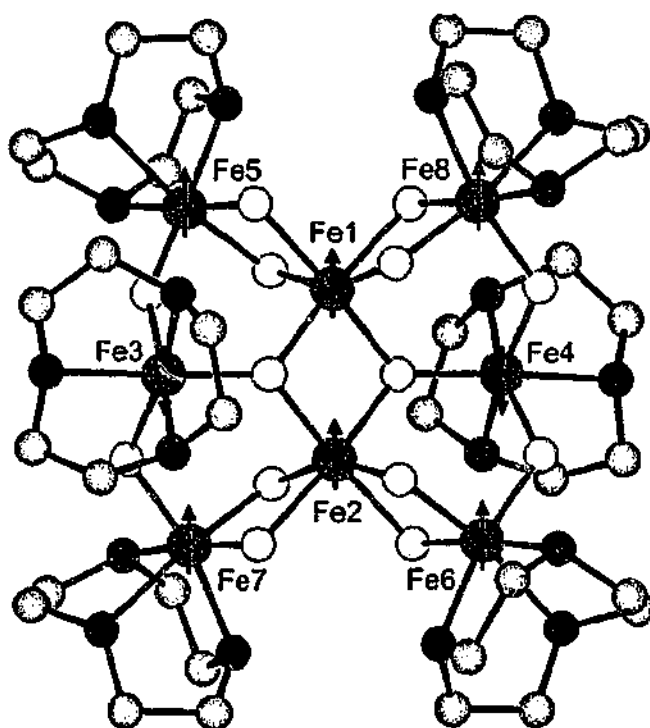


Figure 7.42 The crystal structure of $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{6+}$, where nitrogen atoms are in blue and the remainder of colour codes are as in Figure 7.41. The arrows indicate the spin structure determined by single crystal polarised neutron diffraction experiments.¹⁹¹ Reproduced from reference 96.

The $\text{Fe}^{\text{III}}_{10}$ cage complex $[\text{Fe}_{10}\text{Na}_2\text{O}_6(\text{OH})_4(\text{O}_2\text{CPh})_{10}(\text{chp})_6(\text{H}_2\text{O})_2(\text{Me}_2\text{CO})_2]$ (where chp = 6-chloropyridonato), reported recently by Benelli and Winpenny *et al.*,^{77,78} has an $S = 11$ ground state with an activation barrier to reorientation of the magnetisation of 5.3 K. It is the third Fe SMM known and one of the most rapidly relaxing SMMs.⁸⁴ The core can be described as close packed array of oxygen atoms with iron ions occupying the octahedral holes in the lattice (Figure 7.43).

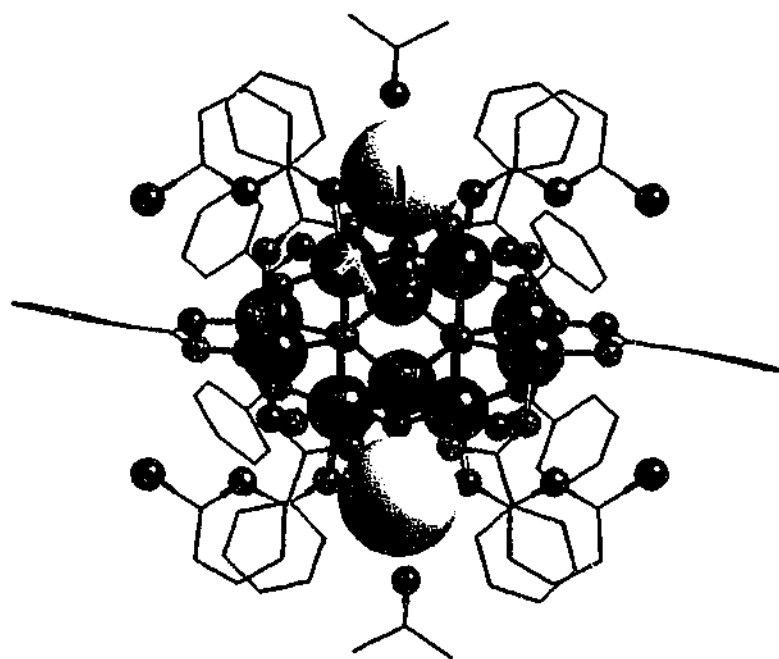


Figure 7.43 The crystal structure of $[\text{Fe}_{10}\text{Na}_2\text{O}_6(\text{OH})_4(\text{O}_2\text{CPh})_{10}(\text{chp})_6(\text{H}_2\text{O})_2(\text{Me}_2\text{CO})_2]$, where iron atoms are shown in dark red, oxygen atoms in red, nitrogens in blue, chlorines in purple and sodium ions in yellow (reproduced from reference 84).

The fourth class of iron based SMM consists of the Fe_{19} oxy-hydroxide clusters reported by Powell *et al.*⁷⁹ Following their work on the co-crystallized $\text{Fe}_{17}/\text{Fe}_{19}$ system with the tripodal ligand H_3heidi (*N*-1-(hydroxyethyl)iminodiacetic acid, $\text{N}(\text{CH}_2\text{CO}_2\text{H})_2(\text{CH}_2\text{CH}_2\text{OH})$),^{182,192} they found that by altering the alcohol side arms of the ligand, i.e. by making methyl and ethyl derivatives, they were able to isolate the Fe_{19}

clusters. The complexes $[\text{Fe}_{19}(\text{L})_{10}(\text{OH})_{14}\text{O}_6(\text{H}_2\text{O})_{12}]\text{X}$,⁷⁹ where $\text{LH}_3 = \text{H}_3\text{metheidi}$ (*N*-(1-Hydroxymethylethyl)iminodiacetic acid), $\text{H}_3\text{etheidi}$ (*N*-(1-Hydroxymethylpropyl)iminodiacetic acid); $\text{X} = \text{NO}_3^-$, Cl^- , like many polynuclear oxo-bridged clusters, possess a core with the CdI_2 type structure and can be described as captured portions of the layered $\text{Fe}(\text{OH})_2^+$ lattice ("captured rusts" or "crusts"). $[\text{Fe}_{19}(\text{metheidi})_{10}(\text{OH})_{14}\text{O}_6(\text{H}_2\text{O})_{12}]^+$ is shown in Figure 7.44. Initial magnetic studies indicated very high ground state spin values, but the presence of both Fe_{17} and Fe_{19} clusters restricted discussion.¹⁰⁵ The more recent studies have indicated $[\text{Fe}_{19}(\text{metheidi})_{10}(\text{OH})_{14}\text{O}_6(\text{H}_2\text{O})_{12}]\text{NO}_3 \cdot 24\text{H}_2\text{O}$ has an $S = 33/2$ ground state, zero-field splitting parameter of $D = -0.035 \text{ cm}^{-1}$ and a spin reversal energy barrier of $\Delta E = 15.7 \text{ K}$ (10.7 cm^{-1}), which is small considering the large value of S . The value of S for the etheidi analogue was estimated to lie between $S = 31/2$ and $33/2$.⁷⁹

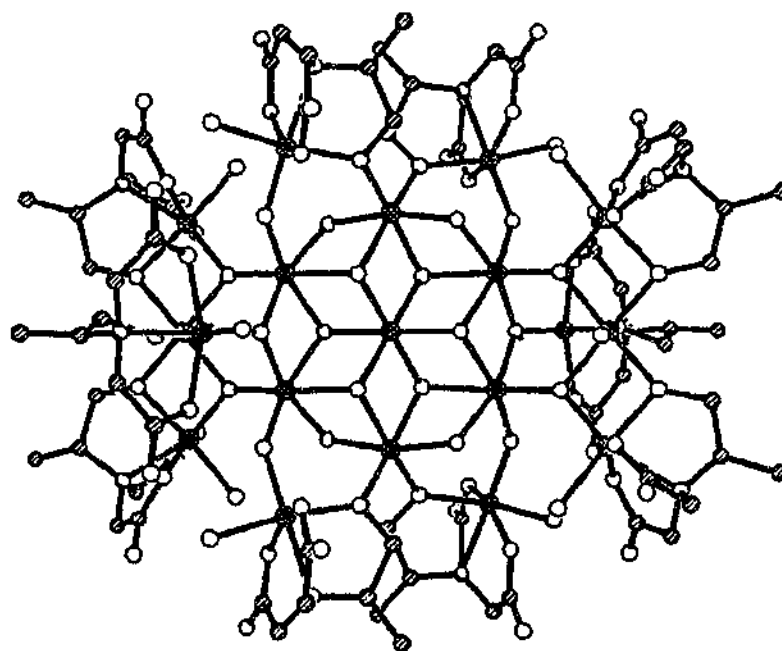


Figure 7.44 The crystal structure of $[\text{Fe}_{19}(\text{metheidi})_{10}(\text{OH})_{14}\text{O}_6(\text{H}_2\text{O})_{12}]^+$, where Fe^{III} ions are cross-hatched circles, oxygen atoms are open circles, carbon atoms are shaded top right to bottom left and nitrogen atoms are shaded circles (reproduced from reference 79).

A small number of vanadium based SMMs have been discovered.^{80,81,183} They belong to the familiar $[M_4O_2]$ butterfly like core structural family, which also includes many Mn, Cr and Fe examples.¹¹² The complexes $[V^{III}_4O_2(O_2CR)_7(bipy)_2](ClO_4)$ ($R = Et, Ph$ and $bipy = 2,2'$ -bipyridine) and $(Et_4N)[V^{III}_4O_2(O_2CEt)_7(pic)_2]$ ($pic^- = picolinate$) have $S = 3$ ground states ($D \approx -1.5 \text{ cm}^{-1}$) with a barrier potential energy of $\Delta E \approx 13.5 \text{ cm}^{-1}$ (cf. Mn_{12} -carboxylates $\Delta E \approx 42 \text{ cm}^{-1}$). The structure of a representative complex is shown in Figure 7.45.

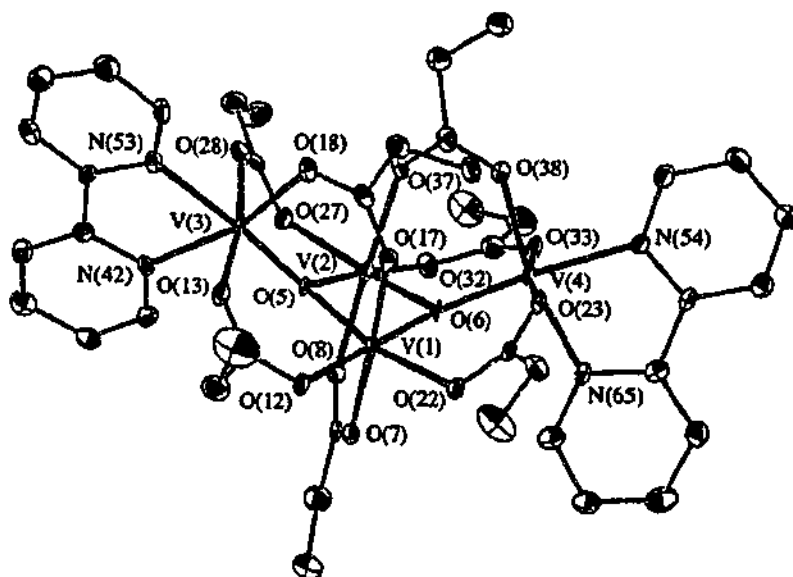


Figure 7.45 The crystal structure of $[V^{III}_4O_2(O_2CEt)_7(bipy)_2]^+$ (thermal ellipsoids shown at 50 % probability). Reproduced from reference 81.

In addition to Mn, Fe and V based SMMs, a small but growing number of other first row transition metal (Ni and Co) based SMMs have appeared in the literature in the last few years. Recently, Winpenny *et al.* reported the first Ni cluster complex to display SMM behaviour,^{82,83} the cyclic dodecanuclear complex $[Ni_{12}(chp)_{12}(OAc)_{12}(H_2O)_6(THF)_6]$ (where $chp = 6$ -chloro-2-pyridonate) shown in Figure 7.46. It has an $S = 12$ ground state, due to ferromagnetic coupling between the twelve $S = 1$ Ni^{II} centres, an energy barrier to

reversal of magnetisation of 10 K and exhibits out-of-phase AC susceptibility signals in the region of 0.4 K.⁸³ The second and larger Ni based SMM is the complex $[\text{Ni}_{21}(\text{cit})_{12}(\text{OH})_{10}(\text{H}_2\text{O})_{10}]^{16-}$ (cit^{4-} = citrate, $\text{C}(\text{O})(\text{CO}_2^-)(\text{CH}_2\text{CO}_2^-)_2$), reported by Güdel *et al.*⁸⁵ The complex exists as different stereoisomers. Of the two compounds structurally characterised, one contains an achiral cluster (Figure 7.47) and the second contains a pair of enantiomers. As is the common trend, the core of these clusters, a $[\text{Ni}_7(\mu_3\text{-OH})_6]^{8+}$ unit is a fragment of the extended layered network $\text{Ni}(\text{OH})_2$. Magnetic measurements of the achiral compound in the millikelvin range indicate the cluster possesses an $S = 3$ ground state and a negative magnetic anisotropy ($D = -0.32$ K) with an energy barrier, $\Delta E = 2.9$ K, to magnetisation reversal at low temperatures.

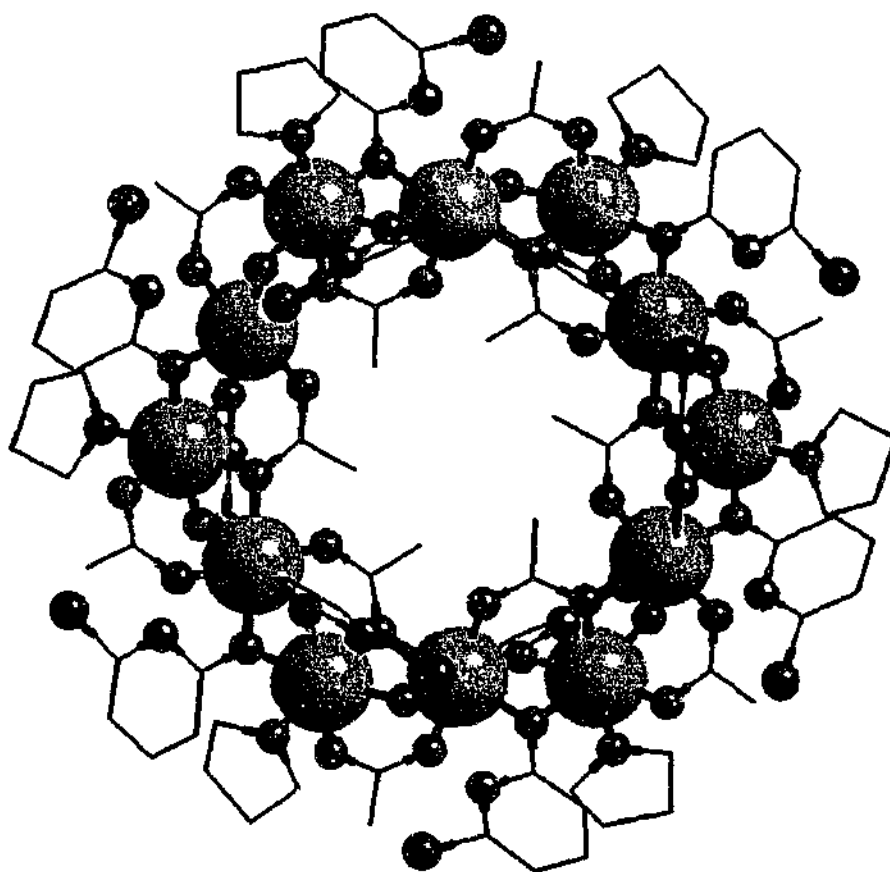


Figure 7.46 The structure of $[\text{Ni}_{12}(\text{chp})_{12}(\text{OAc})_{12}(\text{H}_2\text{O})_6(\text{THF})_6]$, where Ni centres are light blue spheres, oxygen atoms are red, nitrogen atoms are blue and chlorine atoms are purple (reproduced from reference 82).

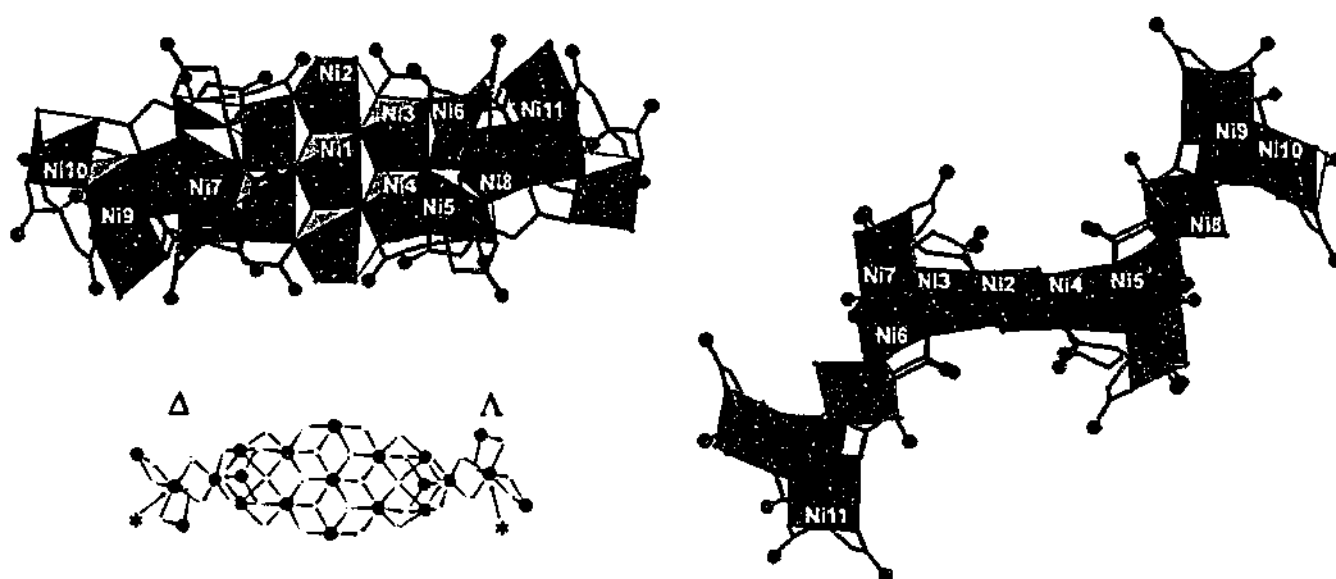


Figure 7.47 Different views of the structure of the achiral cluster of $[\text{Ni}_{21}(\text{cit})_{12}(\text{OH})_{10}(\text{H}_2\text{O})_{10}]^{16-}$ (Ni are black at the centre of green polyhedra, oxygens are red and carbons are grey) and, lower left, a diagram indicating the Δ - Δ configuration of the cluster (reproduced from reference 85).

Recently, Christou and Hendrickson *et al.* reported the Co^{II} and Ni^{II} based SMMs, $[\text{Co}_4(\text{hmp})_4(\text{MeOH})_4\text{Cl}_4]^{86}$ and $[\text{Ni}_4(\text{OMe})_4(\text{sal})_4(\text{MeOH})_4]$ (where Hsal = salicylaldehyde).⁸⁷ Both complexes consist of M_4O_4 cubane units. Many such cubanes are known in the literature.¹¹² The Co^{II} complex, shown in Figure 7.48, possesses an $S = 6$ ground state with an axial zero field splitting parameter of $D \approx -4$ K, and shows hysteresis below 1.2 K. The Ni^{II} complex has an $S = 4$ ground state and exhibits slow magnetisation relaxation below 0.3 K, with a very low energy barrier of ~ 5 K (*c.f.* 62 K for Mn_{12} -acetate). As in the case of a Mn_4 hydrogen bonded dimer,⁴¹ this compound shows inter-dimer antiferromagnetic exchange bias such that there is no step in the hysteresis loop at $H = 0$.

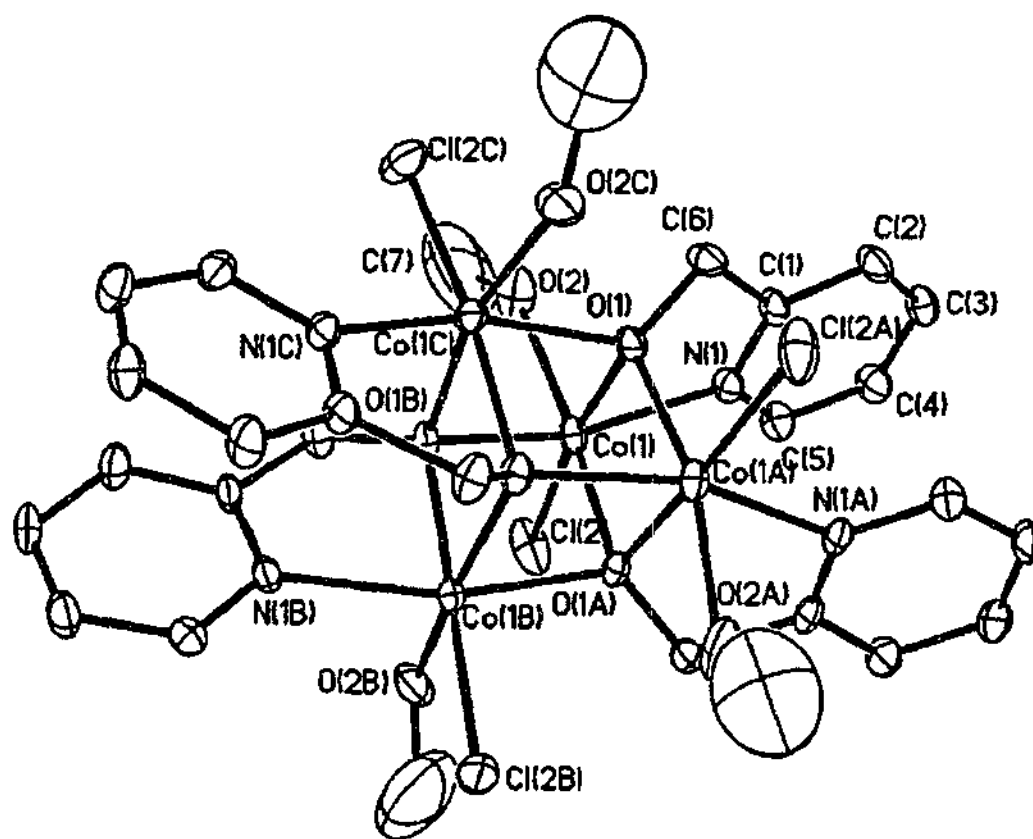


Figure 7.48 The crystal structure of $[\text{Co}_4(\text{hmp})_4(\text{MeOH})_4\text{Cl}_4]$ (reproduced from reference 86).

Finally, much recent research has focused on producing large high-spin metal cyanide clusters that display SMM behaviour, as the S and D values can potentially be readily adjusted by substitution of the metal ions involved.^{88,193-203} However, the chief obstacle that needs to be overcome to obtain high negative magnetic anisotropies is the high symmetry often observed in the structures of cyano-based clusters.²⁰³ Recently, Long *et al.* reported the first well documented cyano-bridged SMM, $\text{K}[(\text{Me}_3\text{tacn})_6\text{MnMo}_6(\text{CN})_{18}](\text{ClO}_4)_3$, (where $\text{Me}_3\text{tacn} = N,N',N''$ -trimethyl-1,4,7-triazacyclononane), shown in Figure 7.49.⁸⁸ The cluster has an $S = 13/2$ ground state with $D = -0.33 \text{ cm}^{-1}$ and a fitted spin reversal barrier potential of $\Delta E = 10 \text{ cm}^{-1}$.

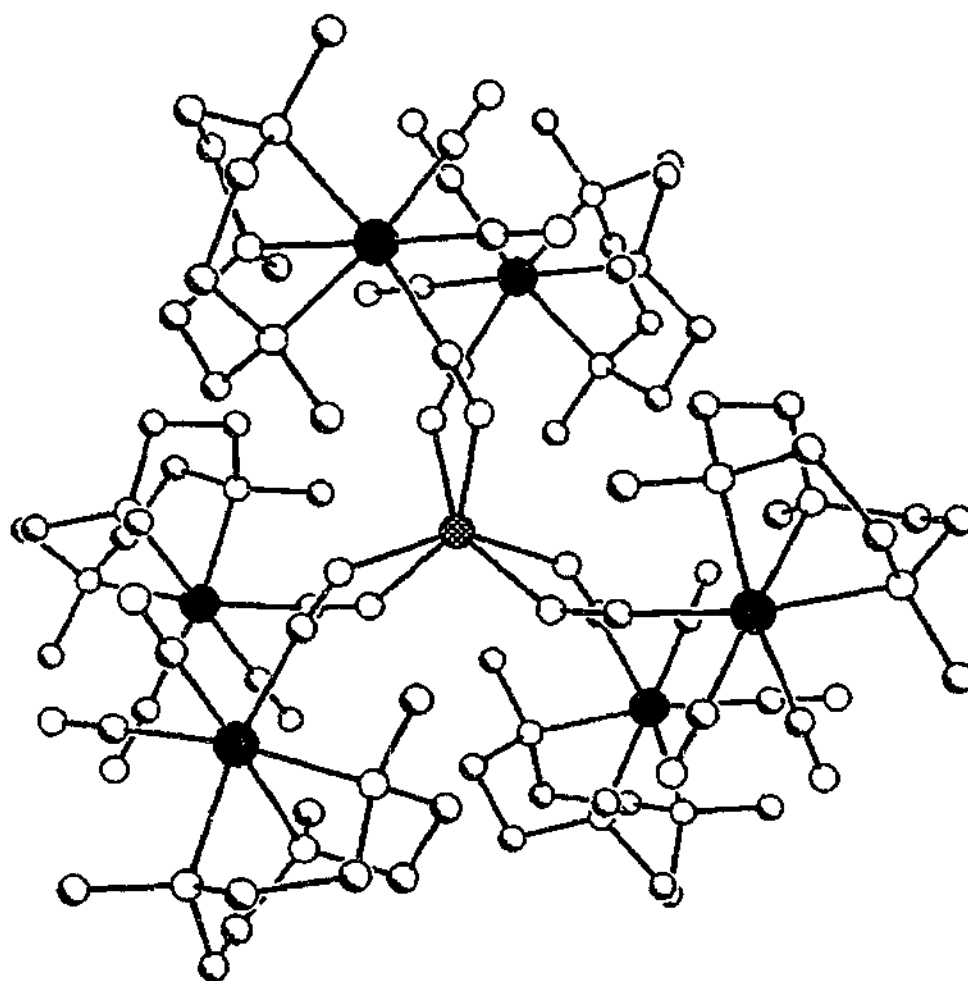


Figure 7.49 The crystal structure of the trigonal prismatic anion $[(\text{Me}_3\text{tacn})_6\text{MnMo}_6(\text{CN})_{18}]^{2-}$, where Mn ions are cross-hatched, Mo ions are black, C atoms are shaded and N atoms are white (reproduced from reference 88).

As detailed in Chapter 1, Decurtins *et al.*^{197,204,205} and Hashimoto *et al.*¹⁹⁸ have recently reported very large cyanide bridged clusters. For instance, $[\text{Mn}^{\text{II}}\{\text{Mn}^{\text{II}}(\text{MeOH})_3\}_8(\mu\text{-CN})_{30}\{\text{Mo}^{\text{V}}(\text{CN})_3\}_6]\cdot 5\text{MeOH}\cdot 2\text{H}_2\text{O}$ ($\text{Mn}^{\text{II}}_9\text{Mo}^{\text{V}}_6$), shown in Figure 7.50, has a very high $S = 51/2$ ground state spin and displays long-range ferromagnetic ordering below 44 K due to inter-cluster ferromagnetic coupling. The structurally analogous $\text{Mn}^{\text{II}}_9\text{W}^{\text{V}}_6$,¹⁹⁸ $\text{Ni}^{\text{II}}_9\text{Mo}^{\text{V}}_6$,²⁰⁴ and $\text{Ni}^{\text{II}}_9\text{W}^{\text{V}}_6$,²⁰⁴ clusters also have high spin ground states of $S = 39/2$, 12 and 12 respectively. No evidence for SMM behaviour was detected for these clusters.

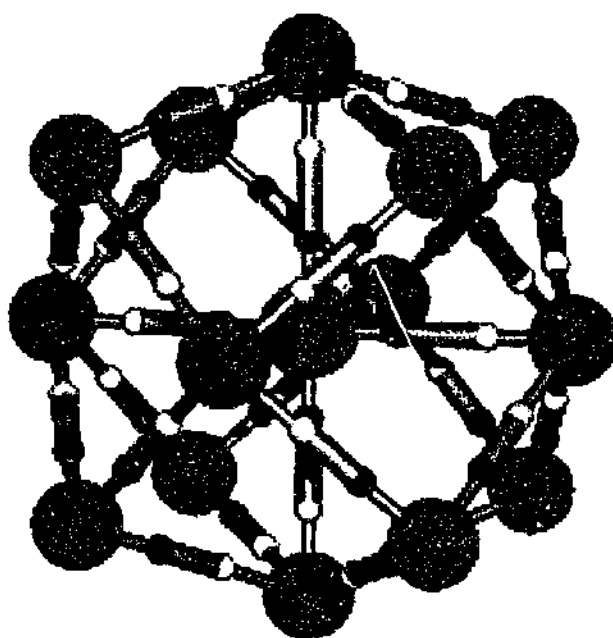


Figure 7.50 A representation of the $[\text{Mn}^{\text{II}}_9(\mu\text{-CN})_{30}\text{Mo}^{\text{V}}_6]$ ($\text{Mn}^{\text{II}}_9\text{Mo}^{\text{V}}_6$) cluster core with idealised O_h symmetry to accentuate the cluster topology. Red spheres represent Mn centres, green spheres represent Mo centres and the bonds between them are the cyanide ligands (reproduced from reference 197).

Recently, Long *et al.*¹⁹³ reported two ‘giant’ nickel-chromium-cyanide clusters, the smaller being $[(\text{Me}_3\text{tacn})_{12}\text{Cr}_{12}\text{Ni}_{12}(\text{CN})_{48}]^{12+}$ (24 metal-species; where $\text{Me}_3\text{tacn} = N,N',N''$ -trimethyl-1,4,7-triazacyclononane), shown in Figure 7.51(a). It consists of a cube of eight Cr^{III} centres linked along the edges by twelve *trans* coordinated $[\text{Ni}(\text{CN})_4]^{2-}$ units. The larger of the two, and the largest to date, is $[(\text{Me}_3\text{tacn})_{14}\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}]^{20+}$ (27 metal-species), shown in Figure 7.51(b). It consists of a double face-centred cubic unit sharing a Ni vertex. Magnetic data were not reported, but as the larger complex is geometrically highly anisotropic, it is thought these types of clusters will be likely to show appreciable magnetic anisotropy and hence SMM behaviour.¹⁹³

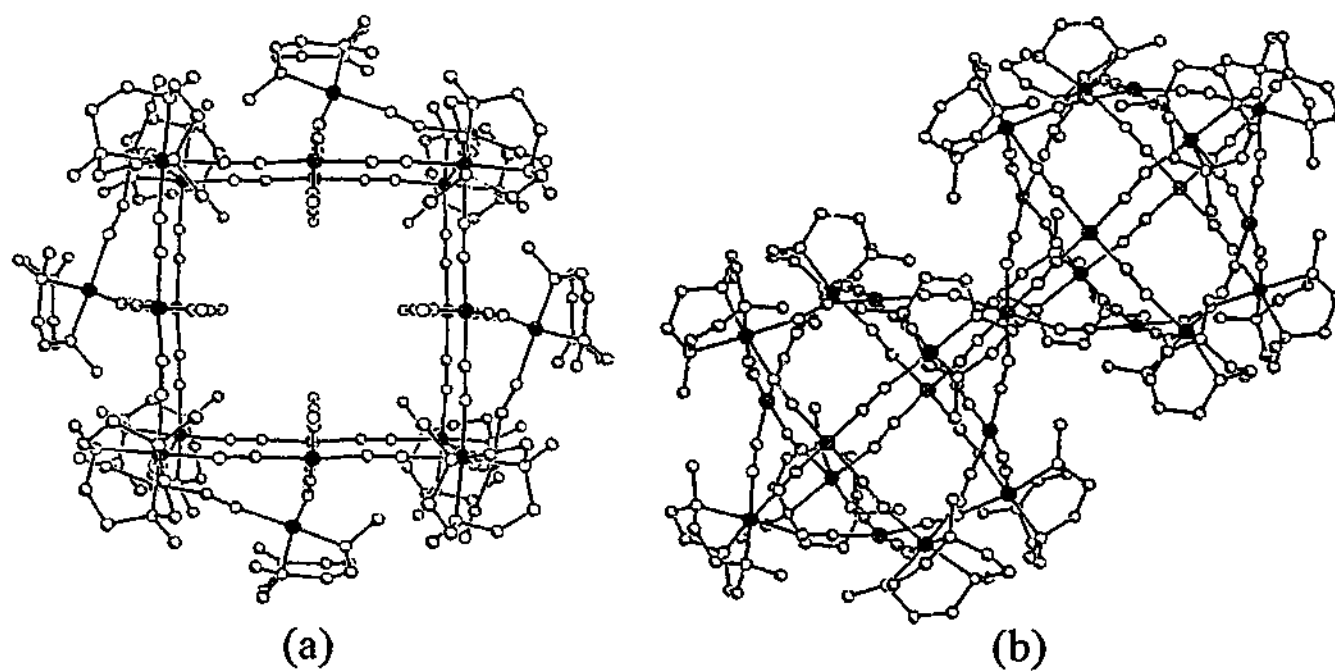


Figure 7.51 The crystal structure of (a) $[(\text{Me}_3\text{tacn})_{12}\text{Cr}_{12}\text{Ni}_{12}(\text{CN})_{48}]^{12+}$ and (b) $[(\text{Me}_3\text{tacn})_{14}\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}]^{20+}$. Black, crosshatched, shaded and white spheres correspond to Cr, Ni, C and N atoms respectively (hydrogen atoms are omitted for clarity). Reproduced from reference 193.

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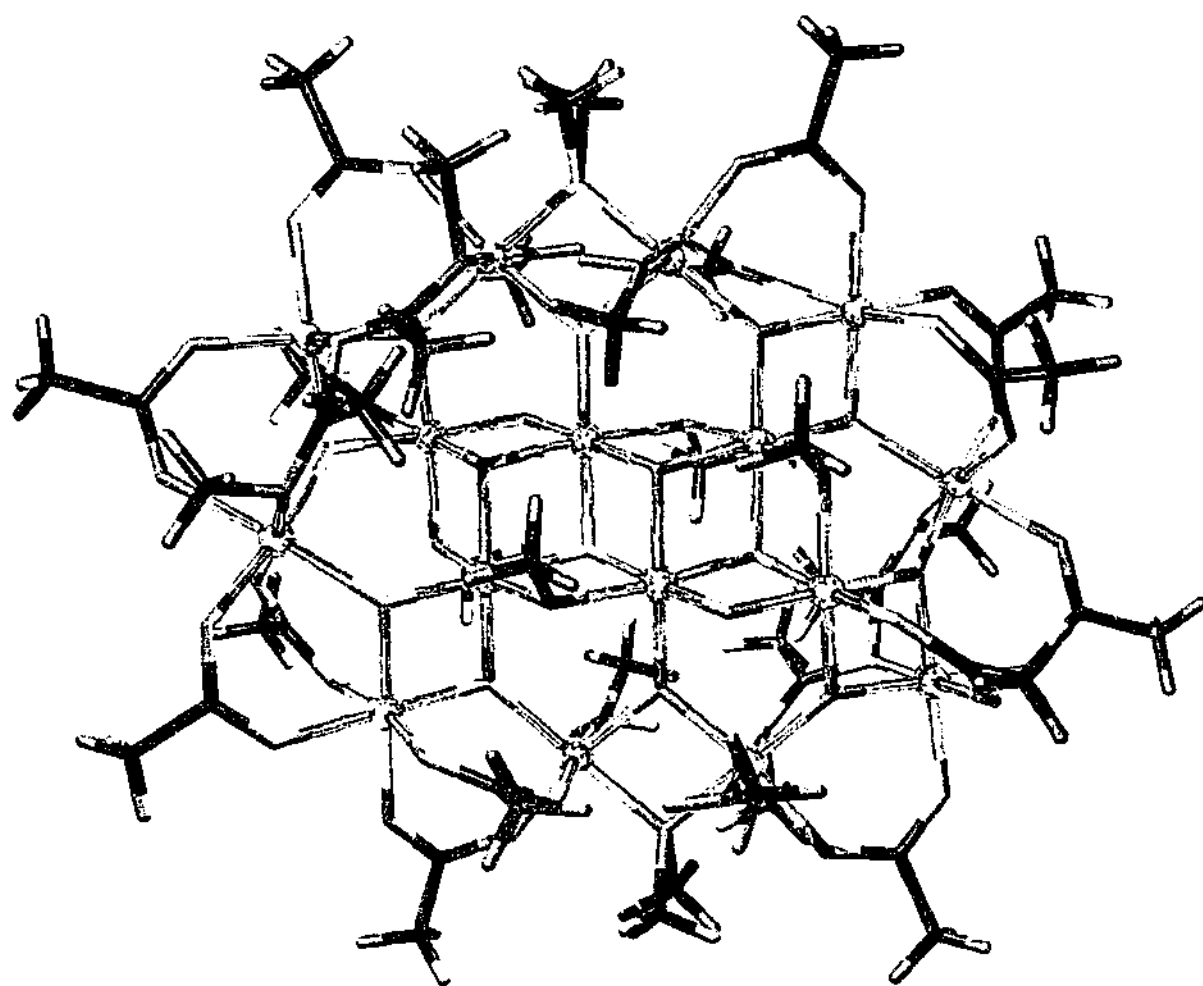
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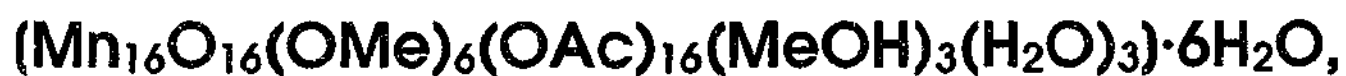
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**CHAPTER 8: SYNTHESIS, STRUCTURE AND
MAGNETISM OF A NEW
SINGLE MOLECULE MAGNET,**



AND OF A LINEAR MIXED BRIDGE CHAIN,



8.1 Introduction

The synthetic and physicochemical studies made by Christou and Hendrickson *et al.*,¹ Gatteschi and Sessoli *et al.*,² and Powell *et al.*³ on high nuclearity manganese and iron oxo/carboxylato cluster complexes have led to significant advances being made in the understanding of nanoscale magnets known as 'single molecule magnets' (SMMs). The archetypal cluster, $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{HOAc} \cdot 4\text{H}_2\text{O}$ (' Mn_{12} -acetate'), was first structurally characterised in 1980 by Lis⁴ and in 1993 it was shown to behave as a single magnetic domain with slow relaxation of magnetisation on the order of several months below a temperature of 4 K.⁵

In the case of manganese, the nuclearities known to date to display SMM behaviour include particular examples of Mn_4 ,⁶ Mn_9 ,^{7,8} Mn_{10} ,⁹ Mn_{12} ,¹⁰ Mn_{18} ,¹¹ and Mn_{30} (the largest Mn carboxylate cluster isolated to date).¹² Very recently a $\text{Mn}^{\text{III}}_{26}$ cage complex has shown preliminary evidence of SMM behaviour.¹³ Other nuclearities such as Mn_3 , Mn_6 ,^{14,15} Mn_7 ,¹⁶ Mn_8 ,^{8,15,17,18} Mn_{13} ,¹⁹ $(\text{Ba}_8\text{Na}_2)\text{Mn}_{16}(\text{II/III})$,²⁰ Mn_{21} ²¹ do not, even though some have high-spin ground states, one of the prerequisites for being an SMM. Another key prerequisite for SMM behaviour is a negative anisotropy in the axial zero-field splitting term D , which in the Mn clusters is introduced into the cluster ground state by Mn^{III} single-ion centres. The subject of SMMs is dealt with in more detail in Chapter 7.

A limited number of examples of SMM clusters containing metals other than manganese also exist. These include Fe_4 ,²² Fe_8 ,²³⁻²⁷ Fe_{10} ,^{28,29} Fe_{19} ,³ and V_4 ³⁰ complexes, and very recently particular Ni_{12} ,³¹ Ni_{21} ,³² Co_4 ,³³ and Ni_4 ³⁴ clusters have been reported to display SMM behaviour in the millikelvin temperature range. The SMM family is not limited to oxo-based species, and now includes a few examples of cyano-bridged clusters.^{35,36}

While attempting to link Mn_3 or Mn_4 carboxylate clusters together using the dicyanamide ligand, in work aimed at making molecule-based magnetic materials, a new manganese(III/IV) carboxylate cluster $[Mn_{16}O_{16}(OMe)_6(OAc)_{16}(MeOH)_3(H_2O)_3] \cdot 6H_2O$ (Mn_{16} -acetate) and a new linear chain Mn^{III} complex $[Mn(\mu-OMe)(\mu-OAc)_2]_n$ were obtained. The synthesis and properties are now described and compared to related species.

8.2 Synthesis and Characterisation of

$[Mn_{16}O_{16}(OMe)_6(OAc)_{16}(MeOH)_3(H_2O)_3] \cdot 6H_2O$ (Mn_{16} -acetate) and $[Mn(\mu-OMe)(\mu-OAc)_2]_n$

Addition of solid $n-Bu_4NMnO_4$ to a stirred solution of $Mn(NO_3)_2 \cdot 4H_2O$ in a mixture of methanol and acetic acid yielded a dark brown solution which was allowed to stand for several weeks. Black, block-like crystals of Mn_{16} -acetate were reproducibly formed, albeit in low yield. If $Na(dca)$ and Me_4NBr are included in the reaction, Mn_{16} -acetate is formed first, followed by small red crystals of $[Mn(\mu-OMe)(\mu-OAc)_2]_n$. Successive filtrations of the reaction to remove the product mixture formed, and subsequent standing yields a pure sample of $[Mn(\mu-OMe)(\mu-OAc)_2]_n$. Infrared spectra show an absorption due to $\nu(C=O)$ at 1558 and 1568 cm^{-1} for Mn_{16} -acetate and $[Mn(\mu-OMe)(\mu-OAc)_2]_n$ respectively. The crystals of the two products are readily differentiated by visual inspection.

Attempts were also made to synthesise the benzoate analogue of the Mn_{16} -acetate complex. One method involved using similar reaction conditions to those for Mn_{16} -acetate, but replacing benzoic acid for acetic acid. Another route explored was to attempt to replace the acetate groups of Mn_{16} -acetate with benzoate, in a similar method utilised by Christou *et al.* and other groups to synthesise a series of $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ derivatives of Mn_{12} -acetate, where R groups include Ph, CH_2Ph , CH_2Bu^t , Et, *p*-Tol, and *m*-Cl-Ph, by

substituting acetate groups on Mn_{12} -acetate.³⁷⁻⁴⁰ However, these attempts were unsuccessful and were not extensively pursued. The latter method presents difficulties as the Mn_{16} -acetate complex decomposes when removed from its mother liquor, and it did not dissolve in a range of common solvents tried.

8.3 Crystal Structures

8.3.1 $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_{16}(\text{MeOH})_3(\text{H}_2\text{O})_3] \cdot 6\text{H}_2\text{O}$

Crystal data are summarized for $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_{16}(\text{MeOH})_3(\text{H}_2\text{O})_3] \cdot 6\text{H}_2\text{O}$ (Mn_{16} -acetate) in Table 8.1. Selected interatomic distances and angles are given in Table 8.2 and Table 8.3 (see pages 360-362). Mn_{16} -acetate crystallizes in the triclinic space group $P\bar{1}$. The cluster lies on an inversion centre relating one half of the cluster to the other. The asymmetric unit contains half of the molecule and three lattice water molecules. The complex consists of six Mn^{IV} and ten Mn^{III} ions held together by fourteen $\mu_3\text{-O}^{2-}$, two $\mu\text{-O}^{2-}$, four $\mu\text{-OMe}^-$ and two $\mu\text{-OAc}^-$ groups to give an approximately elliptical planar $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_4(\text{OAc})_2]^{16+}$ core (Figure 8.1). Peripheral ligation consists of the remaining fourteen $\mu\text{-OAc}^-$, two $\mu\text{-OMe}^-$ groups and three axial water and methanol molecules.

The Mn_{16} core can be divided into two sub-units, a central $[\text{Mn}^{\text{IV}}_6\text{O}_6(\text{OMe})_4]^{8+}$ unit connected to an outer perimeter of ten Mn^{III} ions by ten $\mu_3\text{-O}^{2-}$ ions in the plane of the molecule and two $\mu\text{-OAc}^-$ groups perpendicular (above and below) to the plane of the molecule. The central unit contains six Mn^{IV} ions in two rows of three ($\text{Mn}(1)$, $\text{Mn}(2)$, $\text{Mn}(3)$ and the symmetry related $\text{Mn}(1^i)$, $\text{Mn}(2^i)$, $\text{Mn}(3^i)$) lying in a plane that is sandwiched between two planes of oxygen atoms. Each oxygen plane contains two $\mu_3\text{-O}^{2-}$, one $\mu\text{-O}^{2-}$ and two $\mu\text{-OMe}^-$ ions. One oxygen plane contains $\text{O}(1)$ and $\text{O}(3)$ ($\mu_3\text{-O}^{2-}$), $\text{O}(2^i)$ ($\mu\text{-O}^{2-}$) and $\text{O}(4^i)$ and $\text{O}(6^i)$ ($\mu\text{-OMe}^-$). The other oxygen plane contains $\text{O}(1^i)$ and $\text{O}(3^i)$

(μ_3 -O²⁻), O(2) (μ -O²⁻) and O(4) and O(6) (μ -OMe⁻). The Mn^{IV} ions occupy distorted octahedral sites between these two hexagonal close-packed O layers, in the manner seen in many layered manganese oxide minerals,⁴¹⁻⁴³ metal dihalides, dihydroxides and disulphides.⁴⁴ A recent review by Winpenny³¹ describes this phenomenon, whereby the cores of many large polynuclear complexes adopt a layered mineral or general CdI₂ type structure. For example, two Fe₁₇ and Fe₁₉ oxyhydroxide clusters are related to fragments of goethite or lepidocrocite.^{3,45} The CdI₂ structure is also present in several examples of manganese clusters, Mn^{III}₆Na,⁴⁶ Mn₇ (4Mn^{II}, 3Mn^{III}),¹⁶ Mn₁₀,¹ and Mn₁₉ (albeit all Mn^{II})⁴⁷ clusters and in a recently reported Mn₂₁ (12Mn^{III}, 9Mn^{IV}) cluster.²¹ Winpenny *et al.* reported a large Co₂₄ cluster, in which the core bears a very obvious relationship to Co(OH)₂.⁴⁸ Therefore, just as the Fe₁₇ and Fe₁₉ complexes have been termed "captured rusts" or "crusts",^{3,45} Mn₁₆-acetate could be thought of as a captured portion of a manganese oxide mineral. The Mn₁₂-acetate cluster, [Mn₁₂O₁₂(OAc)₁₆(H₂O)₄]·2HOAc·4H₂O,⁴ can be described as consisting of two subunits, a central [Mn^{IV}₄O₄]⁸⁺ cubane unit connected to an outer ring of [Mn^{III}₈O₈]⁸⁺.

Peripheral ligation around the Mn^{III}₁₀ perimeter in the Mn₁₆-acetate cluster consists of eight equatorial μ -OAc⁻ groups, six axial μ -OAc⁻ groups (three either side of the cluster in an alternating up-down-up fashion) and two μ -OMe⁻ ligands (bridging Mn(6) and Mn(7)). In addition there are three axially coordinated monodentate water and methanol molecules. Eight of the ten perimeter Mn^{III} ions experience Jahn-Teller (JT) axial elongation in the direction perpendicular to the plane of the cluster (Figure 8.2). The remaining two (Mn(4) and Mn(4')) experience JT axial compression roughly parallel to the plane of the cluster in the direction of a μ -OAc⁻ and a core μ_3 -O²⁻. The orientation of the JT axes of SMMs has been shown to be important to the overall cluster magnetic anisotropy and consequently the AC χ'' behaviour,⁴⁹ described later (see section 8.4.1).

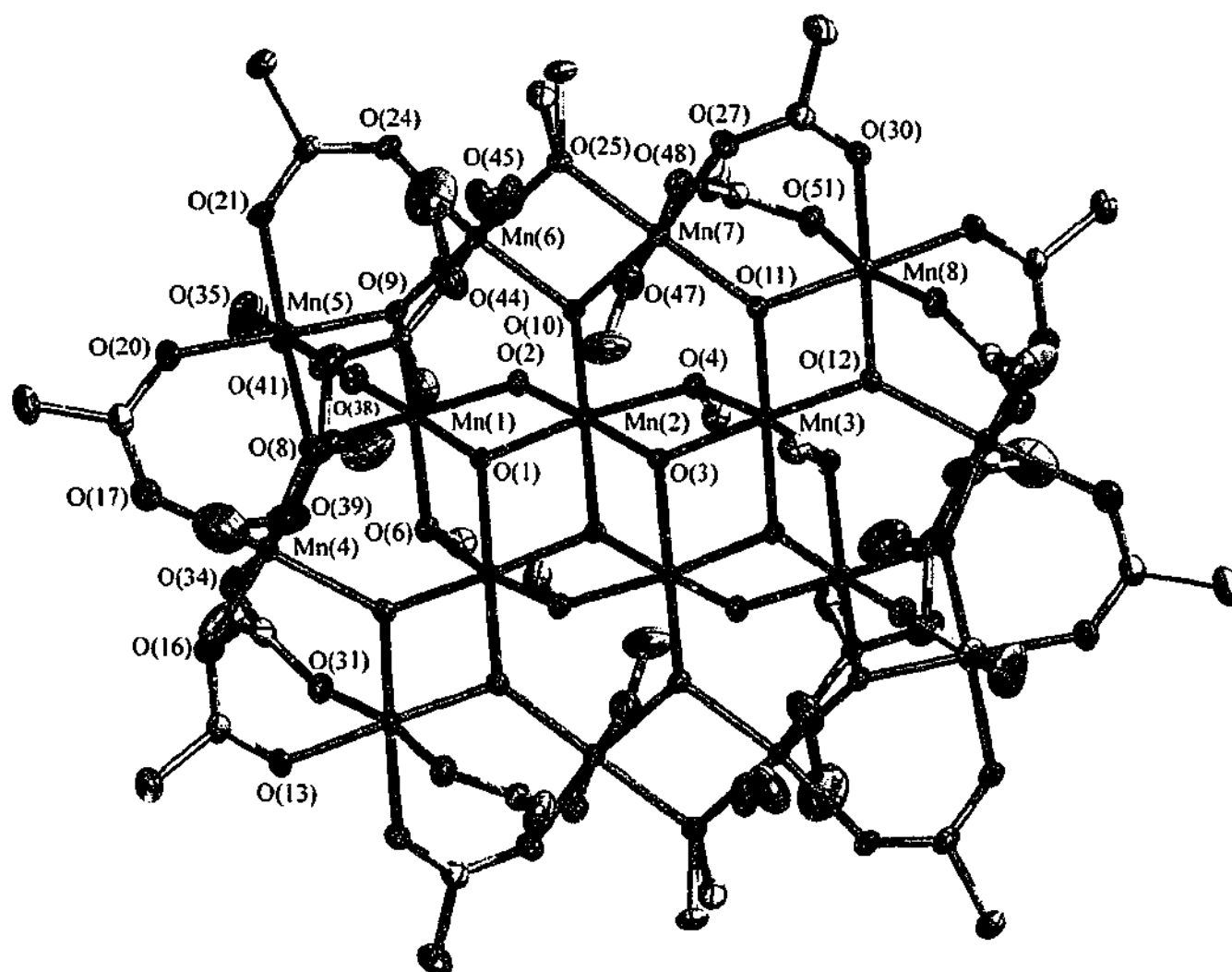


Figure 8.1 The crystal structure of $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_{16}(\text{MeOH})_3(\text{H}_2\text{O})_3] \cdot 6\text{H}_2\text{O}$ (Mn_{16} -acetate) with atom labelling scheme of manganese and oxygen atoms only (hydrogen atoms are omitted for clarity and thermal ellipsoids shown at 50 % probability). The central $[\text{Mn}^{\text{IV}}_6\text{O}_6(\text{OMe})_4]^{8+}$ sub-unit is highlighted in green.

Table 8.1 Crystal data for $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_{16}(\text{MeOH})_3(\text{H}_2\text{O})_3] \cdot 6\text{H}_2\text{O}$ (Mn_{16} -acetate) and $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$.

Compound	Mn_{16} -acetate	$[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$
Formula	$\text{C}_{41}\text{H}_{96}\text{Mn}_{16}\text{O}_{66}$	$\text{C}_5\text{H}_9\text{MnO}_5$
M	2524.22	204.06
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pbcn$
$a/\text{\AA}$	12.8547(2)	14.2547(5)
$b/\text{\AA}$	14.4366(2)	7.1796(2)
$c/\text{\AA}$	14.4590(2)	6.8865(2)
$\alpha/^\circ$	108.276(1)	
$\beta/^\circ$	116.273(1)	
$\gamma/^\circ$	96.900(1)	
$U/\text{\AA}^3$	2176.49(5)	704.79(4)
Z	1	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.926	1.923
T/K	123(2)	123(2)
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	2.343	1.842
Crystal dimensions/mm	$0.2 \times 0.15 \times 0.15$	$0.09 \times 0.05 \times 0.03$
θ ranges / $^\circ$	2.76 – 28.30	4.34 – 28.33
Index ranges	$-17 \leq h \leq 17,$ $-18 \leq k \leq 18,$ $-19 \leq l \leq 19$	$-18 \leq h \leq 18,$ $-9 \leq k \leq 8,$ $-9 \leq l \leq 9$
Completeness to $2\theta = 55^\circ$ / %	99.6	99.8
Data collected	37016	9731
Unique data (R_{int})	10573 (0.0609)	873 (0.0703)
Observed reflections [$I > 2\sigma(I)$]	8648	632
Parameters	669	66
Final R_1, wR_2 [$I > 2\sigma(I)$] ^(a)	0.0424, 0.1032	0.0337, 0.0613
(all data)	0.0580, 0.1101	0.0601, 0.0679
Goodness of fit, S	1.051	1.082
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}/\text{e \AA}^{-3}$	-0.687, 1.794	-0.449, 0.410

^(a) $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$

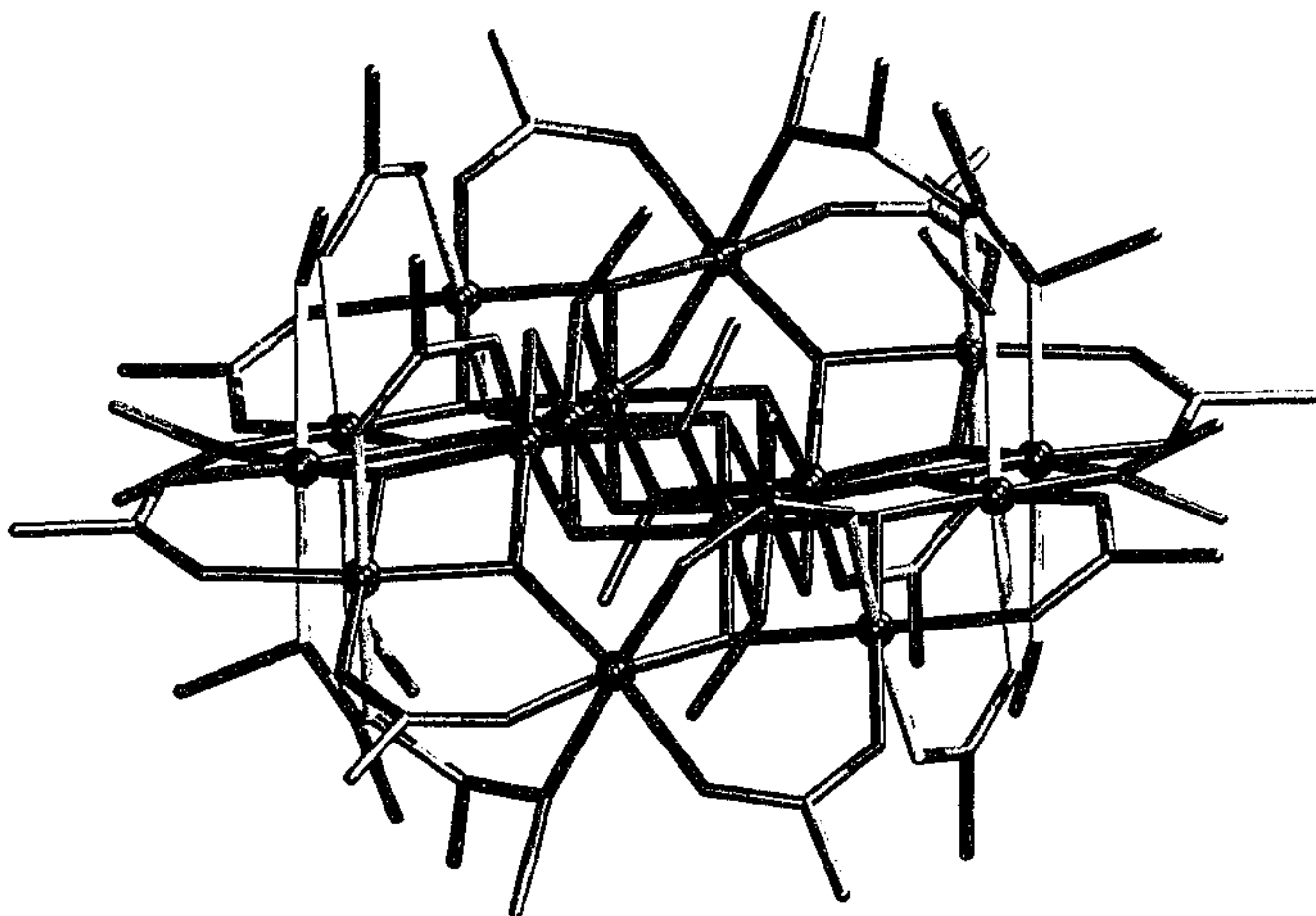


Figure 8.2 The crystal structure of Mn_{16} -acetate showing Jahn-Teller elongation (yellow) and compression (green) distortions, of the perimeter Mn^{III} atoms of Mn_{16} -acetate. Spheres represent Mn atoms.

Several regions of disorder were observed in Mn_{16} -acetate and in the lattice waters. Full details of this disorder are given in Experimental Section 8.6.3. There is positional disorder of the peripheral ligands. In particular, three terminal water ligands and one methanol ligand are disordered over four axial coordination sites (O(45), O(47) and symmetry related partners). Also, another terminal methanol and adjacent acetate group are disordered over two positions (Figure 8.3 and also Figure 8.4). A similar type of disorder has also been seen in mixed carboxylate derivatives of Mn_{12} -acetate, observed by ^1H NMR solution studies by Christou *et al.* Axial H_2O and RCO_2^- ligands exchange rapidly at room temperature.⁵⁰

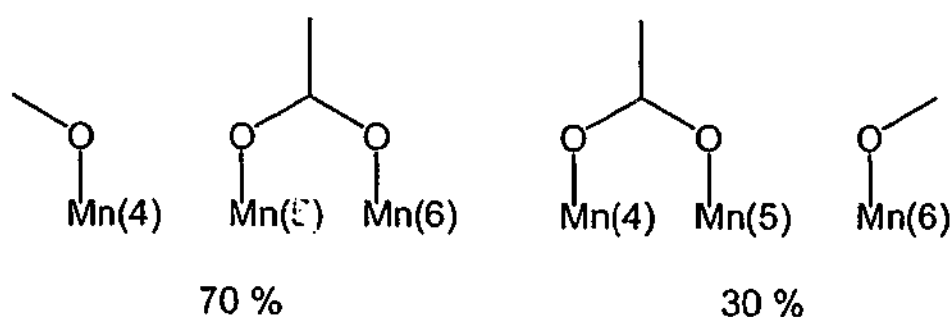


Figure 8.3 A schematic representation of the positional disorder of adjacent axial μ -OAc⁻ and terminal methanol ligands, with approximate percentage occupancies of each configuration of the ligands.

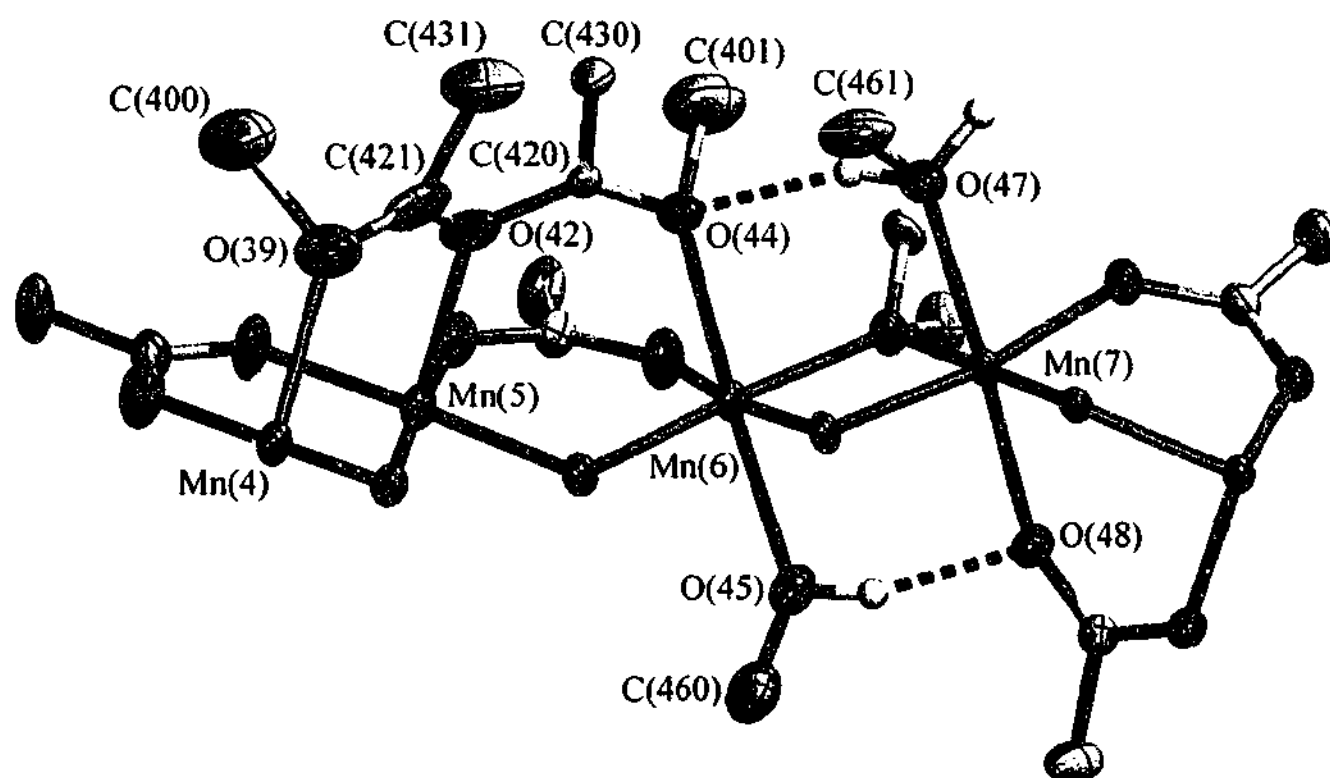


Figure 8.4 The crystal structure of a portion of the Mn^{III} perimeter of Mn₁₆-acetate, showing intra-cluster hydrogen bonding (dashed green), and disordered methanol/acetate and water/methanol (see text).

Several hydrogen bonding interactions were located in this structure (Table 8.4, see page 362). They can be divided into two types: intra-cluster and inter-cluster. Intra-cluster hydrogen bonding exists on the $\text{Mn}^{\text{III}}_{10}$ perimeter (Figure 8.4). The axially coordinated terminal disordered water/methanol (O(45)) on Mn(6) hydrogen bonds to the adjacent $\mu\text{-OAc}^-$ oxygen (O(48)) coordinated to Mn(7). In addition, the coordinated water/methanol (O(47)) on Mn(7) (*trans* to the aforementioned acetate) hydrogen bonds to the adjacent disordered methanol/acetate oxygen (O(44)) on Mn(6). Each Mn_{16} cluster is hydrogen bonded to two adjacent Mn_{16} clusters through two lattice water molecules (O(52)) located between each cluster. The lattice waters hydrogen bond to adjacent clusters *via* the axial water/methanol, O(47), on Mn(7) and an axial $\mu\text{-OAc}^-$ oxygen, O(31) on Mn(6). The lattice water molecules also hydrogen bond to their symmetry related neighbour. These hydrogen bonded chains of clusters propagate parallel to the *c*-axis direction (Figure 8.5).

The role that hydrogen bonding may play in the properties of these high-spin polynuclear manganese clusters is now being studied more closely. Recently Cornia and Gatteschi *et al.* reported the crystal structure of $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{HOAc} \cdot 4\text{H}_2\text{O}$ at 83 K^{51,52} in an effort to explain the significant magnetic anisotropy displayed by this complex despite it being highly structurally symmetrical (S_4 crystallographic symmetry). They found the two disordered acetic acid molecules of solvation transfer this disorder to the cluster by hydrogen bonding interactions thus lowering the effective symmetry of the cluster. Hence increasing magnetic anisotropy. They also reported that the water of solvation hydrogen bonds to a water ligand coordinated to one of the peripheral Mn^{III} atoms. The water ligand also hydrogen bonds to an adjacent bridging acetate. This pattern of hydrogen bonding is very similar to that seen in Mn_{16} -acetate. However, no mention is made of inter-cluster hydrogen bonding interactions.

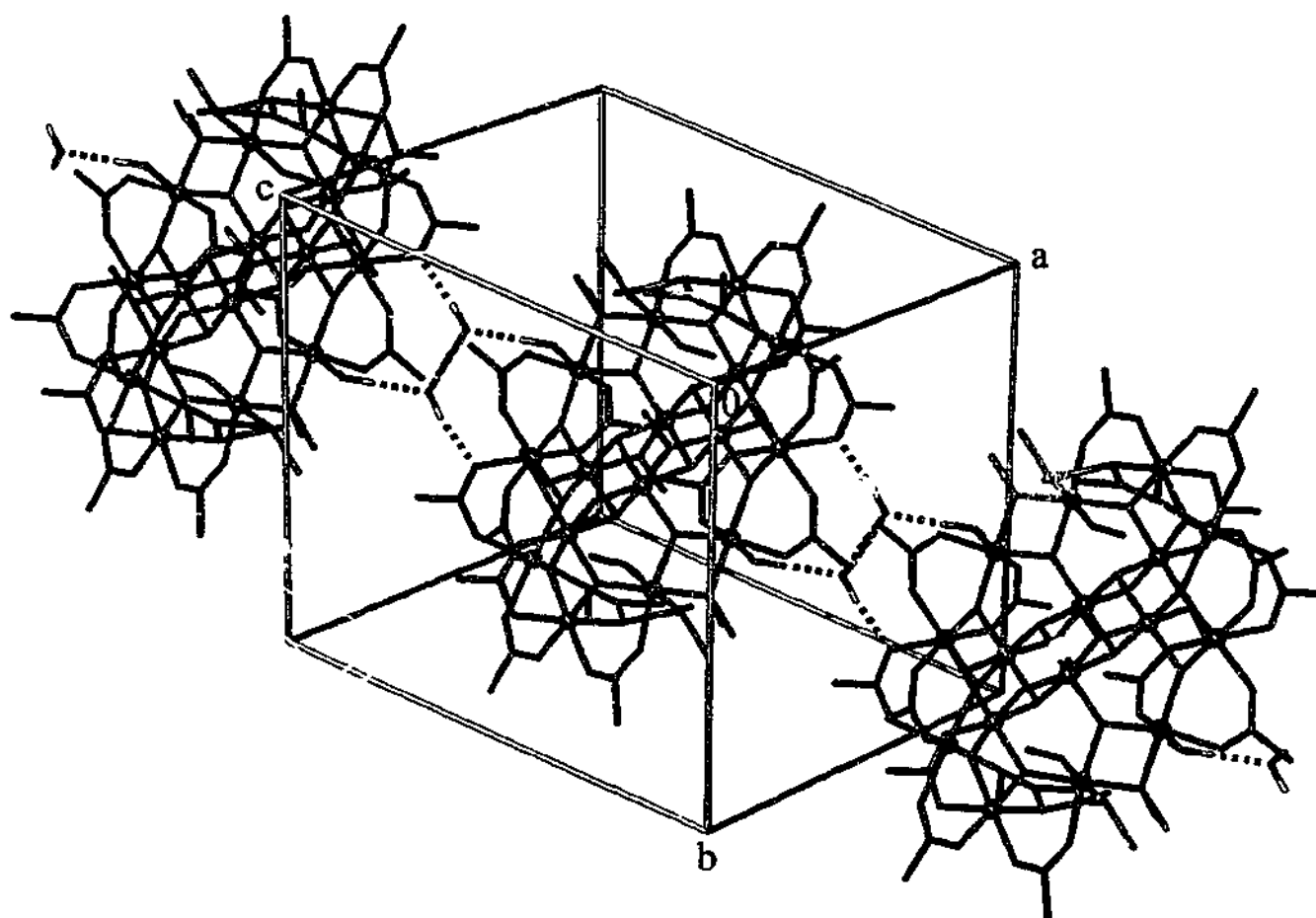


Figure 8.5 A single hydrogen bonded chain of Mn_{16} -acetate running parallel to the c -axis direction (hydrogen bonds shown in dashed green).

Wernsdorfer and Christou *et al.* have also recently reported a supramolecular dimer of Mn_4 SMMs.⁶ They find that due to antiferromagnetic coupling, between the two components, the dimer displays quantum behaviour different from that of the individual tetranuclear components, possibly *via* six $\text{C-H}\cdots\text{Cl}$ hydrogen bonds and a $\text{Cl}\cdots\text{Cl}$ interaction. The dimer displays an exchange-bias of the quantum tunnelling transition with no tunnelling (i.e. no hysteresis step) at $H = 0$. Hendrickson *et al.*^{33,34} have also made similar observations on M_4 cubane clusters of Co^{II} and Ni^{II} .

Table 8.2 Selected interatomic distances (Å) and angles (°) for the central $[\text{Mn}^{\text{IV}}_6\text{O}_5(\text{OMe})_4]^{8+}$ unit and surrounds of Mn_{16} -acetate.

Mn(1)–O(1)	1.898(2)	Mn(2)–O(1)	1.893(2)	Mn(3)–O(1 ⁱ)	1.917(2)
Mn(1)–O(2)	1.827(2)	Mn(2)–O(2)	1.835(2)	Mn(3)–O(3)	1.920(2)
Mn(1)–O(6)	1.937(2)	Mn(2)–O(3)	1.941(2)	Mn(3)–O(4)	1.942(2)
Mn(1)–O(8)	1.920(2)	Mn(2)–O(3 ⁱ)	1.916(2)	Mn(3)–O(6 ⁱ)	1.926(2)
Mn(1)–O(9)	1.857(2)	Mn(2)–O(4)	1.945(2)	Mn(3)–O(11)	1.860(2)
Mn(1)–O(38)	1.924(2)	Mn(2)–O(10)	1.896(2)	Mn(3)–O(12)	1.861(2)
Mn(1)···Mn(2)	2.7593(6)	Mn(2)···Mn(3 ⁱ)	2.8906(6)	Mn(3)···Mn(1 ⁱ)	2.8644(6)
Mn(1)···Mn(3 ⁱ)	2.8644(6)	Mn(2)···Mn(2 ⁱ)	2.9082(9)	Mn(3)···Mn(2 ⁱ)	2.8906(6)
		Mn(2)···Mn(3)	2.9149(6)		
O(2)–Mn(1)–O(9)	93.9(1)	O(1)–Mn(2)–O(3)	96.80(9)		
O(2)–Mn(1)–O(1)	84.33(9)	O(10)–Mn(2)–O(3)	90.40(9)		
O(9)–Mn(1)–O(1)	91.90(9)	O(3 ⁱ)–Mn(2)–O(3)	82.13(9)		
O(2)–Mn(1)–O(8)	172.9(1)	O(2)–Mn(2)–O(4)	96.87(9)		
O(9)–Mn(1)–O(8)	82.44(1)	O(1)–Mn(2)–O(4)	174.33(9)		
O(1)–Mn(1)–O(8)	89.77(9)	O(10)–Mn(2)–O(4)	91.87(9)		
O(2)–Mn(1)–O(38)	92.4(1)	O(3 ⁱ)–Mn(2)–O(4)	92.28(9)		
O(9)–Mn(1)–O(38)	94.2(1)	O(3)–Mn(2)–O(4)	81.79(9)		
O(1)–Mn(1)–O(38)	173.2(1)	O(11)–Mn(3)–O(12)	85.19(9)		
O(8)–Mn(1)–O(38)	93.7(1)	O(11)–Mn(3)–O(1 ⁱ)	176.90(9)		
O(2)–Mn(1)–O(6)	91.56(9)	O(12)–Mn(3)–O(1 ⁱ)	96.73(9)		
O(9)–Mn(1)–O(6)	172.4(1)	O(11)–Mn(3)–O(3)	96.73(9)		
O(1)–Mn(1)–O(6)	83.47(9)	O(12)–Mn(3)–O(3)	178.02(9)		
O(8)–Mn(1)–O(6)	91.52(9)	O(1 ⁱ)–Mn(3)–O(3)	81.37(9)		
O(2)–Mn(1)–O(6)	90.7(1)	O(11)–Mn(3)–O(6 ⁱ)	94.36(9)		
O(2)–Mn(2)–O(1)	84.22(9)	O(12)–Mn(3)–O(6 ⁱ)	88.84(9)		
O(2)–Mn(2)–O(10)	92.86(9)	O(1 ⁱ)–Mn(3)–O(6 ⁱ)	83.26(9)		
O(1)–Mn(2)–O(10)	93.63(9)	O(3)–Mn(3)–O(6 ⁱ)	91.44(9)		
O(2)–Mn(2)–O(3 ⁱ)	94.73(9)	O(11)–Mn(3)–O(4)	91.09(9)		
O(1)–Mn(2)–O(3 ⁱ)	82.08(9)	O(12)–Mn(3)–O(4)	97.12(9)		
O(10)–Mn(2)–O(3 ⁱ)	170.85(9)	O(1 ⁱ)–Mn(3)–O(4)	91.08(9)		
O(2)–Mn(2)–O(3)	176.51(9)	O(3)–Mn(3)–O(4)	82.43(9)		
		O(6 ⁱ)–Mn(3)–O(4)	172.24(9)		

Symmetry transformation: (i) 1-x, 1-y, 1-z.

Table 8.3 Selected interatomic distances (Å) and angles (°) for the outer Mn^{III}₁₀ perimeter of Mn₁₆-acetate.

Mn(4)–O(8)	1.863(2)	Mn(5)–O(41)	2.203(3)	Mn(7)–O(11)	1.900(2)
Mn(4)–O(16)	1.948(3)	Mn(5)–O(35)	2.244(3)	Mn(7)–O(25)	1.934(2)
Mn(4)–O(34)	2.029(3)	Mn(6)–O(9)	1.869(2)	Mn(7)–O(27)	1.941(2)
Mn(4)–O(12 ⁱ)	2.049(2)	Mn(6)–O(25)	1.908(2)	Mn(7)–O(48)	2.216(2)
Mn(4)–O(17)	2.093(3)	Mn(6)–O(10)	1.917(2)	Mn(7)–O(47)	2.237(3)
Mn(4)–O(39)	2.125(3)	Mn(6)–O(24)	1.964(2)	Mn(8)–O(12)	1.883(2)
Mn(5)–O(9)	1.879(2)	Mn(6)–O(44)	2.217(3)	Mn(8)–O(11)	1.905(2)
Mn(5)–O(8)	1.883(2)	Mn(6)–O(45)	2.269(3)	Mn(8)–O(13 ⁱ)	1.959(2)
Mn(5)–O(20)	1.914(2)	Mn(6)–Mn(7)	2.9321(6)	Mn(8)–O(30)	1.974(2)
Mn(5)–O(21)	1.956(2)	Mn(7)–O(10)	1.897(2)	Mn(8)–O(51)	2.169(2)
Mn(4)···Mn(5)	3.3818(7)	Mn(4)···Mn(1)	3.4746(7)	Mn(8)–O(31 ⁱ)	2.191(2)
Mn(5)···Mn(6)	3.3509(7)	Mn(5)···Mn(1)	2.8066(7)	Mn(7)···Mn(3)	3.3965(6)
Mn(6)···Mn(7)	2.9321(6)	Mn(6)···Mn(1)	3.3761(7)	Mn(8)···Mn(3)	2.7845(6)
Mn(7)···Mn(8)	3.3330(6)	Mn(6)···Mn(2)	3.4126(6)	Mn(4 ⁱ)···Mn(3)	3.5317(6)
Mn(8)···Mn(4 ⁱ)	3.3828(7)	Mn(7)···Mn(2)	3.4521(6)		
O(8)–Mn(4)–O(16)	172.2(1)	O(25)–Mn(6)–O(44)	87.7(1)		
O(8)–Mn(4)–O(34)	91.4(1)	O(10)–Mn(6)–O(44)	90.3(1)		
O(16)–Mn(4)–O(34)	91.1(1)	O(24)–Mn(6)–O(44)	90.6(1)		
O(8)–Mn(4)–O(12 ⁱ)	94.71(9)	O(9)–Mn(6)–O(45)	87.4(1)		
O(16)–Mn(4)–O(12 ⁱ)	92.4(1)	O(25)–Mn(6)–O(45)	90.1(1)		
O(34)–Mn(4)–O(12 ⁱ)	95.39(9)	O(10)–Mn(6)–O(45)	87.4(1)		
O(8)–Mn(4)–O(17)	90.1(1)	O(24)–Mn(6)–O(45)	91.4(1)		
O(16)–Mn(4)–O(17)	82.6(1)	O(44)–Mn(6)–O(45)	177.0(1)		
O(34)–Mn(4)–O(17)	88.1(1)	O(10)–Mn(7)–O(11)	99.45(9)		
O(12 ⁱ)–Mn(4)–O(17)	174.0(1)	O(10)–Mn(7)–O(25)	79.94(9)		
O(8)–Mn(4)–O(39)	93.4(1)	O(11)–Mn(7)–O(25)	178.8(1)		
O(16)–Mn(4)–O(39)	83.4(1)	O(10)–Mn(7)–O(27)	167.4(1)		
O(34)–Mn(4)–O(39)	172.8(1)	O(11)–Mn(7)–O(27)	92.7(1)		
O(12 ⁱ)–Mn(4)–O(39)	89.6(1)	O(25)–Mn(7)–O(27)	88.0(1)		
O(17)–Mn(4)–O(39)	86.5(1)	O(10)–Mn(7)–O(48)	89.96(9)		
O(9)–Mn(5)–O(8)	82.86(9)	O(11)–Mn(7)–O(48)	93.25(9)		
O(9)–Mn(5)–O(20)	176.9(1)	O(25)–Mn(7)–O(48)	85.66(9)		
O(8)–Mn(5)–O(20)	97.6(1)	O(10)–Mn(7)–O(47)	88.9(1)		
O(9)–Mn(5)–O(21)	93.41(1)	O(11)–Mn(7)–O(47)	92.4(1)		
O(8)–Mn(5)–O(21)	175.2(1)	O(25)–Mn(7)–O(47)	88.7(1)		
O(20)–Mn(5)–O(21)	86.0(1)	O(27)–Mn(7)–O(47)	87.1(1)		

O(9)–Mn(5)–O(41)	92.9(1)	O(48)–Mn(7)–O(47)	174.4(1)
O(8)–Mn(5)–O(41)	92.0(1)	O(12)–Mn(8)–O(11)	83.32(9)
O(20)–Mn(5)–O(41)	90.1(1)	O(12)–Mn(8)–O(13 ⁱ)	96.8(1)
O(21)–Mn(5)–O(41)	91.3(1)	O(11)–Mn(8)–O(13 ⁱ)	178.6(1)
O(9)–Mn(5)–O(35)	85.6(1)	O(12)–Mn(8)–O(30)	178.6(1)
O(8)–Mn(5)–O(35)	86.4(1)	O(11)–Mn(8)–O(30)	95.42(9)
O(20)–Mn(5)–O(35)	91.5(1)	O(13 ⁱ)–Mn(8)–O(30)	84.4(1)
O(21)–Mn(5)–O(35)	90.2(1)	O(12)–Mn(8)–O(51)	90.79(9)
O(41)–Mn(5)–O(35)	177.91(9)	O(11)–Mn(8)–O(51)	94.74(9)
O(9)–Mn(6)–O(25)	177.2(1)	O(13 ⁱ)–Mn(8)–O(51)	83.85(9)
O(9)–Mn(6)–O(10)	98.60(9)	O(30)–Mn(8)–O(51)	89.9(1)
O(25)–Mn(6)–O(10)	80.09(9)	O(12)–Mn(8)–O(31 ⁱ)	94.46(9)
O(9)–Mn(6)–O(24)	91.1(1)	O(11)–Mn(8)–O(31 ⁱ)	93.26(9)
O(10)–Mn(6)–O(24)	170.2(1)	O(13 ⁱ)–Mn(8)–O(31 ⁱ)	88.1(1)
O(9)–Mn(6)–O(44)	94.8(1)	O(30)–Mn(8)–O(31 ⁱ)	84.97(9)
		O(51)–Mn(8)–O(31 ⁱ)	170.89(9)

Symmetry transformation: (i) 1-x, 1-y, 1-z.

Table 8.4 Hydrogen bonding distances (Å) angles (°) for Mn₁₆-acetate.

O(45)–H(45)	0.87(2)	O(47)–H(47A)	0.95(7)
H(45)···O(48)	1.90(3)	H(47A)···O(52)	1.81(7)
O(45)···O(48)	2.734(3)	O(47)···O(52)	2.732(4)
O(52)–H(52A)	0.89(2)	O(52)–H(52B)	0.90(2)
H(52A)···O(52 ⁱⁱ)	1.96(4)	H(52B)···O(31 ⁱⁱⁱ)	1.89(2)
O(52)···O(52 ⁱⁱ)	2.768(8)	O(52)···O(31 ⁱⁱⁱ)	2.781(4)
O(47)–H(47B)	0.87(2)		
H(47B)···O(44)	2.01(3)		
O(47)···O(44)	2.851(4)		
O(45)–H(45)···O(48)	159(5)	O(47)–H(47A)···O(52)	163(6)
O(52)–H(52A)···O(52 ⁱⁱ)	150(6)	O(52)–H(52B)···O(31 ⁱⁱⁱ)	168(5)
O(47)–H(47B)···O(44)	160(6)		

Symmetry transformations: (ii) 1-x, 1-y, -z; (iii) x, y, z-1.

8.3.2 $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$

Crystal data are summarised for $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$ in Table 8.1 (see page 355). Selected interatomic distances and angles are given in Table 8.5 (see page 365). $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$ crystallises in the orthorhombic space group $Pbcn$. The asymmetric unit contains one bridging acetate ligand, half a manganese(III) atom and half a bridging methoxide ligand. The structure (Figure 8.6) consists of infinite linear 1D chains of manganese(III) atoms bridged by two $\mu\text{-OAc}^-$ ligands and one $\mu\text{-OMe}^-$. Each manganese(III) is coordinated in a distorted octahedral environment. As expected for a high-spin d^4 ion, the metal centres are Jahn-Teller distorted with elongation of the axial bonds to one oxygen atom each of the two $\mu\text{-OAc}^-$ ligands ($\text{Mn}(1)\text{--O}(6^{\text{ii}}) = 2.171(2) \text{ \AA}$). The equatorial coordination plane consists of two oxygen atoms from two $\mu\text{-OMe}^-$ ligands ($\text{Mn}(1)\text{--O}(1) = 1.946(1) \text{ \AA}$) and the other two oxygens of the two $\mu\text{-OAc}^-$ ligands ($\text{Mn}(1)\text{--O}(3) = 1.932(2) \text{ \AA}$). The hydrogen atoms of the bridging methoxide group are disordered over two positions due to the methoxide lying on a rotational 2-fold axis. The chains run parallel to the c -axis direction. The intra-chain $\text{Mn}\cdots\text{Mn}$ distance is equal to half the unit cell length c ($3.4433(1) \text{ \AA}$). The inter-chain $\text{Mn}\cdots\text{Mn}$ distance to adjacent chains in the b -axis direction is equal to the unit cell length b ($7.1796(2) \text{ \AA}$). The next shortest inter-chain $\text{Mn}\cdots\text{Mn}$ distance is equal to half the diagonal of the ab -unit cell face ($7.9803(2) \text{ \AA}$). Figure 8.7 shows five chains viewed parallel to the c -axis.

The structure of $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$ is rather similar to a related complex, $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$, described in Chapter 6. The latter also consists of a triply bridged linear chain of manganese(III) atoms and these chains hydrogen bond to adjacent chains *via* the $\mu\text{-OH}$ and lattice acetic acid and water molecules to form pseudo 2D sheets. It displays long-range antiferromagnetic order ($T_N = 6.1 \text{ K}$) that is probably facilitated by the hydrogen bonding pathways. The lack of magnetic order in the complex

described here (see Section 8.4.2) would seem to support this conclusion, as it is superficially identical but without the hydrogen bonding network.

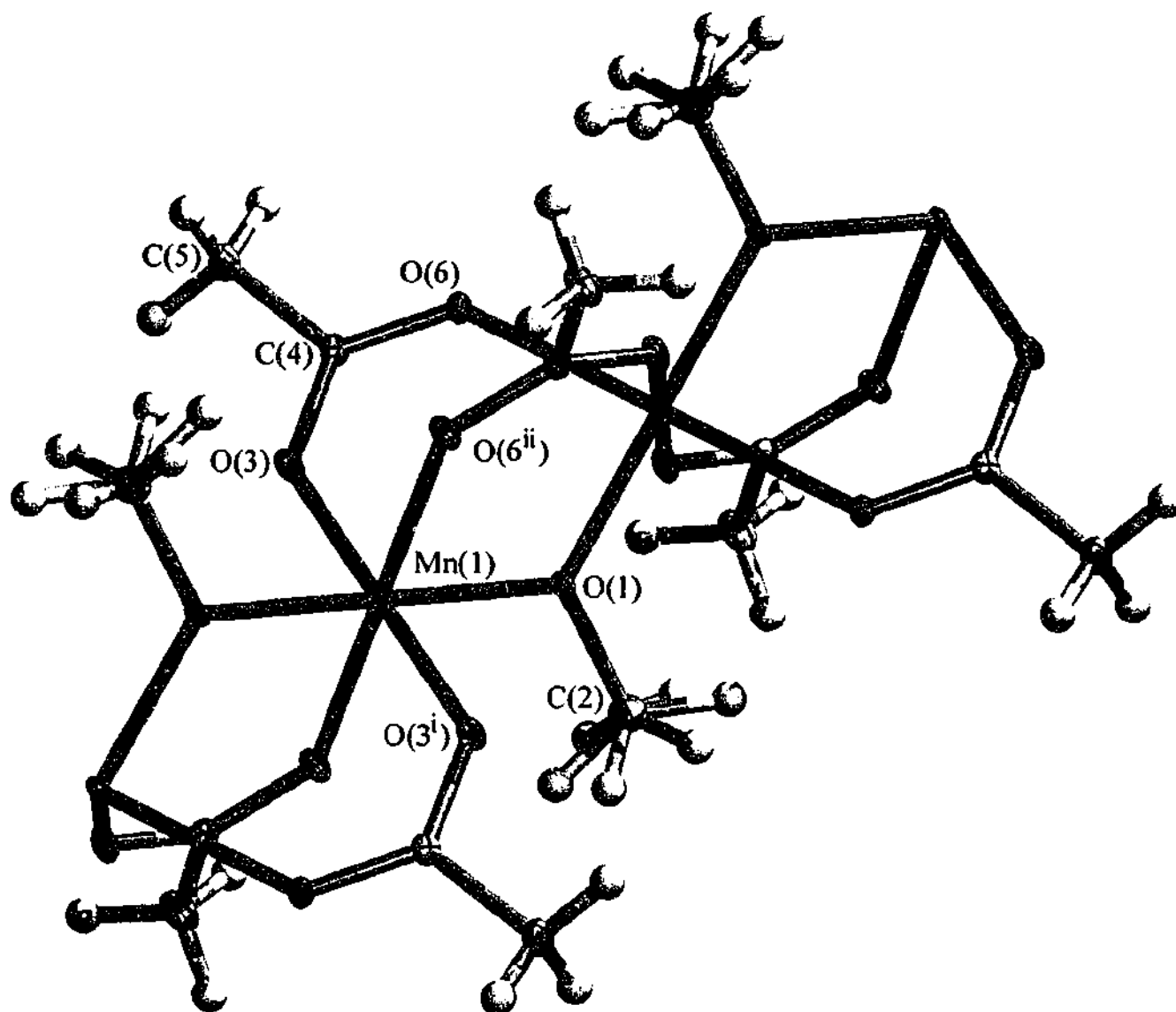


Figure 8.6 The crystal structure of $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$ with atom labelling scheme shown (thermal ellipsoids shown at 50% probability). Disorder of methoxide hydrogen atoms is due to site symmetry (see text).

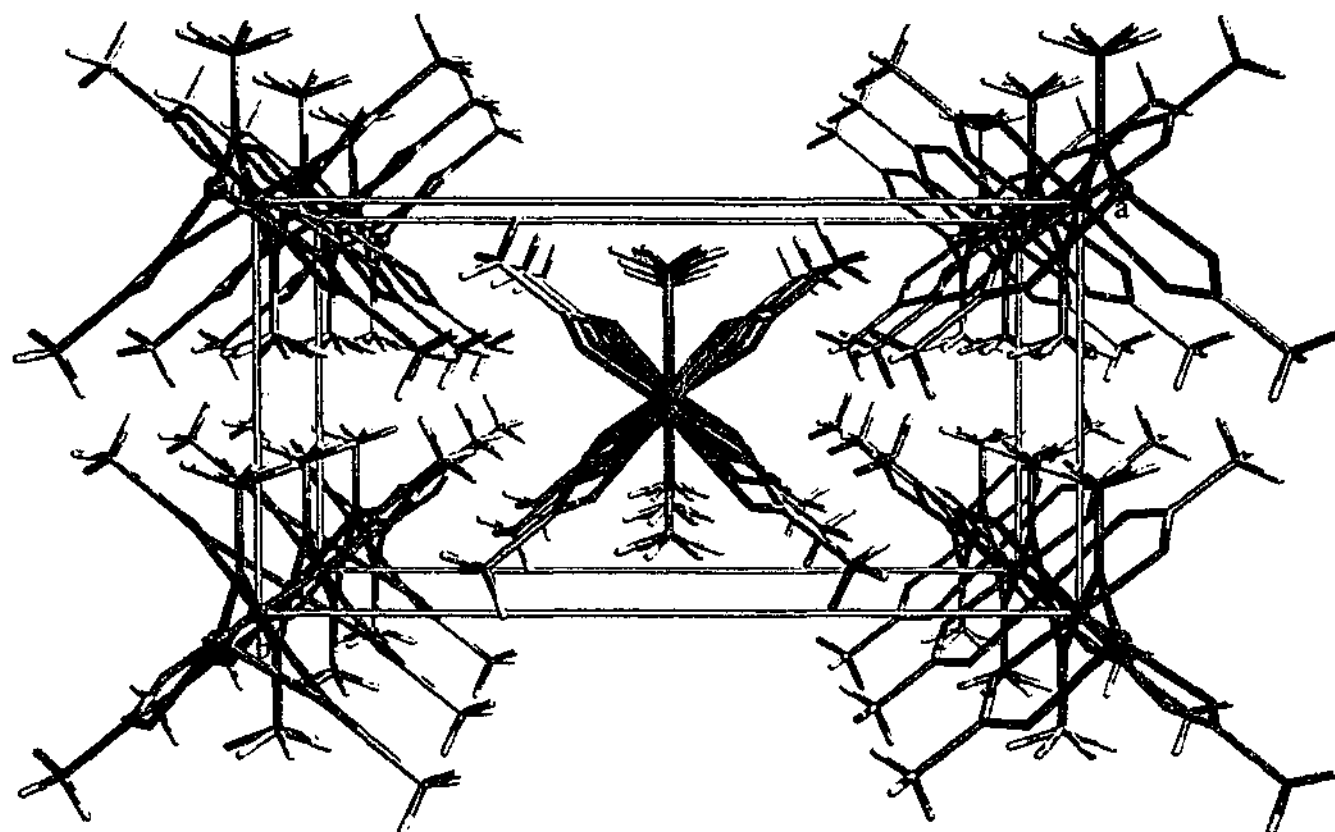


Figure 8.7 Packing diagram of $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$ viewed parallel to the c -axis (spheres represent Mn ions).

Table 8.5 Selected interatomic distances (Å) and angles (°) for $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$.

Mn(1)–O(1)	1.946(1)	Mn(1)–O(6 ⁱⁱ)	2.171(2)
Mn(1)–O(3)	1.932(2)		
O(1)–Mn(1)–O(3)	93.15(6)	O(1)–Mn(1)–O(3 ⁱ)	86.85(6)
O(1)–Mn(1)–O(6 ⁱⁱ)	90.54(6)	O(3)–Mn(1)–O(6 ⁱⁱ)	91.54(8)
O(1)–Mn(1)–O(6 ⁱⁱⁱ)	90.54(6)	O(3)–Mn(1)–O(6 ⁱⁱⁱ)	88.46(8)

Symmetry transformations: (i) $1-x, 1-y, -z$; (ii) $1-x, y, 1/2-z$; (iii) $x, 1-y, z-1/2$.

8.4 Magnetism

8.4.1 $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_{16}(\text{MeOH})_3(\text{H}_2\text{O})_3]\cdot 6\text{H}_2\text{O}$

Magnetic susceptibilities were measured as a function of temperature on freshly isolated samples of Mn_{16} -acetate in a field of 1 T over the range 2–300 K (Figure 8.8). The same results were obtained on neat powders and on Vaseline mulls. The effective magnetic moment, per Mn_{16} , decreases gradually from $14.0 \mu_{\text{B}}$ at 300 K to *ca.* $10.5 \mu_{\text{B}}$, then more rapidly, reaching $5.7 \mu_{\text{B}}$ at 2 K and still decreasing. The value of μ_{eff} at 300 K compares to the value of $18.16 \mu_{\text{B}}$ calculated for six uncoupled Mn^{IV} ($S = 3/2$) and ten Mn^{III} ($S = 4/2$) and is thus indicative of overall antiferromagnetic coupling.

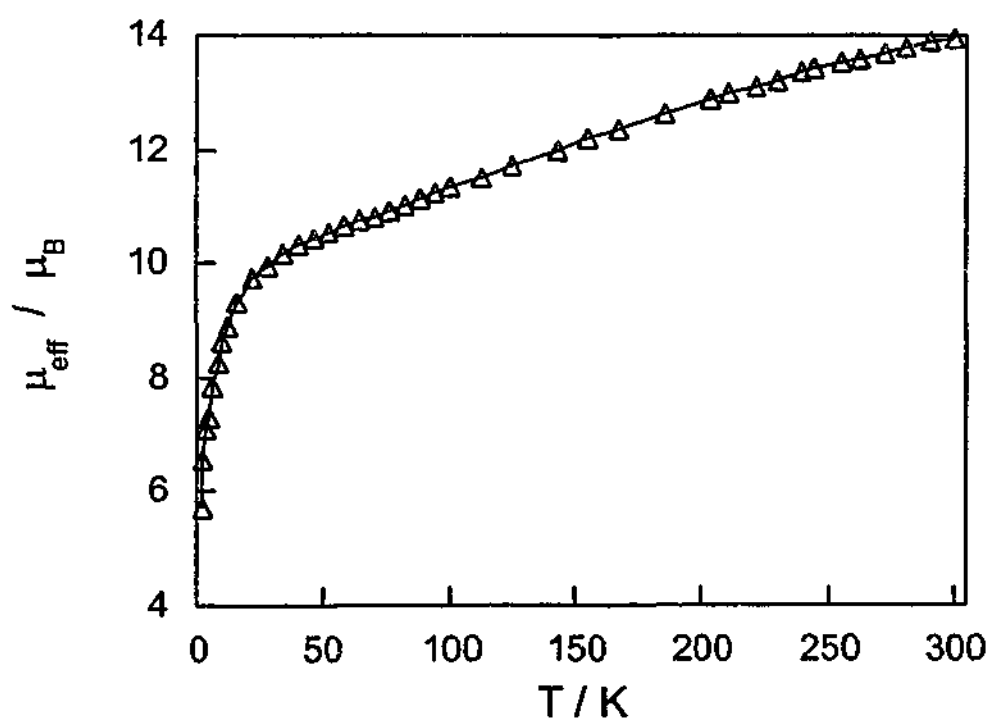


Figure 8.8 Plot of μ_{eff} vs. temperature in $H = 1$ T for Mn_{16} -acetate.

To try to identify the ground spin state of Mn_{16} -acetate, magnetization (M) measurements were made in the ranges of $H = 0$ –5 T and temperature = 2–20 K (Figure 8.9). It can be seen that, at 2 K, the M values increase in a smooth, curved fashion between

0 and 5 T to reach *ca.* $7 N\beta$ in the 5 T field. The M values are still increasing and saturation is not achieved. This is most likely due to thermal population of the ground-state and of other low lying spin-states occurring even at 2 K. Zero-field splitting and Zeeman effects will also influence the shape and size of the M vs. H plots. Weak cluster-cluster interactions, *via* hydrogen bonding pathways, may also play a part. It is therefore not possible, without fitting of the M/H data, to unambiguously assign the ground state spin. When the M/H data are plotted as M vs. $H/\text{temperature}$ in the way commonly employed by Hendrickson and Christou, Figure 8.10 is obtained. The separation of the lines indicates zero-field splitting is occurring.

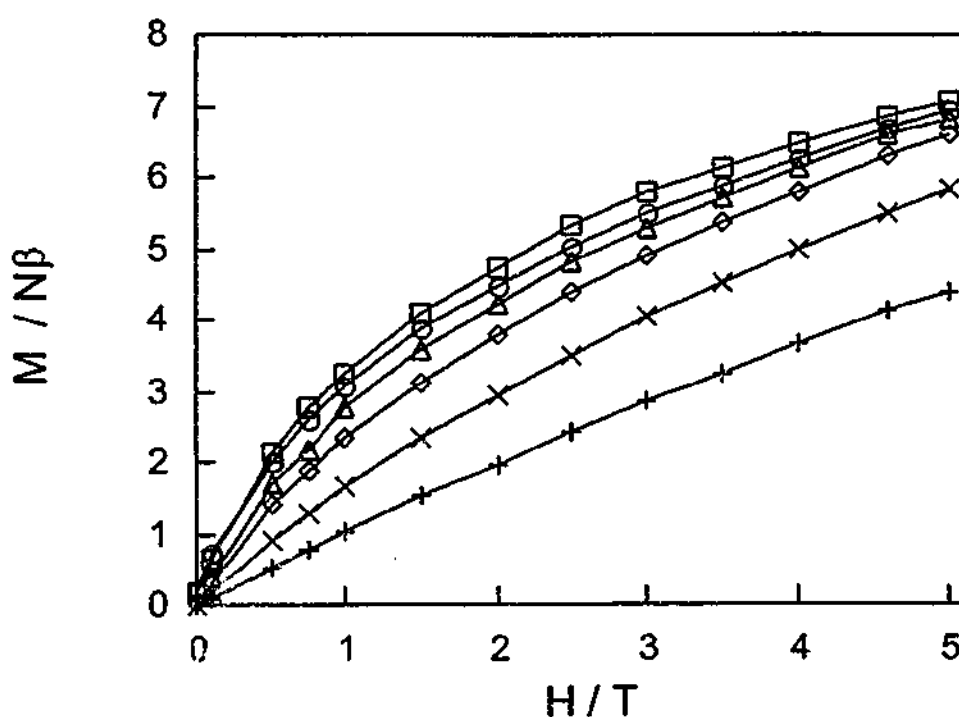


Figure 8.9 Plots of magnetization, M vs. applied field (Tesla) for Mn_{16} -acetate, at various temperatures 2 K ($\square$), 3 K ($\circ$), 4 K (Δ), 5.5 K ($\diamond$), 10 K ($\times$), and 20 K ($+$). The solid lines simply join the isothermal points and are not fitted curves.

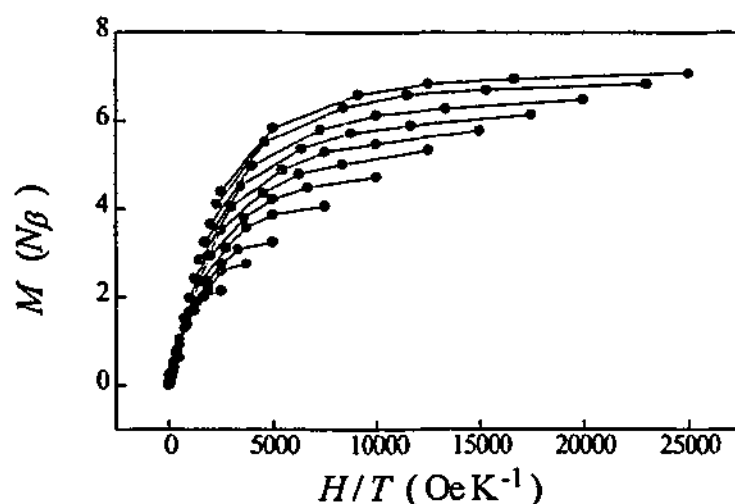


Figure 8.10 Plots of Magnetisation, M vs. H/T for the field values (from top): $H = 5, 4.6, 4, 3.5, 3, 2.5, 2, 1.5, 1, 0.75$ and 0.5 Tesla.

A hysteresis loop measured in low fields (± 0.2 T) on a neat powder at 2 K shows a rapid increase in M in the ± 250 Oe region (Figure 8.11). To observe the characteristic 'stepped' hysteresis loops of SMMs, due to quantum tunnelling, requires the use of single crystals or collections of oriented crystals and so this rapid increase through zero field is unlikely to be such a step.

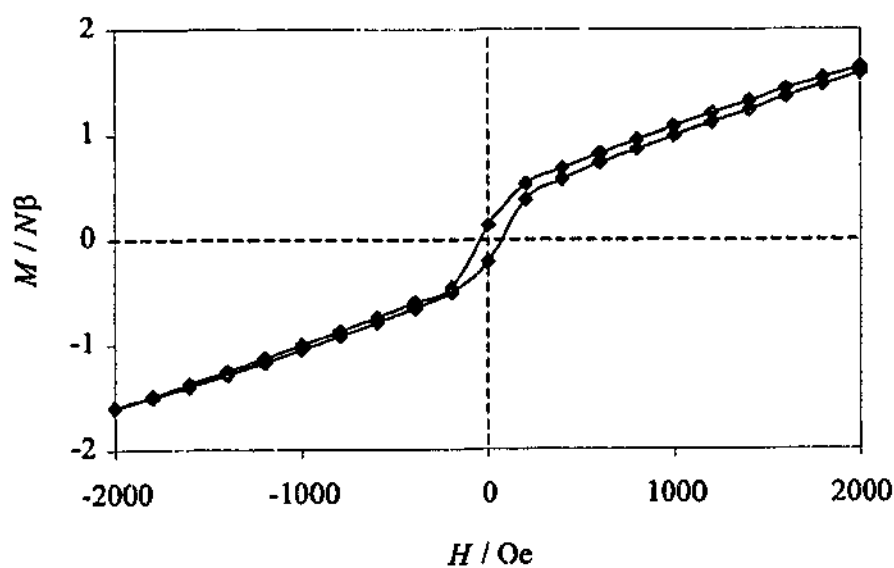


Figure 8.11 Hysteresis plot of a powder sample of Mn_{16} -acetate dispersed in Vaseline, at 2 K.

Detailed AC susceptibility studies were made as a function of frequency (50 - 1500 Hz) in the temperature range 2-10 K, and these are plotted as $\chi'_M T$ vs. T and χ''_M vs. T in Figure 8.12. The $\chi'_M T$ values between 8-10 K ($\sim 8.5 \text{ cm}^3 \text{mol}^{-1} \text{K}$) are independent of frequency and are of similar magnitude to the DC values of $\chi_M T$ in this temperature range. If all the Mn_{16} molecules were populating an isolated $S = 3$ ground state, and assuming $g = 2.0$, the $\chi'_M T$ value would be $6.01 \text{ cm}^3 \text{mol}^{-1} \text{K}$, while population of only an $S = 4$ ground state would yield $\chi'_M T = 10.01 \text{ cm}^3 \text{mol}^{-1} \text{K}$. The observed $\chi'_M T$ value is of an intermediate value, as is the DC magnetisation value, M , at a temperature of 2 K and a field of 5 T ($M \sim 7 N\beta$). Thus, as indicated earlier, the data suggest that there is not an isolated ground S level, but that levels are close together and zero-field splitting and Zeeman effects play a part. Below 8 K the $\chi'_M T$ values for Mn_{16} -acetate decrease rapidly, indicative of the onset of slow magnetic relaxation. At higher frequencies, the decrease in $\chi'_M T$ occurs at higher temperatures. The Mn_{12} -carboxylates behave similarly.⁴⁹ There is a hint of another such decrease in $\chi'_M T$ occurring below ~ 3 K. In Figure 8.12(b), the out-of-phase χ''_M values show maxima in the region 5-7 K, which vary in position, width and magnitude as the frequency is varied, typical of SMM behaviour and similar to that in Mn_{12} -acetate type clusters. In contrast to the Mn_{12} species, the values of the maxima in χ''_M , of 0.25 to $0.20 \text{ cm}^3 \text{mol}^{-1}$, are much smaller than in the Mn_{12} clusters but of similar size to those observed for a Mn_{30} cluster.¹² It is possible that a second series of maxima occur below 2 K, but further measurements on a separate instrument would be required to confirm this and to obtain the relative intensity compared to the 5-7 K maxima. Two such series of maxima, at 4-7 K and 2-3 K, have been observed in some of the Mn_{12} -carboxylate clusters^{37,53} and these originated from the presence of two Jahn-Teller isomers in the samples. In that study each isomer could be isolated separately and assigned to the relevant series of maxima in

χ''_M . It is possible that such isomers can exist in Mn_{16} -acetate, as can be seen in the structural discussion (see section 8.3.1).

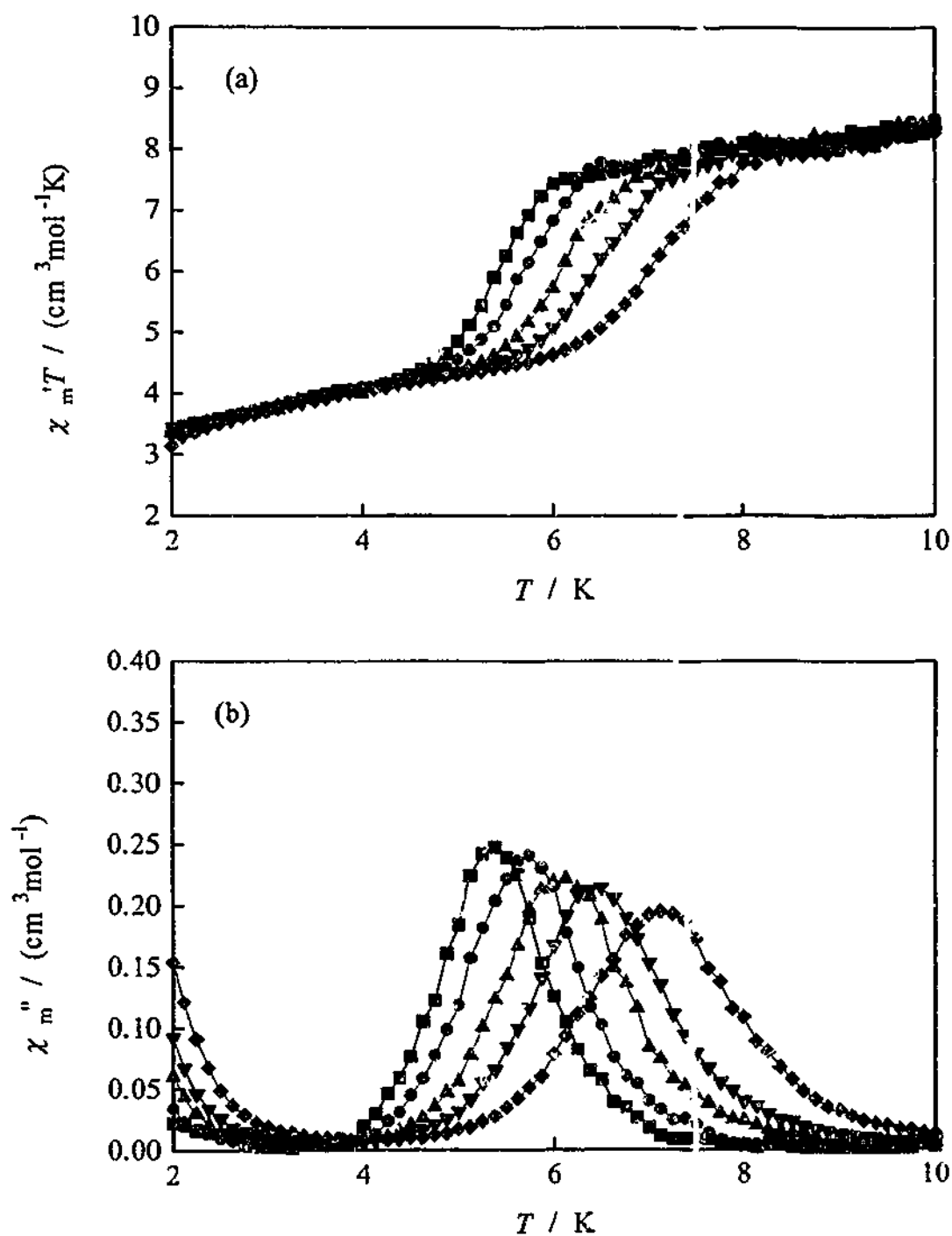


Figure 8.12 (a) AC $\chi'_M T$ vs. temperature and (b) AC χ''_M vs. temperature for Mn_{16} -acetate measured at frequencies 50 (■), 100 (●), 250 (▲), 500 (▼), 1500 (◆) Hz in a DC field of 10 Oe.

The magnetisation relaxation data were analysed using the Arrhenius law for the relaxation time, τ (Equation 8.1):

$$\tau = \tau_0 e^{-\Delta E / kT} \quad \text{Equation 8.1}$$

τ = relaxation time = $1/(2\pi\nu)$ (s),

τ_0 = pre-exponential factor,

ν = AC frequency (Hz) of applied field,

ΔE = activation energy or barrier height of the double potential energy well (cm^{-1}),

k = Boltzmann constant.

The values of T are the temperatures of the maxima in Figure 8.12(b). The relaxation times, τ , are obtained from the frequencies (ν in Hz) of each χ''_{M} measurement using the relation $\tau = 1/(2\pi\nu)$, since at each maximum the relaxation frequency of an SMM is equal to the operating AC frequency, ν . Figure 8.13 shows the plot of $\ln(1/\tau)$ vs. $1/T$, where the solid line is the least-squares best fit to the Arrhenius equation. From this fit, the energy barrier, ΔE , was found to be 52 cm^{-1} (c.f. Mn_{12} -acetate $\Delta E = 43 \text{ cm}^{-1}$, 62 K)^{1,49} with a pre-exponential factor of 3.00×10^{-9} s. Table 8.6 compares these values with those of other SMMs of Mn.

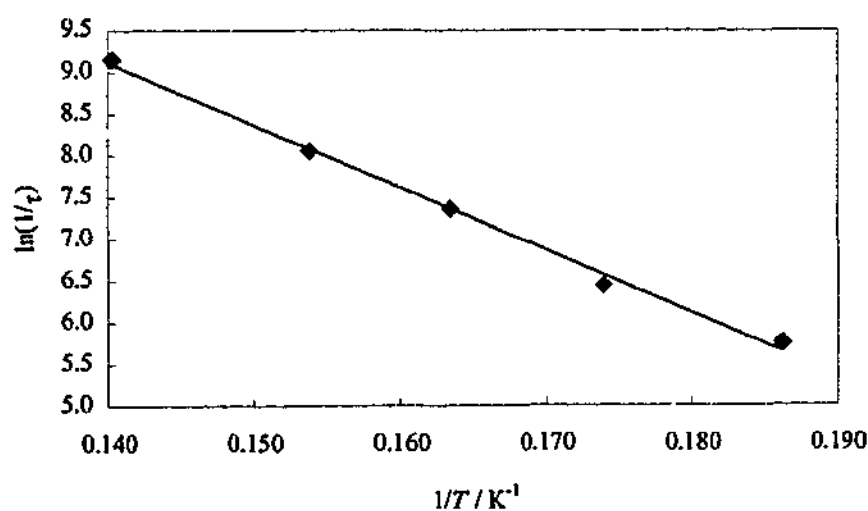


Figure 8.13 Plot of $\ln(1/\tau)$ versus $1/T$ from magnetisation data of Figure 8.12. Solid line represents least squares line of best fit to Arrhenius equation (see text, Equation 8.1).

Table 8.6 Effective energy barrier energies, ΔE , and pre-exponential factors, τ_0 , for some Mn SMM clusters.

Cluster	ΔE (cm ⁻¹)	τ_0 (s)	ref
[Mn ₉ O ₇ (OAc) ₁₁ (thme)(py) ₃ (H ₂ O) ₂] ^(a)	18.9		7
[Mn ₁₂ O ₁₂ (O- <i>p</i> -Me-Bz) ₁₆ (H ₂ O) ₄] $\cdot$ 3H ₂ O ^(b)	45.0	7.9×10^{-9}	53
[Mn ₁₂ O ₈ Cl ₄ (OBz) ₈ (hmp) ₆] ^(c)	21.1	2.5×10^{-9}	10
[Mn ₁₆ O ₁₆ (OMe) ₆ (OAc) ₁₆ (MeOH) ₃ (H ₂ O) ₃] $\cdot$ 6H ₂ O	52.2	3.0×10^{-9}	

(a) H₃thme = 1,1,1-tris(hydroxymethyl)ethane; (b) O-*p*-Me-Bz = *p*-methylbenzoate; (c) hmpH = 2-(hydroxymethyl)pyridine

In the absence of fitting of the M/H data to an appropriate Spin Hamiltonian it is possible to estimate the size of $|D|$, the axial zero-field splitting parameter for the coupled ground state, by use of the relationship: $|D|S_z^2 = \Delta E$, where ΔE is the barrier height.^{2,54} Since the precise value of S is not known, it was assumed to be 4. Thus a $|D|$ value of $52/16 = 3.2$ cm⁻¹ is predicted, which is much larger than those determined for Mn₁₂-acetate systems having a ground $S = 10$ and $D \approx -0.5$ cm⁻¹. It is much more akin to values obtained for Mn^{III} monomeric complexes.⁵⁵

Use of the above relationship assumes that only the ground S state, and its M_S components $0, \pm 1, \pm 2, \dots, \pm S$, are thermally populated. In the present Mn₁₆-acetate cluster there are other low-lying S states as indicated by the nature of the M vs. H isotherms in Figure 8.9.

Attempts are currently being made by Mr. K. J. Berry (Westernport Secondary College, Hastings, Victoria) to try to simulate the M/H data and thus obtain the ground state levels and the D values in a more direct manner. At this point it is clear that

calculations of M , at 2 K and 5 T, for an $S = 4$ level yield, as expected, $8 N\beta$ for $D = 0$; $6.3 N\beta$ for $D = -1 \text{ cm}^{-1}$ and $4 N\beta$ for $D = -3.5 \text{ cm}^{-1}$. Thus, the D value obtained from the AC relaxation data, assuming it is negative (-3.2 cm^{-1}), is not compatible with the Brillouin calculation of M which limits D to being less than $\sim -1 \text{ cm}^{-1}$. The $S = 3$ calculations gave an even bigger discrepancy. There is, therefore, a dilemma.

Güdel *et al.*³² have recently discussed somewhat related anomalies in a Ni_{21} -citrate SMM cluster in which an $S = 3$ state was lowest, but with many other excited states (up to $S = 9$) close in energy and thermally populated in high-fields (up to 8 T) at temperatures below 1 K. The ΔE value obtained from the χ''_M vs. frequency Arrhenius plot was $\sim 3 \text{ K}$ in this Ni_{21} -cluster and D was estimated to be -0.22 cm^{-1} (along the crystallographic c -axis). Rhombic ligand-field terms, E , were thought to be partly responsible for differences in the D value compared to that of Mn_{12} -acetate, and transverse anisotropy terms were also thought to be important, thus rendering the relationship $\Delta E = |D|S^2$ invalid because of admixture of M_S levels. It is also interesting to note that excited S states are now thought to be important in the Mn_{12} -acetate system e.g. $S = 9$ close to $S = 10$ and $S > 10$ under very high fields.⁴⁹

A possible, though unlikely explanation for the AC data and the consequent estimated $|D|$, is that traces of Mn_{12} -acetate are present in the samples and responsible for the frequency dependent AC behaviour. Certainly, there is no evidence for Mn_{12} in the μ_{eff}/T plot of Figure 8.8, since it would show a ferromagnetic like increase in μ_{eff} as the temperature is decreased towards 2 K. A powder XRD measured on one sample showed, by comparison to calculated line positions that Mn_{16} -acetate was the major species present, with traces of the chain $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$ and only a hint of Mn_{12} -acetate. Two of the weakest peaks in the diffractogram could be assigned to Mn_{12} -acetate, being two of the strongest peaks in the calculated pattern for Mn_{12} -acetate.

8.4.2 $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$

The variation of susceptibility and effective magnetic moment, per Mn^{III} with temperature is given in Figure 8.14. A broad maximum in χ_M occurs at ~ 70 K typical of the behaviour of a Heisenberg antiferromagnetically coupled $S = 2$ chain.⁵⁶ The rapid increase in χ_M at low temperature could be due to monomer impurity or to ferromagnetic chain-chain interactions. The corresponding μ_{eff} values decrease gradually from $4.16 \mu_B$ at 300 K (less than the uncoupled $4.87 \mu_B$ value) to $0.98 \mu_B$ at 2 K. The inflection below 10 K is due to monomer impurity or chain-chain effects.

The data were fitted to an $S = 2$ Fisher chain ($-2JS_i \cdot S_j$) model, modified by a $(T - \theta)$ term to give an approximate way of expressing inter-chain interactions. The fit is good and is shown in Figure 8.14. The parameters are $g = 1.91$, $J = -7.0 \text{ cm}^{-1}$ and $\theta = +1.95 \text{ K}$. The J value is of similar magnitude to those of some $[\text{Mn}^{\text{III}}(\text{Schiff-base})\text{X}]_n$ chains ($\text{X} = \text{OAc}^-$, N_3^-),⁵⁵ but much bigger than those obtained in the dca bridged $\text{Mn}^{\text{III}}(\text{Schiff-base})$ systems, described in Chapter 3, because of the large $\text{Mn} \cdots \text{Mn}$ distance and the poor superexchange properties of dca vs. the $\text{OMe}^-/\text{OAc}^-$ combination.

The value of J obtained here is approximately half the value of -13.7 cm^{-1} obtained for the dinuclear $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$ complex $[\text{Mn}^{\text{III}}_2(3\text{-MeO-salpentO})(\mu\text{-OAc})(\mu\text{-OMe})(\text{MeOH})_2]\text{Br}$ (where $3\text{-MeO-salpentOH}^{2-} = 1,5\text{-bis(3-methoxysalicylidenamino)pentan-3-ol}$).⁵⁷ This complex contains one acetate bridge and two alkoxide bridges, one of which is a $\mu\text{-OMe}^-$ group while the other is provided by the Schiff-base ligand, with a $\text{Mn} \cdots \text{Mn}$ distance of $2.9278(6) \text{ \AA}$. The slightly stronger antiferromagnetic coupling for the dinuclear complex can be attributed to the shorter $\text{Mn} \cdots \text{Mn}$ distance compared to $3.4433(1) \text{ \AA}$ for $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$.

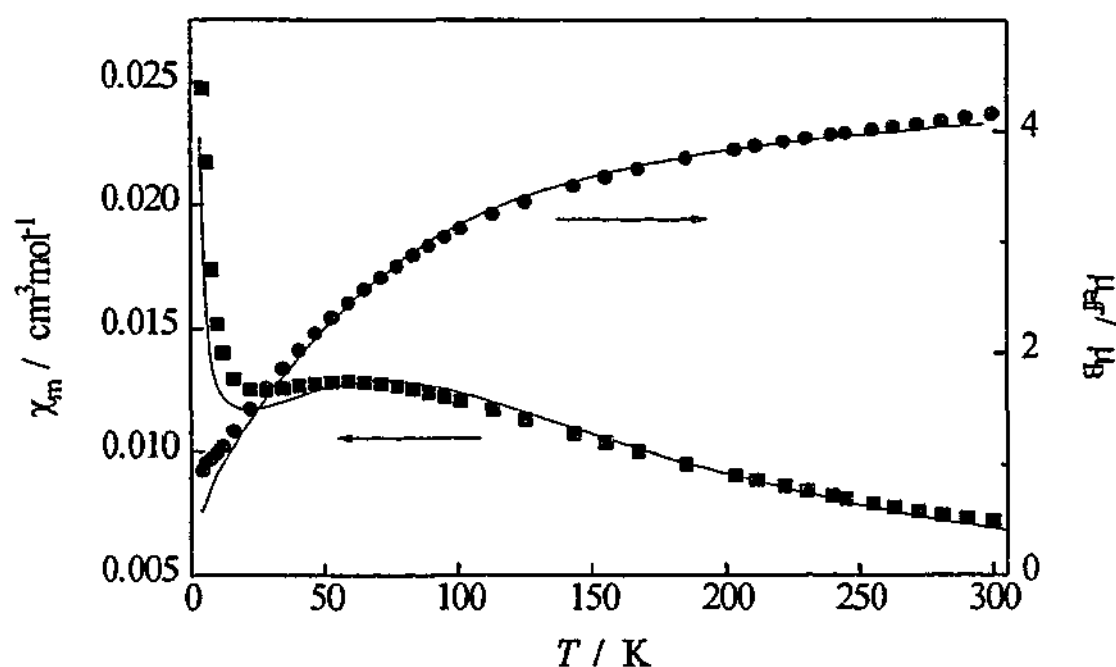


Figure 8.14 Plots of μ_{eff} (■) and χ_M (●), per Mn, *versus* temperature for $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$. The solid lines are those calculated best-fits using the Heisenberg model, $-2J\mathbf{S}_i\cdot\mathbf{S}_j$ (see text).

8.5 Conclusions

A fascinating new manganese(III/IV) alkoxo-carboxylate cluster, $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_{16}(\text{MeOH})_3(\text{H}_2\text{O})_3]\cdot 6\text{H}_2\text{O}$ (Mn_{16} -acetate), has been synthesised and structurally characterised. Extensive magnetic measurements, most notably the frequency dependency observed in the AC χ'' (out-of-phase) signal, have demonstrated that Mn_{16} -acetate is a new member of the family of single-molecule magnets (SMMs). It also represents the first known hexadecanuclear manganese(III/IV) cluster complex. The previously reported Mn_{16} complex, $[\text{Ba}_8\text{Na}_2\text{ClMn}_{16}(\text{OH})_8(\text{CO}_3)_4\text{L}_8]\cdot 53\text{H}_2\text{O}$ where $\text{L} = 1,3$ -diamino-2-hydroxypropane- N,N,N',N' -tetraacetic acid, was determined to be $\text{Mn}^{\text{II}}_{8.5}\text{Mn}^{\text{III}}_{7.5}$ by X-ray absorption spectroscopy.²⁰

Further physical measurements that are desirable on this Mn_{16} -acetate cluster would require external laboratories to be involved. They include (i) high-field/high-frequency EPR (HFEPR) studies in order to determine the D value,⁵⁸⁻⁶⁰ and (ii) the use of strong transverse ($H_{\perp}$) magnetic fields and magnetic specific heat measurements to obtain detailed information on quantum relaxation and quantum coherence in these "mesoscopic-size" clusters.^{61,62}

Future synthetic work in this area could include more rigorous attempts to synthesise different carboxylate derivatives, and mixed ligand Mn_{16} clusters with, for example, nitrate, diphenylphosphinate or diphenylphosphate as reported by Christou *et al.*^{63,64} and Kuroda-Sowa *et al.*⁶⁵ for Mn_{12} -acetate. Partial substitution previously achieved with the Mn_{12} -acetate, of some of the perimeter Mn^{III} centres with Fe^{III} or Cr^{III} ions yielding mixed metal clusters, may also be possible.^{66,67} If these modifications are realised, then the effect these modifications have on the magnetic properties of the resulting cluster can be explored.

In addition, the reaction that formed Mn_{16} -acetate yielded a new linear manganese(III) methoxide-carboxylate chain complex, $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$, also unexpectedly. This complex, whose structure consists of octahedral manganese(III) centres linked by two acetates and one methoxide ligand to form a 1D chain, resembles another complex isolated by the candidate, $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ described in Chapter 6. However, the structure of the latter complex contains a number of important differences. It contains a $\mu\text{-OH}^-$ group in place of the $\mu\text{-OMe}^-$, which hydrogen bonds *via* lattice acetic acid and water molecules to $\mu\text{-OAc}^-$ ligands on adjacent chains to form a 2D sheet structure. Probably as a result of these hydrogen bonding pathways the complex displays long-range antiferromagnetic order, whereas the complex described in this

chapter, $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$, displays antiferromagnetic coupling with no subsequent magnetic order.

8.6 Experimental

8.6.1 Synthesis of $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_{16}(\text{MeOH})_3(\text{H}_2\text{O})_3]\cdot 6\text{H}_2\text{O}$

To a stirred methanolic solution (120 mL) of $\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (2.90 g, 11.57 mmol), and glacial acetic acid (10 mL), $n\text{-Bu}_4\text{NMnO}_4$ (1.14 g, 3.15 mmol) was added in small portions over a period of 30 minutes. The solution was then left to stand. After several weeks a small amount of block-like black crystals of Mn_{16} -acetate formed. The solution was decanted, the crystals collected by filtration and washed quickly with methanol (0.20 g, 8 % based on total available Mn). IR (Nujol, cm^{-1}): 3600m, 3387mbr, 1558s, 1335m, 1027w, 960vw.

Many repeats of the reaction show that crystals of Mn_{16} -acetate decompose with time to yield species containing low content of carbon and poor diffraction quality despite a good external morphology. Presumably slow hydrolysis of OMe^- and OAc^- groups occurs in the solid state. Analysis of a fresh sample, found (%): C, 18.8; H, 3.8; N, 0.0. Calc. for $\text{C}_{41}\text{H}_{96}\text{Mn}_{16}\text{O}_{66}$: C, 19.6; H, 3.5; N, 0.0.

8.6.2 Synthesis of $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$

When the above reaction also had $\text{Na}(\text{dca})$ (2.23 g, 25.0 mmol) and Me_4NBr (3.85 g, 25.0 mmol) added, black crystals of Mn_{16} -acetate formed first, followed by smaller red rectangular block-like crystals of $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$. They were obtained free of the larger black Mn_{16} -acetate crystals by successive filtration of the reaction to remove mixtures of Mn_{16} -acetate and $[\text{Mn}(\text{OMe})(\text{OAc})_2]_n$ that formed, and leaving the filtrate to stand until the product appeared homogenous with respect to the smaller red crystals by

inspection under microscope. The crystals were collected by filtration and washed quickly with methanol (Typical yield 0.25 g, 8 % based on total available Mn). IR (Nujol, cm^{-1}): 3603vw, 1568s, 1401s, 1355m, 1340s, 1018w, 992m, 945w. Anal. (%) Found: C, 29.2; H, 4.6; N, 0.0. Calc. for $\text{C}_5\text{H}_9\text{O}_5\text{Mn}$: C, 29.4; H, 4.4; N, 0.0.

8.6.3 X-Ray Crystallography

Data were collected using a Nonius KappaCCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Integration was carried out by the program DENZO-SMN,⁶⁸ and data were corrected for Lorentz polarisation effects and for absorption using the program SCALEPACK.⁶⁸ No further numerical absorption corrections were applied. Solutions were obtained by direct methods (SHELXS 97)⁶⁹ followed by successive Fourier difference methods, and refined by full matrix least squares on F_{obs}^2 (SHELXL 97)⁶⁹ with the aid of the graphical interface program X-SEED.⁷⁰ All non-hydrogen atoms were refined anisotropically unless otherwise stated. All hydrogen atoms attached to carbons for Mn_{16} -acetate and $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$ were included at calculated positions with isotropic thermal parameters fixed at 1.5 times the U_{eq} of the adjoining carbon atom. For Mn_{16} -acetate, the hydrogens (where assigned) attached to oxygen atoms were located in the difference maps and refined isotropically. The O-H bond distances were restrained with the SHELX⁶⁹ (anti-bumping restraint) DFIX instruction to be 0.90(2) $\text{\AA}$.

The asymmetric unit of Mn_{16} -actetate was found to contain half a Mn_{16} complex as well as three water molecules. Two of the water molecules were disordered. The first disordered water was modelled over two positions, O(540) and O(541), with site occupancies refined to be 0.702 and 0.298 respectively. O(540) and O(541) were refined with isotropic and anisotropic thermal parameters respectively. The second disordered

water was modelled over three positions: O(530), O(531) and O(532), with site occupancies of 0.33(1), 0.36(1) and 0.38(1) respectively. The sum of the occupancies was restrained to be 1.00(1) (calculated 1.07) using the SHELX⁶⁹ SUMP instruction. O(530–532) were refined with anisotropic thermal parameters. The third water, O(52), was ordered and refined with anisotropic thermal parameters. Its hydrogen atoms, H(52A) and H(52B), were located in successive iterations of least squares refinements and difference Fourier maps and refined isotropically with the aforementioned anti-bumping restraints on the O–H bond distances. No hydrogen atom positions were assigned for the two disordered lattice water molecules.

Three areas of disorder were located within the cluster. Firstly, an axial μ -OAc[−] and an adjacent methanol ligand, both on the outer Mn^{III}₁₀ perimeter, were disordered over two positions. The three oxygen donor atoms O(39), O(41) and O(44) were refined at full occupancy. The positions of the two carbon atoms of the acetate group, C(420) and C(421), C(430) and C(431), and the two positions for the methyl carbon of the methanol, C(400) and C(401), were refined to site occupancies in the ratio of 0.684/0.316 (Figure 8.4).

Secondly, two coordinated oxygens (O(45) and O(47)) were initially assigned as two water ligands, however peaks near each oxygen were located at positions consistent with partially occupied methanol carbon atoms. They were consequently assigned as such and site occupancies of these carbon atoms and the attached hydrogen atoms were fixed at 0.25. Thus over the entire cluster four axial positions are occupied by three waters and one methanol. One hydrogen atom for O(45) and two hydrogen atoms for O(47) were located and refined isotropically with the aforementioned anti-bumping restraints applied. Finally, the carbon atom of the μ -OMe[−] bridging between Mn(6) and Mn(7) was disordered over

two positions. The site occupancies of these carbon atoms (C(260) and C(261)), and the attached hydrogen atoms, were refined to the ratio of 0.496/0.504 respectively.

As O(1) and C(2) of the bridging methoxide of $[\text{Mn}(\mu\text{-OMe})(\mu\text{-OAc})_2]_n$ lie along a 2-fold rotational axis the methyl hydrogens are disordered over two positions with equal site occupancies.

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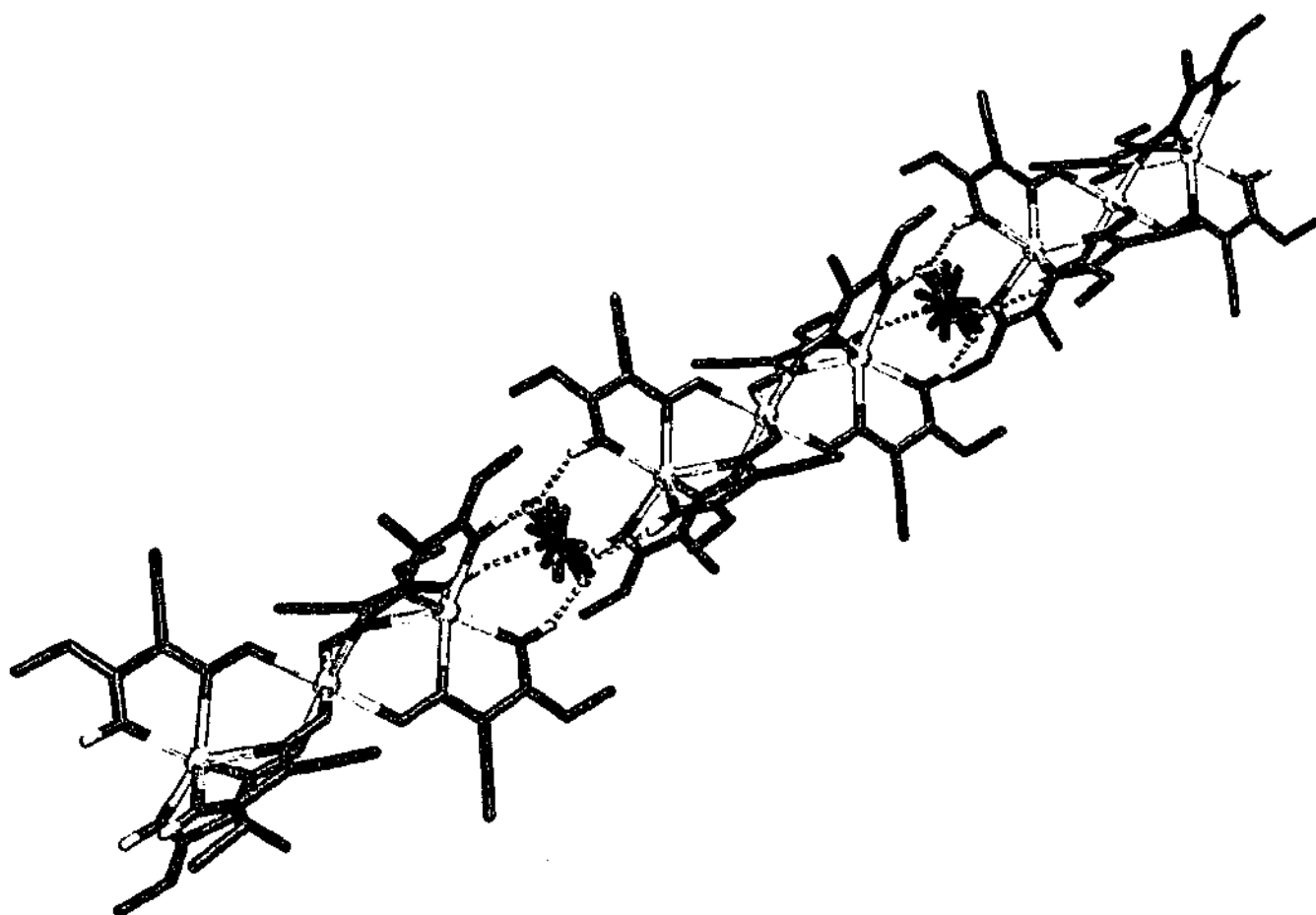
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**CHAPTER 9: SYNTHESIS, STRUCTURE AND
MAGNETISM OF TRINUCLEAR AND
TETRANUCLEAR MIXED VALENT MANGANESE
CLUSTERS, AND COPPER(II) AND NICKEL(II)
MONONUCLEAR COMPLEXES FORMED
FROM DICYANONITROSOMETHANIDE
DERIVED LIGANDS**

9.1 Introduction

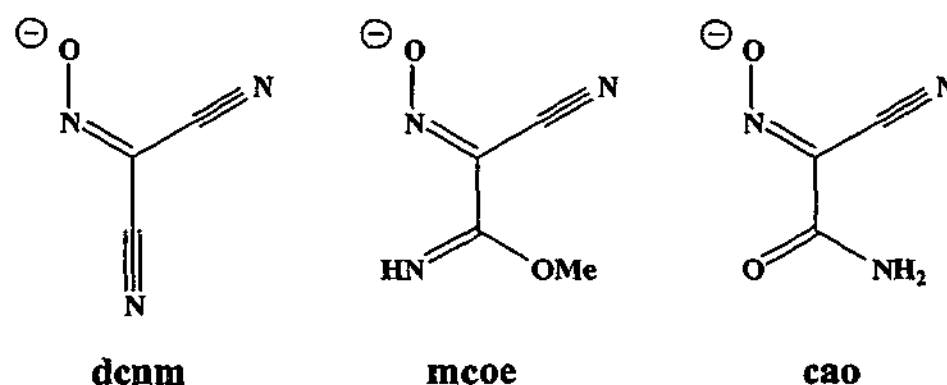
A great deal of recent research in polynuclear mixed-valent manganese complexes has focussed on two main lines of enquiry. Firstly, in the bioinorganic area, many model complexes have been made to replicate the structure and function of manganese containing proteins and enzymes including, significantly, the water oxidation complex (WOC) in the Photosystem II (PSII) of green plants and cyanobacteria, which is responsible for the catalysis of the light driven oxidation of H_2O to O_2 .¹⁻⁴ Detailed spectroscopic, EXAFS, XANES and crystallographic studies have been made to probe the $\text{Mn}_4(\text{Ca})$ μ -oxo cluster in the redox states S_0 to S_4 .^{5,6} The second area of recent Mn cluster research is that of single molecule magnets (SMMs). The archetypal dodecanuclear cluster, $[\text{Mn}^{\text{III/IV}}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{HOAc} \cdot 4\text{H}_2\text{O}$ (' Mn_{12} -acetate') and its derivatives are the best and most comprehensively studied SMMs to date.⁷⁻¹³

Examples of tetranuclear manganese clusters are now known that behave as SMMs and these include the family of complexes with the $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_3\text{O}_3\text{X}]^{6+}$ core,¹⁴⁻¹⁶ where X^- is, for example, a halide, and other Mn_4 complexes such as $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2]$ rhomboidal cores.^{17,18} The subject of SMMs is dealt with in more detail in Chapters 7 and 8.

The results discussed in this chapter arose from a combination of interests in Mn cluster chemistry and in 3D molecule-based magnets containing the pseudohalide ligand dicyanamide (dca, $\text{N}(\text{CN})_2^-$).¹⁹ From such work the candidate isolated the hexadecanuclear manganese(III/IV) cluster, Mn_{16} -acetate, which displays SMM behaviour (see Chapter 8).²⁰

While attempting to synthesise transition metal extended coordination complexes containing the pseudochalcogenide ligand dicyanonitrosomethanide (dcnm, $\text{ONC}(\text{CN})_2^-$), two new mixed-valent manganese complexes were isolated. They are $[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ($\{\text{Mn}_3\}$) and $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$

($\{Mn_4\}$), where mcoe is methyl(2-cyano-2-hydroxyimino)ethanimidate ($ONC(CN)C(NH)OCH_3$) and cao is cyanoacetamidoximate ($ON=C(CN)(CONH_2)^-$) (Scheme 9.1). Separately, two mononuclear complexes were also isolated, $[Ni(cao)_2(H_2O)_2]$ and $[Cu(mcoe)_2(MeOH)_2]$. The chelating-bridging ligands cao and mcoe were formed *in situ* by nucleophilic addition of solvent to dcnm.



Scheme 9.1 Dicyanonitrosomethanide (dcnm, $ONC(CN)_2^-$), methyl(2-cyano-2-hydroxyimino)ethanimidate (mcoe, $ONC(CN)C(NH)OCH_3^-$) and cyanoacetamidoximate (cao, $ON=C(CN)(CONH_2)^-$).

The structures of the complexes $\{Mn_3\}$, $\{Mn_4\}$, $[Cu(mcoe)_2(MeOH)_2]$ and $[Ni(cao)_2(H_2O)_2]$ have been elucidated by single crystal X-ray crystallography. The magnetic properties of $\{Mn_3\}$ and $\{Mn_4\}$ were investigated in some detail. The magnetic properties of the mononuclear copper(II) and nickel(II) complexes are also discussed.

9.2 Synthesis and Characterisation

9.2.1 $[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ and



$[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ($\{\text{Mn}_3\}$) crystallizes out of a solution of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Me}_4\text{N}(\text{dcnm})$ (1:2 molar ratio) in methanol. $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ ($\{\text{Mn}_4\}$) crystallizes out of a solution of equimolar amounts of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Me}_4\text{N}(\text{dcnm})$ in acetonitrile. A brown solid, which from IR spectroscopy is likely to be MnO_2 , is formed in both reactions in small and relatively large quantities for $\{\text{Mn}_3\}$ and $\{\text{Mn}_4\}$, respectively, at the same time as some of the Mn^{II} is oxidized to Mn^{III} , which is then included in the cluster. This brown solid can be filtered off progressively during the course of the reaction. In latter stages, the majority of the product is $\{\text{Mn}_3\}$ or $\{\text{Mn}_4\}$ and can be successfully separated from the remaining MnO_2 powder. The yield of $\{\text{Mn}_4\}$ was very low but quite reproducible. The infrared spectrum of $\{\text{Mn}_3\}$ shows absorbances at 2221 and 1645 cm^{-1} corresponding to the $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{C}=\text{N})$ vibrations, respectively, of the mcoe ligand. Likewise for $\{\text{Mn}_4\}$ absorbances at 2224 and 1682 cm^{-1} correspond to the $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{C}=\text{O})$ vibrations of the cao ligand. Elemental analyses are consistent with the formulations given above. The powder X-ray diffractograms of the bulk samples match those calculated from the crystal structures.

The pseudochalcogenide ligand dicyanonitrosomethanide ($\text{ONC}(\text{CN})_2^-$, dcnm) undergoes nucleophilic addition of solvent (methanol and water for $\{\text{Mn}_3\}$ and $\{\text{Mn}_4\}$ respectively) in the coordination sphere of the metal to form the chelating ligands methyl(2-cyano-2-hydroxyimino)ethanimidate ($\text{ONC}(\text{CN})\text{C}(\text{NH})\text{OCH}_3^-$, mcoe) for $\{\text{Mn}_3\}$ and cyanoacetamidoximate ($\text{ON}=\text{C}(\text{CN})(\text{CONH}_2)^-$, cao) for $\{\text{Mn}_4\}$. The nucleophilic addition of solvent to dcnm has been reported by Hvastijová *et al.* for Co^{II} , Ni^{II} , Cu^{II} and

Pd^{II} complexes (see also sections 9.2.2, 9.3.3 and 9.3.4).²¹⁻²⁴ The protonated caoH ligand, has been synthesized recently by refluxing the filtrate formed from the reaction of $\text{Ag}(\text{dcnm})$ and NH_4Cl in water.²⁵ Compounds $\{\text{Mn}_3\}$ and $\{\text{Mn}_4\}$ are the first examples of compounds in which the mcoe and cao ligands occupy bridging as well as chelating coordination modes. The oxidation of Mn^{II} to Mn^{III} and Mn^{IV} (MnO_2) in these aerobic reactions is not unexpected and the formation of $\text{Mn}^{\text{II}}\text{OMn}^{\text{III}}$ bridges in $\{\text{Mn}_4\}$ under these conditions is common.²⁶

9.2.2 $[\text{Cu}(\text{mcoe})_2(\text{MeOH})_2]$ and $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$

The reaction of a solution of $\text{Me}_4\text{N}(\text{dcnm})$ in methanol with a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in methanol in 2:1 molar ratio yields large well formed dark green needles of $[\text{Cu}(\text{mcoe})_2(\text{MeOH})_2]$. A similar reaction in water with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ instead of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ yields dark red-purple crystals of $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$. Infrared spectra of $[\text{Cu}(\text{mcoe})_2(\text{MeOH})_2]$ and $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$ show absorbances at 2219 and 2228 cm^{-1} due to $\nu(\text{C}\equiv\text{N})$ of mcoe and cao respectively. As for $[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ and $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$, dcnm has undergone nucleophilic addition of solvent on coordination to form the chelating ligands mcoe and cao .

9.3 Crystal Structures

9.3.1 $[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$

Crystallographic data for $[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ($\{\text{Mn}_3\}$) are summarised in Table 9.1. Table 9.2 contains selected distances and angles (see page 395). The compound $\{\text{Mn}_3\}$ crystallizes in the trigonal space group $P\bar{3}1c$. The cation is a linear trinuclear complex (Figure 9.1) with the three manganese ions lying along a common three-fold axis and the central manganese atom situated on an inversion centre ($\bar{3}$). Thus the asymmetric

unit contains 1/6 of the formula unit. The cation contains two symmetry related terminal six-coordinate manganese(II) ions chelated by the N-donor atoms of the imine and oxime groups of three mcoe ligands in a trigonal prismatic N_6 environment ($Mn(2)-N(9) = 2.189(4)$, $Mn(2)-N(2) = 2.324(3)$ Å and $N(2)-Mn(2)-N(9) = 72.2(1)^\circ$). The two terminal manganese(II) ions are bridged to the central manganese(III) by the oxime groups of the six mcoe ligands, providing an O_6 coordination environment in a distorted octahedral fashion ($Mn(1)-O(1) = 2.169(3)$ Å).

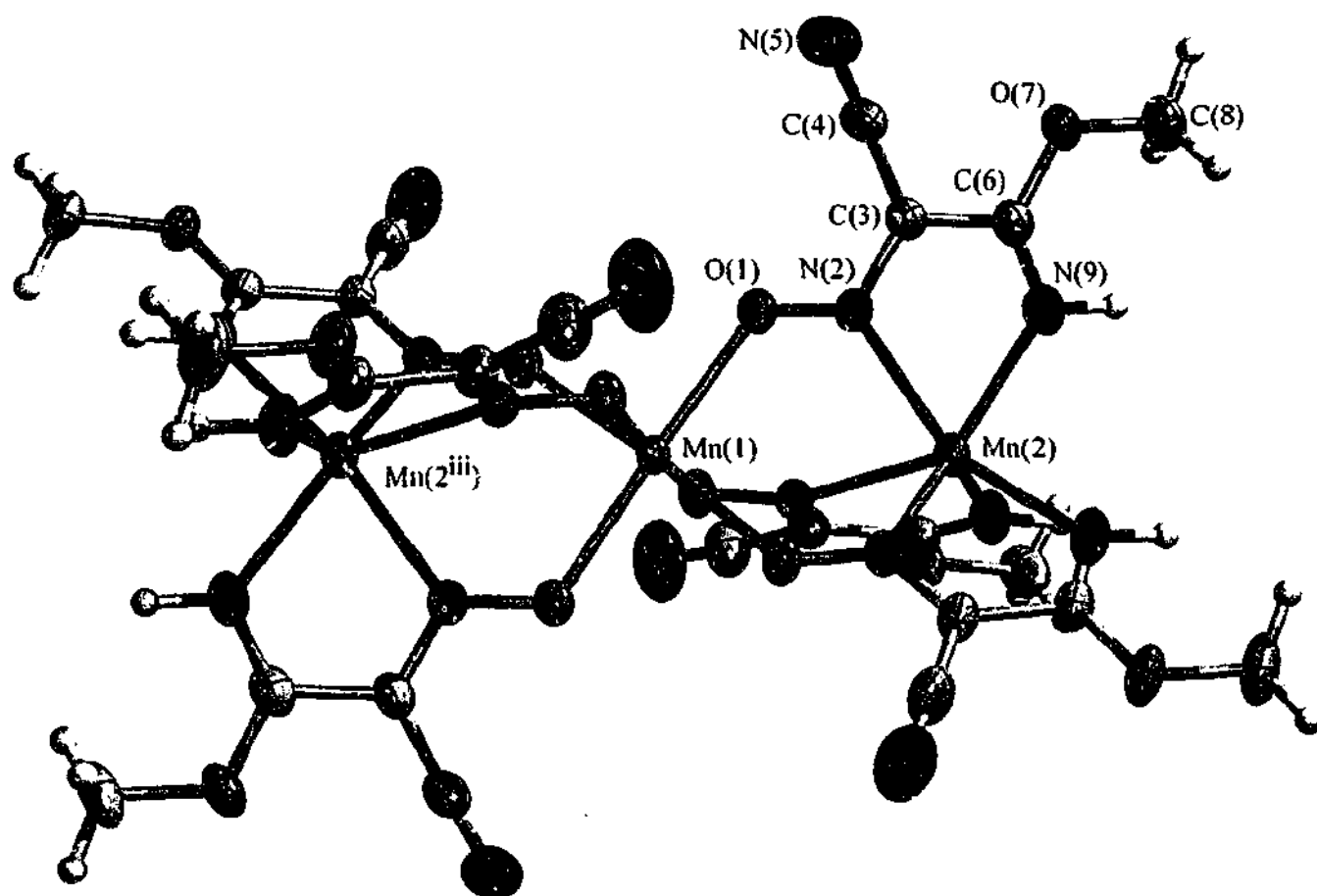


Figure 9.1 The crystal structure of $[Mn_3(mcoe)_6]NO_3 \cdot 2H_2O$ ($\{Mn_3\}$), with the atom labelling scheme shown (thermal ellipsoids shown at 50% probability). Nitrate counterions and lattice water molecules are omitted.

Table 9.1 Crystal data for $[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ($\{\text{Mn}_3\}$) and $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ ($\{\text{Mn}_4\}$).

Compound	$\{\text{Mn}_3\}$	$\{\text{Mn}_4\}$
Formula	$\text{C}_{24}\text{H}_{28}\text{Mn}_3\text{N}_{19}\text{O}_{17}$	$\text{C}_{24}\text{H}_{54}\text{Mn}_4\text{N}_{20}\text{O}_{30}$
<i>M</i>	1019.47	1322.62
Crystal system	Trigonal	Monoclinic
Space group	$P\bar{3}1c$	$C2/c$
<i>a</i> /Å	12.4720(2)	19.2163(3)
<i>b</i> /Å	12.4720(2)	11.4283(2)
<i>c</i> /Å	15.8114(4)	24.0215(2)
$\beta/^\circ$		90.916(1)
<i>U</i> /Å ³	2129.97(7)	5274.7(2)
<i>Z</i>	2	4
<i>T</i> /K	123(2)	123(2)
$\rho_{\text{calc}} / \text{g cm}^{-3}$	1.590	1.666
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	0.965	1.041
Crystal habit, colour	rhomboidal, red	rhomboidal, orange-red
Crystal dimensions / mm	0.15 × 0.125 × 0.1	0.2 × 0.2 × 0.1
θ ranges / °	2.58 – 28.32	2.12 – 28.29
Index ranges	$-16 \leq h \leq 16,$ $-15 \leq k \leq 16,$ $-21 \leq l \leq 21$	$-25 \leq h \leq 25,$ $-15 \leq k \leq 15,$ $-32 \leq l \leq 32$
Completeness to $2\theta = 55^\circ$ / %	99.9	99.2
Data collected	29281	35448
Unique data (<i>R</i> _{int})	1775 (0.0908)	6442 (0.0619)
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	1390	4578
Parameters	106	292
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^(a)	0.0759, 0.2172	0.1134, 0.3314
(all data)	0.0968, 0.2321	0.1502, 0.3563
Goodness of fit, <i>S</i>	1.141	1.097
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}} / \text{e Å}^{-3}$	-1.613, 1.366	-1.483, 1.819

^(a) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

The oxidation states are assigned on the basis of charge balance and on consideration of bond lengths. The two terminal manganese ions are assigned Mn^{II} due to the longer average bond length (2.257(7) Å) compared to the bond length for the central manganese ion (2.169(3) Å), which was assigned as Mn^{III} . It would be expected that the central Mn^{III} ion would show Jahn-Teller distortion, having d^4 configuration in a near octahedral environment. However, due to the $\bar{3}$ symmetry of this metal site, there is only one unique Mn–O bond length.

This compound strongly resembles the linear trinuclear mixed oxidation state manganese compounds $[(\text{Me}_3\text{-tacn})\text{Mn}^{\text{III}}\{(\mu\text{-niox})_3\text{M}^{\text{II}}\}\text{Mn}^{\text{III}}(\text{Me}_3\text{-tacn})](\text{ClO}_4)_2$, ($\text{M}^{\text{II}} = \text{Mn, Cu and Zn}$; $\text{Me}_3\text{-tacn} = 1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane}$; $\text{H}_2\text{niox} = \text{cyclohexane-}1,2\text{-dione}$) published by Birkelbach *et al.*^{27,28} In contrast to $\{\text{Mn}_3\}$, these complexes consist of a central M^{II} ion chelated by three niox^{2-} ligands in a trigonal prismatic environment with an N_6 coordination sphere, and are then bridged to the two terminal Mn^{III} ions by the oxime groups of the niox^{2-} ligands. The terminal Mn^{III} ions are in turn capped by $\text{Me}_3\text{-tacn}$ and thus possess a distorted octahedral N_3O_3 coordination environment. Other linear $\text{Mn}^{\text{III}}\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ examples are also known.²⁹

Each cation in $\{\text{Mn}_3\}$ is linked to its neighbour along the c -axis *via* hydrogen bonding between the cation imine hydrogen atoms and the nitrate counter-ion ($\text{N}(9)\cdots\text{O}(111) = 2.90(1)$ Å) (Figure 9.2), which is disordered over two positions related by a $48.8(1)^\circ$ rotation about the nitrogen atom. This disorder in the nitrate oxygen may be caused by hydrogen bonding between the three imine hydrogens each on adjacent complexes that are staggered 60° with respect to each other.

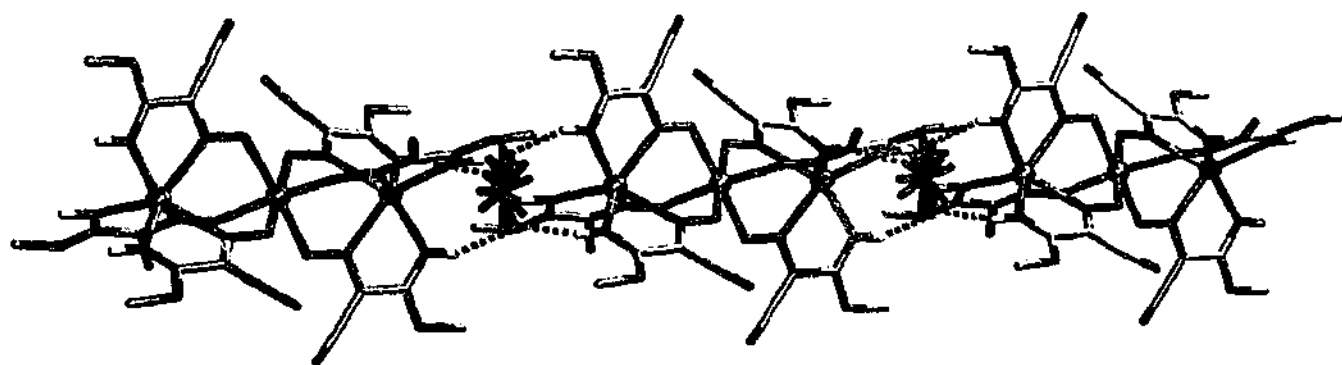


Figure 9.2 Hydrogen bonding of $[\text{Mn}_3(\text{mcoe})_6]^+$ cations alternating with disordered nitrate anions (H-bonds dashed green, methyl hydrogens omitted for clarity).

Table 9.2 Selected interatomic distances (Å) and angles (°) for $[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ($\{\text{Mn}_3\}$).

Mn(1)–O(1)	2.169(3)	Mn(1)···Mn(2)	3.9177(9)
Mn(2)–N(2)	2.324(3)	Mn(2)–N(9)	2.189(4)
O(1)–N(2)	1.301(4)	C(3)–C(6)	1.490(5)
N(2)–C(3)	1.303(5)	C(6)–N(9)	1.250(6)
C(3)–C(4)	1.410(6)	C(6)–O(7)	1.338(5)
C(4)–N(5)	1.14(1)	O(7)–C(8)	1.462(6)
O(1)–Mn(1)–O(1 ⁱ)	90.7(1)	N(2)–Mn(2)–N(9)	72.2(1)
O(1 ⁱ)–Mn(1)–O(1 ⁱⁱ)	82.6(1)	N(9)–Mn(2)–N(9 ⁱⁱ)	92.7(1)
O(1)–Mn(1)–O(1 ⁱⁱ)	93.5(9)	N(2)–Mn(2)–N(2 ⁱⁱ)	85.3(1)
O(1)–Mn(1)–O(1 ⁱⁱⁱ)	174.5(1)	N(2)–Mn(2)–N(9 ⁱⁱ)	138.2(1)
		N(2 ⁱⁱ)–Mn(2)–N(9)	125.9(1)
Hydrogen bonding			
N(9)–H(9)	1.00(7)		
H(9)···O(110)	2.00(7)	H(9)···O(111)	2.02(7)
N(9)···O(110)	2.94(3)	N(9)···O(111)	2.90(2)
N(9)–H(9)···O(110)	156(5)	N(9)–H(9)···O(111)	147(5)

Symmetry transformations: (i) $y-x, y, 3/2-z$; (ii) $-1-y, x-y+1, z$; (iii) $1-y, 1-x, 3/2-z$.

9.3.2 $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$

Crystallographic data for $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ ($\{\text{Mn}_4\}$) are summarised in Table 9.1 (see page 393). Selected interatomic distances and angles for $\{\text{Mn}_4\}$ are contained in Table 9.3 (see page 402). Compound $\{\text{Mn}_4\}$ crystallizes in the monoclinic space group $C2/c$, with the tetranuclear manganese cluster lying on an inversion centre. Figure 9.3 shows the cluster with the atom labelling scheme. The asymmetric unit contains half of the cluster, one tetramethylammonium and two nitrate counter ions and one lattice water. The cluster contains a rhombic $[\text{Mn}_4(\mu_3\text{-O})_2]^{6+}$ core (2Mn^{II} , 2Mn^{III}) in which the four Mn atoms lie in a plane with $\text{Mn}(1) \cdots \text{Mn}(2) = 3.546(2) \text{ \AA}$ being considerably longer than $\text{Mn}(2) \cdots \text{Mn}(2^i) = 2.773(2) \text{ \AA}$. This is due to the latter pair being bridged by two $\mu_3\text{-O}^{2-}$ atoms ($\text{Mn}(2) \cdots \text{O}(1) = 1.844(3) \text{ \AA}$ and $\text{Mn}(2^i) \cdots \text{O}(1) = 1.837(5) \text{ \AA}$), whereas the former pair are bridged by the two atom N–O oxime moiety of the cao ligand ($\text{Mn}(1) \cdots \text{N}(3) = 2.436(6) \text{ \AA}$ and $\text{O}(2) \cdots \text{Mn}(2) = 2.003(5) \text{ \AA}$) and a single $\mu_3\text{-O}^{2-}$ atom ($\text{Mn}(1) \cdots \text{O}(1) = 2.077(5) \text{ \AA}$). The $\mu_3\text{-O}^{2-}$ atom lies $0.190(6) \text{ \AA}$ out of the plane defined by the four manganese atoms. On the periphery of the $[\text{Mn}_4(\mu_3\text{-O})_2]^{6+}$ core are four chelating cao ligands (two of which are unique) that lie roughly coplanar with the core. In the axial positions of the metal coordination spheres are six terminal water molecules, two each on $\text{Mn}(1)$ and $\text{Mn}(1^i)$ and one each on $\text{Mn}(2)$ and $\text{Mn}(2^i)$, and two terminal acetonitrile ligands, one each on $\text{Mn}(2)$ and $\text{Mn}(2^i)$.

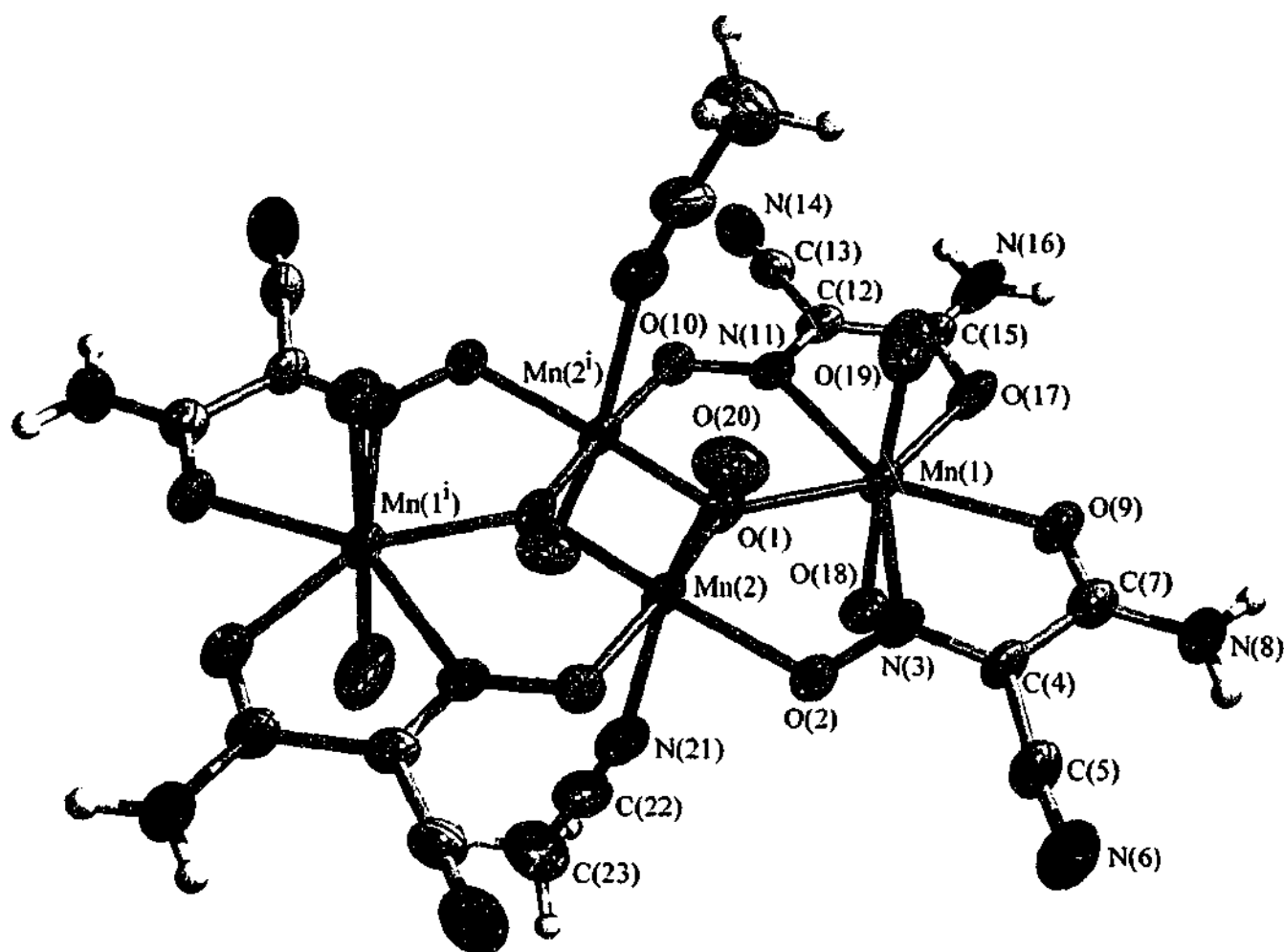


Figure 9.3 Crystal structure of $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ ($\{\text{Mn}_4\}$) with atom labelling scheme (thermal ellipsoids shown at 50% probability). Counter ions and lattice waters omitted.

The two Mn^{II} atoms ($\text{Mn}(1)$ and $\text{Mn}(1^i)$) are thus seven coordinate in an approximate pentagonal bipyramidal arrangement. The carbonyl oxygens ($\text{O}(9)$ and $\text{O}(17)$) and oxime nitrogens ($\text{N}(3)$ and $\text{N}(11)$) of two cao ligands and one $\mu_3\text{-O}^{2-}$ ion ($\text{O}(1)$) make up the pentagonal plane of the bipyramid, whereas the apices are filled by the two axial waters ($\text{O}(18)$ and $\text{O}(19)$). The sum of the five angles around the plane is 360° , attesting to the planarity of the coordination environment. The non-coordinating nitrile groups of the two cao ligands chelating each Mn^{II} ion are bent slightly away from the plane of the $[\text{Mn}_4(\mu_3\text{-O})_2]^{6+}$ core. $\text{Mn}(2)$ (and $\text{Mn}(2^i)$) was assigned as Mn^{III} on the basis of the

significant Jahn-Teller elongation in the direction of the axial water and acetonitrile ligands ($\text{Mn}(2)\text{--O}(20) = 2.296(8) \text{ \AA}$ and $\text{Mn}(2)\text{--N}(21) = 2.372(9) \text{ \AA}$, where the average equatorial bond distance = $1.92 \text{ \AA}$).

A complex network of hydrogen bonding exists between the clusters and the intercalated water and nitrate anions. Inspection of the cluster shows that there are several sites capable of hydrogen bonding, and the cluster packing mode is primarily determined by the hydrogen bonding interactions. Broadly speaking there are two intersecting hydrogen bonding networks. Firstly, a sheet in the *ab*-plane is formed by hydrogen bonding interactions between adjacent clusters (perpendicular to the plane of the clusters) *via* the terminal waters, the nitrate anions and the intercalated water molecule. Secondly, another sheet network is formed in the *ac*-plane by hydrogen bonding between the terminal amine and the nitrile groups of the cao ligand on adjacent clusters. The tetramethylammonium cations pack between the sheets in the *ab*-plane.

The network in the *ab*-plane involves multiple hydrogen bonding interactions and can be broken down into two types of intersecting chains. Firstly, the terminal water oxygen atom O(19) on Mn(2) hydrogen bonds to two symmetry related nitrate anions ($\text{O}(19)\cdots\text{O}(52^{\text{iv}}) = 3.07(2)$, $\text{O}(19)\cdots\text{O}(53) = 2.63(2) \text{ \AA}$ and $\text{O}(52^{\text{iv}})\cdots\text{O}(19)\cdots\text{O}(53) = 124.9(7)^\circ$). Both nitrate anions in turn hydrogen bond to a symmetry related O(19) on an adjacent cluster. The pattern thus formed is a stepped chain of clusters (Figure 9.4). The second chain in this plane involves hydrogen bonding from the water O(18) coordinated to Mn(2) to both a nitrate anion ($\text{O}(18)\cdots\text{O}(43^{\text{i}}) = 2.86(2) \text{ \AA}$) and a disordered water (average $\text{O}\cdots\text{O}$ distance = $2.9(1) \text{ \AA}$), which in turn hydrogen bond to their symmetry related partners (nitrate-water average $\text{O}\cdots\text{O}$ distance = $2.37(9) \text{ \AA}$), which then also hydrogen bond to O(18) on the adjacent cluster (Figure 9.5). The water coordinated to the central Mn(1) also

hydrogen bonds to the nearby nitrate anion that is also hydrogen bonded to O(18) ($\text{O}(20)\cdots\text{O}(43) = 2.82(2) \text{ \AA}$).

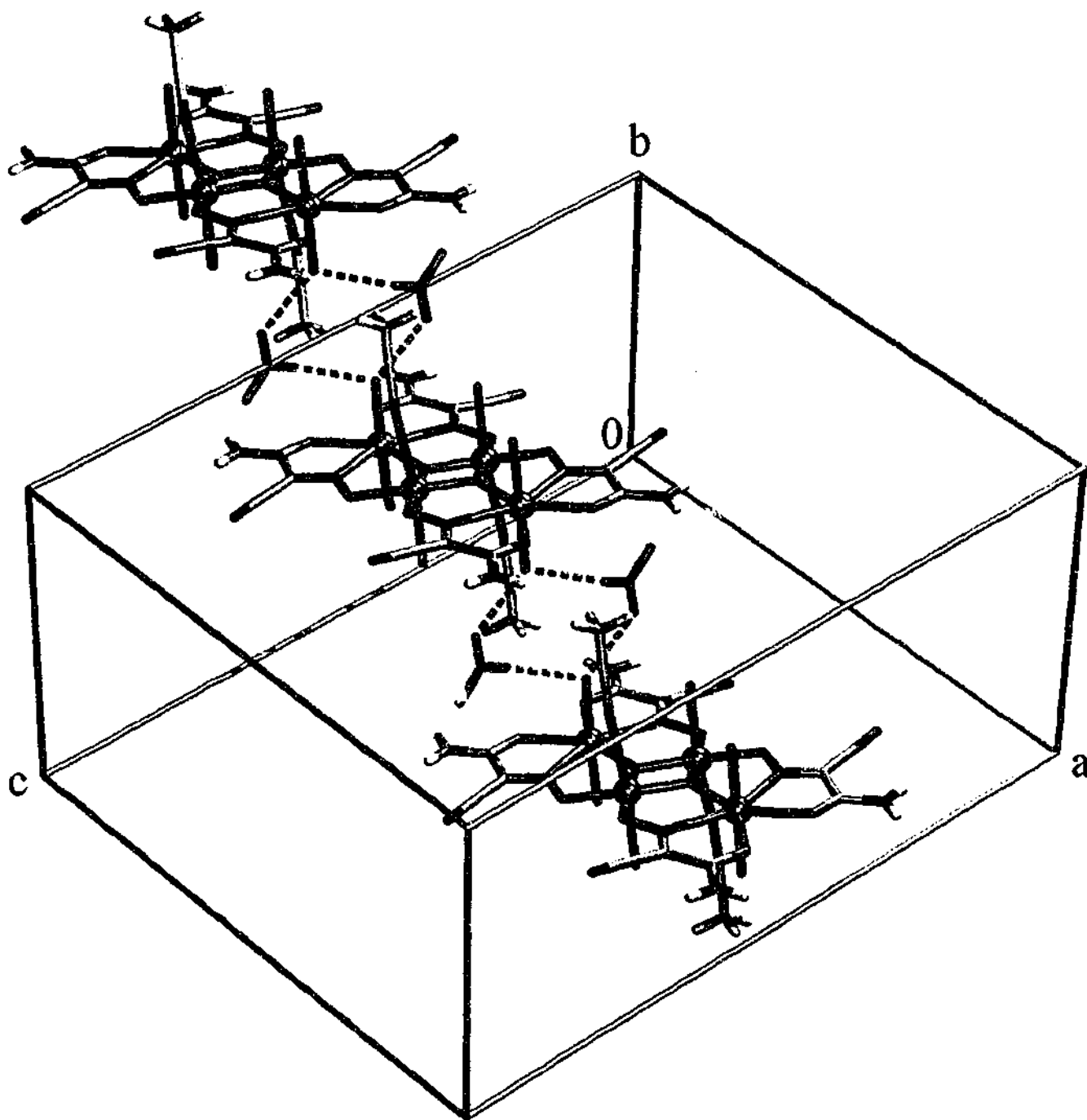


Figure 9.4 The stepped chain section of the hydrogen bond network (dashed green) of $\{\text{Mn}_4\}$ in the ab -plane.

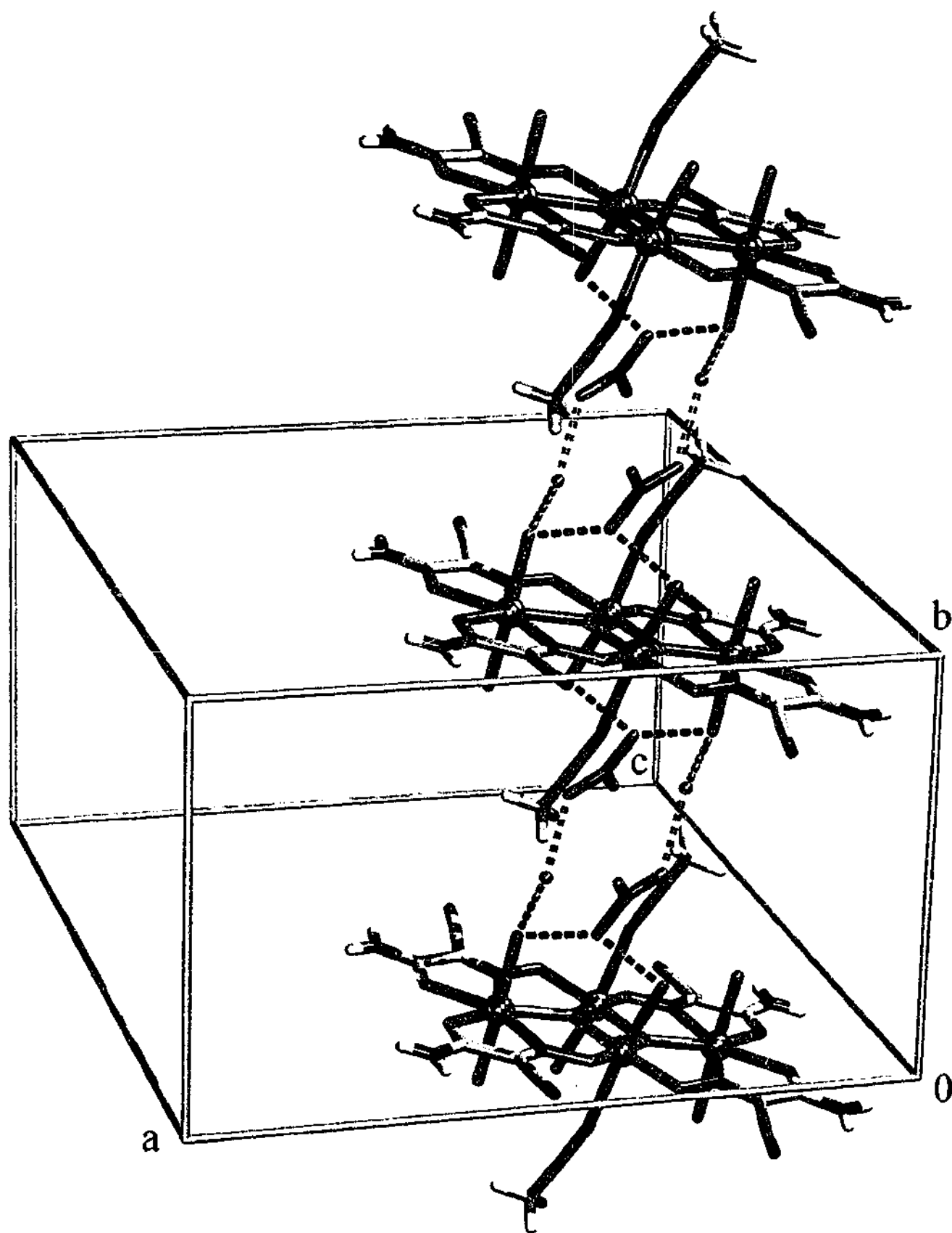


Figure 9.5 Second part of the hydrogen bonded network (dashed green) of $\{Mn_4\}$ in the *ab*-plane.

The sheet in the *ac*-plane (Figure 9.6) is set up by the terminal amines and nitriles of the two unique *cao* ligands, so that the amine on one cluster hydrogen bonds to the nitrile on the adjacent cluster ($N(8) \cdots N(6^{iii}) = 3.00(1) \text{ \AA}$, $N(8)-H(8B) \cdots N(6^{iii}) = 149.4^\circ$ and $N(16) \cdots N(14^v) = 3.03(1) \text{ \AA}$, $N(16)-H(16B) \cdots N(14^v) = 152.9^\circ$). All hydrogen bonds in the plane are directed parallel to the *c*-axis direction. Viewed parallel to the *c*-axis direction the sheets undulate due to the planes of adjacent clusters in the *a*-axis direction being on an angle of $31.48(3)^\circ$ to each other (mean planes of Mn atoms). The terminal amine on one of the *cao* ligands also hydrogen bonds to a nearby nitrate anion ($N(8) \cdots O(43^{ii}) = 2.90(2) \text{ \AA}$, $N(8)-H(8A) \cdots O(43^{ii}) = 175.9^\circ$) and correspondingly the other amine hydrogen bonds to the disordered lattice water molecule with an average distance of $2.79(7) \text{ \AA}$. Thus the amine groups also participate in the hydrogen bonded network in the *ab*-plane.

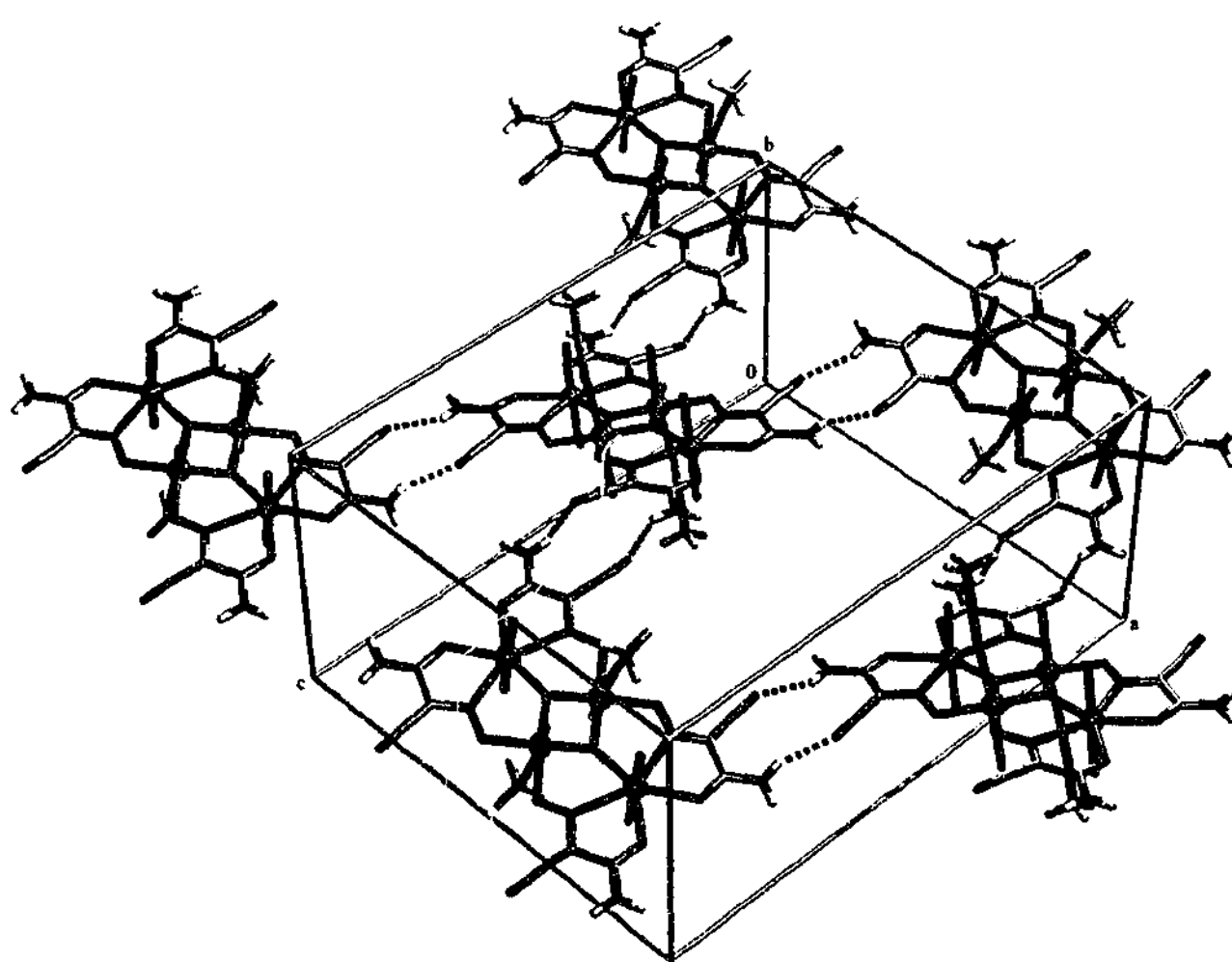


Figure 9.6 Hydrogen bonded network (dashed green) of $\{Mn_4\}$ in the *ac*-plane.

Table 9.3 Selected interatomic distances (Å) and angles (°) for $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ ($\{\text{Mn}_4\}$).

Mn(1)–O(1)	2.077(5)	Mn(2)–O(1)	1.844(5)
Mn(1)–N(3)	1.924(2)	Mn(2)–O(1 ⁱ)	1.837(5)
Mn(1)–O(9)	2.241(6)	Mn(2)–O(2)	2.003(5)
Mn(1)–N(11)	2.425(6)	Mn(2)–O(10 ⁱ)	1.993(5)
Mn(1)–O(17)	2.226(6)	Mn(2)–O(20)	2.296(8)
Mn(1)–O(18)	2.192(7)	Mn(2)–N(21)	2.372(9)
Mn(1)–O(19)	2.180(9)	Mn(2)···Mn(2 ⁱ)	2.773(2)
Mn(1)···Mn(2)	3.546(2)		
O(1)–Mn(1)–O(19)	93.7(3)	O(17)–Mn(1)–N(3)	142.9(2)
O(1)–Mn(1)–O(18)	87.3(2)	O(9)–Mn(1)–N(3)	68.4(2)
O(19)–Mn(1)–O(18)	176.3(3)	O(1)–Mn(2)–O(1 ⁱ)	82.3(2)
O(1)–Mn(1)–O(17)	142.3(2)	O(1 ⁱ)–Mn(2)–O(10 ⁱ)	93.7(2)
O(19)–Mn(1)–O(17)	90.0(4)	O(1)–Mn(2)–O(10 ⁱ)	175.9(2)
O(18)–Mn(1)–O(17)	91.4(3)	O(1 ⁱ)–Mn(2)–O(2)	176.5(2)
O(1)–Mn(1)–O(9)	143.1(2)	O(1)–Mn(2)–O(2)	94.6(2)
O(19)–Mn(1)–O(9)	86.7(3)	O(2)–Mn(2)–O(10 ⁱ)	89.4(2)
O(18)–Mn(1)–O(9)	90.3(3)	O(1 ⁱ)–Mn(2)–O(20)	95.9(3)
O(17)–Mn(1)–O(9)	74.6(2)	O(1)–Mn(2)–O(20)	93.8(3)
O(1)–Mn(1)–N(11)	73.9(2)	O(10 ⁱ)–Mn(2)–O(20)	87.0(3)
O(19)–Mn(1)–N(11)	90.3(3)	O(2)–Mn(2)–O(20)	82.5(3)
O(18)–Mn(1)–N(11)	93.4(2)	O(1 ⁱ)–Mn(2)–N(21)	94.9(3)
O(17)–Mn(1)–N(11)	68.5(2)	O(1)–Mn(2)–N(21)	93.4(3)
O(9)–Mn(1)–N(11)	143.0(2)	O(10 ⁱ)–Mn(2)–N(21)	86.4(3)
O(1)–Mn(2)–N(3)	74.6(2)	O(2)–Mn(2)–N(21)	87.0(3)
O(19)–Mn(1)–N(3)	90.8(3)	O(20)–Mn(2)–N(21)	167.7(3)
O(18)–Mn(1)–N(3)	86.0(2)		
Hydrogen bonding			
O(19)···O(52 ^{iv})	3.07(2)	O(20)···O(43)	2.82(2)
O(19)···O(53)	2.63(2)	N(8)···N(6 ⁱⁱⁱ)	3.00(1)
O(18)···O(43 ⁱ)	2.86(2)	N(16)···N(14 ^v)	3.03(1)
O(18)···O(600 ⁱⁱ)	2.49(5)	N(8)···O(43 ⁱⁱ)	2.90(2)
O(600)···O(41)	2.40(5)	N(16)···O(600 ^{iv})	2.90(4)
O(601)···O(41)	2.34(4)	N(16)···O(601 ^{iv})	2.67(3)
O(52 ^{iv})···O(19)···O(53)	124.9(7)	N(8)–H(8B)···N(6 ⁱⁱⁱ)	149.4
N(8)–H(8A)···O(43 ⁱⁱ)	175.9	N(16)–H(16B)···N(14 ^v)	152.9

Symmetry transformations: (i) $1/2-x, 3/2-y, 1-x$; (ii) $x-1/2, y-1/2, z$; (iii) $-x, y, 3/2-z$; (iv) $-x, 2-y, 1-z$; (v) $-x, y, 3/2-z$.

9.3.3 $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$

X-Ray structural analysis was performed by Dr. P. Jensen on a single crystal prepared by the candidate. Crystallographic data for $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$ are summarised in Table 9.4. Selected interatomic distances and angles are given in Table 9.6 (see page 410). $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$ (Figure 9.7) crystallises in the monoclinic space group $C2/m$. The structure of this mononuclear species consists of a Ni^{II} atom lying on an inversion centre (thus the asymmetric unit contains half of the complex), which is coordinated in a near octahedral environment by the carbonyl oxygen ($\text{Ni}(1)\text{--O}(8) = 2.053(2) \text{ \AA}$) and oxime nitrogen ($\text{Ni}(1)\text{--N}(2) = 2.068(2) \text{ \AA}$) of two cao ligands in the equatorial plane and by two water molecules ($\text{Ni}(1)\text{--O}(9) = 2.016(2) \text{ \AA}$) in the axial positions. The cao ligand lies on a mirror plane and the axial Ni–O bond lies on a perpendicular two-fold rotational axis, therefore the only non-ideal octahedral coordination angles are those within the plane of the cao ligands ($\text{N}(2)\text{--Ni}(1)\text{--O}(8) = 78.87(7)^\circ$ and its complement $\text{O}(8^i)\text{--Ni}(1)\text{--N}(2) = 101.13(7)^\circ$).

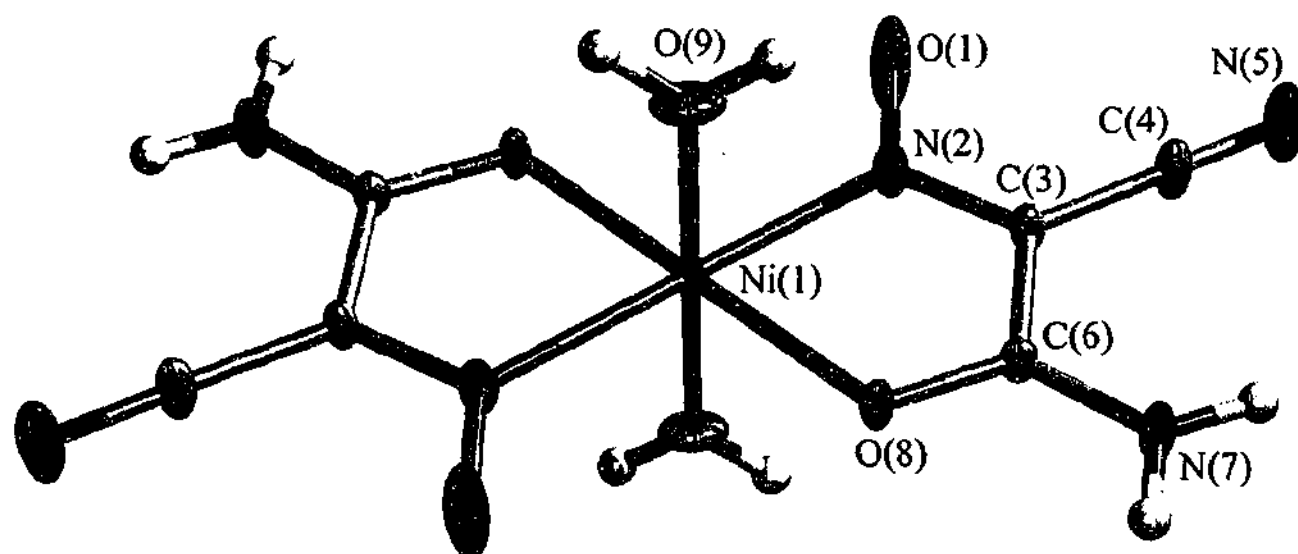


Figure 9.7 Crystal structure of $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$ with atom labelling scheme (thermal ellipsoids shown at 50 % probability).

Table 9.4 Crystal data for [Ni(cao)₂(H₂O)₂] and [Cu(mcoe)₂(MeOH)₂].

Complex	[Ni(cao) ₂ (H ₂ O) ₂]	[Cu(mcoe) ₂ (MeOH) ₂]
Formula	C ₆ H ₈ N ₆ NiO ₆	C ₁₀ H ₁₆ CuN ₆ O ₆
<i>M</i>	318.89	379.83
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/m</i>	<i>P2₁/c</i>
<i>a</i> /Å	6.8712(2)	5.3442(1)
<i>b</i> /Å	7.4908(3)	15.8348(6)
<i>c</i> /Å	11.7493(4)	9.4068(3)
β /°	93.330(2)	97.344(2)
<i>U</i> /Å ³	603.72(4)	789.51(4)
<i>Z</i>	2	2
<i>T</i> /K	123(2)	153(2)
ρ_{calc} / g cm ⁻³	1.754	1.598
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	1.642	1.423
Crystal dimensions / mm	0.2 × 0.1 × 0.07	0.3 × 0.15 × 0.13
θ ranges / °	3.47 – 30.01	3.37 – 32.56
Index ranges	-9 ≤ <i>h</i> ≤ 9, -10 ≤ <i>k</i> ≤ 10, -16 ≤ <i>l</i> ≤ 16	-7 ≤ <i>h</i> ≤ 5, -23 ≤ <i>k</i> ≤ 20, -12 ≤ <i>l</i> ≤ 14
Completeness to 2 θ = 55° / %	99.7	99.1
Data collected	4291	8243
Unique data (<i>R</i> _{int})	937 (0.0271)	2635 (0.0391)
Observed data [<i>I</i> > 2 σ (<i>I</i>)]	913	2023
Parameters	68	138
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] ^(a)	0.0287, 0.0634	0.0340, 0.0626
(all data)	0.0296, 0.0640	0.0613, 0.0898
Goodness of fit, <i>S</i>	1.059	1.111
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ / e Å ⁻³	-0.957, 0.989	-1.057, 0.904

^(a) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

Because of the types of peripheral groups on the cao ligands and the axial H₂O ligands, a series of hydrogen bonds links the mononuclear species to form a 3D hydrogen bonded network. For ease of description, this network can be divided into two orthogonal 2D sheets, one in the *ab*-plane and a second in the *ac*-plane. The sheet in the *ab*-plane (Figure 9.8) is formed by hydrogen bonds from the axial water ligands to the oxime oxygen atoms of adjacent complexes ($H(9)\cdots O(1^{iv}) = 2.08(3) \text{ \AA}$ and $O(9)-H(9)\cdots O(1^{iv}) = 159(5)^\circ$). If each complex is viewed as a node, and the two hydrogen bonds between each adjacent complex are viewed as a single connection, the resulting topology of this sheet is (4,4).

The sheet in the *ac*-plane (Figure 9.9) is formed by hydrogen bonds occurring between one of the amine hydrogens of the cao ligand to the nitrile group of an adjacent complex in the *c*-axis direction ($H(7A)\cdots N(5^{ii}) = 2.14(4) \text{ \AA}$ and $N(7)-H(7A)\cdots N(5^{ii}) = 170(4)^\circ$), and between the other cao amine and the oxime oxygen on an adjacent complex in the *a*-axis direction ($H(7B)\cdots O(1^{iii}) = 2.04(4) \text{ \AA}$ and $N(7)-H(7B)\cdots O(1^{iii}) = 158(3)^\circ$). This sheet also has (4,4) topology and resembles closely the hydrogen bonded sheet of {Mn₄} in the *ac*-plane described in section 9.3.2 (see Figure 9.6). The shortest Ni $\cdots$ Ni distance is equal to half the diagonal of the *ab* face of the unit cell ($5.0825(1) \text{ \AA}$). The next shortest Ni $\cdots$ Ni distances are equal to the *a* ($6.8712(2) \text{ \AA}$) and *c* ($11.7493(4) \text{ \AA}$) unit cell lengths.

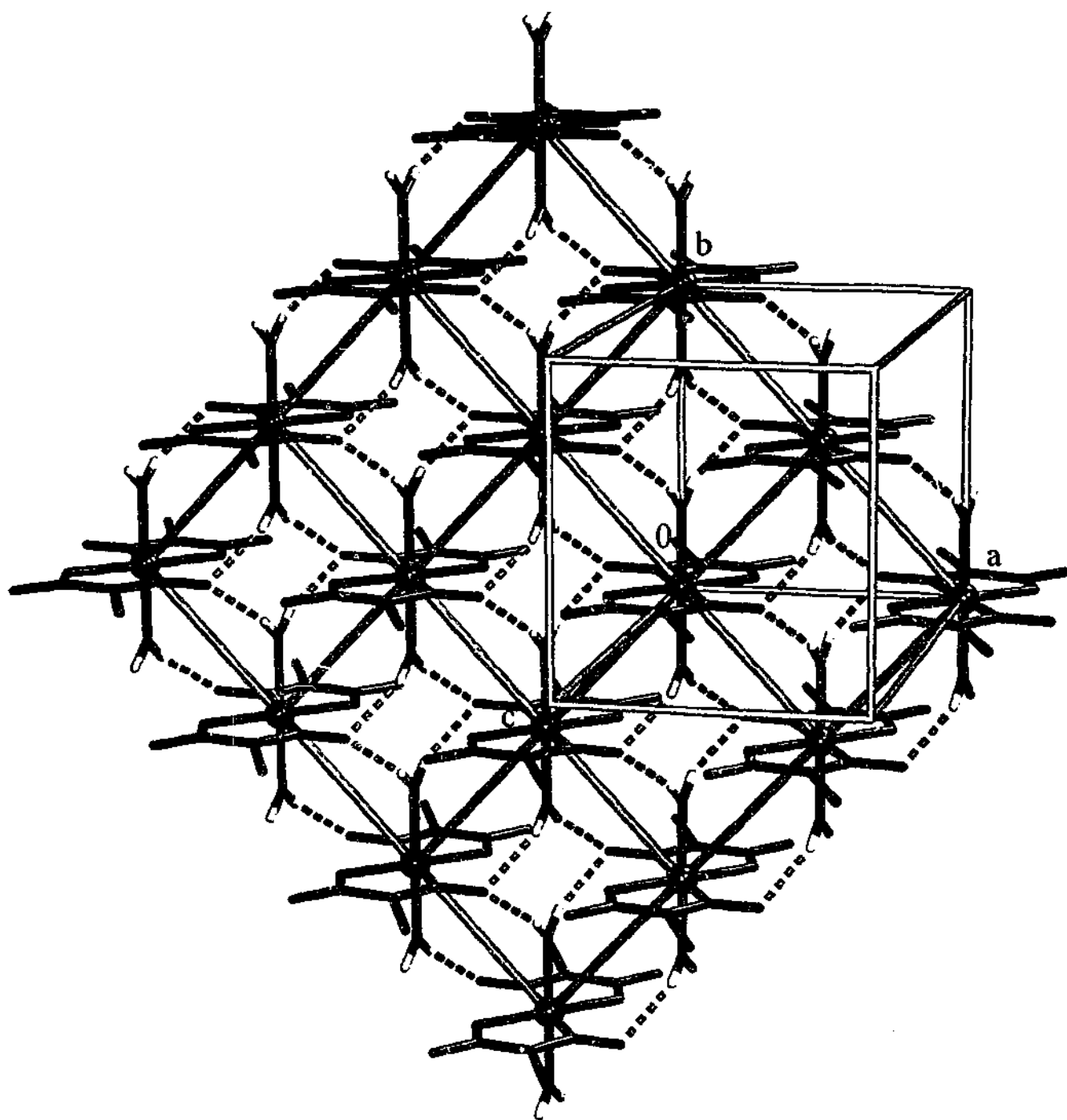


Figure 9.8 2D hydrogen bonded (4,4) sheet network of $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$ in the ab -plane (hydrogen bonds shown in dashed green, (4,4) network shown in red and amine hydrogens omitted for clarity).

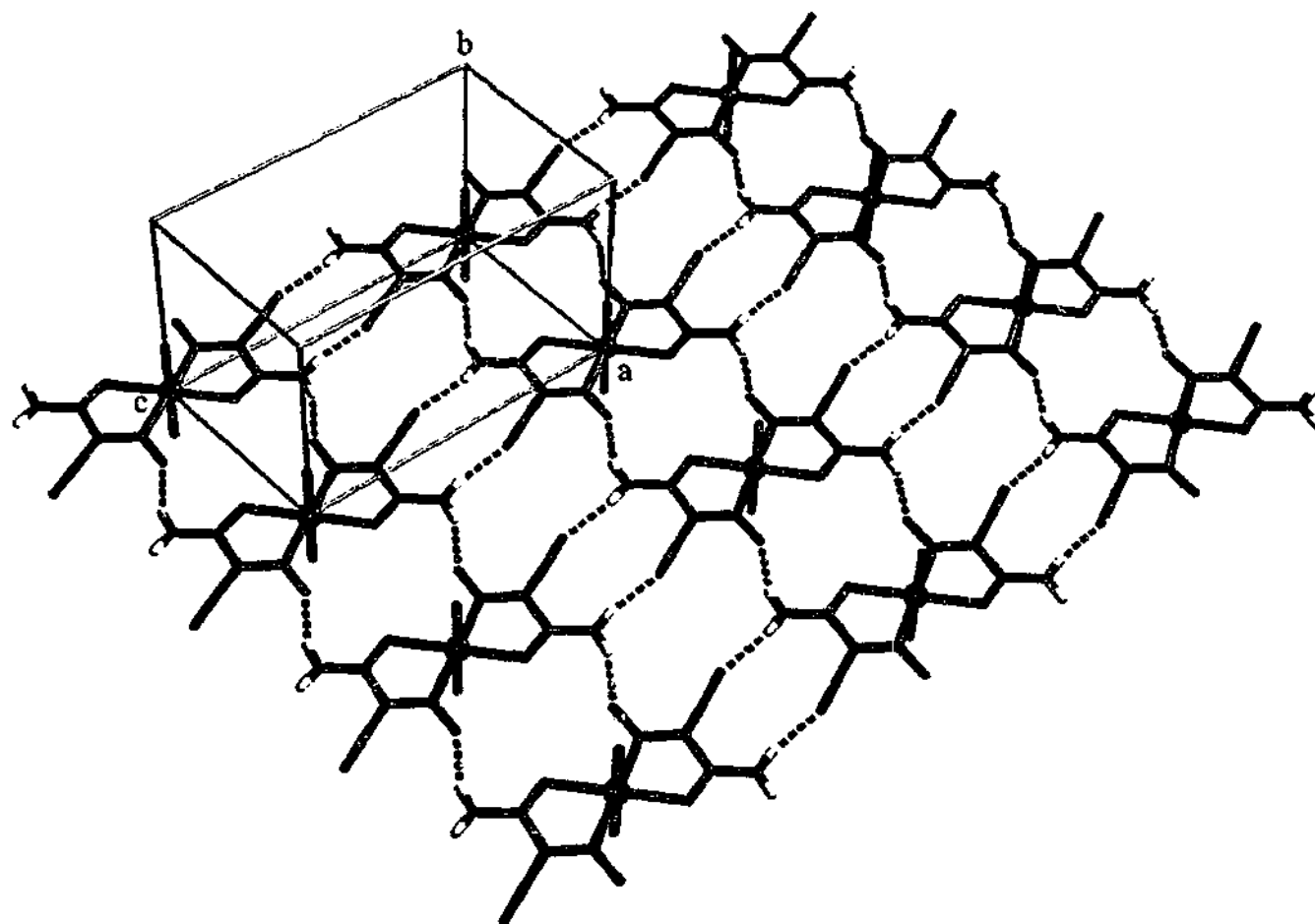


Figure 9.9 View of $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$ showing a hydrogen bonded 2D grid (4,4) sheet in the ac -plane.

In 1983 Skopenko *et al.* reported the structure of this complex at room temperature (295 K).³⁰ Their solution is in the orthorhombic space group $Cmca$. A later unit cell measurement, again at 123 K, on a crystal from another sample of $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$ prepared by the candidate, gave the same parameters as those obtained by Skopenko *et al.* Thus, these are two different phases or polymorphs, as they have the same chemical composition but different packing in the solid state. The unit cell dimensions of the previously reported phase are given in Table 9.5 alongside those of the phase reported here for comparison (the former and latter phases are arbitrarily designated α and β respectively).

Table 9.5 Unit cell parameters for the polymorphs α - and β -[Ni(cao)₂(H₂O)₂] (at 295 K, and 123 K).³⁰

Complex	α -[Ni(cao) ₂ (H ₂ O) ₂] at 295 K ³⁰	β -[Ni(cao) ₂ (H ₂ O) ₂] at 123 K
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Cmca</i>	<i>C2/m</i>
<i>a</i> /Å	7.546(1)	6.8712(2)
<i>b</i> /Å	6.880(1)	7.4908(3)
<i>c</i> /Å	23.382(5)	11.7493(4)
β /°		93.330(2)

Conversion of the α - to the β -phase can conceptually be brought about by taking every second molecule along the *c*-axis direction and translating them in the *b*-axis direction (α -phase) a distance of $1/2b$ and then rotating these molecules 180° about the *c*-axis. Consequently, the overall hydrogen bonding networks of the two phases are different. The 2D H-bond network in the axial direction of the molecules (*ab*-plane) is identical, although every second *ab*-plane network is rotated 180° about the *c*-axis with respect to the other phase. The H-bond network in the equatorial plane of the molecules in the α -phase, however, has (3,6) topology as opposed to the (4,4) net of the β -phase reported here. Figure 9.10 shows the hydrogen bonding networks in the equatorial plane of the α - and β -phases for comparison.

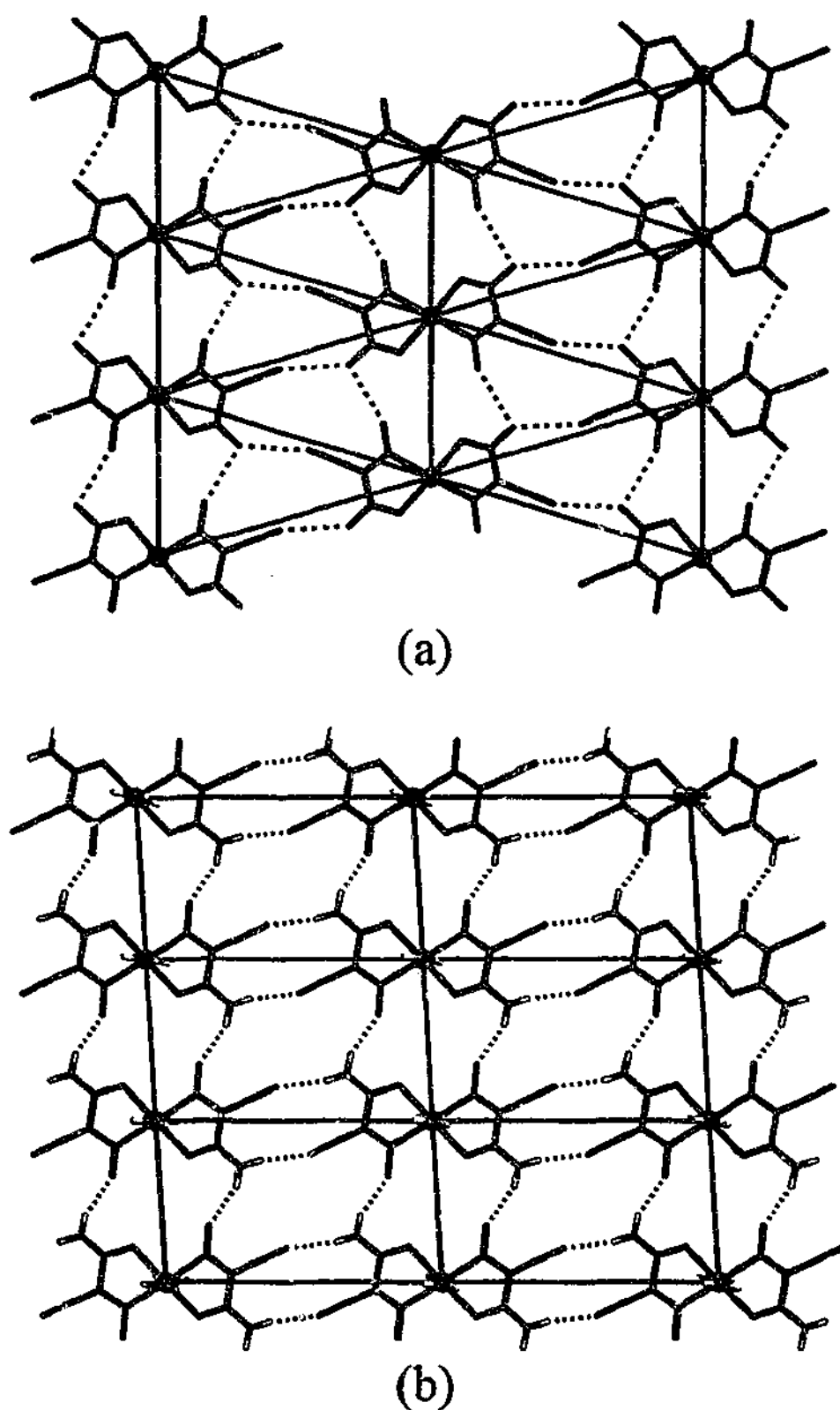


Figure 9.10 The hydrogen bonding networks in the equatorial plane of the $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$ molecules for (a) the α -phase (3,6) and (b) the β -phase (4,4). The topologies of the nets are indicated by the blue lines. The structure of α - $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$ reported by Skopenko *et al.*,³⁰ was rendered from a simulated SHELX res file of CSD entry CABTUU.

Table 9.6 Selected interatomic distances (Å) and angles (°) for [Ni(cao)₂(H₂O)₂].

Ni(1)–N(2)	2.068(2)	Ni(1)–O(8)	2.053(2)
Ni(1)–O(9)	2.016(2)		
N(2)–Ni(1)–O(8)	78.87(7)	O(8 ⁱ)–Ni(1)–N(2)	101.13(7)
Hydrogen bonding			
In the <i>ab</i> -plane			
O(9)–H(9)	0.86(2)	O(9)···O(1 ^{iv})	2.898(2)
H(9)···O(1 ^{iv})	2.08(3)	O(9)–H(9)···O(1 ^{iv})	159(5)
In the <i>ac</i> -plane			
N(7)–H(7A)	0.88(4)	N(7)–H(B)	0.88(4)
H(7A)···N(5 ⁱⁱ)	2.14(4)	H(7B)···O(1 ⁱⁱⁱ)	2.04(4)
N(7)···N(5 ⁱⁱ)	3.010(3)	N(7)···O(1 ⁱⁱⁱ)	2.878(3)
N(7)–H(7A)···N(5 ⁱⁱ)	170(4)	N(7)–H(7B)···O(1 ⁱⁱⁱ)	158(3)

Symmetry transformations: (i) $-x, -y, -z$; (ii) $-x, -y, 1-x$; (iii) $x-1, y, z$; (iv) $1/2-x, 1/2-y, -z$.

9.3.4 [Cu(mcoe)₂(MeOH)₂]

X-Ray structural analysis was performed by Dr. S. R. Batten on a single crystal prepared by the candidate. Crystallographic data for [Cu(mcoe)₂(MeOH)₂] are summarised in Table 9.4 (see page 404). Selected interatomic distances and angles are given in Table 9.7 (see page 413). The mononuclear complex [Cu(mcoe)₂(MeOH)₂] crystallises in the monoclinic space group $P2_1/c$. It consists of a copper(II) atom, which lies on an inversion centre, coordinated in a Jahn-Teller distorted octahedral environment by the imine nitrogen (Cu(1)–N(9) = 1.963(2) Å) and oxime nitrogen (Cu(1)–N(2) = 2.034(2) Å) of two mcoe ligands in the equatorial plane and by two methanol ligands (Cu(1)–O(10) = 2.494(2) Å) in the elongated axial positions (Figure 9.11).

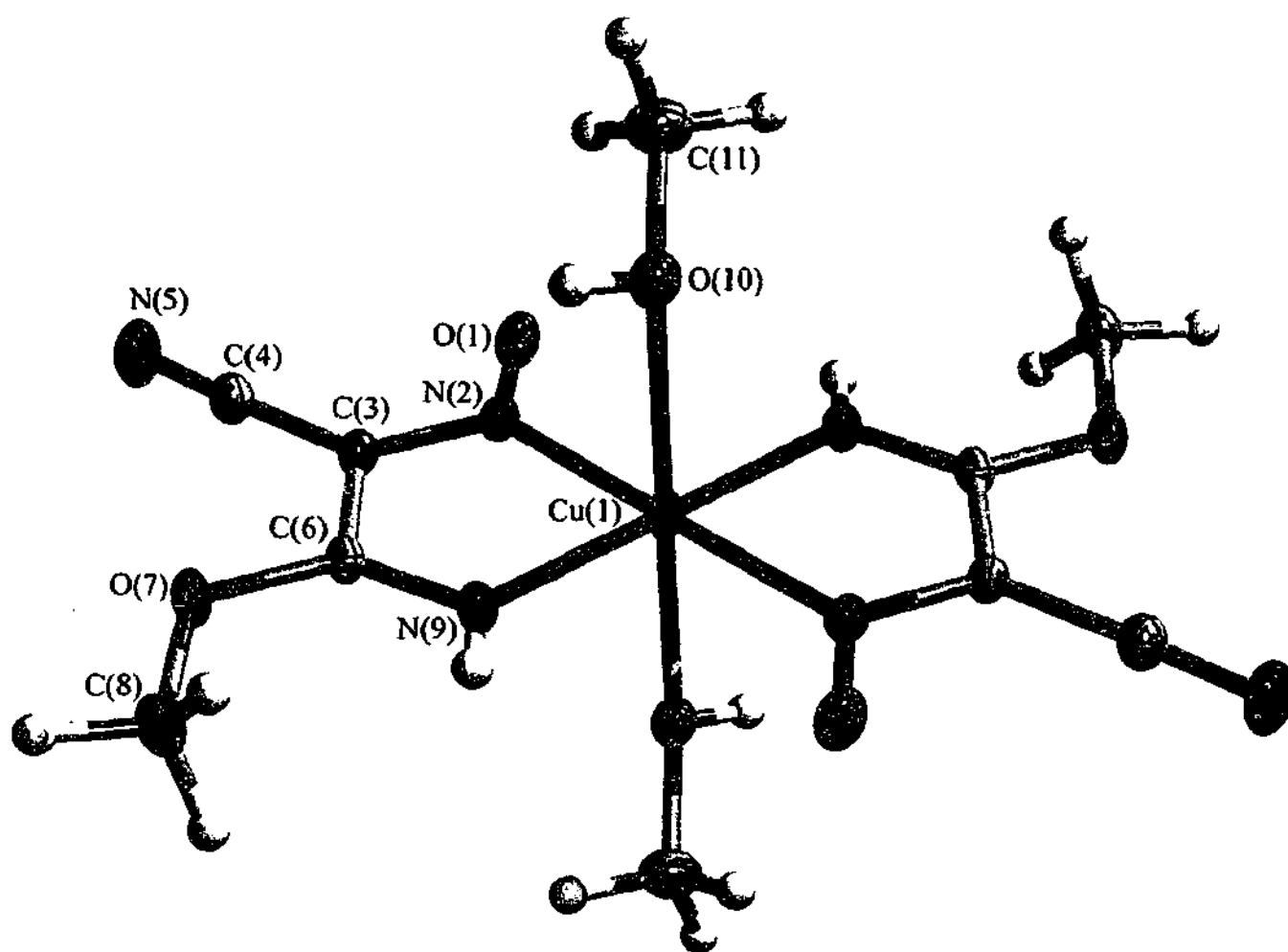


Figure 9.11 The crystal structure of $[\text{Cu}(\text{mcoe})_2(\text{MeOH})_2]$ with the atom labelling scheme shown (thermal ellipsoids shown at 50 % probability).

Once again, because of the types of peripheral groups on the mcoe ligands, these mononuclear species are linked by intermolecular hydrogen bonds formed between the axial methanol and the mcoe oxime oxygen ($\text{H}(10)\cdots\text{O}(1^{\text{iii}}) = 1.94(4) \text{ \AA}$ and $\text{O}(10)-\text{H}(10)\cdots\text{O}(1^{\text{iii}}) = 178(4)^\circ$), and the imine of the mcoe ligand and the methanol oxygen ($\text{H}(9)\cdots\text{O}(10^{\text{ii}}) = 2.27(3) \text{ \AA}$ and $\text{N}(9)-\text{H}(9)\cdots\text{O}(10^{\text{ii}}) = 153(3)^\circ$). Linear 1D chains are formed that run parallel to the a -axis direction (Figure 9.12). The intra-chain $\text{Cu}\cdots\text{Cu}$ distance is equal to the unit cell length a ($5.3442(1) \text{ \AA}$). The shortest inter-chain $\text{Cu}\cdots\text{Cu}$ distance is equal to half the diagonal of the bc -plane ($9.2091(3) \text{ \AA}$).

The hydrogen bonding interactions link ligands which lie along $\text{Cu}(d_{z^2})$ and $\text{Cu}(d_{x^2-y^2})$ directions and thus any magnetic exchange will be expected to be very weak.

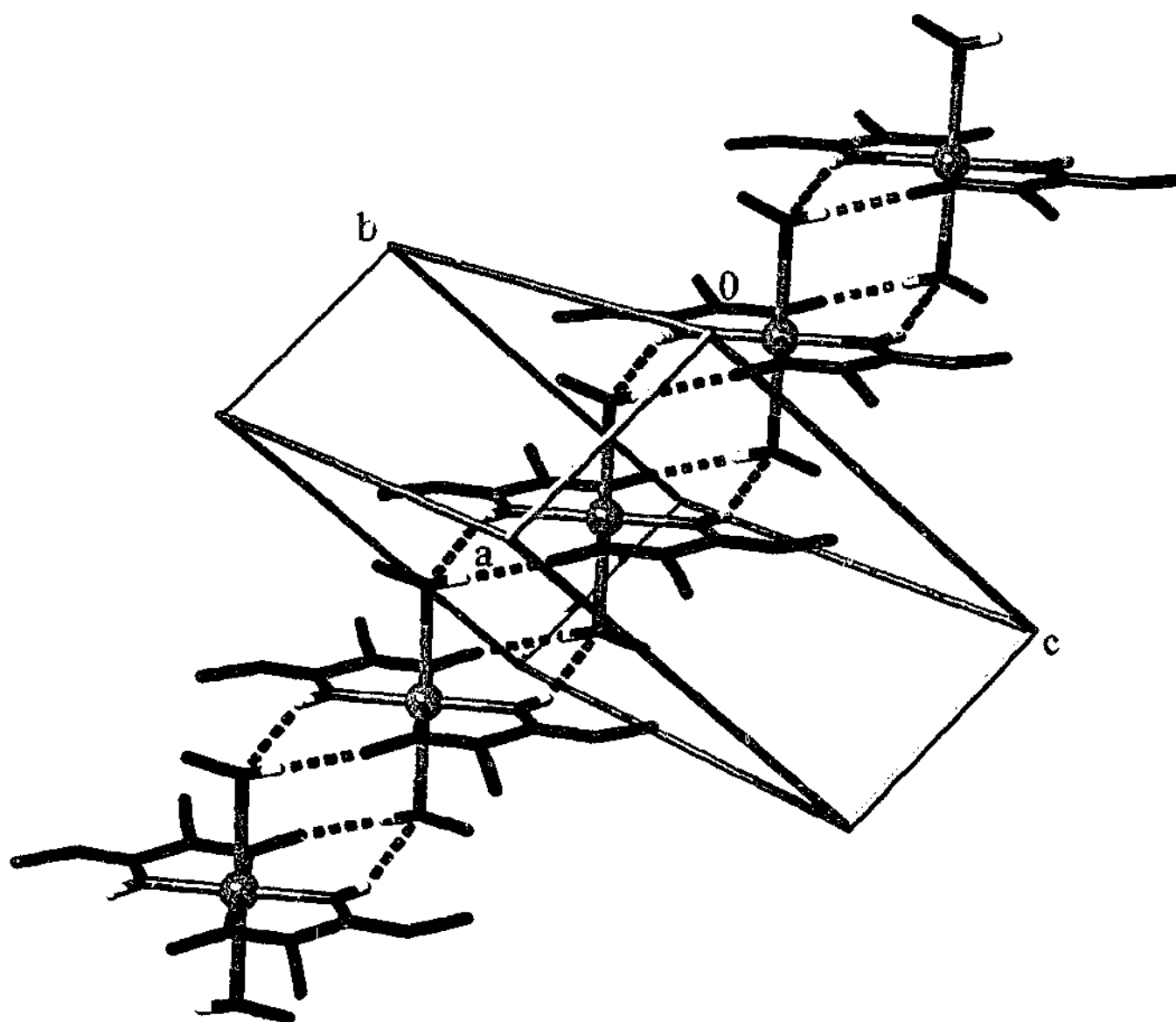


Figure 9.12 A Linear 1D hydrogen bonded chain of $[\text{Cu}(\text{mcoe})_2(\text{MeOH})_2]$ running parallel to the a -axis direction.

Table 9.7 Selected interatomic distances (Å) and angles (°) for [Cu(mcoe)₂(MeOH)₂].

Cu(1)–N(2)	2.034(2)	Cu(1)–N(9)	1.963(2)
Cu(1)–O(10)	2.494(2)	C(3)–N(2)	1.321(3)
N(2)–Cu(1)–N(9)	81.39(7)	N(2)–Cu(1)–N(9 ⁱ)	98.61(7)
N(2)–Cu(1)–O(10)	90.74(6)	N(9)–Cu(1)–O(10)	88.64(7)
Hydrogen bonding			
N(9)–H(9)	0.78(3)	O(10)–H(10)	0.79(4)
H(9)···O(10 ⁱⁱ)	2.27(3)	H(10)···O(1 ⁱⁱⁱ)	1.94(4)
N(9)···O(10 ⁱⁱ)	2.989(2)	O(10)···O(1 ⁱⁱⁱ)	2.726(2)
N(9)–H(9)···O(10 ⁱⁱ)	153(3)	O(10)–H(10)···O(1 ⁱⁱⁱ)	178(4)

Symmetry transformations: (i) 1-x, 1-y, 1-z; (ii) -x, 1-y, 1-z; (iii) x-1, y, z.

9.4 Magnetism

The help of Mr. Kevin Berry (Westernport Secondary College, Hastings, Victoria) with calculations is gratefully acknowledged.

9.4.1 [Mn₃(mcoe)₆]NO₃·2H₂O

In Figure 9.13 it can be seen that the magnetic moment, per Mn₃, decreases a little from 9.5 μ_B at 300 K to ~9 μ_B at ~100 K, then more rapidly to reach a shoulder value of 5.5 μ_B at 5 K, before reaching 4.7 μ_B at 2 K. The uncoupled ($g = 2.0$) value for $S_1 = 5/2$, $S_2 = 4/2$, $S_3 = 5/2$ is 9.70 μ_B and very weak antiferromagnetic coupling is therefore occurring. The 2 K value is suggestive of a $S_T = 2$ coupled ground-state but, since the J values are small, there will be many M_S energy levels populated because of their close spacing of a few cm^{-1} .

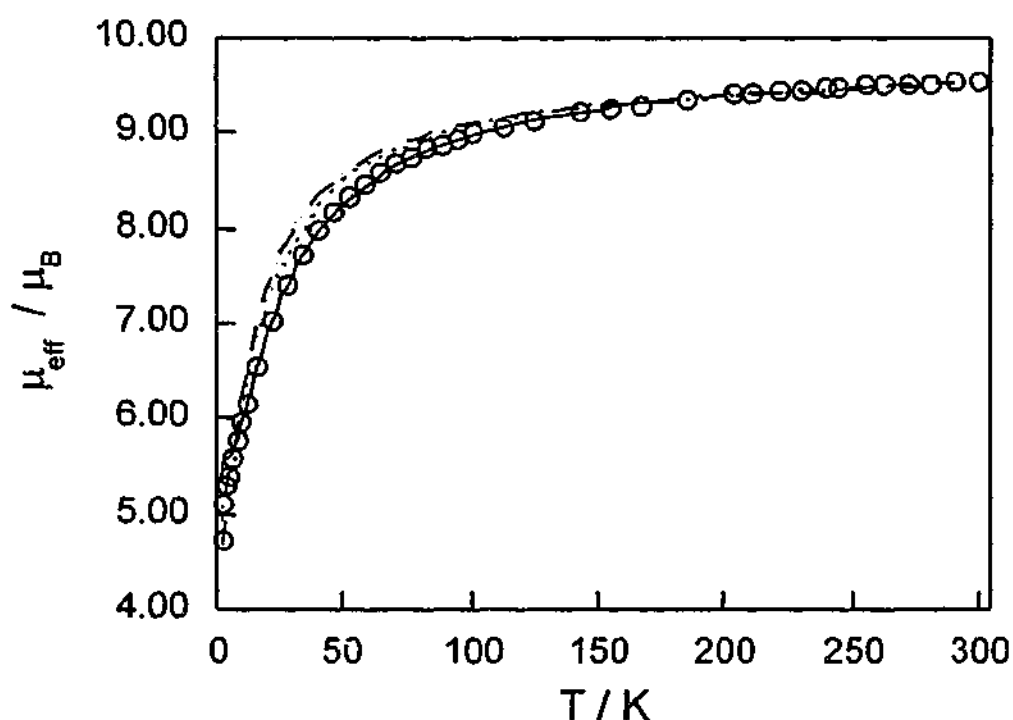


Figure 9.13 Plot of observed μ_{eff} data for $\{\text{Mn}_3\}$ (2–300 K, $H = 1$ T). Calculated lines are obtained using the parameter sets (a) to (c) (see text) are given. (a) ---, (b) ·····, (c) —.

The crossover of relevant S_T levels occur at the following α values where $\alpha = J_{13}/J_{12}$ and J_{12} is negative;

$$S_T = 3 \quad \alpha < 0.4$$

$$S_T = 2 \quad 0.4 < \alpha < 0.5$$

$$S_T = 1 \quad \alpha > 0.5$$

The spin Hamiltonian employed is that commonly used for a linear trimer:

$$H = -2J_{12}(S_1 \cdot S_2 + S_2 \cdot S_3) - 2J_{13}S_1 \cdot S_3 \quad \text{Equation 9.1}$$

The field-dependent thermodynamic form of susceptibility was employed.^{17,18,31} Wide ranges of parameter values were explored in trying to fit the whole susceptibility data

between 2-300 K. The region 12-120 K was the hardest to reproduce. Using χ_{TIP} of $300 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, the following three sets gave quite good fits.

- (a) $g = 1.99$, $J_{12} = -1.02 \text{ cm}^{-1}$, $J_{13} = -0.53 \text{ cm}^{-1}$, $\alpha = 0.52$, $S_{\text{T}} = 1$ ground;
- (b) $g = 2.00$, $J_{12} = -1.16 \text{ cm}^{-1}$, $J_{13} = -0.58 \text{ cm}^{-1}$, $\alpha = 0.50$, $S_{\text{T}} = 1$ or 2 ground;
- (c) $g = 2.02$, $J_{12} = -1.59 \text{ cm}^{-1}$, $J_{13} = -0.67 \text{ cm}^{-1}$, $\alpha = 0.42$, $S_{\text{T}} = 2$ ground.

Fit (c) was better than (a) and (b) between 10-120 K but worse below 6 K (Figure 9.14). It is possible that the small discrepancy below 6 K arises through trimer-trimer interactions. Variable field magnetisation isotherms ($T = 2\text{-}20 \text{ K}$, $H = 0\text{-}5 \text{ T}$) were measured to help to identify the S_{T} ground state. Saturation in M is not complete even at 2 K and 5 T.

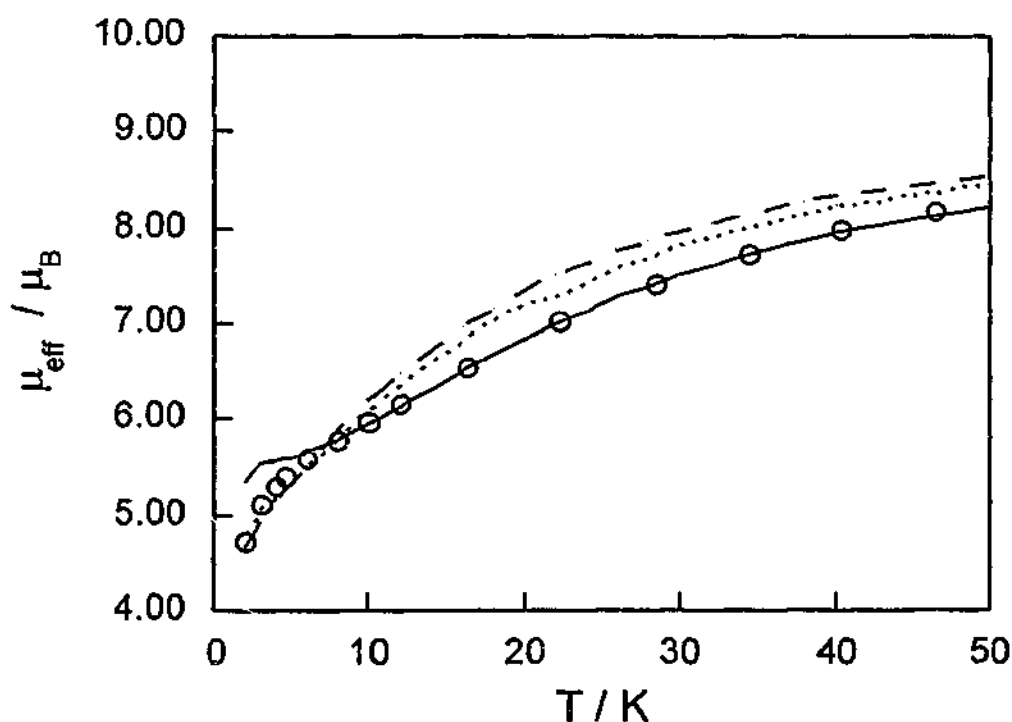


Figure 9.14 Plot of observed μ_{eff} data for $\{\text{Mn}_3\}$ in region 2-50 K with calculated lines for parameter sets (a) ----, (b) ·····, (c) — (see text).

Calculation of the M vs. H plots at 2 K and 0-5 T using the parameter sets (a) to (c) gave the worst agreement for set (c) with calculated M values being bigger than observed at all temperature and field combinations. Sets (a) and (b) gave similar calculated values and showed good agreement for the three temperatures with fields between 0-1.5 T but with calculated M values greater than those observed above 1.5 T (Figure 9.15). It is interesting to note that the 2 K/5 T calculated values of M are significantly greater than $4N\beta$ anticipated for $S_T = 2$ lowest in energy because of thermal population of the $S_T = 3$ and $S_T = 1$ Zeeman levels close by. In summary, the α value appears to be close to 0.5, the crossover point of $S_T = 1$ and 2. The discrepancies between observed and calculated M values above fields of 1.5 T are most likely because of zero-field splitting effects combined with Zeeman effects from closely spaced S_T levels. There is not an isolated S_T ground-state for $\{\text{Mn}_3\}$ and so further attempts to calculate D values have not been made. Plots of observed M vs. H / T (K), either isothermal (2-20 K) or isofield,^{17,18} show non-superposition of the lines and are thus indicative of zero-field splitting effects. Weak trimer-trimer effects may also play a minor part in the higher field regimes.

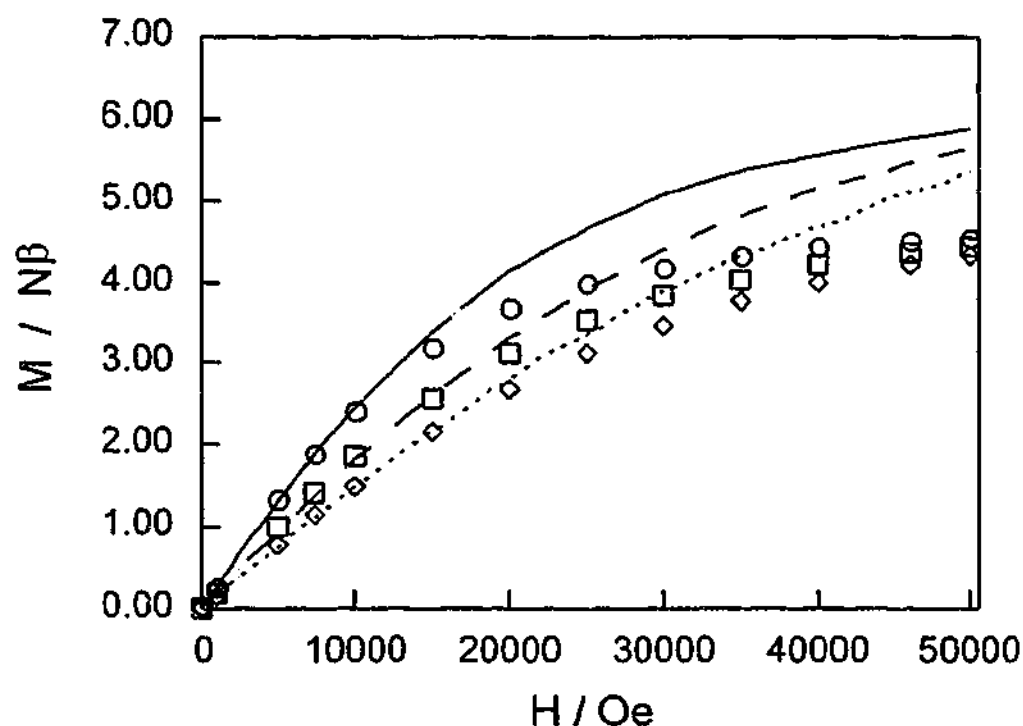


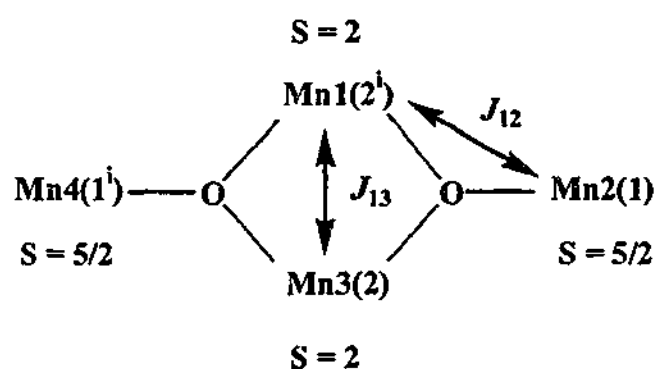
Figure 9.15 Plots of isothermal (2, 3, 4 K) magnetisation data *versus* field, H , for $\{\text{Mn}_3\}$. Calculated lines (— 2 K, ---- 3 K, 4 K) use parameter set (a) given in the text and the spin Hamiltonian given, which does not include zero-field splitting terms.

The J_{12} value for $\{\text{Mn}_3\}$ of $\sim -1 \text{ cm}^{-1}$, which results from $\text{Mn}^{\text{III}}\text{--O--N(R)--Mn}^{\text{II}}$ superexchange pathways, can be compared to the related nioximato- and dimethylglyoximato-bridging in the work of Birkelbach *et al.*^{27,28} in which J_{12} was $+4.7 \text{ cm}^{-1}$ (with $J_{13} = -3.0 \text{ cm}^{-1}$). The difference in sign of J_{12} results from the net effects of the ferromagnetic and antiferromagnetic contributions to J_{12} , which in turn will be influenced by subtle coordination differences on the Mn^{III} and Mn^{II} centres and, to a lesser degree, by the terminal binding groups. These structural differences have been described above in section 9.3.1.

9.4.2 $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$

Two freshly prepared samples were measured and very similar μ_{eff} (per Mn_4) data were obtained when measured in a field of 1 T and dispersed in Vaseline to prevent

torquing.³² The moment decreases, gradually, from $8.65 \mu_B$ at 300 K to reach a plateau value of $\sim 7.8 \mu_B$ between 50-10 K, then more rapidly, reaching $6.85 \mu_B$ at 2 K and still decreasing (Figure 9.16). The spin-only value for two Mn^{III} ($S = 2$) plus two Mn^{II} ($S = 5/2$) of $\mu = 10.86 \mu_B$ is bigger than the observed value at 300 K and thus antiferromagnetic coupling is occurring. The 'butterfly' tetranuclear arrangement of spins, with two Mn^{III} ($2, 2^i$) in the body positions and two Mn^{II} ($1, 1^i$) at the wingtips, was employed in the $(-2J\mathbf{S}_i \cdot \mathbf{S}_j)$ spin Hamiltonian below^{17,18,31} with the spin centres numbered as in Scheme 9.2 and the approximation $J_{12} = J_{14} = J_{34} = J_{23}$.



Scheme 9.2

$$H = -J_{12}(\mathbf{S}_T^2 - \mathbf{S}_{13}^2 - \mathbf{S}_{24}^2) - J_{13}(\mathbf{S}_{13}^2 - \mathbf{S}_1^2 - \mathbf{S}_3^2) \quad \text{Equation 9.2}$$

Where $\mathbf{S}_{13} = \mathbf{S}_1 + \mathbf{S}_3$, $\mathbf{S}_{24} = \mathbf{S}_2 + \mathbf{S}_4$, and $\mathbf{S}_T = \mathbf{S}_{13} + \mathbf{S}_{24}$. The Kambe vector coupling approach has been described for this spin combination.^{17,18,31} There are 110 possible spin states with $\mathbf{S}_T$, the total spin of the cluster, varying from 0 to 9. The field dependent thermodynamic form of susceptibility was employed, in combination with matrix diagonalisation methods,³¹ to fit the susceptibility data.

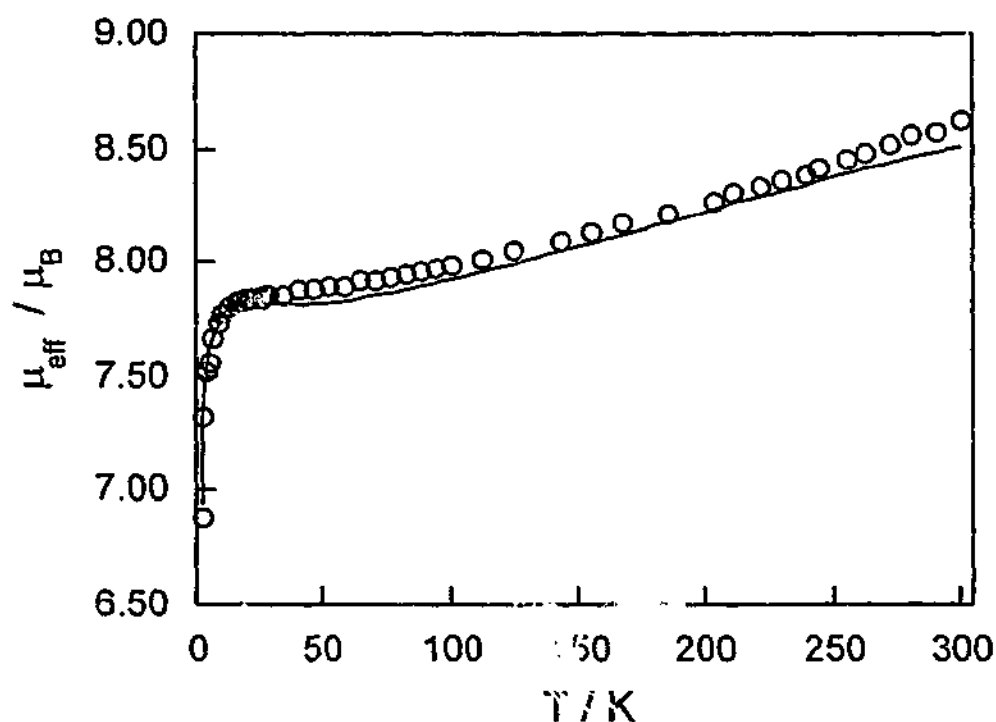


Figure 9.16 Plot of observed μ_{eff} data for $\{\text{Mn}_4\}$ (2–300 K, $H = 1$ T). Best-fit calculated line obtained using the parameter set given in the text.

The best-fit to the data is obtained for the parameter set $g = 1.88$, $J_{12} = -2.5 \text{ cm}^{-1}$, $J_{13} = -46.0 \text{ cm}^{-1}$, $\alpha = J_{13} / J_{12} = 18.4$, $J_{24} = 0$. These parameters also give good agreement with the 2, 3 and 4 T magnetisation isotherms (Figure 9.17). Interestingly, the ground state under these conditions, viz $\alpha > 6$, J_{12} and J_{13} negative and with J_{13} large, is made up of the six degenerate levels $S_T = 0, 1, 2, 3, 4, 5$ and they correspond to $S_{13} = 0$. Introduction of a tiny J_{24} value of -0.02 cm^{-1} has only a minimal effect on the quality of fit. Larger J_{24} values such as $\pm 0.1 \text{ cm}^{-1}$, which correspond to splitting up of the six S_T levels, lead to much poorer fits. Thus, an isolated S_T ground level is not present in $\{\text{Mn}_4\}$ and plots of M versus H / temperature, much used by Hendrickson and Christou^{17,18} to show zero-field splitting of isolated ground states, yield isofield lines all superimposed on each other indicating a lack of zero-field splitting.

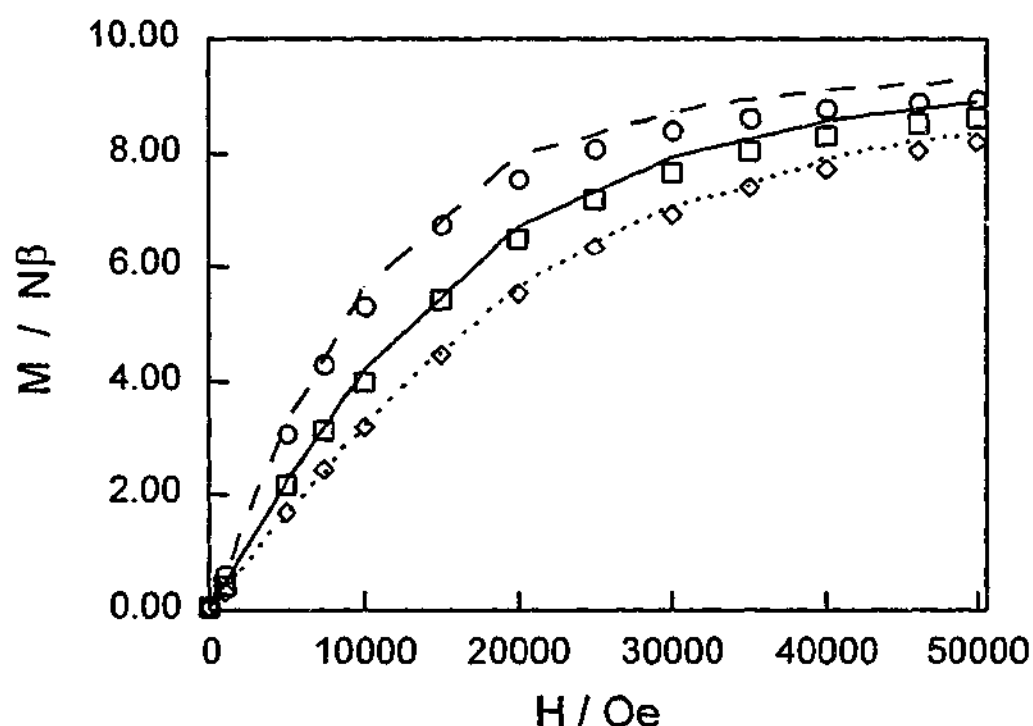


Figure 9.17 Plots of isothermal (2, 3, 4 K) magnetisation data *versus* field, H , for $\{\text{Mn}_4\}$. Calculated lines (----- 2 K, ——— 3 K, 4 K) use the parameter set given in the text and in Table 9.8. The kinks in the calculated curves reflect the number of calculated points used in the plotting routine.

The J and g values and ground S_T states for other recently reported $\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_2$ planar-rhomboidal compounds are compared to those of $\{\text{Mn}_4\}$ in Table 9.8. Lower than expected g values are a common feature, the second and third examples being particularly low. The first three compounds have μ_3 -oxo bridges and J_{13} (body-body $\text{Mn}^{\text{III}}\cdots\text{Mn}^{\text{III}}$) is much more negative for $\{\text{Mn}_4\}$ than for the others. The μ_3 -phenoxo bridged compounds containing pdmH^- and hmp^- ligands show ferromagnetic J_{12} and J_{13} values possibly because of the nature of the orbital overlap involving the phenoxo oxygen. These J values lead to large S_T ground state values with negative zero-field splitting. Such features are prerequisites for single-molecule magnetic (SMM) behaviour and this was confirmed for these molecules by observing frequency dependent out-of-phase components χ''_M . $\{\text{Mn}_4\}$

would be predicted not to exhibit SMM behaviour because of a lack of zero-field splitting. Measurements of the AC χ''_M values *versus* temperature (2-10 K; oscillation frequencies 10, 50, 100, 250, 500, 1500 Hz; AC field amplitude 3.5 Oe) were therefore made and showed no maximum in this temperature range and thus $\{Mn_4\}$ does not display SMM behaviour.

Table 9.8 Comparison of J values (cm^{-1}) and ground spin states for $Mn^{II}_2Mn^{III}_2$ planar rhomboidal species where $Mn_1 = Mn_3 = Mn^{III}$ at body sites.

Cluster	J_{12}	J_{13}	$\alpha = J_{13}/J_{12}$	g	Ground S_T	ref
$\{Mn_4\}$	-2.5	-46.0	18.4	1.88	0.5 ^(d)	(e)
$Mn_4O_2(O_2CMe)_6(bipy)_2$ ^(a)	-1.97	-3.12	1.59	1.70	2	33
$Mn_4O_2(O_2CCPh_3)_6(OEt_2)_2$	-1.50	-2.80	1.89	1.47	2	34
$[Mn_4(O_2CMe)_2(pdmH)_6](ClO_4)_2$ ^(b)	+0.40 ^(f)	+8.1 ^(f)	20.4	1.84	8 ± 1	17
$[Mn_4(O_2CMe)_2(pdmH)_6](ClO_4)_2 \cdot 2.5H_2O$	+1.1 ^(f)	+8.7 ^(f)	7.94	1.89	9	17
$[Mn_4(hmp)_6Br_2(H_2O)_2]Br_2 \cdot 4H_2O$ ^(c)	+0.92 ^(f)	+8.66 ^(f)	9.43	1.94	9	18

^(a) bipy = 2,2'-bipyridine, ^(b) pdmH⁻ = monoanion of pyridine-2,6-dimethanol, ^(c) hmp⁻ = anion of 2-hydroxymethylpyridine, ^(d) six degenerate levels, ^(e) this work, ^(f) these values were incorrectly divided by a factor of two in Price *et al.*³⁵ (see Appendix 2, page 450).

9.4.3 $[Ni(cao)_2(H_2O)_2]$ and $[Cu(mcoe)_2(MeOH)_2]$

The magnetic data (Figure 9.18 (Ni) and Figure 9.19 (Cu)) show Curie-Weiss dependence of susceptibility ($C = 1.272 \text{ cm}^3\text{mol}^{-1}\text{K}$; $\theta = -4.3 \text{ K}$ (Ni) and $C = 0.38 \text{ cm}^3\text{mol}^{-1}\text{K}$; $\theta = 0.32 \text{ K}$ (Cu)). For $[Ni(cao)_2(H_2O)_2]$ the corresponding μ_{eff} values decrease marginally between 300 - 15 K, then more rapidly reaching $1.95 \mu_B$ at 2 K. This behaviour is anticipated for a combination of zero-field splitting of the $^3A_{2g}$ state and weak antiferromagnetic coupling, occurring *via* the hydrogen bonding pathways. For

$[\text{Cu}(\text{mcoe})_2(\text{MeOH})_2]$ μ_{eff} remains at $1.77 \mu_{\text{B}}$ between 300-10 K, with a small decrease to $1.58 \mu_{\text{B}}$ at 2 K. Likewise, the latter behaviour may be indicative of extremely weak coupling occurring *via* the hydrogen bonding pathways (*vide supra*).

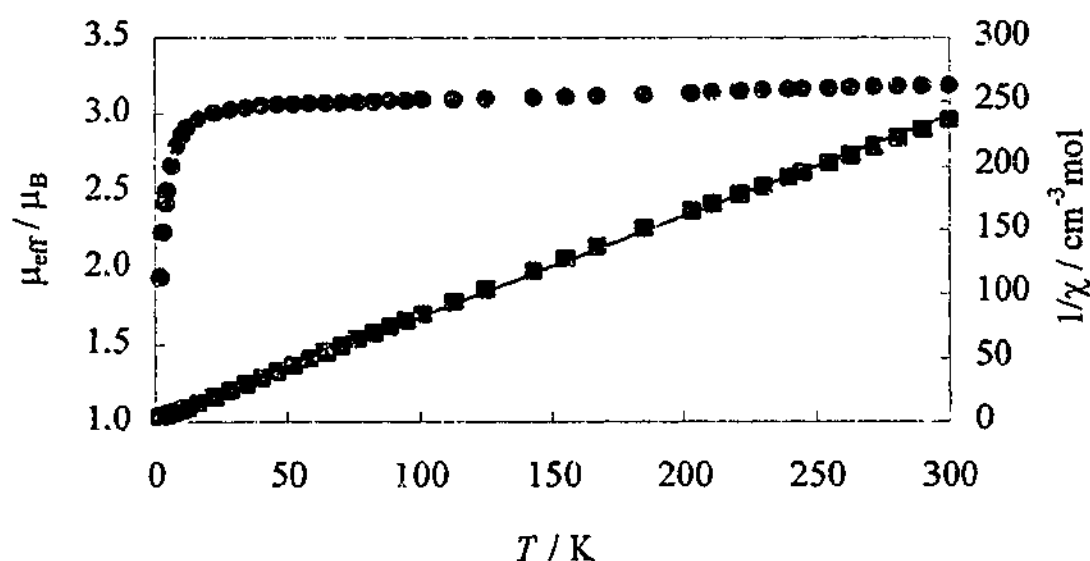


Figure 9.18 Plots of magnetic moment, μ_{eff} (●), and inverse susceptibility, $1/\chi$ (■), for $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$ (the solid line in the $1/\chi$ plot is the fit to the Curie-Weiss law).

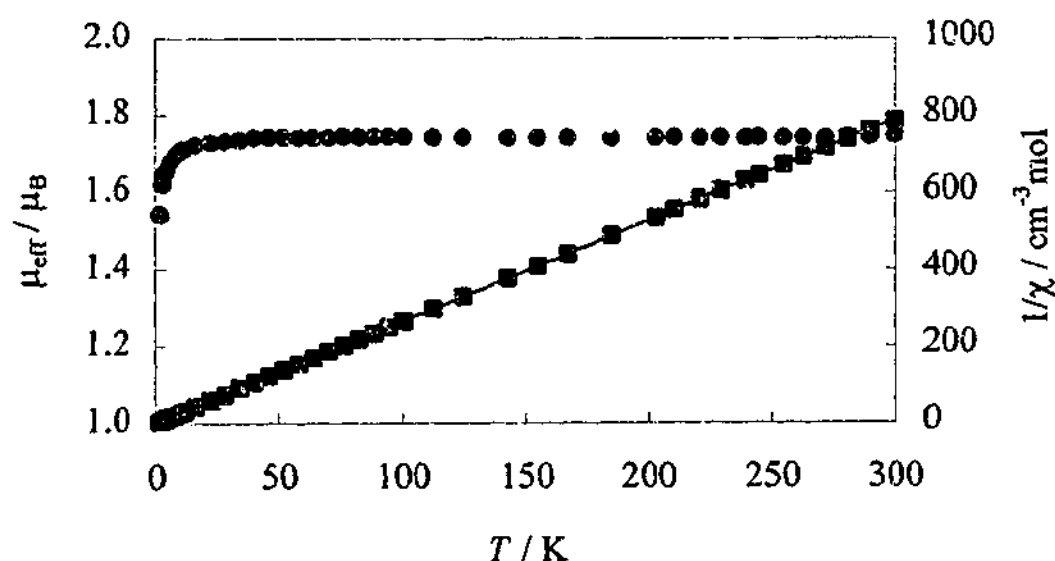


Figure 9.19 Plots of magnetic moment, μ_{eff} (●), and inverse susceptibility, $1/\chi$ (■), for $[\text{Cu}(\text{mcoe})_2(\text{MeOH})_2]$ (the solid line in the $1/\chi$ plot is the fit to the Curie-Weiss law).

9.5 Conclusions

Two new mixed valent manganese(II)/(III) compounds and two mononuclear nickel(II) and copper(II) complexes were synthesised in which the starting pseudochalcogenide ligand, dicyanonitrosomethanide ($\text{ONC}(\text{CN})_2^-$, dcnm), undergoes nucleophilic addition of methanol in $\{\text{Mn}_3\}$ and $[\text{Cu}(\text{mcoe})_2(\text{MeOH})_2]$, and water in $\{\text{Mn}_4\}$ and $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$ during coordination to the metal ions. The crystal structures of $\{\text{Mn}_3\}$ and $\{\text{Mn}_4\}$ show the former is a linear trinuclear $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}\text{Mn}^{\text{II}}$ compound containing bridging oxime moieties from the chelating ligand, mcoe. The latter compound has a planar rhomboidal (butterfly) arrangement of $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ with the Mn^{III} ions in 'body' positions bridged to the 'wingtip', seven coordinate Mn^{II} ions by μ_3 -oxo atoms and by the NO^- oxime groups of the chelating ligand, cao.

A second phase of $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$ was found, termed the β -phase, where the first phase, α - $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$, was reported by Skopenko *et al.* in 1983.³⁰ The α -phase differs in the overall 3D hydrogen bonding network between the molecules, and is related to the β -phase by translation and rotation of half of the molecules (*vide supra*).

Each of the complexes described in this chapter exhibits interesting supramolecular hydrogen bonding networks largely as a consequence of the functional groups on the ligands cao and mcoe. In particular, the ligand cao has peripheral nitrile and amine groups positioned so that complementary hydrogen bonds can occur between two cao complexes.

Several reasonable fits to the variable temperature magnetic susceptibility data for $\{\text{Mn}_3\}$ gave an intramolecular coupling constant, J_{12} , of $\sim -1 \text{ cm}^{-1}$ (*vide supra*), indicating

weak antiferromagnetic exchange. The complex $\{\text{Mn}_3\}$ does not possess an isolated ground spin state, S_T , but rather thermally populates closely spaced S_T levels of 1 and 2.

The best fit to the variable temperature magnetic susceptibility data for $\{\text{Mn}_4\}$ yielded 'wingtip-to-body' and 'body-to-body' (*vide supra*) coupling constants of $J_{12} = -2.5 \text{ cm}^{-1}$ and $J_{12} = -46.0 \text{ cm}^{-1}$ respectively. These values indicate antiferromagnetic coupling within the complex. The 'body-to-body' exchange is particularly strongly antiferromagnetic in comparison to other similar 'butterfly' type tetranuclear complexes. $\{\text{Mn}_4\}$ also does not possess an isolated ground state spin, S_T , but instead six degenerate levels of 0 to 5. No negative zero-field splitting values were observed for either $\{\text{Mn}_3\}$ or $\{\text{Mn}_4\}$, indicating that they are not single molecule magnets (SMMs). The magnetism of the mononuclear Ni^{II} and Cu^{II} complexes follow the Curie-Weiss law, with perhaps the suggestion of extremely weak coupling occurring *via* the hydrogen bonding pathways.

The initial intention of this work was to synthesise extended network complexes containing dcnm. However the structural and magnetic results obtained, although largely unexpected, were most interesting.

9.6 Experimental

9.6.1 Synthesis of $\text{Ag}(\text{dcnm})$ and $\text{Me}_4\text{N}(\text{dcnm})$

$\text{Ag}(\text{dcnm})$ was synthesized by Dr. Stuart Batten according to the literature.³⁶ $\text{Me}_4\text{N}(\text{dcnm})$ was synthesised by adding a solution of Me_4NBr (4.929 g, 32.0 mmol) in a solvent mixture of 100 mL acetonitrile and 40 mL methanol to a stirred suspension of $\text{Ag}(\text{dcnm})$ (6.059 g, 30.0 mmol) in 50 mL dichloromethane. AgBr was removed by filtration through Celite on a large sinter. The solvent was evaporated from the filtrate by rotary evaporation and the resulting yellow oil recrystallised by vapour diffusion of diethyl ether into a solution in methanol (Yield 5.08 g, 95%). IR (Nujol mull, cm^{-1}): 3438mbr,

2212s, 1654m, 1583w, 1487s, 1418m, 1273s, 1233s, 1169m, 951s, 879vw, 832vw, 779m, 669m, 580m.

9.6.2 Synthesis of $[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$

A methanolic solution (5 mL) of $\text{Me}_4\text{N}(\text{dcnm})$ (0.336 g, 2.0 mmol) was added to a methanolic solution (5 mL) of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.251 g, 1.0 mmol). The resultant solution was an orange colour. After one week many red crystals were present in the deep red solution. The crystals had a hexagonal or half-hexagonal cross-section and did not lose solvent in air. The solution was decanted. A fine light-brown solid, which coprecipitated with the crystals was removed by suspending it in methanol (the crystals were far less mobile, sinking rapidly) and decanting the suspension. This process was repeated several times until the methanol wash was free of the light-brown solid. The crystals were collected by filtration, washed with methanol and dried in air. Yield 0.17 g (50 % based on total available Mn). An irregular shaped crystal was chosen for X-ray diffraction structural analysis. IR (Nujol mull, cm^{-1}): 3258s, 2221m, 1645s, 1434s, 1385m, 1356s, 1266s, 1192s, 1125s, 952w, 823w, 779m. Anal. (%) Found: C, 29.5; H, 3.1; N, 24.8. Calc. for $\text{C}_{24}\text{H}_{28}\text{N}_{19}\text{O}_{17}\text{Mn}_3$: C, 28.3; H, 2.8; N, 26.1. Powder XRD: The diffractogram of the bulk product matches that calculated from the crystal structure.

9.6.3 Synthesis of $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$

$\text{Me}_4\text{N}(\text{dcnm})$ (0.596 g, 3.54 mmol) was stirred in 10 mL of hot acetonitrile to dissolve. There remained a small amount of yellow residue. A solution of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.889 g, 3.54 mmol) in acetonitrile (10 mL) was then added to this mixture, resulting in an instant colour change to deep red. Over a period of about 30 minutes of stirring the hot mixture changed to an orange colour. The mixture was then filtered several times to remove a fine brown precipitate (most likely manganese oxide), then covered and left to

stand. After four days the solution was a red/brown colour with a small amount of fine brown precipitate mixed with many red/orange crystals. The fine brown precipitate was removed by suspending it in the solution (the crystals were far less mobile, the majority remaining attached to the glass of the vessel) and filtering the suspension. The filtrate was returned to the crystals, which were then filtered and washed with acetonitrile (Yield 50 mg, 4 % based on total available Mn). IR (Nujol, cm^{-1}): 3390sbr, 2268vw, 2224s, 1682s, 1606s, 1470s, 1317s, 1224s, 1136s, 1041m, 950m, 831m, 708sh, 666sh. Anal. (%) Found: C, 22.2; H, 3.0; N, 22.4. Calc. for $\text{C}_{24}\text{H}_{54}\text{N}_{20}\text{O}_{30}\text{Mn}_4$: C, 21.8; H, 4.1; N, 21.2. Powder XRD: The diffractogram of the bulk product matches that calculated from the crystal structure.

9.6.4 Synthesis of $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$

An aqueous solution (5 mL) of $\text{Me}_4\text{N}(\text{dcnm})$ (0.081 g, 0.50 mmol) was added to an aqueous solution (5 mL) of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.091 g, 0.25 mmol) in a large sample vial. The resultant yellow solution was sealed and left to stand. After approximately one month several clusters of dark red/purple crystals were present as well as a small amount of colourless crystals. The latter were most likely Me_4NClO_4 . The red/purple crystals were very sensitive to solvent loss, thus were kept in the mother liquor. IR (Nujol, cm^{-1}): 3356sbr, 3192sbr, 2751w, 2589vw, 2228s, 1667s, 1628s, 1586s, 1454, 1393s, 1299s, 1178s, 1102s, 771m, 717s, 650m.

A crystal suitable for X-ray diffraction was cut from one of the clusters and data were collected by Dr. Paul Jensen.

9.6.5 Synthesis of $[\text{Cu}(\text{mcoe})_2(\text{MeOH})_2]$

A methanolic solution (10 mL) of $\text{Me}_4\text{N}(\text{dcnm})$ (0.081 g, 0.50 mmol) was added to a methanolic solution (10 mL) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.060 g, 0.25 mmol) in a large

sample vial. The resultant dark green solution was sealed and left to stand. After one day large dark green needles had formed. The needles were very sensitive to solvent loss, thus were kept in the mother liquor. IR (Nujol, cm^{-1}): 3499s, 3296s, 2219m, 1644s, 1431s, 1311s, 1238vw, 1207s, 1159m, 1144s, 955vw, 787m.

A crystal suitable for X-ray crystallographic study was cut from one of the dark green needles and data were collected by Dr. Stuart Batten.

9.6.6 X-Ray Crystallography

Data were collected using a Nonius KappaCCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Integration was carried out by the program DENZO-SMN,³⁷ and data were corrected for Lorentz polarisation effects and for absorption using the program SCALEPACK.³⁷ Solutions were obtained by direct methods (SHELXS 97)³⁸ followed by successive Fourier difference methods, and refined by full matrix least squares on F_{obs}^2 (SHELXL 97)³⁸ with the aid of the graphical interface program X-SEED.³⁹

For $[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ all non-hydrogen atoms of the cation complex, the two waters of crystallization and the nitrogen atom of the nitrate were refined anisotropically. The unique oxygen atom of the nitrate was found to be disordered over two positions. The two contributions (assigned equal quarter site occupancies) were refined isotropically. The imine hydrogen atom was located in the difference Fourier map and was subsequently refined isotropically. The methoxy hydrogen atoms of the mcoe ligand were included at calculated positions with U values 1.5 times the U_{eq} of the carbon atom. Two regions of electron density not connected to each other were assigned as two water molecules.

For $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ all non-hydrogen atoms of the cluster were refined anisotropically. Due to significant disorder that was difficult to

model, the non-hydrogen atoms of the tetramethylammonium and nitrate counter ions were refined isotropically and no hydrogen atoms were assigned. A region of residual electron density was assigned as a water molecule disordered over two positions (O(600) and O(601)). Hydrogen atoms on the coordinating acetonitrile molecules and the amine groups of the cao ligands were assigned to calculated positions with U values 1.5 times (for methyl hydrogen atoms) and 1.2 times (for amine hydrogen atoms) the U_{eq} of the attached atom, whereas those on the coordinating water molecules were not located. As can be seen in Table 9.1 the final R -value was relatively high. The crystals were quite small and weakly diffracting and many were tried with poorer quality diffraction. A number of solutions were obtained for different crystals, the best giving the refined structure presented here. Despite the extreme disorder in the counter ions and in a water molecule the cluster itself is well refined.

For $[\text{Cu}(\text{mcoe})_2(\text{MeOH})_2]$ and $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$ all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the Fourier difference maps and refined freely with isotropic thermal parameters, except for the water hydrogen (H(9)) of $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$ to which was applied an anti-bumping restraint using the DFIX⁴⁰ instruction, but was otherwise refined isotropically. The structures of $[\text{Cu}(\text{mcoe})_2(\text{MeOH})_2]$ and $[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$ were solved by Dr. Stuart Batten and Dr. Paul Jensen respectively.

9.6.7 Magnetic Measurements

Magnetic measurements were kindly carried out by Dr. B. Moubaraki as described previously¹⁹ using a Quantum Design MPMS 5 Squid magnetometer for DC magnetisation measurements and a PPMS instrument for AC susceptibility measurements. Since Mn^{III} complexes display torquing at low temperatures,³² the powder was dispersed in Vaseline.

9.6.8 X-Ray Powder Diffraction of $[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ and $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$

Powder X-ray diffraction data were collected by Mr. Rod Mackie (School of Physics and Materials Engineering, Monash University, Clayton) on a Scintag Automated Powder Diffractometer using a Cu-K α monochromatic radiation source ($\lambda = 154.059$ pm), a solid state Ge detector, 2 mm divergence slit and a 3 mm receiving slit at room temperature. The programs Crystal Diffract⁴¹ and Unit Cell⁴² were used by Dr. Stuart Batten (School of Chemistry, Monash University, Clayton) to confirm that the single crystals were representative of the bulk samples.

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APPENDIX 1: INSTRUMENTATION

Infrared Spectra

Were recorded on a Perkin Elmer 1600 series FTIR spectrometer in the range 500 – 4000 cm^{-1} with a resolution of 4 cm^{-1} . Samples were prepared as Nujol mulls between NaCl plates. Intensities are described by the following abbreviations: s = strong; m = medium; w = weak; vw = very weak; sh = shoulder and br = broad.

Single Crystal X-Ray Diffraction Data

Were collected on a Nonius KappaCCD Diffractometer using the phi and/or omega scan collection methods with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$).

X-Ray Powder Diffraction Data

Were collected by Mr. Rod Mackie (School of Physics and Materials Engineering, Monash University, Clayton) on a Scintag Automated Powder Diffractometer using a Cu- $K\alpha$ monochromatic radiation source ($\lambda = 154.059 \text{ pm}$), a solid state Ge detector, 2 mm divergence slit and a 3 mm receiving slit at room temperature.

Variable Temperature Magnetic Data

Were collected by Dr. Boujemaa Moubaraki (School of Chemistry, Monash University, Clayton). DC susceptibilities were measured using a Quantum Design Magnetic Properties Measurement System (MPMS 5) SQUID magnetometer calibrated by use of a standard palladium sample (Quantum Design) of accurately known magnetisation or by use of magnetochemical calibrants such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$. AC susceptibilities were measured with a Quantum Design Physical Property Measurement

System (PPMS 7) fitted with an Option P-500 (ACMS) attachment for AC measurements. Samples were contained in gelatine capsules held in the middle of a drinking straw, which was fixed to the end of a sample rod.

Microanalyses

Microanalytical measurements (C, H, N) were performed by Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, Dunedin, New Zealand.

Thermogravimetric Analyses

Thermal degradation studies were performed on a Simultaneous Thermal Analyzer (Rheometric Scientific, STA 1500), which was calibrated using a four point melt series (indium, tin, lead, and zinc). Experiments were performed in aluminium pans, under either an atmosphere of nitrogen or dried air.

APPENDIX 2: PUBLICATIONS

Pages 438-447

Self-penetration - A Structural Compromise Between Single Networks and Interpenetration: Magnetic Properties and Crystal Structures of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ and $[\text{M}(\text{dca})(\text{tcm})]$, $\text{M} = \text{Co}, \text{Ni}, \text{Cu}$, $\text{dca} = \text{Dicyanamide}, \text{N}(\text{CN})_2^-$, $\text{tcm} = \text{Tricyanomethanide}, \text{C}(\text{CN})_3^-$.

Paul Jensen, David J. Price, Stuart R. Batten, Boujemaa Moubaraki and Keith S. Murray, *Chem. Eur. J.*, 2000, 6, 3186-3195.

Page 448-449

Synthesis, Structure and Magnetism of a New Manganese Carboxylate Cluster: $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_{16}(\text{MeOH})_3(\text{H}_2\text{O})_3] \cdot 6\text{H}_2\text{O}$.

David J. Price, Stuart R. Batten, Boujemaa Moubaraki and Keith S. Murray, *Chem. Commun.*, 2002, 762-763.

Pages 450-461

Structure and magnetism of trinuclear and tetranuclear mixed valent manganese clusters from dicyanonitrosomethanide derived ligands.

David J. Price, Stuart R. Batten, Kevin J. Berry, Boujemaa Moubaraki and Keith S. Murray, *Polyhedron*, 2003, 22, 165-176.

Synthesis, structure and magnetism of $\{[\text{Mn}(\mu\text{-OH})(\mu\text{-OAc})_2]\cdot\text{HOAc}\cdot\text{H}_2\text{O}\}_n$ and the facilitation of long-range magnetic order through hydrogen bonding.

David J. Price, Stuart R. Batten, Boujemaa Moubaraki and Keith S. Murray, *Polyhedron*, in press.

1D Manganese(III) and iron(III) coordination polymers containing Schiff-base ligands and dicyanamide

David J. Price, Stuart R. Batten, Boujemaa Moubaraki and Keith S. Murray, *Indian J. Chem.*, submitted.

FULL PAPER

Self-Penetration—A Structural Compromise between Single Networks and Interpenetration: Magnetic Properties and Crystal Structures of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ and $[\text{M}(\text{dca})(\text{tcm})]$, $\text{M} = \text{Co}, \text{Ni}, \text{Cu}$, $\text{dca} = \text{Dicyanamide}, \text{N}(\text{CN})_2^-$, $\text{tcm} = \text{Tricyanomethanide}, \text{C}(\text{CN})_3^-$

Paul Jensen, David J. Price, Stuart R. Batten, Boujemaa Moubaraki, and Keith S. Murray*^[a]

Dedicated to the memory of Professor Olivier Kahn

Abstract: The three-dimensional coordination polymers $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ (1) and $[\text{M}(\text{dca})(\text{tcm})]$, $\text{M} = \text{Co}$ (2), Ni (3), Cu (4), $\text{dca} = \text{dicyanamide}, \text{N}(\text{CN})_2^-$, $\text{tcm} = \text{tricyanomethanide}, \text{C}(\text{CN})_3^-$, have isomorphous structures. In 1 half the dca ligands coordinate directly (through all three nitrogen atoms) to three Mn atoms (all metal atoms are six-coordinate), while the other half coordinate to two Mn atoms (through the nitrile nitrogens) and hydrogen bond to water molecules coordinated to a third Mn atom (through the amide nitrogen). This $\text{dca} \cdot \text{H}_2\text{O}$ structural moiety is disordered over a mirror plane, and is replaced by the structurally equivalent tcm ligand in

compounds 2–4. The resulting structures display a new self-penetrating 3,6-connected (2:1) network topology that can be related to, but is different from, the rutile net. The self-penetrating $[\text{M}(\text{dca})(\text{tcm})]$ network can be viewed as a structural compromise between the two interpenetrating rutile-like networks of $[\text{M}(\text{tcm})_2]$ and the single rutile-like network of $\alpha\text{-}[\text{M}(\text{dca})_2]$.

Keywords: coordination chemistry · crystal engineering · dicyanamide · magnetic properties · tricyanomethanide

The temperature and field dependence of the DC and AC magnetic susceptibilities and magnetisations has been measured for complexes 1–4. Compounds 1–3 exhibit long-range magnetic order with critical temperatures of 6.3 K for 1, 3.5 K for 2 and 8.0 K for 3. The Cu^{II} compound 4 does not order and is essentially a paramagnet. Hysteresis measurements of coercive field and remnant magnetisation show that 1, 2 and 3 are soft magnets, 1 being a canted-spin antiferromagnet (weak ferromagnet), while 2 and 3 are ferromagnets that display some unusual features in their high-field magnetisation isotherms in comparison to their related $\alpha\text{-}[\text{M}(\text{dca})_2]$ phases.

Introduction

Entangled systems are of great chemical interest due to the interesting topological and physical properties displayed by such systems. Molecular entanglement, in the form of catenanes, rotaxanes and knots is well known.^[1] Entanglement of ordered polymeric networks, that is, *interpenetration*, is also of great current interest, and numerous well-characterised systems are known.^[2] Interpenetration occurs when two or more unconnected infinite networks pass through each

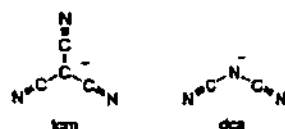
other such that they cannot be separated without breaking of bonds within the networks. They are polymeric equivalents of catenanes and rotaxanes.

The polymeric equivalent of a molecular knot is a *self-penetrating* (self-entangled or intrapenetrating) network. These networks are single networks that nonetheless contain regions in which rods pass through rings in a similar fashion to interpenetrating systems. While rods and rings in any network can be chosen such that a rod passes through a ring, a useful and necessary restriction is to define a network as self-penetrating only when the *smallest topological circuits* are penetrated by rods.^[3,4] A smallest circuit is defined as the minimum number of nodes it takes to leave a chosen node along one link and return to the starting node through a different link. The smallest topological circuits are not necessarily all the same size.

[a] Prof. K. S. Murray, P. Jensen, D. J. Price, Dr. S. R. Batten, Dr. B. Moubaraki
Department of Chemistry, P.O. Box 23
Monash University 3800 (Australia)
Fax: (+61)3-9905-4597
E-mail: keith.s.murray@sci.monash.edu.au

3186–3195

We report here four new compounds that possess a new self-penetrating network topology. Three of the compounds also show long-range magnetic ordering, which is related to their unusual structures. The structures arise from our ongoing interest in the structural and magnetic properties of coordination polymers containing the pseudohalide ligands tricyanomethanide (tcm , $\text{C}(\text{CN})_3^-$) and dicyanamide (dca , $\text{N}(\text{CN})_2^-$). The compounds $[\text{M}(\text{tcm})_2]$, $\text{M}^{\text{II}} = \text{Cr}$, Mn , Fe , Co ,



Ni , Cu , Zn , Cd and Hg , contain two interpenetrating rutile-related networks.^{12–14} Similarly, the compounds $\alpha\text{-}[\text{M}(\text{dca})_2]$, $\text{M}^{\text{II}} = \text{Cr}$, Mn , Fe , Co , Ni and Cu , also contain rutile-related networks, although in this case no interpenetration occurs.¹⁵ Although investigation of the magnetic properties of $[\text{M}(\text{tcm})_2]$ uncovered only weak coupling and no long-range ordering, the magnetic properties of $\alpha\text{-}[\text{M}(\text{dca})_2]$ were much more varied and interesting, ranging from long-range ferromagnetism (Co , Ni) to spin-canted antiferromagnetism (Mn , Fe) to simple paramagnetism (Cu).

A number of other coordination polymers containing either tcm ^{12,16–17} or dca ^{18–21} have also been crystallographically characterised by different teams. In particular, we have already reported the formation of two products obtained from the reaction of Mn^{II} and dca in water— $\alpha\text{-}[\text{Mn}(\text{dca})_2]$, which has a single rutile-like network, and $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, which contains linear chains penetrating (4,4) sheets.^{16,22} We report here the structure and magnetism of a third product, namely $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ (1), and of $[\text{M}(\text{dca})(\text{tcm})]$, $\text{M} = \text{Co}$ (2), Ni (3) and Cu (4). They all contain the same self-penetrating network structure. Indeed, although 1 was obtained fortuitously, compounds 2–4 were the result of a deliberate crystal-engineering strategy based on the structure of 1. We have also found that 1 is responsible for a magnetic transition noted²³ weakly at 6 K in the magnetisation versus temperature plot of the parent $[\text{Mn}(\text{dca})_2]$, a spin-canted antiferromagnet with $T_N = 16$ K. The hydrate was present as a trace impurity. The compounds 2 and 3 are new homometallic long-range-ordered magnets, while 4 is essentially a paramagnet.

Results and Discussion

Synthesis and crystal structures: Crystals of 1 were obtained by slow evaporation of either solutions of $[\text{Mn}(\text{dca})_2]$ in wet methanol/ethanol, or of aqueous solutions of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}(\text{dca})$. Unlike $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, compound 1 appears not to lose solvent at room temperature upon removal from the mother liquor. The structure of 1 was solved by X-ray crystallography (Table 1).

The structure contains octahedral Mn atoms coordinated to (on average) five dca ligands and one water ligand. The dca ligands are of two types—one coordinates to three Mn atoms through each of the three nitrogen atoms ($\text{dca}1$), while the other coordinates directly to two Mn atoms through the nitrile nitrogens only ($\text{dca}2$). The $\text{dca}2$ ligands also form hydrogen bonds through the amide nitrogens to the water molecules, which are also coordinated to the Mn atoms. This $\text{dca}2 \cdot \text{H}_2\text{O}$ moiety, however, is disordered over two positions which are related by a mirror plane. While the amide nitrogen and one of the nitrile groups of $\text{dca}2$ (and the Mn atom coordinated to this nitrile) lie on the mirror plane, the other nitrile group and the water ligand do not. In fact they have symmetry-related positions that superimpose on each other, with the affected nitrogen and oxygen atoms given the same positional parameters. Consequently the $\text{O} \cdots \text{N}$ hydrogen-bonding distance is constrained to be the same as the NCN distance within the $\text{dca}2$ ligand ($\text{O}1 \cdots \text{N}4 = 2.633(7)$ Å), and the position of the disordered carbon is the only site without full occupancy by a non-hydrogen atom. The result of this disorder is the creation of a trigonal moiety within the

Table 1. Selected crystallographic and data collection parameters for compounds 1–4.

	$[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ (1)	$[\text{Co}(\text{dca})(\text{tcm})]$ (2)	$[\text{Ni}(\text{dca})(\text{tcm})]$ (3) ^a	$[\text{Cu}(\text{dca})(\text{tcm})]$ (4)
formula	$\text{MnC}_5\text{N}_6\text{H}_2\text{O}$	CoC_3N_4	NiC_3N_4	CuC_3N_4
M_r	205.06	215.05	214.83	219.66
crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	$\text{Am}a2$ (no. 40)	$\text{Am}a2$ (no. 40)	$\text{Am}a2$ (no. 40)	$\text{Am}a2$ (no. 40)
a [Å]	7.5743(2)	7.4129(3)	7.309(2)	7.2041(3)
b [Å]	17.4533(7)	17.0895(6)	16.799(6)	17.4837(6)
c [Å]	5.6353(2)	5.5991(2)	5.562(2)	5.7395(3)
V [Å ³]	744.97(4)	709.31(5)	691.0(3)	721.48(5)
Z	4	4	4	4
T [K]	293(2)	173(2)	295(1)	123(2)
ρ_{calc} [g cm ⁻³]	1.83	2.014	2.065	2.022
μ [cm ⁻¹]	17.28	23.67		29.75
$F(000)$	404	420		428
$2\theta_{\text{max}}$ [°]	60.06	55.68	64.64	60.06
hkl ranges	$0 \leq h \leq 9$ $-24 \leq k \leq 0$ $0 \leq l \leq 7$	$-9 \leq h \leq 9$ $-22 \leq k \leq 22$ $-6 \leq l \leq 6$		$-10 \leq h \leq 10$ $-22 \leq k \leq 23$ $-8 \leq l \leq 8$
data collected	5465	5006		5272
unique data (R_{int})	611 (0.037)	888 (0.044)		1115 (0.045)
observed data [$I > 2\sigma(I)$]	554	856		1076
parameters	68	66		66
final R_1 , wR_2 [$I > 2\sigma(I)$] ^b	0.0262, 0.0571	0.0228, 0.0528		0.0240, 0.0585
R_1 , wR_2 (all data)	0.0333, 0.0615	0.0244, 0.0534		0.0259, 0.0593
weighting scheme (a , b) ^a	0.0184, 0.7932	0.0155, 1.5132		0.0276, 1.0625
goodness of fit	1.199	1.108		1.148
Flack parameter	0.02(12)	0.01(3)		0.01(2)
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ [e Å ⁻³]	0.53, -0.38	0.36, -0.33		0.42, -0.45

[a] From X-ray powder diffraction ($\lambda = 1.54059$ Å) at 295 K. [b] $R_1 = \sum |\Delta F|/\sum |F_o|$, $wR_2 = [\sum (F_o^2 - F_c^2)^2/\sum F_o^2]^{1/2}$ in which $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [F_o^2 + 2F_c^2]/3$.

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structure, as shown in Figure 1. A more informative formula for the structure would thus be $[\text{Mn}(\text{dca1})(\text{dca2} \cdot \text{H}_2\text{O})]$. Selected bond lengths and angles are given in Table 2.

The disordered $\text{dca2} \cdot \text{H}_2\text{O}$ moiety was recognised to be geometrically very similar to the tcm anion (Figure 1), so we attempted to engineer new materials which had the same

not obtained for 3, powder X-ray diffraction was used to show it was isomorphous with 1, 2 and 4). In fact, they possess the same space group and similar cell parameters (Table 1) as 1. Bond lengths and angles are given in Table 3. The network topology is perhaps explained more easily for $[\text{M}(\text{dca})(\text{tcm})]$, and in comparison to the rutile networks of $[\text{M}(\text{dca})_2]$ (1 net)

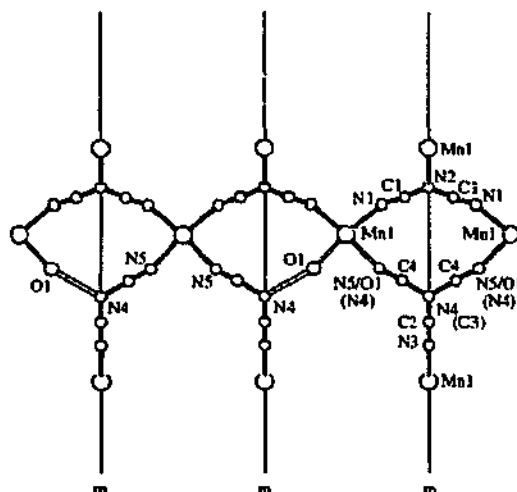


Figure 1. A chain in the structure of $[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$ (1) showing the disorder of the $\text{dca2} \cdot \text{H}_2\text{O}$ system over the mirror plane (thin line). The two different orientations of the system are shown (left and middle) as well as the resultant sum of the disorder (right). The hydrogen bond is denoted by the open bond, and the atom numbering scheme for $[\text{M}(\text{dca})(\text{tcm})]$ (where different to 1) is shown in brackets. Symmetry related atoms are not distinguished.

Table 2. Selected interatomic distances (Å) and angles (°) for 1.^(a)

Mn1–N1	2.191(4)	Mn1–N3	2.171(5)
Mn1–N5 ⁱ	2.100(4)	Mn1–O1 ^b	2.190(4)
Mn1–N2 ⁱⁱ	2.417(4)	N1–C1	1.148(4)
C1–N2	1.307(4)	N3–C2	1.146(7)
C2–N4	1.325(8)	N4–C3	1.460(7)
N5–C3	1.175(6)	O1...N1	2.633(7)
N3–Mn1–N1	94.8(2)	N3–Mn1–N1 ⁱⁱⁱ	94.8(2)
N3–Mn1–N5 ⁱ	96.5(1)	N1–Mn1–N5 ⁱ	87.7(1)
N1–Mn1–N5 ^{iv}	167.7(2)	N1–Mn1–N1 ⁱⁱⁱ	95.9(2)
N3–Mn1–N2 ⁱⁱ	178.7(3)	N1–Mn1–N2 ⁱⁱ	178.7(3)
N1–Mn1–N2 ⁱⁱ	84.3(1)	C1–N1–Mn1	157.3(4)
C1–N2–C1 ^v	118.3(4)	C1–N2–Mn1 ^{vi}	120.6(2)
C2–N3–Mn1	162.9(5)	C2–N4–C3	118.0(3)
C3–N4–C3 ⁱⁱⁱ	119.2(7)	C3–N5–Mn1 ^{vii}	161.7(4)
N1–C1–N2	174.5(4)	N3–C2–N4	178.4(6)
N5–C3–N4	176.2(6)		

[a] Symmetry transformations: I: $-x, -y, z-1$; II: $-x, 1/2-y, z-1/2$; III: $1/2-x, y, z$; IV: $x+1/2, -y, z-1$; V: $-x-1/2, y, z$; VI: $-x, 1/2-y, z+1/2$; VII: $-x, -y, z+1$.

network, but with tcm replacing the disordered $\text{dca2} \cdot \text{H}_2\text{O}$ moiety. Half of the dca in the reaction mixture was replaced with tcm , and crystalline products were obtained for Co, Ni and Cu. X-ray crystallography showed the new products, $[\text{M}(\text{dca})(\text{tcm})]$, $\text{M} = \text{Co}$ (2), Ni (3) and Cu (4), did indeed have the desired topology (while useable single crystals were

Table 3. Bond lengths (Å) and angles (°) for 2 and 4.^(a)

	2	4 ^(b)	4 ^(c)
M1–N1	2.099(2)	1.983(2)	1.980(2)
M1–N4 ⁱ	2.101(2)	1.992(2)	1.989(2)
M1–N3	2.122(3)	2.360(3)	2.390(3)
M1–N2 ⁱⁱ	2.192(3)	2.526(3)	2.564(3)
N1–C1	1.152(3)	1.150(3)	1.142(3)
C1–N2	1.319(3)	1.307(3)	1.305(3)
N3–C2	1.182(6)	1.188(6)	1.197(8)
C2–C3	1.464(6)	1.461(6)	1.462(7)
C3–C4	1.390(3)	1.378(3)	1.377(3)
C4–N4	1.147(3)	1.148(3)	1.141(3)
N1–M1–N3	92.59(9)	94.07(9)	94.0(1)
N1–M1–N1 ⁱⁱ	95.7(1)	93.0(1)	93.0(1)
N1–M1–N4 ⁱ	84.63(8)	86.90(8)	86.90(8)
N1–M1–N4 ⁱⁱⁱ	174.97(9)	174.21(9)	174.2(1)
N1–M1–N2 ^{vi}	86.31(8)	86.2(1)	85.7(1)
N3–M1–N4 ⁱ	92.41(9)	91.72(9)	91.83(9)
N3–M1–N2 ^{vi}	178.4(1)	180.0(1)	180.0(1)
N4 ⁱ –M1–N4 ⁱⁱⁱ	94.7(1)	92.6(1)	92.6(1)
N4 ⁱ –M1–N2 ^{vi}	88.70(8)	88.1(1)	88.5(1)
C1–N1–M1	158.4(2)	155.8(2)	155.6(2)
N1–C1–N2	175.9(3)	175.0(3)	174.6(3)
C1–N2–C1 ^v	117.3(3)	119.0(3)	119.2(3)
C1–N2–M1 ^{vii}	121.3(2)	120.5(4)	120.4(4)
C2–N3–M1	158.9(4)	150.1(3)	152.2(4)
N3–C2–C3	178.4(5)	177.8(4)	178.2(5)
C2–C3–C4	120.7(2)	120.8(2)	120.8(2)
C4–C3–C4 ⁱⁱ	117.3(3)	117.8(3)	117.9(3)
C3–C4–N4	179.5(3)	179.8(3)	179.8(3)
C4–N4–M1 ^v	169.1(2)	167.5(2)	167.5(2)

[a] Symmetry transformations: I: $-x, -y, z-1$; II: $1/2-x, y, z$; III: $x+1/2, -y, z-1$; IV: $-x-1/2, y, z$; V: $-x, -y, z+1$; VI: $-x, 1/2-y, z-1/2$; VII: $-x, 1/2-y, z+1/2$. [b] 123 K. [c] 297 K.

and $[\text{M}(\text{tcm})_2]$ (2 nets). Both structures, however, have the same topology and thus the description of $[\text{M}(\text{dca})(\text{tcm})]$ applies equally as well for 1.

As implied above, the structure is closely related to the rutile network. Network topology is an important consideration in the design, construction, analysis and exploitation of new, ordered, polymeric networks (whether coordination polymers or hydrogen-bonded networks), and the rutile network (Figure 2a) is one of the important basic networks that result from the combination of three-connecting and six-connecting centres (in the ratio 2:1).¹⁴

The rutile structure (TiO_2 ; octahedral Ti, trigonal O) can be described in terms of square channels in which the three-connecting centres form the sides of the channels, and the six-connecting centres occupy the corners (Figure 2a). These channels can be constructed by cross-linking TiO_2 chains arranged such that adjacent chains are perpendicular (Figure 2a). The sides of these channels contain six-membered rings (alternating three- and six-connecting centres), which are the second smallest rings within the structure. The smallest are four-membered rings within the afore-mentioned chains,

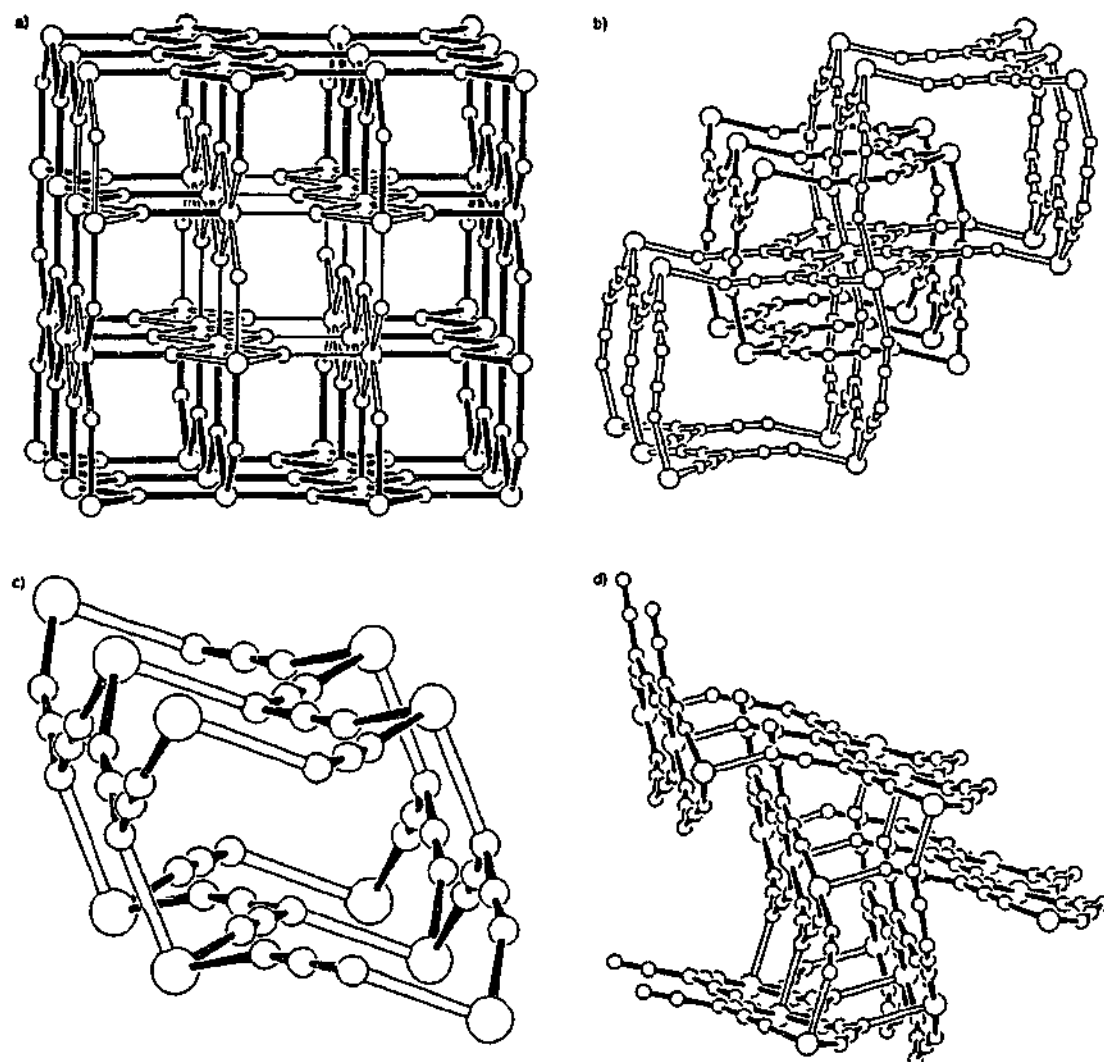


Figure 2. The rutile (TiO_2) framework. Octahedral centres (Ti) are represented by large circles and trigonal centres (O) are represented by small circles. A square channel is highlighted in the centre by the open bonds (the four separate chains) and the thin bonds (the connections between the chains which give the channel). A four-membered ring (left) and a six-membered ring (top left) are also highlighted by open bonds. b) A square channel in the rutile-like structure of $[\text{M}(\text{tcm})_2]$ interpenetrated by a second identical network. c) A square channel in the rutile-like structure of $\alpha\text{-}[\text{M}(\text{dca})_2]$. The $\text{M}-\text{N}_{\text{amide}}$ connections between the four perpendicular chains which generate the channel are highlighted by the open bonds. d) The connection of four perpendicular chains in the structure of $[\text{M}(\text{dca})(\text{tcm})]$. The interchain connections are highlighted by the open bonds. Compare the result to the square channels generated in $[\text{M}(\text{tcm})_2]$ and $\alpha\text{-}[\text{M}(\text{dca})_2]$. All figures are viewed from equivalent angles.

which also contain alternating three- and six-connecting centres. Both the four- and six-membered rings are, however, "smallest circuits" in a topological sense.

In the $[\text{M}(\text{tcm})_2]$ structures, the distance between the octahedral centres and the trigonal centres is large (ca. 4.5–5.0 Å), and thus a porous network results. This allows the interpenetration of a second network. The interpenetration is such that rods of one network pass through the six-membered rings (from a topological point of view—i.e., only the nodes are counted) of the second network (Figure 2b). The four-

membered rings are too small to sterically allow penetration of a rod from the second network.

In the rutile-like structure of $[\text{M}(\text{dca})_2]$, while two-thirds of the trigonal to octahedral node distances are similar to those in $[\text{M}(\text{tcm})_2]$, one-third are considerably shorter ($\text{M}-\text{N}_{\text{amide}}$ vs. $\text{M}-\text{NC}-\text{C}$). This results in a considerably denser, less spacious rutile network, which does not allow interpenetration. Structurally, the bonds which are shorter are the bonds between the chains that form the square channels (Figure 2c). This means that the sizes of the four-membered rings are not affected, but

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the six-membered rings, through which the rods of the second network pass in the interpenetrating $[M(\text{tcm})_2]$ structures, are considerably smaller. Too small, it appears, to allow penetration, and thus interpenetration does not occur.

In the structure of $[M(\text{dca})(\text{tcm})]$, we combine the three long links of tcm and the one short/two long links of dca. In this structure the short dca link again occurs *between* the ML_2 chains. If we examine the connections between four adjacent chains analogous to those which form the square channels in the two previous rutile-like structures, the similarities and differences of the new network to rutile become apparent. The chains, all of which are crystallographically equivalent, have the formula $[M(\text{dca})(\text{tcm})]$ and have tcm ligands on one side of the chain and dca ligands on the other. Again, adjoining chains are mutually inclined to each other, and are connected by the third link of the three-connecting centres joining to the axial positions of the six-connecting metal centres. The requirement that the $M \cdots M$ distance within the chains must be the same for the dca bridge as for the tcm bridge means that the metal to amide nitrogen link of the dca must be the *interchain* bond. This means, however, that the interchain linkages of the three-connecting centres to the six-connecting centres are of different lengths, depending on whether the ligand is tcm or dca. In other words, in this structure we have two types of trigonal nodes—one with three long links of equal length (tcm) and one with two long links and one short link (dca). The structural consequences of this are shown in Figure 2d. The first two interchain linkages are of the long tcm type. The second two linkages between chains, however, are of the short dca type. Therefore, while the four chains in rutile connect to form a square channel, the network of interconnected chains in $[M(\text{dca})(\text{tcm})]$ falls short of returning to its starting point, and folds back through itself in the spiral fashion shown in Figure 2d. As for $[M(\text{tcm})_2]$, the penetration occurs such that the six-membered $\text{M}_3(\text{tcm})_3$ rings are penetrated by C—CN—M rods of the tcm anions. In this case, however, it is a single network penetrating itself. Penetration does not occur through the four-membered rings or the smaller $\text{M}_3(\text{dca})_3$ six-membered rings.

In summary, we find that if we combine octahedral metal ions with a ligand with three long links (tcm) we get two interpenetrating rutile-like networks, while combination of octahedral metals with a ligand that contains one short and two long links (dca) results in a single rutile-like network. If, however, we use *both* ligands, we get a structural compromise between the two parent structures—a single, self-penetrating network with a topology different but closely related to rutile.

A schematic view of the overall network is shown in Figure 3. We mentioned previously the importance of smallest circuits in the topology of a network for defining a self-penetrating network. The total number of smallest circuits from any given p -connected node in a network (which is simply equal to the number of possible combinations of any two links radiating from the node) is equal to $p(p-1)/2$. The value is halved so that each circuit is only counted once. To illustrate, inspection of the rutile network (Figure 2a) reveals that there are 15 smallest circuits that start from a six-connecting centre ($p=6$): two four-membered, ten six-membered and three eight-membered rings. The smallest

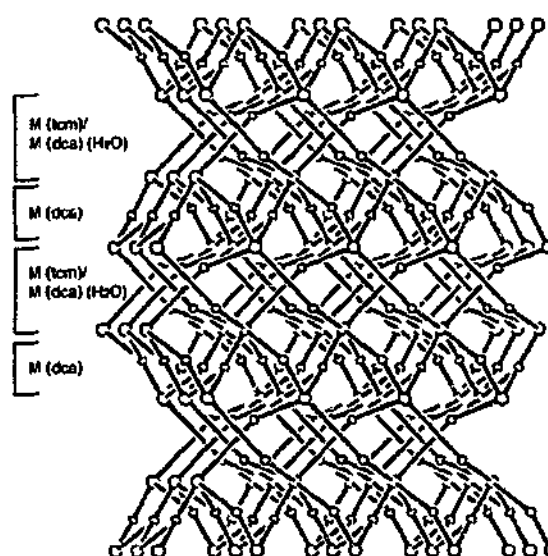


Figure 3. A schematic view of the $[M(\text{dca})(\text{tcm})]$ network, with only the octahedral and trigonal centres shown. Layers of $M(\text{tcm})$ (or $M(\text{dca})(\text{H}_2\text{O})$) and $M(\text{dca})$ in the structure are highlighted (see text).

circuits starting from the three-connecting centres ($p=3$) are one four-membered and two six-membered rings. In the self-penetrating network (Figure 3), the distribution and size of the smallest rings are the same as rutile: four-, six- and eight-membered rings (2:10:3) for the six-connecting nodes, and four- and six-membered rings (1:2) for each of the two types of three-connecting centres. Thus although they have different topologies, rutile and $[M(\text{dca})(\text{tcm})]$ have the same Schläfli notation: $(4^2 6^{10} 8^3)(4^1 6^2)$.

As mentioned above, in the interpenetrating rutile networks of $[M(\text{tcm})_2]$ the penetration occurs through the six-membered rings, which are a "smallest circuit" of the rutile network. Similarly, the penetration in the $[M(\text{dca})(\text{tcm})]$ network also occurs through the six-membered "smallest circuits". Thus we can describe the network as *self-penetrating*. Recently a number of other self-penetrating networks have been reported.^[3, 4, 10] The structure also represents a new network topology for 3,6-connected networks with the connectors in the ratio 2:1. Previously described topologies include the above-mentioned rutile^[3, 4, 9] and $[\text{Hg}(\text{tpt})_2(\text{ClO}_4)_2] \cdot 6\text{C}_2\text{H}_2\text{Cl}_4$.^[10]

The close similarity of the tcm and dca·H₂O structural moieties also resulted in the structures of 2–4 being doped by small random amounts of dca·H₂O (in place of tcm). The IR spectra contained sharp H₂O bending frequencies at 1618 (2), 1616 (3) and 1619 cm⁻¹ (4), and the elemental analyses showed the presence of small amounts of hydrogen. In each structure the thermal parameters for one of the tcm carbon atoms (C2; the only atom not replaced by a similar non-hydrogen atom when tcm is replaced by dca·H₂O is a nitrile carbon) were higher than most of the other atoms in the structures. This last fact, along with analysis of the powder X-ray diffraction pattern (which showed that the only other

phase present is $[M(\text{tcm})_2]$ —the analysis was also consistent with some $[M(\text{tcm})_2]$ impurities, leads us to believe that the water is present as a doping in the crystal structure of the tcm moiety by the $\text{dca} \cdot \text{H}_2\text{O}$ moiety, rather than as separate phases of $[M(\text{dca})(\text{tcm})]$ and $[M(\text{dca})_2(\text{H}_2\text{O})]$. In addition, no evidence of $[M(\text{dca})_2(\text{H}_2\text{O})]$ was seen in the magnetism or powder X-ray diffraction of samples of $[M(\text{dca})_2]$ previously prepared from water for $M = \text{Co}$, Ni or Cu ,^[6] unlike $M = \text{Mn}$, as discussed elsewhere. This indicates that tcm, although it is partially replaced by $\text{dca} \cdot \text{H}_2\text{O}$, is still an essential component in the Co , Ni and Cu structures.

Magnetic properties: Complex 1 is another example of the growing number of homometallic spin-canted antiferromagnets (weak ferromagnets).^[1b, ed. no. 12–16] In a field of 0.3 T this high spin d^3 species shows a μ_{Mn} value at 300 K of $5.64 \mu_B$ ($\chi T = 3.98 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$). As the temperature is decreased the μ_{Mn} values gradually decrease due to antiferromagnetic coupling, reaching $2.62 \mu_B$ ($\chi T = 0.86 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) at 4.2 K (Figure 4). The Weiss constant from the χ versus $1/T$ plot is

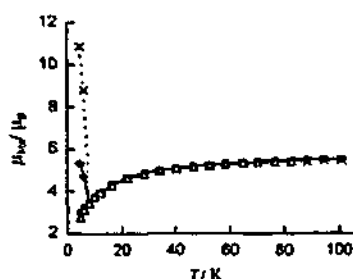


Figure 4. Plots of magnetic moment, μ_{Mn} , versus temperature in various applied fields for 1. Field values 20 Oe ($\times$), 200 Oe ($\circ$), 1000 Oe ($\diamond$), 3000 Oe (Δ). (Note that the $\chi_{\text{Mn}}T$ values can be obtained from $\mu_{\text{Mn}}^2 = 7.997 \chi_{\text{Mn}}T$)

–4.2 K. In field values below about 200 Oe the magnetic moments show an abrupt increase at approximately 6 K due to the occurrence of long-range order. Thus μ_{Mn} is $10.9 \mu_B$ at 4.2 K in a field of 20 Oe. The T_N value of 6.3 K was confirmed by measuring the magnetisation (M) values in zero-field-cooled (ZFCM) and field-cooled (FCM, 5 Oe) modes (Figure 5). The χ' versus T plot of the AC in-phase susceptibility

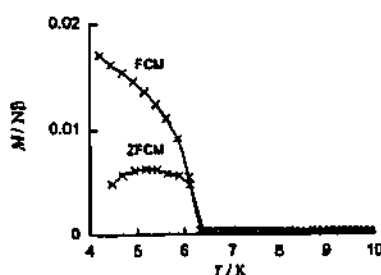


Figure 5. Plots of magnetisation, M , versus temperature for 1 measured with zero-field cooling (ZFCM) and field cooling (FCM; DC field = 5 Oe).

showed a very sharp maximum at 6.3 K typical of a weak ferromagnet. Hysteresis measurements on a neat powder at 2 K showed a remnant magnetisation (RM) of $112 \text{ cm}^3 \text{ mol}^{-1} \text{ Oe}$ and coercive field of 250 Oe, values typical of a soft magnet (Figure 6). High-field magnetisation data, with tem-

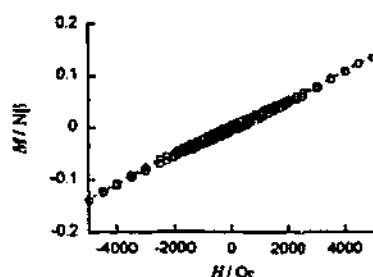


Figure 6. Hysteresis loop for 1 measured on a powder sample at 2 K.

peratures above and below the ordering temperature, again show evidence for spin-canted antiferromagnetism in terms of linear behaviour and low values of M at the highest field used, for example, $1.7 \text{ N}\beta$ at 5 T and 2 K (M_{Mn} for Mn^{II} would be $5 \text{ N}\beta$).

The key structural features of 1 that give rise to the antiferromagnetic coupling are the three-connecting dca and $\text{dca} \cdot \text{H}_2\text{O}$ bridges, dominated by the chains of Mn^{II} ions bridged through the nitrile nitrogen atoms, as in the cases of $[\text{Mn}(\text{dca})_2]$ and $[\text{Mn}(\text{dca})_2\text{L}_2]$ chain systems.^[1b, ed. no. 6] Use of Rushbrooke and Wood theory^[17] for the coupling of $S = 5/2$ centres led to a best fit set of parameters of the 0.3 T susceptibility data of $g = 1.93$ and $J = -0.19 \text{ cm}^{-1}$, agreement below 30 K being poor. The J value is similar to those in the $[\text{Mn}(\text{dca})_2\text{L}_2]$ series.^[1b, ed.]

The occurrence of long-range spin-canting arises through a combination of bridging through the amide nitrogen atom and, importantly, the disposition of adjacent Mn chromophores at 60.6° to each other along the N_{amide} -bridged pathways. This appears to be a common structural feature in other recent molecule-based examples of spin-canting.^[12–14, 19] Self-penetration of the polymeric network does not appear to lead to any interactions between chains.

The mixed ligand, high-spin complexes $[\text{M}(\text{dca})(\text{tcm})]$, $M = \text{Co}$ (2) and Ni (3), display long-range order at T_c values of 3.5 K and 8.0 K, respectively, temperatures that are approximately one-third of those displayed by the $[\text{M}(\text{dca})_2]$ parents.^[1b, ed. no. 6] The magnetic moment data for 3 in a field of 1 T are shown in Figure 7. The μ_{Ni} value at 300 K of $3.05 \mu_B$ ($\chi T = 1.16 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) shows a small but gradual increase as the temperature is decreased, typical of ferromagnetic coupling, with a rapid increase to a maximum of $5.39 \mu_B$ at 7.9 K, followed by a rapid decrease to $3.02 \mu_B$ at 2 K. The Weiss constant for susceptibility is $+4.9 \text{ K}$ over the temperature range 4–300 K. In smaller applied fields the rise to a sharp maximum becomes more abrupt such that in a field of 200 Oe the μ_{Ni} value is $23 \mu_B$ ($\chi T = 66.1 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$). Such behaviour is typical of the occurrence of a magnetic phase transition. Confirmation is provided in Figure 8, which shows

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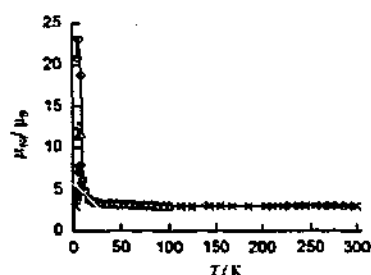


Figure 7. Plots of μ_{eff} versus temperature for 3 in applied fields of 1000 Oe (x), 3000 Oe (o), 2000 Oe (Δ), 20 Oe (◊).

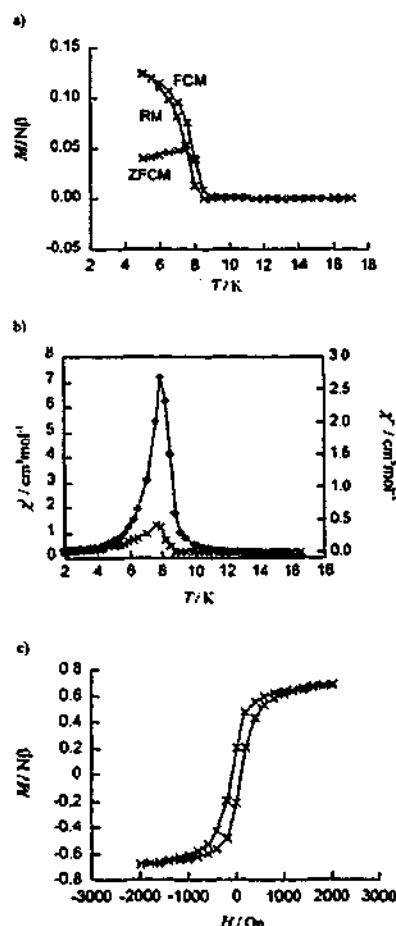


Figure 8. a) Plots of FCM, ZFCM and RM (remnant magnetisation) for 3 using a field of 5 Oe. b) Plots of in-phase (o) and out-of-phase (x) AC susceptibilities of 3 versus temperature in a field of 3.5 Oe oscillating at 20 Hz. c) Hysteresis loop for 3 measured as a powder at 5 K.

plots of FCM, ZFCM and RM in a DC field of 5 Oe, a hysteresis loop at 5 K in fields of ± 2000 Oe and the in-phase and out-of-phase components of AC susceptibilities, the in-phase plot showing a maximum at T_c . The RM is $1151 \text{ cm}^3 \text{ mol}^{-1} \text{ Oe}$ and the coercive field is 100 Oe, which

can be compared with those for $[\text{Ni}(\text{dca})_2]$ of $5027 \text{ cm}^3 \text{ mol}^{-1} \text{ Oe}$ and 220 Oe (at 5 K; dependent on temperature and particle size^[16, 44, 16]). The high-field M versus H plots measured at temperatures between 2 and 20 K show differences in detail when compared with those of the ferromagnet $[\text{Ni}(\text{dca})_2]$ ^[16, 44, 16] particularly below T_c . Thus, at 2 K, after a very rapid, almost spontaneous, increase in M at low fields, as anticipated for a ferromagnet, the M values then slowly increase and do not saturate below a field of 5 T, being $1.75 \text{ N}\beta$ at 5 T. This may be due to a competing antiferromagnetic ordering, also responsible for the decrease in μ_{eff} which occurs at very low temperatures below μ_{max} . It may also be due to spin-canting as in 1, but the shape of the χ' peak in the AC data of Figure 8 is much more ferromagnetic-like.

DC and AC measurements show that 2 orders at 3.5 K. In Figure 9 it can be seen that the μ_{eff} versus temperature plot in

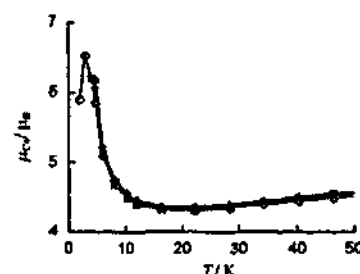


Figure 9. Plots of μ_{eff} versus temperature (2 to 100 K) for 2 in applied fields of 3000 Oe (o), 1000 Oe (x), 200 Oe (◊). Not shown here are the 20 Oe data, which rise abruptly to a maximum of $21.95 \mu_B$ at very low temperatures.

a DC field of 0.3 T shows a moment at 290 K of $5.20 \mu_B$ ($\chi T = 3.39 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$), which decreases very gradually to reach a broad minimum of $4.32 \mu_B$ at 22 K, reminiscent of ferrimagnetic behaviour but possibly due mainly to single-ion spin-orbit splitting combined with ferromagnetic order.^[16] In a field of 200 Oe, the moment reaches a sharp maximum of $6.51 \mu_B$ before decreasing to reach $5.89 \mu_B$ at 4.2 K. In smaller applied fields such as 20 Oe (not shown) the moments increase sharply below temperatures of 10 K, due to long-range order, such that a value of $21.95 \mu_B$ is observed at a sharp maximum at 3 K. Similarly shaped μ_{eff} versus temperature curves have recently been observed for other octahedral Co^{II} systems.^[19, 20] The ordering temperature is confirmed by measurements of ZFCM and FCM (5 Oe DC field) and a χ' maximum in the AC susceptibilities (Figure 10). The hysteresis loop measured at 2.5 K between ± 1000 Oe has an RM value of $186 \text{ cm}^3 \text{ mol}^{-1} \text{ Oe}$ and coercive field of 17 Oe, indicative of a very soft magnet with values much reduced from those in the ferromagnet $[\text{Co}(\text{dca})_2]$ ^[16, 44, 16] Plots of M versus H at temperatures above and below the ordering temperature are shown in Figure 11. At 2 K, the M values increase very rapidly in very low fields on account of ordering, then begin to saturate above 2 T reaching $2.1 \mu_B$ at 5 T, a value well below the $S = 3/2 M_{\text{sat}}$ value of $3 \text{ N}\beta$. Similarly reduced values were observed in $[\text{Co}(\text{dca})_2]$ and $[\text{Co}(\text{tcm})_2]$ (not ordered) and are due primarily

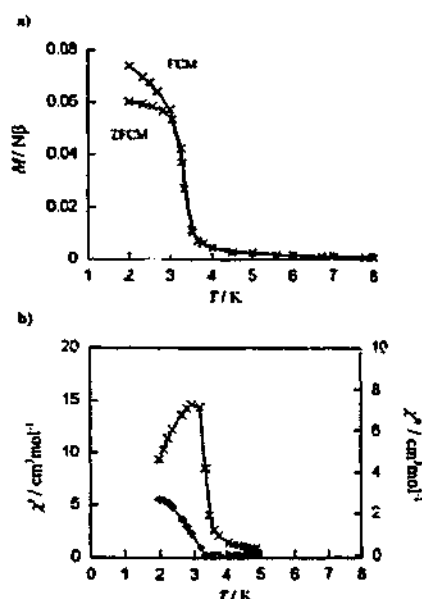


Figure 10. a) FCM (DC field of 5 Oe) and ZFCM data for 2. b) In-phase, χ' (x), and out-of-phase, χ'' (o). AC susceptibilities for 2 in a field of 3.5 Oe oscillating at 20 Hz.

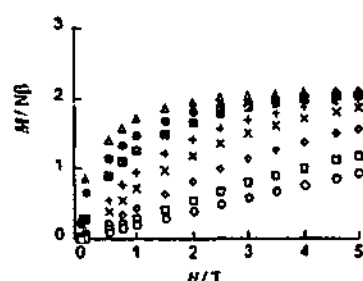


Figure 11. Magnetization isotherms for 2 measured at 2 K (Δ), 3 K (●), 4 K (◐), 5.5 K (+), 7 K (x), 10 K (◊), 15 K (◑), 20 K (○).

to spin-orbit coupling effects within the 4T_1 single ion states.^{19a, 19b, 20} The shapes of the M/H plots are quite unlike those of a recently reported canted-spin antiferromagnet ($T_N = 9$ K), $[\text{Co}(\text{HCONH}_2)_2(\text{HCO}_2)_2]^{12b}$ in which the M values increase approximately linearly with H , do not saturate and are of the order of $0.66 N\beta$ at $H = 5.5$ T and 2 K. The $[\text{Co}(\text{dca})(\text{tcm})]$ complex is much more weakly antiferromagnetically coupled, if at all, than is the formate example. Consideration of all the magnetic data for $[\text{Co}(\text{dca})(\text{tcm})]$, including the ferromagnetic-like shape of the AC χ' versus T plot, would suggest that spin-canting is not important.

A plot of μ_{eff} versus temperature for $[\text{Cu}(\text{dca})(\text{tcm})]$, in an applied field of 1 T, is Curie-like over the whole range ($\mu_{\text{eff}} = 1.76 \mu_B$), except for a very small increase in μ_{eff} evident at low temperatures. This is reminiscent of the behaviour reported for a sample of $[\text{Cu}(\text{dca})_2]$ prepared from ethanol.^{16b} The present compound does not show any long-range order, most likely due to the Jahn–Teller lengthening of the Cu–N_{amide} bond (Table 3).

We have noted above that these $[\text{M}(\text{dca})(\text{tcm})]$ compounds consist of a single-phase material plus traces of a separate $[\text{M}(\text{tcm})_2]$ phase. The single phase is effectively $[\text{M}(\text{dca})(\text{tcm})_x(\text{dca} \cdot \text{H}_2\text{O})_{1-x}]$, in which tcm is randomly replaced with small quantities of $\text{dca} \cdot \text{H}_2\text{O}$. The magnetic studies have clearly shown that the bulk samples of 2 and 3 display a single, well-defined magnetic phase transition. The traces of $[\text{M}(\text{tcm})_2]$ present in the samples will not influence the long-range order since the $[\text{M}(\text{tcm})_2]$ compounds are not ordered.^{16c} While we believe that the $[\text{M}(\text{dca})(\text{tcm})]$ host is responsible for the observed long-range order, it is possible that neat samples of this and of $[\text{M}(\text{dca})(\text{dca} \cdot \text{H}_2\text{O})]$ would behave similarly magnetically and have near-identical powder X-ray diffraction patterns. Work is in progress to obtain such undoped single phases for $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ and Cu , the monohydrate of Mn (1) being described here.

Finally, it is of interest to look at an alternative view of the three-dimensional networks of 1–4 to try to explain the magnetic features. Parallel two-dimensional zig-zag (6,3) sheets of $\text{M}(\text{dca})$ can be distinguished within the network (Figure 3), which alternate with layers that contain two interpenetrating $\text{M}(\text{tcm})$ (or $\text{M}(\text{dca} \cdot \text{H}_2\text{O})$) (6,3) sheets which give rise to the self-penetration. Within the $\text{M}(\text{dca})$ sheets the tridentate dca bridges will dominate the exchange coupling and lead to long-range order (except for Cu), as observed in the parent α - $[\text{M}(\text{dca})_2]$ rutile-like phases. The anionic linking groups between the sheets will give rise to weaker coupling. In separate work, we are investigating structure–magnetism relations in complexes of the type $[\text{R}_4\text{E}][\text{M}(\text{dca})_2]$, $\text{E} = \text{As}, \text{P}, \text{N}$, in which two-dimensional sheets are separated by R_4E^+ organic cations of different sizes.²¹ Day et al.²² have recently noted the sensitivity of the type of long-range order and the size of T_c in the $[\text{R}_4\text{E}][\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3]$ sheet structures to the nature of the R_4E^+ cation used.

Experimental Section

Synthesis of 1

Method A: $[\text{Mn}(\text{dca})_2]^{19a}$ (30 mg, 0.16 mmol) was dissolved in hot methanol (5 mL). On cooling to room temperature ethanol (5 mL) was added. Crystals of 1 suitable for X-ray diffraction were afforded by slow evaporation of this solution over a period of several months. The majority of the crystals were triangular in habit and insensitive to solvent loss. IR (Nujol): $\nu = 3611, 3577, 3521, 3389, 3113, 2310, 2258, 2185, 1626, 1359, 1326, 955, 937, 679, 668 \text{ cm}^{-1}$; elemental analysis calcd (%) for $\text{C}_4\text{H}_2\text{MnN}_4\text{O}$ (205.06): C 23.4, N 41.0, H 1.0; found: C 23.6, N 41.3, H 0.8.

Method B: Aqueous solutions (5 mL each) of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (362 mg, 1.0 mmol) and $\text{Na}(\text{dca})$ (176 mg, 2.0 mmol) were combined. Slow evaporation over two weeks yielded several aggregates of crystals and a small number of mainly irregularly shaped single crystals (some of which were of triangular habit) that were filtered and washed with ethanol. Yield: 82 mg (40%); IR (Nujol): $\nu = 3520, 3222, 3111, 2309, 2257, 2183, 1625, 1359, 1324, 1057, 1006, 956, 938, 681, 667 \text{ cm}^{-1}$; elemental analysis calcd (%) for $\text{C}_4\text{H}_2\text{MnN}_4\text{O}$ (205.06): C 23.4, N 41.0, H 1.0; found: C 23.5, N 41.4, H 0.8. The powder X-ray diffraction pattern matched that calculated from the crystal structure data.

Synthesis of 2: A hot solution (6 mL) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (390 mg, 1.34 mmol) was added to a hot aqueous solution (6 mL) of $\text{Na}(\text{dca})$ (100 mg, 1.12 mmol) and $\text{K}(\text{tcm})$ (145 mg, 1.12 mmol). The resulting solution was allowed to cool and a pink/red microcrystalline product formed over several days. The product was filtered and washed with water. Yield: 150 mg (62%); IR (Nujol): $\nu = 3462, 2295, 2262, 2264, 2215\text{sh}, 2197$.

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1618, 1357, 1314, 1268, 1253, 1070, 966 cm^{-1} ; elemental analysis calcd (%) for CoC_2N_6 (215.05): C 33.51, N 39.09, H 0.00; found: C 33.99, N 37.73, H 0.25. The analytical figures are indicative of the presence of small amounts of $\text{dca} \cdot \text{H}_2\text{O}$ in place of tcm. Powder X-ray diffraction also showed the presence of traces of $[\text{Co}(\text{tcm})_2]$. Single crystals were grown by layering an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}(\text{dca})$ with H_2O , MeOH , then a solution of $(\text{Me}_4\text{N})(\text{tcm})$ in MeOH . Small pink crystals formed after several days.

Synthesis of 3: A hot aqueous solution (3 mL) of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (408 mg, 1.40 mmol) was added to a hot aqueous solution (3 mL) of $\text{Na}(\text{dca})$ (100 mg, 1.12 mmol) and $\text{K}(\text{tcm})$ (147 mg, 1.14 mmol). The resulting solution was allowed to cool and a blue microcrystalline product formed over several days. The product was filtered and washed with water. Yield: 210 mg (87%); IR (Nujol): $\nu = 3389, 3456, 2350, 2304, 2290, 2270, 2212, 1616, 1316, 1268, 1254, 1088, 972 \text{ cm}^{-1}$; elemental analysis calcd (%) for NiC_2N_6 (214.83): C 33.54, N 39.13, H 0.00; found: C 32.12, N 37.59, H 0.40. As in 2, these figures are indicative of the presence of small amounts of $\text{dca} \cdot \text{H}_2\text{O}$ in place of tcm. Powder X-ray diffraction also showed the presence of traces of $[\text{Ni}(\text{tcm})_2]$.

Synthesis of 4: A hot aqueous solution (6 mL) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (288 mg, 1.19 mmol) was added to a hot aqueous solution (6 mL) of $\text{Na}(\text{dca})$ (100 mg, 1.12 mmol) and $\text{K}(\text{tcm})$ (145 mg, 1.12 mmol). The resulting solution was allowed to cool and a green/brown crystalline product formed over several days. The product was filtered and washed with water. Yield: 195 mg (79%); IR (Nujol): $\nu = 3620, 3482, 2332, 2271, 2206, 2181 \text{ (sh)}, 1619, 1360, 1259, 1088, 964 \text{ cm}^{-1}$; elemental analysis calcd (%) for CuC_2N_6 (219.66): C 32.79, N 38.26, H 0.00; found: C 30.54, N 38.30, H 0.29. As in 2 and 3, these figures are indicative of the presence of small amounts of $\text{dca} \cdot \text{H}_2\text{O}$ in place of tcm.

Crystallography: Crystal data and details of the structure determinations are presented in Table 1. Data were collected on a Nonius KappaCCD diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$), using ϕ and ω rotations with 1° frames. The images were processed with the HKL suite of programs.^[24] Data for 4 were collected at two different temperatures (123 and 297 K). Absorption corrections (face-indexed) were applied only to the data for 4, at both temperatures (min/max. transmission factors = 0.717/0.862 (123 K), 0.721/0.863 (297 K)). Solutions were obtained by using either SHELXS-97^[25] or teXsan^[26] followed by successive difference Fourier transform methods, and structures were refined against F^2 using SHELXL-97.^[24] The absolute configurations of 2 and 4 were assigned on the basis of the Flack parameter (Table 1), while 1 was refined as a racemic twin. All non-hydrogen atoms were made anisotropic, while the hydrogen atoms in 1 were neither detected nor assigned. In 1 atoms C3, O1 and N5 were refined at half occupancy due to the disorder over the mirror plane, and O1 and N5 were constrained to have identical x, y, z and U_{ij} parameters. The structure of 1 was also solved in P1, which indicated that the disorder was present even in the absence of any crystallographically imposed symmetry.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 138773 (1), CCDC 138774 (2), CCDC 138775 (4 at 123 K) and CCDC 138776 (4 at 297 K). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

Magnetic studies: Details of the measurements of DC susceptibilities and magnetizations using a Quantum Design MPMS5 SQUID magnetometer have been given previously.^[20] The AC susceptibilities were measured with a Quantum Design Physical Property Measurement System (PPMS-7) fitted with an Option P-500 (ACMS) for AC measurements. Samples of about 20 mg were contained in gelatine capsules held at the end of a drinking straw, which was fixed to the sample rod. The AC field used was 3.5 Oe oscillating at 20 Hz.

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Self-Penetration

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www.rsc.org/chemcommSynthesis, structure and magnetism of a new manganese carboxylate cluster: $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_{16}(\text{MeOH})_3(\text{H}_2\text{O})_3]\cdot 6\text{H}_2\text{O}$

David J. Price, Stuart R. Batten, Boujemaa Moubarki and Keith S. Murray*

School of Chemistry, Monash University, Clayton, Victoria 3800, Australia.

E-mail: Keith.S.Murray@sci.monash.edu.au

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A new manganese(III/IV) carboxylate cluster $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_{16}(\text{MeOH})_3(\text{H}_2\text{O})_3]\cdot 6\text{H}_2\text{O}$ has been structurally characterised and shown to display net antiferromagnetic coupling with preliminary evidence for single-molecule magnetic behaviour.

The synthetic and physicochemical studies made by Christou and Hendrickson *et al.*,¹ Gatteschi and Sessoli *et al.*,² and Powell *et al.*³ on high nuclearity manganese and iron oxo/carboxylate cluster complexes have led to significant advances being made in the understanding of nanoscale magnets termed 'single molecule magnets' (SMMs). In the case of manganese, the nuclearities known to date to display SMM behaviour include Mn_4 , Mn_{12} and Mn_{30} .⁴ Other nuclearities such as Mn_3 , Mn_6 , Mn_7 , Mn_8 , Mn_9 , Mn_{10} , Mn_{13} , Mn_{15} do not, even though some have high-spin ground states, one of the prerequisites for being a SMM. Another key prerequisite for SMM behaviour is a negative anisotropy in the axial zero-field splitting term D , which in the Mn clusters is introduced into the cluster ground state by Mn^{III} single-ion centres.

The archetypal cluster, $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ (Mn_{12} -acetate'), contains a central cubane $\text{Mn}^{\text{IV}}_4\text{O}_4$ core, bridged to an outer belt of eight Mn^{III} ions by $\mu_3\text{-O}^{2-}$ bridges, the eight Mn^{III} being bridged by OAc^- ligands.

We report here details of a new manganese carboxylate cluster, $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_{16}(\text{MeOH})_3(\text{H}_2\text{O})_3]\cdot 6\text{H}_2\text{O}$ (**1**). This complex was first obtained accidentally when attempting to expand our dicyanamide (dca^- , $\text{N}(\text{CN})_2^-$) molecule-based magnet work into networks of Mn_3 or Mn_4 clusters bridged by dca^- ligands.⁵ It was subsequently found that dca^- was not necessary for its formation. Thus, addition of solid $n\text{-Bu}_4\text{NMnO}_4$ to a stirred solution of $\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ in a mixture of methanol and acetic acid yielded a dark brown solution which was allowed to stand for several weeks, with the formation of black block-like crystals of **1**.† If $\text{Na}(\text{dca})$ and Me_4NBr are included in the reaction, **1** is formed first followed by small red crystals, identified as a triply-bridged linear chain complex $[\text{Mn}^{\text{III}}(\text{OMe})(\text{OAc})_2]_n$, which will be described elsewhere.⁶ The presence of alkoxide bridges in **1** is rare in Mn clusters and probably responsible for the nuclearity obtained.⁷

In the structure of **1**,† the cluster lies on an inversion centre relating one half of the cluster to the other. The asymmetric unit contains half of the molecule and three lattice water molecules. The cluster consists of six Mn^{IV} and ten Mn^{III} ions⁸ held together by fourteen $\mu_3\text{-O}^{2-}$, two $\mu_2\text{-O}^{2-}$, four $\mu\text{-OMe}^-$ and two $\mu\text{-OAc}^-$ groups to give a roughly elliptical planar $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_2]^{16+}$ core (Fig. 1). Peripheral ligation consists of the remaining fourteen $\mu\text{-OAc}^-$, two $\mu\text{-OMe}^-$ groups and three axial water and methanol molecules.

The Mn_{16} core can be divided into two sub-units, a central $[\text{Mn}^{\text{IV}}_6\text{O}_6(\text{OMe})_4]^{8+}$ unit connected to an outer perimeter of ten Mn^{III} ions by ten $\mu_3\text{-O}^{2-}$ ions in the plane of the molecule and two $\mu\text{-OAc}^-$ groups perpendicular (above and below) to the plane of the molecule. The central unit contains six Mn^{IV} ions in two rows of three ($\text{Mn}(1)$, $\text{Mn}(2)$, $\text{Mn}(3)$) and the symmetry related $\text{Mn}(1')$, $\text{Mn}(2')$, $\text{Mn}(3')$) lying in a plane that is sandwiched between two planes of oxygen atoms. Each plane contains two $\mu_3\text{-O}^{2-}$, one $\mu_2\text{-O}^{2-}$ and two $\mu\text{-OMe}^-$ ions. One

oxygen plane contains $\text{O}(1)$ and $\text{O}(3)$ ($\mu_3\text{-O}^{2-}$), $\text{O}(2')$ ($\mu_2\text{-O}^{2-}$), and $\text{O}(4')$ and $\text{O}(6')$ ($\mu\text{-OMe}^-$). The other oxygen plane

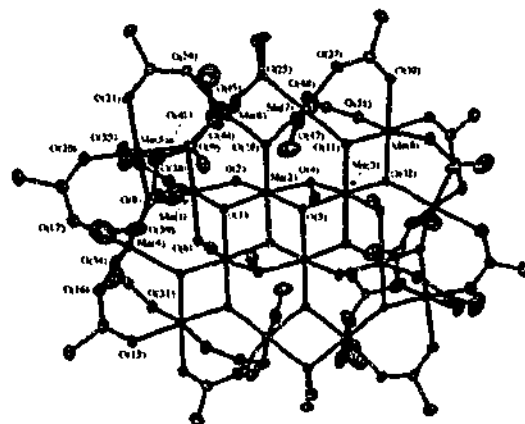


Fig. 1 $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{OAc})_{16}(\text{MeOH})_3(\text{H}_2\text{O})_3]\cdot 6\text{H}_2\text{O}$ with atom labelling scheme of manganese and oxygen atoms only (hydrogen atoms have been omitted for clarity). The central $[\text{Mn}^{\text{IV}}_6\text{O}_6(\text{OMe})_4]^{8+}$ sub-unit is highlighted in green.

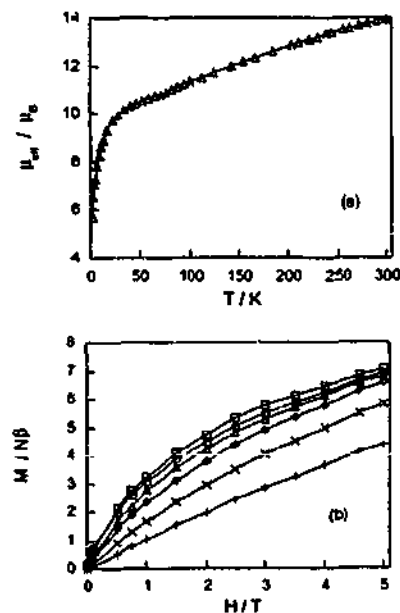


Fig. 2 (a) Plot of χ_M vs. temperature at 1 T and (b) Plots of magnetization, M (in units $N\beta$) vs. applied field at various temperatures: ($\square$) 2 K, ($\circ$) 3 K, ($\triangle$) 4 K, ($\diamond$) 5.5 K ($\times$) 10 K, (+) 20 K. Solid lines are not fits.

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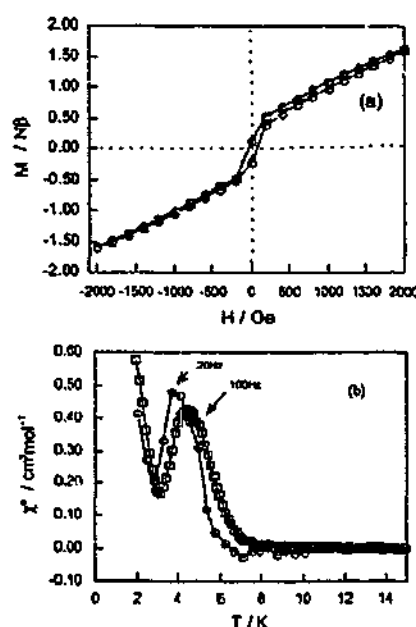


Fig. 3 (a) Hysteresis plot of a powder sample dispersed in vaseline, at 2 K and (b) out of phase AC χ'' plots with $H = 3.5$ Oe.

contains O(1') and O(3') (μ_3 -O $^{2-}$), O(2) (μ_2 -O $^{2-}$), and O(4) and O(6) (μ -O $^{2-}$). The Mn^{IV} ions occupy distorted octahedral sites between these two hexagonal close-packed O layers, in the manner seen in manganese oxide minerals,⁹ and within two related Fe₁₇ and Fe₁₉ oxyhydroxide clusters.¹⁰ Thus 1 could be thought of as a captured portion of a layered manganese oxide mineral. Such is not the case in Mn₁₂-acetate.

Peripheral ligation around the Mn^{III}₁₀ perimeter contains eight equatorial μ -OAc⁻ groups, six axial μ -OAc⁻ groups (three each on either side of the cluster in an alternating up-down fashion) and two μ -OMe⁻ ligands (bridging Mn(6) and Mn(7)). Eight of the ten perimeter Mn^{III} ions experience Jahn-Teller (JT) axial elongation in the direction perpendicular to the plane of the cluster. The remaining two (Mn(4) and Mn(4')) experience JT axial compression roughly parallel to the plane of the cluster in the direction of a μ -OAc⁻ and a core μ_3 -O $^{2-}$. This may be important in regard to AC χ'' behaviour.¹¹ Hydrogen bonding from an axial disordered water/methanol and an axial μ -OAc⁻ via two lattice water molecules between each cluster links them into chains that propagate parallel to the c-axis direction.

Variable temperature magnetic susceptibilities were measured on freshly isolated samples of 1 in a field of 1 T over the range 2–300 K (Fig. 2(a)). The same results were obtained on neat powders and on vaseline mulls. The effective magnetic moment, per Mn₁₀, decreases gradually from 14.0 μ_B at 300 K to ca. 10.5 μ_B , then more rapidly, reaching 5.7 μ_B at 2 K and still decreasing. The value of μ_{eff} at 300 K compares to the value of 18.16 μ_B calculated for six uncoupled Mn^{IV} ($S = 3/2$) and ten Mn^{III} ($S = 4/2$) and is thus indicative of overall antiferromagnetic coupling. To try to identify the ground spin state of 1, magnetization (M) measurements were made in the ranges of $H = 0$ –5 T and temperature = 2–20 K (Fig. 2(b)). It can be seen that, at 2 K, the M values increase in a gradual curved fashion between 0 and 5 T to reach ca. 7 $N\beta$ in the 5 T field. The M values are still increasing and saturation is not achieved. This is most likely due to thermal population of the ground-state and of other low lying spin-states occurring even at 2 K. Zero-field splitting and Zeeman effects will also influence the shape and

size of the M vs. H plots. Cluster-cluster interactions, via hydrogen bonding pathways, may also play a part. It is therefore not possible, without fitting of the M/H data, to unambiguously assign the ground state spin. A hysteresis loop (± 0.2 T) at 2 K shows a rapid increase in M in the ± 250 Oe region (Fig. 3(a)). Preliminary AC χ'' susceptibility measurements made in the range 2–15 K, at two frequencies (20 and 100 Hz) and $H = 3.5$ Oe, show a clear maximum which moves from 3.9 K at 20 Hz to 4.6 K at 100 Hz (Fig. 3(b)). This frequency dependence of χ''_{max} is one of the key experimental criteria for SMM behaviour and we are presently confirming this at different frequencies.

This work was supported by a Large Grant (to K. S. M.) and a Fellowship (to S. R. B.) from the Australian Research Council.

Notes and references

[†] Typical synthetic procedure: to a stirred methanolic solution (120 mL) of Mn(NO₃)₂·4H₂O (11.57 mmol, 2.90 g), and glacial acetic acid (10 mL), *n*-Bu₄NMnO₄ (3.15 mmol, 1.14 g) was added in small portions over a period of 30 min. The solution was then left to stand. After several weeks a small amount of block-like black crystals of Mn₁₂-acetate formed. The solution was decanted and the crystals collected (0.20 g, 8% based on total Mn). $\nu(\text{OH})$ 3387 cm⁻¹ (br), $\nu(\text{C}=\text{O})$ 1558 cm⁻¹.

In reactions which also had NaOAc (25.0 mmol, 2.23 g) and Me₄NBr (25.0 mmol, 3.85 g) added, black crystals of Mn₁₂-acetate, 1, formed first, followed by smaller red crystals of [Mn^{IV}(OMe)(OAc)₂]_n, the latter in higher yield. $\nu(\text{C}=\text{O})$ 1568 cm⁻¹.

Many repeats of the reaction show that crystals of 1 decompose with time to yield species containing low content of carbon and poor diffraction quality despite a good external morphology. Presumably slow hydrolysis of OMe⁻ and OAc⁻ groups occurs in the solid state. Analysis of a fresh sample, found: C, 18.8; H, 3.8. Calc. for C₄₁H₄₀Mn₁₀O₆₆: C, 19.6; H, 3.5%.

[‡] Crystal data for C₄₁H₄₀Mn₁₀O₆₆, $M = 2524.22$, triclinic, space group $P\bar{1}$, $a = 12.8547(2)$, $b = 14.4366(2)$, $c = 14.4590(2)$ Å, $\alpha = 108.276(1)^\circ$, $\beta = 116.273(1)^\circ$, $\gamma = 96.900(1)^\circ$, $U = 2176.49(5)$ Å³, $T = 123(2)$ K, $Z = 1$, $F(000) = 1270$, $D_c = 1.926$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 2.343$ mm⁻¹, $2\theta_{max} = 56.6^\circ$. A black block (0.2 × 0.15 × 0.15 mm), 37016 total reflections, 10573 independent reflections ($R_{int} = 0.0609$), of which 8648 were observed [$I > 2\sigma(I)$]. At final convergence $R_1 [I > 2\sigma(I)] = 0.0424$, wR_2 (all data) = 0.1101 for 669 parameters, $S = 1.051$, CCDC reference number 176429. See <http://www.rsc.org/suppdata/csb1/b111404/v> for crystallographic data in CIF or other electronic format.

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- The oxidation states were so assigned for the following reasons. The central Mn^{IV} ions have bond lengths comparable to those seen in the central {Mn^{IV}₄O₄}⁴⁺ cubane of Mn₁₂-acetate (T. Lis, *Acta Crystallogr., Sect. B*, 1980, 36, 2042) and lack the Jahn-Teller distortion common for Mn^{III}, e.g. α -Mn^{III}O(OH) (T. Kohler, T. Armbruster and E. Libowitzky, *J. Solid State Chem.*, 1997, 133, 486). In contrast, the perimeter Mn^{III} ions did show significant Jahn-Teller distortion. This oxidation state assignment therefore requires the pyramidal oxygen atoms to be O²⁻ rather than OH⁻, again consistent with Mn₁₂-acetate.
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Structure and magnetism of trinuclear and tetranuclear mixed valent manganese clusters from dicyanonitrosomethanide derived ligands

David J. Price^a, Stuart R. Batten^a, Kevin J. Berry^b, Boujemaa Moubaraki^a,
Keith S. Murray^{a,*}

^a School of Chemistry, Monash University, PO Box 23, Clayton, Vic. 3800, Australia

^b Westernport Secondary College, Hastings, Vic. 3915, Australia

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Abstract

Two new mixed valent clusters of manganese have been synthesised in which the starting pseudochalcogenide ligand, dicyanonitrosomethanide, $(\text{ONC}(\text{CN})_2)^-$ (dcnm^-) undergoes nucleophilic addition of methanol in complex 1 and water in complex 2 during coordination to the metal ions. Crystal structures show that complex 1 is a linear trinuclear $\text{Mn}(\text{II})\text{Mn}(\text{III})\text{Mn}(\text{II})$ compound, $[\text{Mn}_3(\text{meoc})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$, containing bridging oximate moieties from the chelating ligand methyl(2-cyano-2-hydroxyimino)ethanimidate $[\text{ONC}(\text{CN})\text{C}(\text{NH})\text{OCH}_3]^-$, meoc^- . Compound 2 has a planar rhomboidal (butterfly) arrangement of $\text{Mn}(\text{II})\text{Mn}(\text{II})\text{Mn}(\text{II})\text{Mn}(\text{III})$ with the $\text{Mn}(\text{III})$ ions in 'body' positions bridged to the 'wingtip', seven coordinate $\text{Mn}(\text{II})$ ions by μ_3 -oxo atoms and by the NO^- oximate groups of the cyanoacetamidooximate chelating ligand, cao^- , $[\text{ON}=\text{C}(\text{CN})\text{CONH}_2]^-$. 2 has the formula $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$. There are hydrogen bonded cluster-cluster interactions in both compounds. Detailed susceptibility and magnetisation measurements on 1 and 2 reveal intra-cluster antiferromagnetic coupling with a total spin ground state at the crossover point of $S_T = 2$ and 1 for 1, with other states very close in energy, and a rare sixfold degenerate set of S_T levels, 0, 1, 2, 3, 4, 5, lying lowest in the case of 2. In the latter case this is largely because of the large J_{13} ($\text{Mn}(\text{III})\text{Mn}(\text{II})$; body-body) value (-46.0 cm^{-1}) compared with the wing-body ($\text{Mn}(\text{II})\text{Mn}(\text{III})$) J_{12} value of -2.5 cm^{-1} . These coupling constants and S_T states are compared with those of other recent examples of planar rhomboidal mixed valent clusters, some of which show ferromagnetic J values and very large S_T ground states, with single-molecule magnetic behaviour exhibited in those cases. AC susceptibility studies show that complex 2 does not exhibit single-molecule magnetism behaviour. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Dicyanonitrosomethanide derived oximate ligands; Mixed valent manganese clusters; Trinuclear; Tetranuclear; Magnetism; Crystal structures

1. Introduction

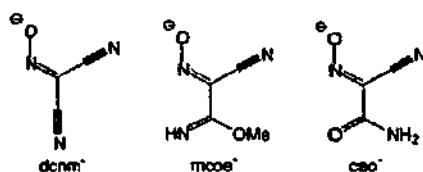
A great deal of recent research in polynuclear mixed valent manganese complexes has focussed on two main lines of enquiry. Firstly, in the bioinorganic area, many model complexes have been made to replicate the structure and function of manganese containing proteins and enzymes including, significantly, the water oxidation complex (WOC) in the Photosystem II (PSII) of green plants and cyanobacteria, which is responsible for

the catalysis of the light driven oxidation of H_2O to O_2 [1–4]. Detailed spectroscopic, EXAFS, XANES and crystallographic studies have been made to probe the $\text{Mn}_4(\text{Ca}) \mu_3\text{-oxo}$ cluster in the redox states S_0 to S_4 [5,6]. Secondly, in the field of nanomagnetic materials, some large high-spin manganese carboxylate clusters display magnetic properties previously only associated with nano-sized particles of magnetic metal oxides, that is, they can be magnetised and as such have been termed single-molecule magnets (SMMs). They also display unusual quantum mechanical effects in their single-crystal magnetisation hysteresis plots. The archetypal cluster, $[\text{Mn}(\text{III}/\text{IV})_2\text{O}_2(\text{OAc})_4(\text{H}_2\text{O})_4] \cdot 2\text{HOAc} \cdot 4\text{H}_2\text{O}$ (' Mn_{12} -acetate') and its derivatives are the best and most comprehensively studied SMMs to date [7–13]. Other

* Corresponding author. Tel.: +61-3-9905-4512; fax: +61-3-9905-4597.

E-mail address: keith.s.murray@sci.monash.edu.au (K.S. Murray).

examples of SMMs include the family of complexes with the $[\text{Mn(IV)Mn(III)}_2\text{O}_3\text{X}]^{6+}$ core [14–16], where X^- is, for example, a halide, and other Mn_4 complexes such as $[\text{Mn(III)}_2\text{Mn(II)}_2]$ rhomboidal cores [17,18] as well as a number of Fe_4 , Fe_8 and V_4 complexes [19–23]. More recently, a Ni_{12} wheel complex [24] and the first non-oxo-based SMM, the cyano bridged $\text{MnMo}_6(\text{CN})_{18}$ cluster [25], have been isolated.



We present here two new mixed valent manganese complexes $[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ (1) and $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ (2), where mcoe^- is methyl(2-cyano-2-hydroxyimino)ethanimidate $[(\text{ONC}(\text{CN})\text{C}(\text{NH})\text{OCH}_3)]^-$ and cao^- is cyanoacetamidoximate $[(\text{ON}=\text{C}(\text{CN})\text{CONH}_2)]^-$. Their structures and magnetic properties are described.

This work arose from a combination of interests in Mn cluster chemistry and in 3D-molecular magnets based on pseudohalide and pseudochalcogenide bridges of cyano based ligands [26]. From such work we have recently reported a Mn_{16} cluster which displays aspects of SMM behaviour [27].

2. Experimental

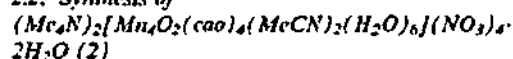
$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, methanol and acetonitrile were used as received. All reactions were performed under aerobic conditions. $\text{Me}_4\text{N}(\text{dcnm})$ was prepared by a metathesis reaction by adding an acetonitrile solution of Me_4NBr to a suspension of $\text{Ag}(\text{dcnm})$ in dichloromethane (dcnm^- is $\text{ONC}(\text{CN})_2^-$). AgBr was removed by filtration. The solvent was removed and the resulting yellow oil was recrystallised by vapour diffusion of diethyl ether into a solution in methanol (Yield 95%). $\text{Ag}(\text{dcnm})$ was synthesised according to the literature [28].

2.1. Synthesis of $[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ (1)

A methanolic solution (5 ml) of $\text{Me}_4\text{N}(\text{dcnm})$ (0.336 g, 2.0 mmol) was added to a methanolic solution (5 ml) of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.251 g, 1.0 mmol). The resultant solution was an orange colour. After 1 week many red crystals were present in the deep red solution. The crystals had a hexagonal or half-hexagonal appearance and did not lose solvent in air. The solution was decanted. A fine light-brown solid, which coprecipitated

with the crystals was removed by suspending it in methanol (the crystals were far less mobile, sinking rapidly) and decanting the suspension. This process was repeated several times until the methanol wash was free of the light-brown solid. The crystals were collected by filtration, washed with methanol and dried in air. Yield 0.17 g (50% based on total available Mn). An irregular shaped crystal was chosen for X-ray diffraction structural analysis. IR (Nujol, cm^{-1}): 3258s, 2221m, 1645s, 1434s, 1385m, 1356s, 1266s, 1192s, 1125s, 952w, 823w, 779m. Anal. Found: C, 29.5; H, 3.1; N, 24.8. Calc. for $\text{C}_{24}\text{H}_{28}\text{N}_{19}\text{O}_{17}\text{Mn}_3$: C, 28.3; H, 2.8; N, 26.1%. Powder XRD: The diffractogram of the bulk product matches that calculated from the crystal structure.

2.2. Synthesis of



$\text{Me}_4\text{N}(\text{dcnm})$ (0.596 g, 3.54 mmol) was stirred in 10 ml of hot acetonitrile to dissolve. There remained a small amount of yellow residue. A solution of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.889 g, 3.54 mmol) in acetonitrile (10 ml) was then added to this mixture, resulting in an instant colour change to deep red. Over a period of about 30 min of stirring the hot mixture changed to an orange colour. The mixture was then filtered several times to remove a fine brown precipitate (most likely manganese oxide), then covered and left to stand. After 4 days the solution was a red/brown colour with a small amount of fine brown precipitate mixed with many red/orange crystals. The fine brown precipitate was removed by suspending it in the solution (the crystals were far less mobile, the majority remaining attached to the glass of the vessel) and filtering the suspension. The filtrate was returned to the crystals, which were then filtered and washed with acetonitrile (Yield 50 mg, 4% based on total available Mn). IR (Nujol, cm^{-1}): 3390sbr, 2268vw, 2224s, 1682s, 1606s, 1470s, 1317s, 1224s, 1136s, 1041m, 950m, 831m, 708sh, 666sh. Anal. Found: C, 22.2; H, 3.0; N, 22.4. Calc. for $\text{C}_{24}\text{H}_{34}\text{N}_{20}\text{O}_{30}\text{Mn}_4$: C, 21.8; H, 4.1; N, 21.2%. Powder XRD: The diffractogram of the bulk product matches that calculated from the crystal structure.

2.3. X-ray crystallographic studies

Crystal data for 1 and 2 are summarised in Table 1. Data were collected using a Nonius KappaCCD diffractometer with graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Integration was carried out by the program DENZO-SMN [29], and data were corrected for Lorentz polarisation effects and for absorption using the program SCALEPACK [29]. Solutions were obtained by direct methods (SHELXS-97 [30]) followed by successive Fourier difference methods, and

Table 1
Summary of crystal data

	1	2
Formula	C ₂₄ H ₂₈ MnN ₃ O ₁₇	C ₂₄ H ₃₄ MnN ₃ O ₁₆
<i>M</i>	1019.47	1322.62
Crystal system	trigonal	monoclinic
Space group	<i>P</i> 3 ₁ <i>c</i>	<i>C</i> 2 ₁ <i>c</i>
<i>a</i> (Å)	12.4720(2)	19.2163(3)
<i>b</i> (Å)	12.4720(2)	11.4283(2)
<i>c</i> (Å)	15.8114(4)	24.0215(2)
β (°)		90.916(1)
<i>U</i> (Å ³)	2129.97(7)	5274.7(2)
<i>Z</i>	2	4
<i>T</i> (K)	123(2)	123(2)
μ (Mo-K α) (mm ⁻¹)	0.965	1.041
Crystal habit, colour	rhomboidal, red	rhomboidal, orange-red
Crystal size (mm)	0.15 × 0.125 × 0.1	0.2 × 0.2 × 0.1
Index ranges	−16 ≤ <i>h</i> ≤ 16, −15 ≤ <i>k</i> ≤ 16, −21 ≤ <i>l</i> ≤ 21	−25 ≤ <i>h</i> ≤ 25, −15 ≤ <i>k</i> ≤ 15, −32 ≤ <i>l</i> ≤ 32
Completeness to 2 θ = 55° (%)	99.9	99.2
Data collected	29 281	35 448
Unique data [<i>R</i> _{int}]	1775 [0.0908]	6442 [0.0619]
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	1390	4578
Parameters	106	292
Final <i>R</i> ₁ , <i>wR</i> ₂	0.0759, 0.2172, 0.0968,	0.1134, 0.3314,
[<i>I</i> > 2 σ (<i>I</i>)] (all data) *	0.2321	0.1502, 0.3563
Goodness-of-fit, <i>S</i>	1.141	1.097

$$^* R_1 = \sum [|F_o| - |F_c|] / \sum |F_o|, wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}.$$

refined by full-matrix least-squares on F_{obs}^2 (SHELXL-97 [30]).

For complex 1 all non-hydrogen atoms of the cation complex, the two waters of crystallisation and the nitrogen atom of the nitrate were refined anisotropically. The unique oxygen atom of the nitrate was found to be disordered over two positions. The two contributions (assigned equal quarter site occupancies) were refined isotropically. The imidate proton was located in the difference Fourier map and was subsequently refined isotropically. The methoxy protons of the meoc[−] ligand were included at calculated positions with *U* values 1.5 times the *U*_{eq} of the carbon atom. Two regions of electron density not connected to each other were assigned as two water molecules. Table 2 contains selected distances and angles.

For complex 2 all non-hydrogen atoms of the cluster were refined anisotropically. Due to significant disorder that was difficult to model the non-hydrogen atoms of the tetramethylammonium and nitrate counter ions were refined isotropically and no hydrogen atoms were assigned. A region of residual electron density was assigned as a water molecule disordered over two

Table 2
Selected bond distances (Å) and angles (°) of 1

Bond lengths			
Mn(1)–O(1)	2.169(3)	Mn(1)···Mn(2)	3.9177(9)
Mn(2)–N(2)	2.324(3)	Mn(2)–N(9)	2.189(4)
O(1)–N(2)	1.301(4)	C(3)–C(6)	1.490(5)
N(2)–C(3)	1.303(5)	C(6)–N(9)	1.250(6)
C(3)–C(4)	1.410(6)	C(6)–O(7)	1.338(5)
C(4)–N(5)	1.14(1)	O(7)–C(8)	1.462(6)
Bond angles			
O(1)–Mn(1)–O(1')	90.7(1)	N(2)–Mn(2)–N(9)	72.2(1)
O(1')–Mn(1)–O(1'')	82.6(1)	N(9)–Mn(2)–N(9')	92.73(14)
O(1)–Mn(1)–O(1'')	93.5(9)	N(2)–Mn(2)–N(2')	85.33(12)
O(1)–Mn(1)–O(1'')	174.5(1)	N(2)–Mn(2)–N(9')	138.15(13)
		N(2')–Mn(2)–N(9)	125.91(12)
Hydrogen bonding			
N(9)–H(9)	1.00(7)		
H(9)···O(110)	2.00(7)	H(9)···O(111)	2.02(7)
N(9)···O(110)	2.94(3)	N(9)···O(111)	2.90(2)
N(9)–H(9)···O(110)	156(5)	N(9)–H(9)···O(111)	147(5)

Symmetry transformations (i) $-x+y, y, -z+3/2$; (ii) $-y+1, x-y+1, z$; (iii) $-y+1, -x+1, -z+3/2$.

positions O(600) and O(601)). Hydrogen atoms on the coordinating acetonitrile molecules and the amine groups of the cao[−] ligands were assigned to calculated positions with *U* values 1.5 times (for methyl protons) and 1.2 times (for amine protons) the *U*_{eq} of the attached atom, whereas those on the coordinating water molecules were not located. As can be seen in Table 1 the final *R*-value was relatively high. The crystals were quite small and weakly diffracting and many were tried with poorer quality diffraction. A number of solutions were obtained for different crystals, the best giving the refined structure presented here. Despite the extreme disorder in the counter ions and in a water molecule the cluster itself is well refined. Table 3 contains selected distances and angles.

2.4. Magnetic measurements

Magnetic measurements were carried out as described previously [26] using a Quantum Design MPMS 5 Squid magnetometer for DC magnetisation measurements and a PPMS instrument for AC susceptibility measurements. Since Mn(III) complexes display torquing at low temperatures [31], the powder samples were dispersed in Verelene.

3. Results and discussion

3.1. Synthesis and characterisation

Complex 1 crystallises out of a solution of Mn(NO₃)₂·4H₂O and Me₄N(dcnm) (1:2 molar ratio) in methanol. Complex 2 crystallised out of a solution of equimolar

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Table 3
Selected bond distances (Å) and angles (°) of 2

Bond lengths			
Mn(1)–O(1)	2.077(5)	Mn(2)–O(1)	1.844(5)
Mn(1)–N(3)	1.924(2)	Mn(2)–O(1')	1.837(5)
Mn(1)–O(9)	2.241(6)	Mn(2)–O(2)	2.003(5)
Mn(1)–N(11)	2.425(6)	Mn(2)–O(10')	1.993(5)
Mn(1)–O(17)	2.226(6)	Mn(2)–O(20)	2.296(8)
Mn(1)–O(18)	2.192(7)	Mn(2)–N(21)	2.372(9)
Mn(1)–O(19)	2.183(9)	Mn(2)–Mn(2')	2.773(2)
Mn(1)–Mn(2)	3.546(2)		
Bond angles			
O(1)–Mn(1)–O(19)	93.7(3)	O(17)–Mn(1)–N(3)	142.9(2)
O(1)–Mn(1)–O(18)	87.3(2)	O(9)–Mn(1)–N(3)	68.4(2)
O(19)–Mn(1)–O(18)	176.3(3)	O(1)–Mn(2)–O(1')	82.3(2)
O(1)–Mn(1)–O(17)	142.3(2)	O(1')–Mn(2)–O(10')	93.7(2)
O(19)–Mn(1)–O(17)	90.0(4)	O(1)–Mn(2)–O(10')	175.9(2)
O(18)–Mn(1)–O(17)	91.4(3)	O(1')–Mn(2)–O(2)	176.5(2)
O(1)–Mn(1)–O(9)	143.1(2)	O(1)–Mn(2)–O(2)	94.6(2)
O(19)–Mn(1)–O(9)	86.7(3)	O(2)–Mn(2)–O(10')	89.4(2)
O(18)–Mn(1)–O(9)	90.3(3)	O(1')–Mn(2)–O(20)	95.9(3)
O(17)–Mn(1)–O(9)	74.6(2)	O(1)–Mn(2)–O(20)	93.8(3)
O(1)–Mn(1)–N(11)	73.9(2)	O(10')–Mn(2)–O(20)	87.0(3)
O(19)–Mn(1)–N(11)	90.3(3)	O(2)–Mn(2)–O(20)	82.5(3)
O(18)–Mn(1)–N(11)	93.4(2)	O(1')–Mn(2)–N(21)	94.9(3)
O(17)–Mn(1)–N(11)	68.5(2)	O(1)–Mn(2)–N(21)	93.4(3)
O(9)–Mn(1)–N(11)	143.0(2)	O(10')–Mn(2)–N(21)	86.4(3)
O(1)–Mn(2)–N(3)	74.6(2)	O(2)–Mn(2)–N(21)	87.0(3)
O(19)–Mn(2)–N(3)	90.8(3)	O(20)–Mn(2)–N(21)	167.7(3)
O(18)–Mn(2)–N(3)	86.0(2)	Mn(2)–O(1)–Mn(2')	97.7(2)
Hydrogen bonding			
O(19)–O(52 ^{iv})	3.07(2)	O(20)–O(43)	2.82(2)
O(19)–O(53)	2.63(2)	N(8)–N(6 ^{iv})	3.00(1)
O(18)–O(43)	2.86(2)	N(16)–N(14 ^v)	3.03(1)
O(18)–O(600 ⁱⁱ)	2.49(5)	N(8)–O(43 ⁱⁱ)	2.90(2)
O(600)–O(41)	2.40(5)	N(16)–O(600 ^{iv})	2.90(4)
O(601)–O(41)	2.34(4)	N(16)–O(601 ^{iv})	2.67(3)
O(52 ^{iv})–O(19)–O(53)	124.9(7)	N(8)–H(8B)–N(6 ^{iv})	149.4
N(8)–H(8A)–O(43 ⁱⁱ)	175.9	N(16)–H(16B)–N(14 ^v)	152.9

Symmetry transformations (i) $-x+1/2, -y+3/2, -z+1$; (ii) $x-1/2, y-1/2, z$; (iii) $-x, y, 3/2-z$; (iv) $-x, 2-y, 1-z$; (v) $-x, y, 3/2-z$.

amounts of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Me}_4\text{N}(\text{dcnm})$ in hot acetonitrile. A brown solid, which from IR spectroscopy is likely to be MnO_2 , is formed in relatively large quantities at the same time as some of the $\text{Mn}(\text{II})$ is oxidised to $\text{Mn}(\text{III})$, which is then included in the tetranuclear cluster. This solid can be filtered off progressively during the course of the reaction. In latter stages, the majority of the product is 2 and can be relatively successfully separated from remaining MnO_2 powder. The yield of 2 was very low but quite reproducible.

Infrared spectroscopy of complex 1 shows absorbances at 2221 and 1645 cm^{-1} corresponding to the $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{C}=\text{N})$ vibrations, respectively, from the mcoe^- ligand. Likewise for complex 2 absorbances at 2224 and 1682 cm^{-1} correspond to the $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{C}=\text{O})$ vibrations of the cao^- ligand.

The pseudochalcogenide ligand dicyanonitrosomethanide ($\text{ONC}(\text{CN})_2^-$, dcnm^-) undergoes nucleophilic addition of solvent (methanol and water for complexes 1 and 2, respectively) in the coordination sphere of the metal to form the chelating ligands, methyl(2-cyano-2-hydroxyimino)ethanimidate ($[\text{ONC}(\text{CN})\text{C}(\text{NH})\text{OCH}_3]^-$, mcoe^-) for 1 and cyanoacetamidoximate ($[\text{ON}=\text{C}(\text{CN})(\text{CONH}_2)]^-$, cao^-) for 2. The nucleophilic addition of solvent to dcnm^- has been reported by Hvastijová et al. for $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Pd}(\text{II})$ complexes [32–36]. The protonated form of the ligand, caoH , has been synthesised recently by refluxing the filtrate formed from the reaction of $\text{Ag}(\text{dcnm})$ and NH_4Cl in water [37]. Compounds 1 and 2 are the first examples of complexes in which the mcoe^- and cao^- ligands occupy bridging as well as chelating coordination modes. The oxidation of $\text{Mn}(\text{II})$ to $\text{Mn}(\text{III})$ and $\text{Mn}(\text{IV})$ (MnO_2) in these aerobic reactions is not unexpected and the formation of $\text{Mn}(\text{II})\text{OMn}(\text{III})$ bridges in 2 under these conditions is common.

3.2. Crystal structures

3.2.1. $[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ (1)

Complex 1 crystallises in the trigonal space group $P\bar{3}1c$. The cation is a linear trinuclear complex (Fig. 1) with the three manganese ions lying along a threefold axis and the central manganese atom situated on an inversion centre. Thus the asymmetric unit contains 1/6 of the formula unit. The cation contains two symmetry related terminal six-coordinate manganese(II) ions chelated by the N-donor atoms of the imidate and oxime groups of three mcoe^- ligands in a trigonal prismatic environment ($\text{Mn}(2)-\text{N}(9)=2.189(4)$, $\text{Mn}(2)-\text{N}(2)=2.324(3)$ Å and $\text{N}(2)-\text{Mn}(2)-\text{N}(9)=72.2(1)^\circ$). The two terminal manganese(II) ions are bridged to the central manganese(III) by the oxime groups of the six mcoe^- ligands, providing an entirely O-donor atom coordination environment in a distorted octahedral fashion ($\text{Mn}(1)-\text{O}(1)=2.169(3)$ Å).

The oxidation states are assigned on the basis of charge balance and on consideration of bond lengths. The two terminal manganese ions are assigned $\text{Mn}(\text{II})$ due to the longer average bond length (2.257(7) Å) compared with the bond length for the central manganese ion, which was assigned as $\text{Mn}(\text{III})$. It would be expected that the central $\text{Mn}(\text{III})$ ion would show Jahn–Teller distortion, having d^4 configuration in a near-octahedral environment. However, in this case, there is only one unique Mn–O bond length.

This complex strongly resembles the linear trinuclear mixed oxidation state manganese complexes $[(\text{Me}_3\text{-tacn})\text{Mn}(\text{III})\{\mu\text{-niox}\}_2\text{M}(\text{II})\{\text{Me}_3\text{-tacn}\}](\text{ClO}_4)_2$ ($\text{M}(\text{II})=\text{Mn}, \text{Cu}$ and Zn ; $\text{Me}_3\text{-tacn}=1,4,7$ -trimethyl-1,4,7-triazacyclononane; $\text{H}_2\text{niox}=\text{cyclohexane-1,2-dione}$) published by Birkelbach et al. [38,39]. In

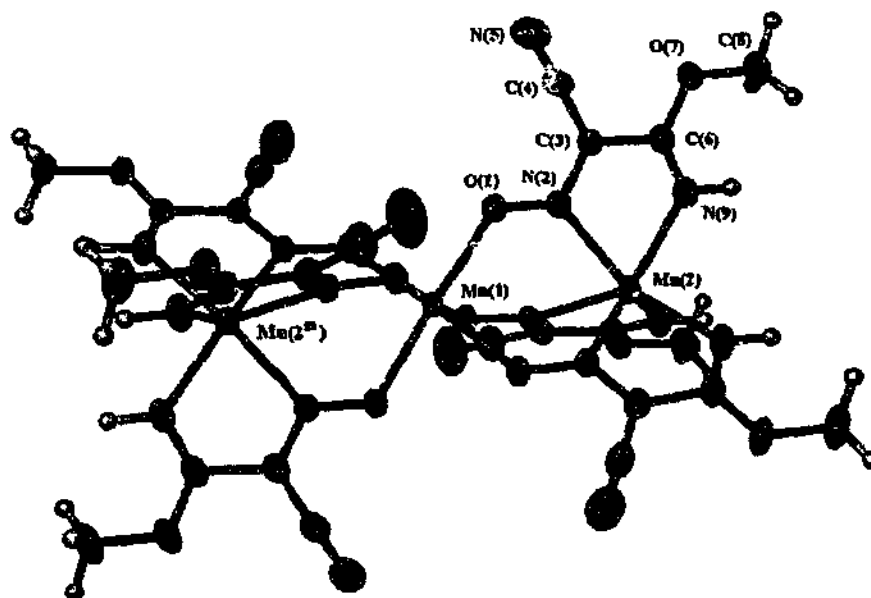


Fig. 1. Crystal structure of $[\text{Mn}_3(\text{mcoe})_3]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ (1) with atom labelling scheme (thermal ellipsoids shown at 50% probability). NO_3^- and lattice waters omitted.

contrast to 1, these complexes consist of a central $\text{M}(\text{II})$ ion chelated by three niox^{2-} ligands in a trigonal prismatic environment with an entirely N-donor atom coordination sphere, and are then bridged to the two terminal $\text{Mn}(\text{III})$ ions by the oxime groups of the niox^{2-} ligands. The terminal $\text{Mn}(\text{III})$ ions are in turn capped by $\text{Me}_3\text{-tacn}$ and thus possess a distorted octahedral N_3O_3 coordination environment. Other linear $\text{Mn}(\text{II})\text{Mn}(\text{III})$ examples are known [40].

Each cation in 1 is linked to its neighbour along the c -axis via hydrogen bonding between the cation imidate protons and the nitrate counter ion ($\text{N}(9) \cdots \text{O}(11) = 2.90(1) \text{ \AA}$) (Fig. 2), which is disordered over two positions related by a $48.8(1)^\circ$ rotation about the nitrogen atom. This disorder in the nitrate oxygen may be due to the hydrogen bonding between the three imidate protons each on adjacent complexes that are staggered 60° with respect to each other.

3.2.2. $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ (2)

Complex 2 crystallises in the monoclinic space group $C2/c$, with the tetranuclear manganese cluster lying on an inversion centre. Table 3 contains selected bond distances and angles for 2. Fig. 3 shows the cluster and the atom labelling scheme. The asymmetric unit contains half of the cluster, one tetramethylammonium and two nitrate counter ions and one lattice water. The cluster contains a $[\text{Mn}_4(\mu_3\text{-O})_2]^{6+}$ core ($2\text{Mn}(\text{II})$, $2\text{Mn}(\text{III})$) in which the four Mn atoms lie in a diamond shaped plane with $\text{Mn}(1) \cdots \text{Mn}(2) = 3.546(2) \text{ \AA}$ being considerably longer than $\text{Mn}(2) \cdots \text{Mn}(2^i) = 2.773(2) \text{ \AA}$. This is due to the latter pair being bridged by two $\mu_3\text{-O}^{2-}$ atoms ($\text{Mn}(2)\text{--O}(1) = 1.844(3)(2) \text{ \AA}$ and $\text{Mn}(2^i)\text{--O}(1) = 1.837(5) \text{ \AA}$), whereas the former pair are bridged by the two atom N–O moiety of the cao^- ligand ($\text{Mn}(1)\text{--N}(3) = 2.436(6) \text{ \AA}$ and $\text{O}(2)\text{--Mn}(2) = 2.003(5) \text{ \AA}$).

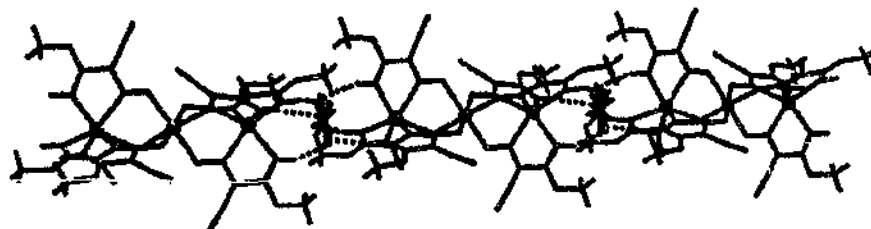


Fig. 2. Hydrogen bonding of $[\text{Mn}_3(\text{mcoe})_3]^+$ cations alternating with disordered nitrate anions (H-bonds dashed, methyl protons omitted for clarity).

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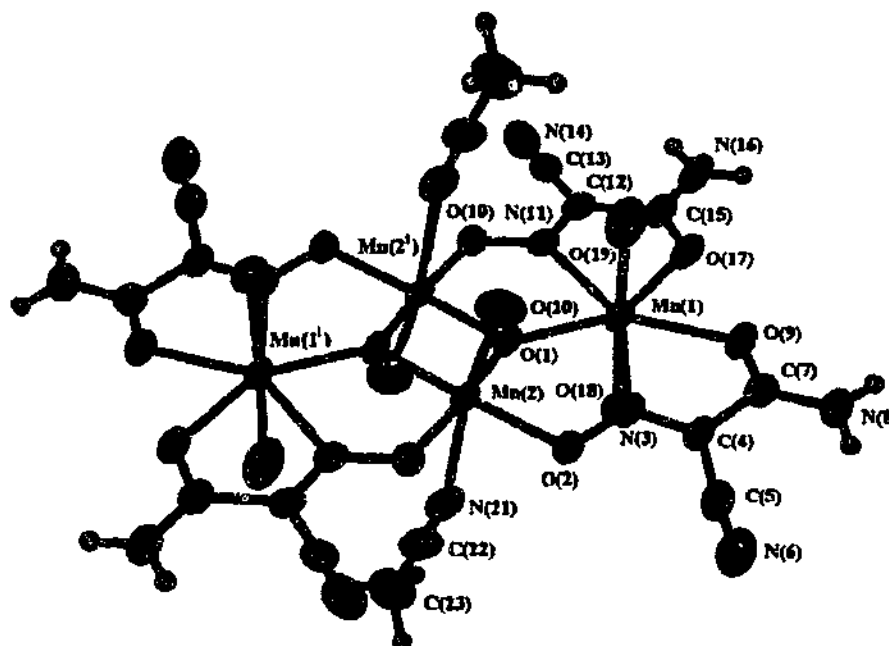


Fig. 3. Crystal structure of 2 with atom labelling scheme (thermal ellipsoids shown at 50% probability). Hydrogen atoms, counter ions and lattice waters omitted.

Å) and a single $\mu_3\text{-O}^{2-}$ atom ($\text{Mn}(1)\text{--O}(1) = 2.077(5)$ Å). The $\mu_3\text{-O}^{2-}$ atom lies 0.190(6) Å out of the plane defined by the four manganese atoms. On the periphery of the $[\text{Mn}_4(\mu_3\text{-O})_2]^{6+}$ core are four chelating cao^- ligands (two of which are unique) which lie roughly coplanar with the core. In the axial positions of the metal coordination spheres are six terminal water molecules, two each on Mn(1) and Mn(1') and one each on Mn(2) and Mn(2'), and two terminal acetonitrile ligands, one each on Mn(2) and Mn(2').

The two Mn(II) atoms (Mn(1) and Mn(1')) are thus seven coordinate in an approximate pentagonal bipyramidal arrangement. The carbonyl oxygens (O(9) and O(17)) and oxime nitrogens (N(3) and N(11)) of two cao^- ligands and one $\mu_3\text{-O}^{2-}$ ion (O(1)) make up the pentagonal plane of the bipyramid, whereas the apices are filled by the two axial waters (O(18) and O(19)). The five angles around the plane are $68.4(2)^\circ$, $68.5(2)^\circ$, $73.9(2)^\circ$, $74.6(2)^\circ$ and $74.6(2)^\circ$. The sum of these angles being 360° attests to the planarity of the coordination environment. The non-coordinating nitrile groups of the two cao^- ligands chelating each Mn(II) ion are bent slightly away from the plane of the $[\text{Mn}_4(\mu_3\text{-O})_2]^{6+}$ core. Mn(2) and Mn(2') were assigned as Mn(III) ions on the basis of the significant Jahn–Teller elongation in the direction of the axial water and acetonitrile ligands ($\text{Mn}(2)\text{--O}(20) = 2.296(8)$ Å and $\text{Mn}(2)\text{--N}(21) = 2.372(9)$ Å, where the average equatorial bond dis-

tance = 1.92 Å), as expected for a high-spin Mn(III) (d^4) in near-octahedral geometry.

A complex network of hydrogen bonding exists between the clusters and the intercalated water and nitrate anions. Inspection of the cluster shows that there are several sites capable of hydrogen bonding, and the cluster packing is determined by the hydrogen bonding interactions. Broadly speaking there are two intersecting hydrogen bonding networks. Firstly, a sheet in the ab -plane is formed by hydrogen bonding interactions between adjacent clusters (perpendicular to the plane of the clusters) via the terminal waters, the nitrate anions and the intercalated water molecule. Secondly, another sheet network is formed in the ac -plane by hydrogen bonding between the terminal amine and the nitrile groups of the cao^- ligand on adjacent clusters. The tetramethylammonium cations pack between the sheets in the ab -plane.

The network in the ab -plane involves multiple hydrogen bonding interactions and can be broken down into two types of intersecting chains. The terminal water oxygen atom O(19) on Mn(2) hydrogen bonds to two symmetry related nitrate anions ($\text{O}(19)\cdots\text{O}(52^{\text{iv}}) = 3.07(2)$, $\text{O}(19)\cdots\text{O}(53) = 2.63(2)$ Å and $\text{O}(52^{\text{iv}})\cdots\text{O}(19)\cdots\text{O}(53) = 124.9(7)^\circ$) which in turn both hydrogen bond to a symmetry related O(19) on an adjacent cluster. The pattern thus formed is a stepped chain of clusters (Fig. 4(a)). In addition another chain in

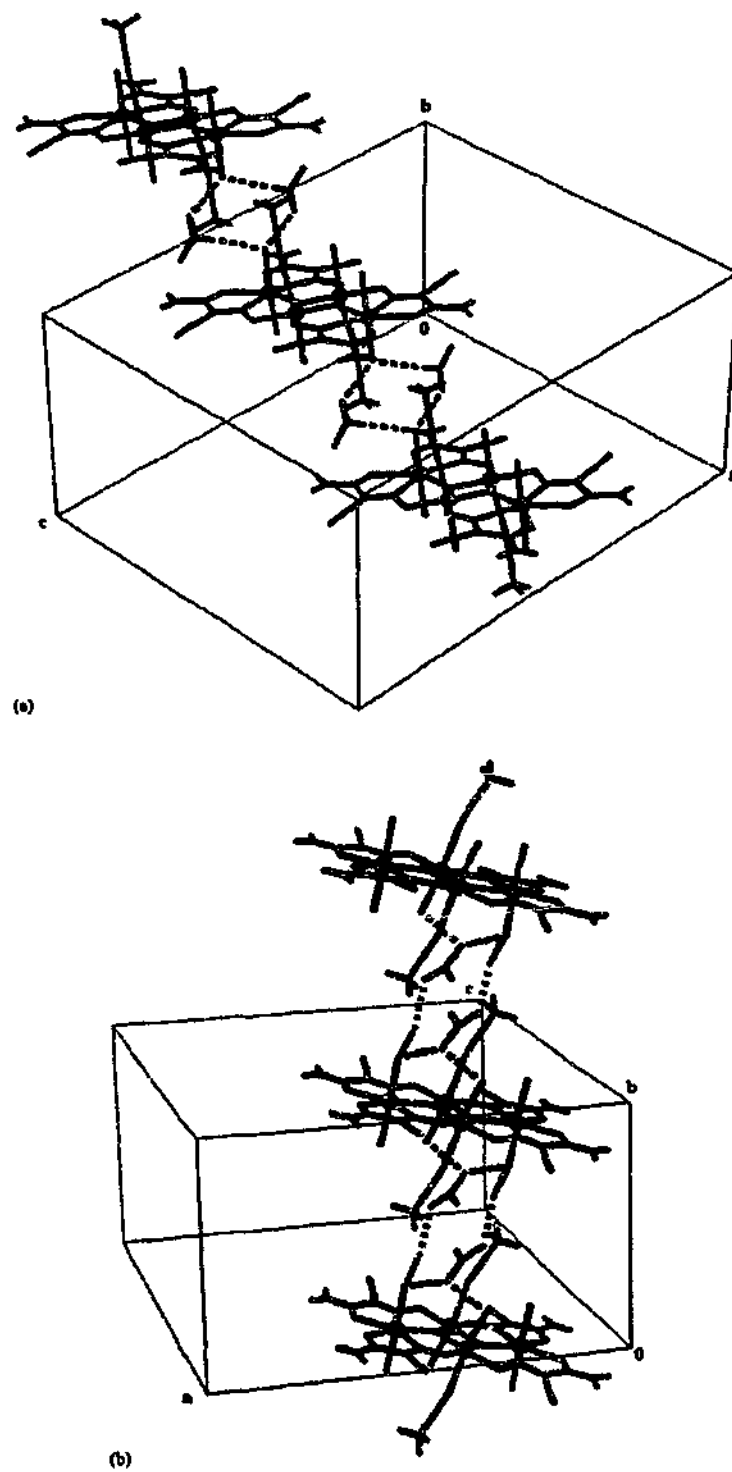


Fig. 4. (a) The stepped chain section of the hydrogen bond network (dashed) of 2 in the *ab*-plane. (b) Second part of the hydrogen bonded network (dashed) of 2 in the *ab*-plane. (c) Hydrogen bonded network (dashed) of 2 in the *ac*-plane.

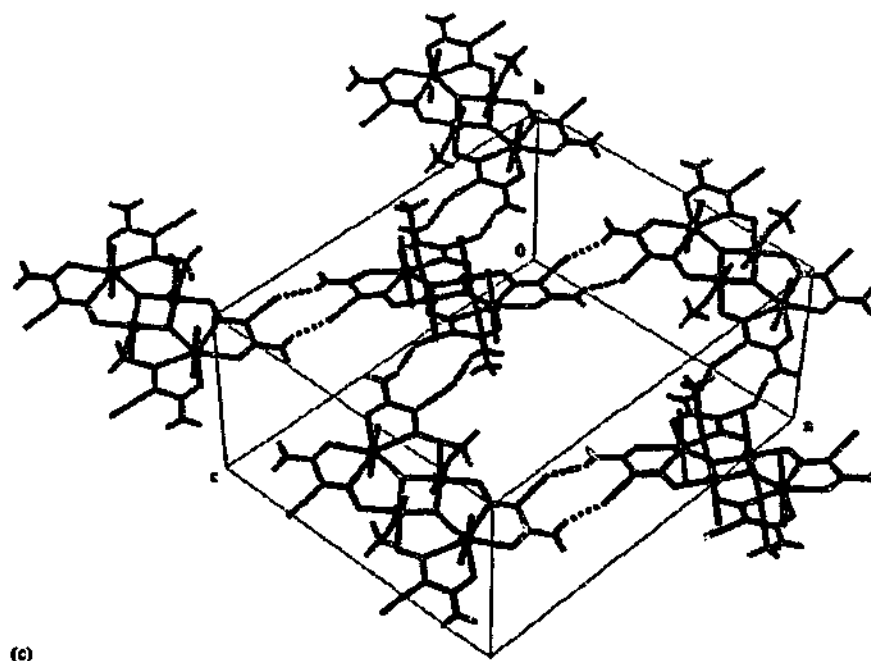


Fig. 4 (Continued)

this plane exists that involves hydrogen bonding from the water O(18) coordinated to Mn(2) to both a nitrate anion (O(18)···O(43^h) = 2.86(2) Å) and a disordered water (average O···O distance = 2.9(1) Å) which in turn hydrogen bond to their symmetry related partners (nitrate-water average O···O distance = 2.37(9) Å), which then also hydrogen bond to O(18) on the adjacent cluster (Fig. 4(b)). The water coordinated to the central Mn(1) also hydrogen bonds to the nearby nitrate anion that is also hydrogen bonded to O(18) (O(20)···O(43) = 2.82(2) Å).

The sheet in the *ac*-plane (Fig. 4(c)) is set up by the terminal amines and nitriles of the two unique *cao*[−] ligands, so that the amine on one cluster hydrogen bonds to the nitrile on the adjacent cluster (N(8)···N(6ⁱⁱⁱ) = 3.00(1) Å, N(8)–H(8B)···N(6ⁱⁱⁱ) = 149.4° and N(16)···N(14^v) = 3.03(1) Å, N(16)–H(16B)···N(14^v) = 152.9°). All hydrogen bonds in the plane are directed parallel to the *c*-axis direction. The topology of this sheet is (4,4). Viewed parallel to the *c*-axis direction the sheets undulate due to the planes of adjacent clusters in the *a*-axis direction being on an angle of 31.48(3)° to each other (mean planes of Mn atoms). The terminal amine on one of the *cao*[−] ligands also hydrogen bonds to a nearby nitrate anion (N(8)···O(43^h) = 2.90(2) Å, N(8)–H(8A)···O(43^h) = 175.9°) and correspondingly the other amine hydrogen bonds to the disordered lattice water molecule with an

average distance of 2.79(7) Å. Thus the amine groups also participate in the hydrogen bonded network in the *ab*-plane.

3.3. Magnetism

3.3.1. $[Mn_3(mcoe)_6]NO_3 \cdot 2H_2O$ (1)

In Fig. 5(a) it can be seen that the magnetic moment, per Mn, decreases a little from 9.5 μ_B at 300 K to ~9 μ_B at ~100 K, then more rapidly to reach a shoulder value of 5.5 μ_B at 5 K, before reaching 4.7 μ_B at 2 K. The uncoupled (*g* = 2.0) value for $S_1 = 5/2$, $S_2 = 4/2$, $S_3 = 5/2$ is 9.70 μ_B and thus very weak antiferromagnetic coupling is occurring. The 2 K value is suggestive of a $S_T = 2$ coupled ground state but, since *J* values are small, there will be many M_S energy levels populated because of their close spacing of a few cm^{-1} . The crossover of relevant S_T levels occur at the following α values where $\alpha = J_{13}/J_{12}$ and J_{12} is negative:

$$S_1 = 3 \quad \alpha < 0.4$$

$$S_T = 2 \quad 0.4 < \alpha < 0.5$$

$$S_T = 1 \quad \alpha > 0.5$$

The spin Hamiltonian employed is that commonly used for a linear trimer:

$$H = -2J_{12}(S_1 \cdot S_2 + S_2 \cdot S_3) - 2J_{13}S_1 \cdot S_3$$

The field-dependent thermodynamic form of suscept-

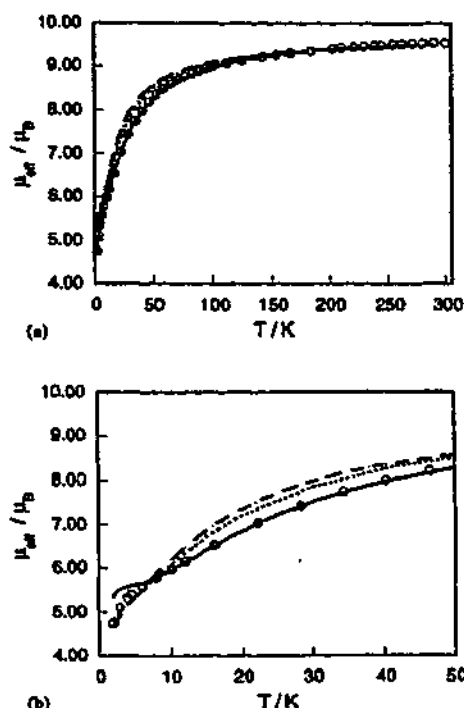


Fig. 5. (a) Plot of observed μ_{eff} data for complex 1 (2–300 K, $H = 1$ T). Calculated lines are obtained using the parameter sets (a) to (c) (see text) are given. (a) $\cdots$, (b) $\cdots$, (c) $\cdots$. (b) Plot of observed μ_{eff} data for complex 1 in region 2–50 K with calculated lines for parameter sets (a) $\cdots$, (b) $\cdots$, (c) $\cdots$ (see text).

ibility was employed [17,18,41]. Wide ranges of parameter values were explored in trying to fit the whole susceptibility data between 2–300 K. The region 12–120 K was the hardest to reproduce. Using χ_{TP} of $300 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, the following three sets gave quite good fits:

- $g = 1.99$, $J_{12} = -1.02 \text{ cm}^{-1}$, $J_{13} = -0.53 \text{ cm}^{-1}$, $\alpha = 0.52$, $S_T = 1$ ground;
- $g = 2.00$, $J_{12} = -1.16 \text{ cm}^{-1}$, $J_{13} = -0.58 \text{ cm}^{-1}$, $\alpha = 0.50$, $S_T = 1$ or 2 ground;
- $g = 2.02$, $J_{12} = -1.59 \text{ cm}^{-1}$, $J_{13} = -0.67 \text{ cm}^{-1}$, $\alpha = 0.42$, $S_T = 2$ ground.

Fit (c) was better than (a) and (b) between 10–120 K but worse below 6 K (Fig. 5(b)). It is possible that the small discrepancy below 6 K arises through trimer–trimer interactions. Variable field magnetisation isotherms ($T = 2$ –20 K, $H = 0$ –5 T) were measured to help to identify the S_T ground state. Saturation in M is not complete even at 2 K and 5 T.

Calculation of the M versus H plots at 2 K and 0–5 T using the parameter sets (a) to (c) gave the worst agreement for set (c) with calculated M values being

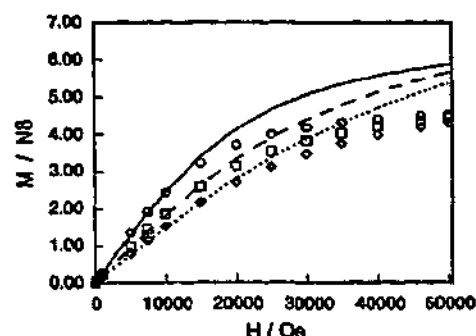


Fig. 6. Plots of isothermal (2, 3, 4 K) magnetisation data vs. field, H , for complex 1. Calculated lines ($\cdots$ 2 K, $\cdots$ 3 K, $\cdots$ 4 K) use parameter set (a) given in the text and the spin Hamiltonian given, which does not include zero-field splitting terms.

bigger than observed at all temperature and field combinations. Sets (a) and (b) gave similar calculated values and showed good agreement for the three temperatures with fields between 0–1.5 T but with calculated M values greater than those observed above 1.5 T (Fig. 6). It is interesting to note that the 2 K/5 T calculated values of M are significantly greater than $4N\beta$ anticipated for $S_T = 2$ lowest in energy because of thermal population of the $S_T = 3$ and $S_T = 1$ Zeeman levels close by. In summary, the α value appears to be close to 0.5, the crossover point of $S_T = 1$ and 2. The discrepancies between observed and calculated M values above fields of 1.5 T are most likely because of zero-field splitting effects combined with Zeeman effects from closely spaced S_T levels. There is not an isolated S_T ground state for complex 1 and so further attempts to calculate D values have not been made. Plots of observed M versus H/T (K), either isothermal (2–20 K) or isofield [17,18], show non-superposition of the lines and are thus indicative of zero-field splitting effects. Weak trimer–trimer effects may also play a minor part in the higher field regimes.

The J_{12} value for 1 of $\sim -1 \text{ cm}^{-1}$, which results from $\text{Mn(III)}\text{--O--N(R)}\text{--Mn(II)}$ superexchange pathways can be compared with the related nitoximato- and dimethylglyoximato-bridging in the work of Birkelbach et al. [38,39] in which J_{12} was $+4.7 \text{ cm}^{-1}$ (with $J_{13} = -3.0 \text{ cm}^{-1}$). The difference in sign of J_{12} results from the net effects of the ferromagnetic and antiferromagnetic contributions to J_{12} which, in turn, will be influenced by subtle coordination differences on the Mn(III) and Mn(II) centres and, to a lesser degree by the terminal binding groups. These structural differences have been described above in Section 3.2.1.

3.3.2. $(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ (2)

Two fresh samples were measured and very similar μ_{eff} (per Mn_4) data were obtained when measured in a

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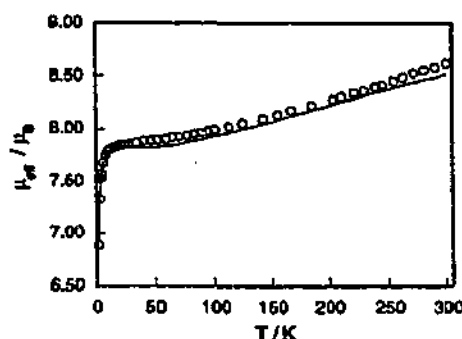


Fig. 7. Plot of observed μ_{eff} data for complex 2 (2–300 K, $H = 1$ T). Best-fit calculated line obtained using the parameter set given in the text.

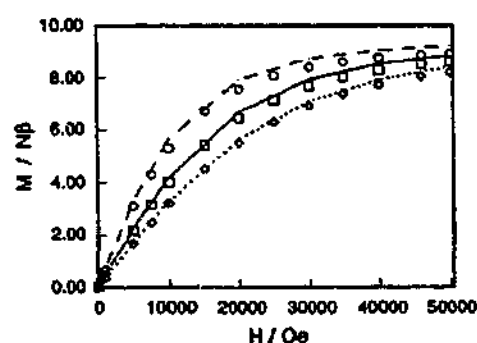
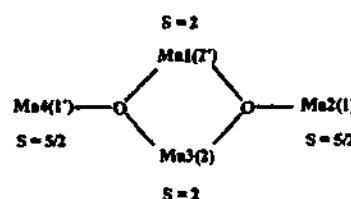


Fig. 8. Plots of isothermal (2, 3, 4 K) magnetisation data vs. field, H , for complex 2. Calculated lines (— 2 K, --- 3 K, 4 K) use the parameter set given in the text and in Table 4. The kinks in the calculated curves reflect the number of calculated points used in the plotting routine.

field of 1 T and dispersed in Vaseline to prevent torquing. The moment decreases, gradually, from $8.65\mu_{\text{B}}$ at 300 K to reach a plateau value of $\sim 7.8\mu_{\text{B}}$ between 50–100 K, then more rapidly reaching $6.85\mu_{\text{B}}$ at 2 K and still decreasing (Fig. 7). The spin-only value for

two Mn(III) ($S = 2$) plus two Mn(II) ($S = 5/2$) of $\mu = 10.86\mu_{\text{B}}$ is bigger than the observed value at 300 K. Thus antiferromagnetic coupling is occurring. The 'butterfly' tetranuclear arrangement of spins, with two Mn(III)(2,2') in the body positions and two Mn(II)(1,1') at the wingtips was employed in the $(-2J_1 - S_2)$ spin Hamiltonian [17,18,41] with the spin centres numbered as follows.



The Kambe vector coupling approach has been described for this spin combination [17,18,41]. There are 110 possible spin states with S_T , the total spin of the cluster, varying from 0 to 9. We use the field-dependent thermodynamic form of susceptibility, in combination with matrix diagonalisation methods, to fit the susceptibility data.

The best-fit to the data is obtained for the parameter set $g = 1.88$, $J_{12} = -2.5 \text{ cm}^{-1}$, $J_{13} = -46.0 \text{ cm}^{-1}$, $\alpha = J_{13}/J_{12} = 18.4$, $J_{24} = 0$. These parameters also give good agreement with the 2, 3 and 4 T magnetisation isotherms (Fig. 8). Interestingly, the ground state under these conditions, viz $\alpha > 6$, J_{12} and J_{13} negative and with J_{13} large, is made up of the six degenerate levels $S_T = 0, 1, 2, 3, 4, 5$ and they correspond to $S_{13} = 0$. Introduction of a tiny J_{24} value of -0.02 cm^{-1} has only a minimal effect on the quality of fit. Larger J_{24} values such as $\pm 0.1 \text{ cm}^{-1}$, which correspond to splitting up of the six S_T levels, lead to much poorer fits. Thus, " " not have an isolated S_T ground level in 2 and plots of M versus H/T temperature, much used by Hendrickson and Christou [17,18] to show zero-field splitting of isolated ground states, yield isofield lines all superimposed on each other thus indicating a lack of zero-field splitting.

Table 4

Comparison of J values (cm^{-1}) and ground spin states for $\text{Mn(II)}_2\text{Mn(III)}_2$ planar rhomboidal cores where $\text{Mn}_1 = \text{Mn}_3 = \text{Mn(II)}$ at body sites

Cluster	J_{12}	J_{13}	$\alpha = J_{13}/J_{12}$	g	Ground S_T	References
2	-2.5	-46.0	18.4	1.88	0–5 ^d	^e
$\text{Mn}_4\text{O}_2(\text{O}_2\text{CCH}_3)_6(\text{bipy})_2$ ^a	-1.97	-3.12	1.59	1.70	2	[42]
$\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_6(\text{OEt})_2$	-1.50	-2.80	1.89	1.47	2	[43]
$[\text{Mn}_4(\text{O}_2\text{CCH}_3)_2(\text{pdmH})_4](\text{ClO}_4)_2$ ^b	+0.20	+4.05	20.4	1.84	8 ± 1	[17]
$[\text{Mn}_4(\text{O}_2\text{CCH}_3)_2(\text{pdmH})_4] \cdot 2.5\text{H}_2\text{O}$	+0.55	+4.35	7.94	1.89	9	[17]
$[\text{Mn}_4(\text{hmp})_4\text{Br}_2(\text{H}_2\text{O})_2]\text{Br}_2 \cdot 4\text{H}_2\text{O}$ ^c	+0.47	+4.42	9.43	1.94	9	[18]

^a bipy = 2,2'-bipyridine.

^b pdmH⁻ = monoanion of pyridine-2,6-dimethanol.

^c hmp⁻ = anion of 2-hydroxymethylpyridine.

^d Six degenerate levels.

^e This work.

The J values and ground S_T states for other recently reported $Mn(II)_2Mn(III)_2$ planar-rhomboidal compounds are compared with those of **2** in Table 4. The first three compounds have μ_3 -oxo bridges and J_{13} (body–body $Mn(III)\cdots Mn(III)$) is much more negative for complex **2** than for the others. The μ_3 -phenoxo bridged compounds containing $pdmH^-$ and hmp^- ligands show ferromagnetic J_{12} and J_{13} values possibly because of the nature of the orbital overlap involving the phenoxo oxygen. These J values lead to large S_T ground state values with negative zero-field splitting. Such features are prerequisites for single-molecule magnetic (SMM) behaviour and this was confirmed for these molecules by observing frequency dependent out-of-phase components χ''_M . We would predict that complex **2** should not exhibit SMM behaviour because of a lack of zero-field splitting. Measurements of the AC χ''_M values versus temperature (2–10 K; oscillation frequencies 10, 50, 100, 250, 500, 1500 Hz; AC field amplitude 3.5 Oe) showed no maximum in this temperature range and thus **2** does not display SMM behaviour.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre. CCDC Nos. 190372 and 190373. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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APPENDIX 3: CRYSTALLOGRAPHIC INFORMATION

CD-ROM

The code for each crystal structure gives the file stem for each of the SHELX-97 refinement files on the attached CD-ROM.

CHAPTER 2

Compound	File stem
$[\text{Mn}(\text{dca})_2(\text{H}_2\text{O})]$	dp4_dos
$[\text{Mn}(\text{dca})(\text{NO}_3)(\text{terpy})]_n$	dp14v2
$\{[\text{Mn}(\text{dca})(\text{H}_2\text{O})(\text{terpy})](\text{dca})\}_n$	dp13v2

CHAPTER 3

Compound	File stem
$[\text{Mn}(\text{salen})(\text{dca})]_n$	dp07v2
$[\text{Fe}(\text{salen})(\text{dca})]_n$	tc01
$[\text{Mn}(\text{sal-}o\text{-phen})(\text{dca})]_n$	dp44
$[\text{Fe}(\text{sal-}o\text{-phen})(\text{dca})]_n$	dp17
$[\text{Mn}((\pm)\text{-saltch})(\text{dca})]_n$	dp27
$[\text{Fe}((\pm)\text{-saltch})(\text{dca})]_n$	db02v2

CHAPTER 4

Compound	File stem
[Mn(acenH ₂)(dca) ₂]	dp09v8ba
[Fe(acenH ₂)(dca) ₂]	dp10v2a
[Mn(actchH ₂)(dca) ₂]	dp16v2
[Fe(actchH ₂)(dca) ₂]	dp15
<i>trans</i> -[Mn(acenH ₂) ₂ (denm) ₂]	dp11v4a

CHAPTER 5

Compound	File stem
Ph ₄ P[Co(dca) ₂ NO ₂] $\cdot$ MeCN	dp06abs
Ph ₄ P[Ni(dca) ₂ NO ₂] $\cdot$ MeCN	dp18ov2
Ph ₄ P[Co(dca)Br ₂]	dp36v1

CHAPTER 6

Compound	File stem
{[Mn(μ -OH)(μ -OAc) ₂] $\cdot$ HOAc $\cdot$ H ₂ O} _n }	dp29av5

CHAPTER 7

Compound	File stem
[Mn ₁₆ O ₁₆ (OMe) ₆ (OAc) ₁₆ (MeOH) ₃ (H ₂ O) ₃] $\cdot$ 6H ₂ O	dp24v2
[Mn(μ -OMe)(μ -OAc) ₂] _n	dp26

CHAPTER 9

Compound	File stem
$[\text{Mn}_3(\text{mcoe})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$	dp41v2
$(\text{Me}_4\text{N})_2[\text{Mn}_4\text{O}_2(\text{cao})_4(\text{MeCN})_2(\text{H}_2\text{O})_6](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$	dp21atst
$[\text{Ni}(\text{cao})_2(\text{H}_2\text{O})_2]$	dp01v3
$[\text{Cu}(\text{mcoe})_2(\text{MeOH})_2]$	dp9dos