Mono- vs. bi-metallic assembly on a bulky bis(imino)terpyridine framework: a combined experimental and theoretical study

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The bis(imino)terpyridine ligands, 6,6'-{(2,6-*i*-Pr₂C₆H₃)N=CR}₂-2,2':6',2''-C₁₅H₉N₃ (R = H **L1**, Me **L2**), have been prepared in high yield from the condensation reaction of the corresponding carbonyl compound with two equivalents of 2,6-diisopropylaniline. The molecular structure of **L2** reveals a transoid relationship between the imino and pyridyl nitrogen groups throughout the ligand framework. Treatment of aldimine-containing **L1** with one equivalent or an excess of MX₂ in *n*-BuOH at 110 °C gives the mononuclear five-coordinate complexes, [(**L1**)MX₂] (M = Fe, X = Cl **1a**; M = Ni, X = Br **1b**; M = Zn, X = Cl **1c**), in which the metal centre occupies the terpyridine cavity and the imino groups pendant. Conversely, reaction of ketimine-containing **L2** with excess MX₂ in *n*-BuOH at 110 °C affords the binuclear complexes, [(**L2**)M₂X₄] (M = Fe, X = Cl **3a**; M = Ni, X = Br **3b**; M = Zn, X = Cl **3c**), in which one metal centre occupies a bidentate pyridylimine cavity while the other a tridentate bipyridylimine cavity. ¹H NMR studies on diamagnetic **3c** suggests a fluxional process is operational at ambient temperature in which the central pyridine ring undergoes an exchange between metal coordination. Under less forcing conditions (room temperature in dichloromethane), the monometallic counterpart of **1b** [(**L2**)NiBr₂] (**2b**) has been isolated which can be converted to **3b** by addition of one equivalent of (DME)NiBr₂ (DME = 1,2-dimethoxyethane) in *n*-BuOH at 110 °C. Quantum mechanical calculations (DFT) have been performed on [(**L1**)ZnCl₂] and [(**L2**)ZnCl₂] for different monometallic conformations and show that **1a** is the energetically preferred structure for **L1** while there is evidence for dynamic behaviour in **L2**-containing species leading to bimetallic formation. Single-crystal X-ray diffraction studies have been performed on **1a**, **1b**, **1c**, **2b**, **3a**, **3b**(H₂O) and **3c**.

1 Introduction

The application of 2,6-linked oligopyridine ligands, C₅H₄N-(C₅H₃N)_{*n*}-C₅H₄N (*n* = 2–7), in coordination chemistry is now well established with mono-, double- or triple-stranded helicates being a feature of the structural types.¹ For example quinquepyridine (*n* = 3) can readily form homobimetallic salts of the type [(quinquepyridine)₂M₂]²⁺ with a variety of 3d metal ions including cobalt,² nickel³ and copper.⁴

We have been interested recently in developing oligopyridine ligands featuring sterically demanding imino end-groups, ArN=CR(C₅H₃N)_{*n*}CR=NAr (*n* = 3, 4, 5; Ar = 2,6-substituted aryl group; R = H or hydrocarbyl), and have termed this family of ligands as oligopyridylimines (Fig. 1).⁵ It was envisaged that the steric attributes of these ligands would to some extent inhibit multi-stranded helicate formation and allow access to well-defined polymetallic complexes of the form [(oligopyridylimine)M_{*x*}X_{*y*}] (X = anionic monodentate ligand) that could be amenable to further functionalisation at the metal centres and/or for catalytic applications.

Herein we report our efforts at developing the coordination chemistry of the potentially pentadentate (*n* = 3) member of

Fig. 1 Oligopyridylimines (R = H or hydrocarbyl, Ar = aryl).

the family, bis(imino)terpyridine (**Lx**). To the knowledge of the authors, **Lx** has received scarcely any attention as a supporting ligand for binding to transition metals.⁶ Specifically, we focus on the reactivity of 6,6'-{(2,6-*i*-Pr₂C₆H₃)N=CR}₂-2,2':6',2''-C₁₅H₉N₃ (**Lx** = **L1** R = H; **Lx** = **L2** R = Me) towards divalent metal halides of iron, nickel and zinc and pay particular attention to the effect of the imino-carbon substituent R on the nuclearity of the product. Furthermore, DFT calculations are used to support and complement the synthetic work.

2 Results and discussion

(a) Syntheses of the ligands

The ligands 6,6'-{(2,6-*i*-Pr₂C₆H₃)N=CR}₂-2,2':6',2''-C₁₅H₉N₃ (R = H **L1**, R = Me **L2**) were synthesised in good yield by the acid catalysed condensation reaction of 6,6'-bis-formyl-2,2':6',2''-terpyridine^{5,7} and 6,6'-bis-acetyl-2,2':6',2''-terpyridine⁵ with two equivalents of 2,6-diisopropylaniline in ethanol, respectively (Scheme 1). Alternatively, **L2** can be prepared by carrying out

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Scheme 1 Reagents and conditions: 2 eq. 2,6-*i*-Pr₂C₆H₃NH₂, EtOH, cat. H⁺, heat.

Table 1 Selected bond distances (Å) and angles (°) for **L2**

C(13)–N(1)	1.284(6)	C(18)–C(19)	1.506(6)
C(29)–N(5)	1.255(6)	C(23)–C(24)	1.458(7)
C(29)–N(5)–C(30)	119.8(4)		

the reaction in neat 2,6-diisopropylaniline at elevated temperature over short time periods.⁵ Both ligands have been characterised by IR, ¹H and ¹³C NMR spectroscopy along with ES mass spectrometry (see Experimental section). **L2** has also been the subject of a single-crystal X-ray diffraction study.

Pale yellow crystals of **L2** suitable for the X-ray determination were grown by the slow evaporation of a dichloromethane solution containing the compound. A view of **L2** is shown in Fig. 2; selected bond distances and angles are listed in Table 1. The structure of **L2** consists of three 2,6-linked pyridine rings with the imino groups occupying the ends of the oligopyridylimine chain. The nitrogen atoms of the pyridine groups adopt a mutually transoid conformation which is also extended to the terminal imine groups in a manner reminiscent of that found in 2,6-oligopyridines.^{1,8} A slight twist [torsion angles: N(1)–C(13)–C(14)–N(2) 1.8°; N(2)–C(18)–C(19)–N(3) 6.9°; N(3)–C(23)–C(24)–N(4) 3.4°; N(4)–C(28)–C(29)–N(5) 3.5°] from planarity is displayed throughout the imine-pyridine backbone as has been observed for **L1**.⁵ The 2,6-diisopropyl substituents on the terminal aryl groups sit above and below the planes of the nearest pyridine units within the chain. The N(1)–C(13) and N(5)–C(29) bond lengths of 1.284(6) and 1.255(6) Å are consistent with their being double bond character. The IR spectra of **L1** and **L2** confirm the presence of the imine with ν(C=N) bands at *ca.* 1645 cm^{−1} which is supported by the ¹³C NMR spectra which show peaks at δ 163.5 (**L1**) and δ 166.1 (**L2**) corresponding to the imino carbon atoms.

(b) Complexation reactions

(i) Reaction of MX₂ with L1. The reaction of **L1** with one equivalent of MX₂ [MX₂ = FeCl₂, (DME)NiBr₂, ZnCl₂] in *n*-butanol at 110 °C gave complexes [(**L1**)MX₂] (M = Fe, X = Cl

1a; M = Ni, X = Br **1b**; M = Zn, X = Cl **1c**) in high yield (Scheme 2). No evidence for bimetallic products was apparent on addition of two equivalents or greater of MX₂ or after stirring for longer periods. All products have been characterised by microanalysis, FAB mass spectrometry, IR spectroscopy and, in the cases of **1a** and **1b**, by magnetic measurements and **1c** by ¹H NMR spectroscopy (see Table 2 and Experimental section). In addition, crystals of **1a**, **1b** and **1c** have been subjected to single-crystal X-ray diffraction studies.

Crystals of **1a**, **1b** and **1c** suitable for the X-ray determinations were grown by slow cooling of hot acetonitrile solutions containing the complexes. The structures of **1a**, **1b** and **1c** are similar and only **1a** will be discussed in any detail. A view of **1a** is depicted in Fig. 3; selected bond distances and angles for **1a**, **1b** and **1c** are listed in Table 3. The molecular structure of **1a** depicts a single iron centre bound by **L1** and two terminal chloride ligands. The metal centre occupies the tridentate terpyridine cavity with the two imine groups pendant and *exo* to the coordinated terpyridine moiety. The geometry at the metal centre can be best described as distorted trigonal bipyramidal with N(2) and N(2A) defining the axial sites [N(2)–Fe(1)–N(2A) 150.8(3)°] and N(3), Cl(1) and Cl(1A) the equatorial ones [N(3)–Fe(1)–Cl(1) 120.99(5); Cl(1)–Fe(1)–Cl(1A) 118.03(9)°]. The complex has molecular C₂ symmetry about an axis containing the metal, the pyridyl–N(3) and C(21) atoms. The central M–N_{pyridyl} distance [2.073(6) Å] is noticeably less than the M–N(2)_{pyridyl} and M–N(2A)_{pyridyl} bond lengths [2.234(5) Å], probably as a consequence of satisfying the tridentate chelating constraint of the ligand and that it occupies a equatorial site within the trigonal bipyramid. The C=N bond distance [1.283(8) Å] is similar to that found in **L2** [av. 1.258 Å].

The FAB mass spectra for **1a–c** show fragmentation peaks corresponding to the loss of one halide group from the corresponding molecular ion peak. The IR spectra for **1a–c** display ν(C=N) bands at *ca.* 1635 cm^{−1} and in a similar region to that for free **L1**, supporting the pendant nature of the imino groups. Complexes **1a** and **1b** are paramagnetic and display magnetic moments of 5.3 and 2.8 μ_B (Evans Balance at ambient temperature) which are consistent with high spin configurations possessing four and two unpaired electrons, respectively. In contrast, complex **1c** is

Fig. 2 Molecular structure of **L2** including the atom numbering scheme.

Scheme 2 Reagents and conditions: (i) 1 eq. or xs. MX_2 [$\text{MX}_2 = \text{FeCl}_2, (\text{DME})\text{NiBr}_2, \text{ZnCl}_2$], *n*-BuOH, 110 °C; (ii) 1 eq. $(\text{DME})\text{NiBr}_2$, CH_2Cl_2 , RT; (iii) 2 eq. MX_2 [$\text{MX}_2 = \text{FeCl}_2, (\text{DME})\text{NiBr}_2, \text{ZnCl}_2$], *n*-BuOH, 110 °C; (iv) 1 eq. $(\text{DME})\text{NiBr}_2$, *n*-BuOH, 110 °C; (v) $\text{CHCl}_3/\text{H}_2\text{O}$, RT (Ar = 2,6-*i*-Pr₂C₆H₃).

Table 2 Characterisation data for the new complexes **1**–**3**

Compound	Colour	$\nu(\text{C}=\text{N})^a/\text{cm}^{-1}$	μ_{eff}^b/μ_B	$^1\text{H NMR}^c$ (δ)	FAB mass
1a	Brown	1635	5.3	<i>d</i>	733 $[\text{M}]^+$, 698 $[\text{M} - \text{Cl}]^+$
1b	Yellow	1640	2.8	<i>d</i>	746 $[\text{M} - \text{Br}]^+$, 665 $[\text{M} - 2\text{Br}]^+$
1c	Yellow	1638	<i>e</i>	1.49 (d, 24H, $^3J_{\text{HH}}$ 6.7 Hz, $\text{CH}(\text{CH}_3)_2$), 3.06 (sept, 4H, $^3J_{\text{HH}}$ 6.7 Hz, $\text{CH}(\text{CH}_3)_2$), 7.07 (m, 6H, ArH), 8.10 (dd, 2H, $^3J_{\text{HH}}$ 7.6 Hz, 7.9 Hz, PyH), 8.21 (d, 2H, $^3J_{\text{HH}}$ 7.6 Hz, PyH), 8.28 (m, 3H, PyH), 8.60 (d, 2H, $^3J_{\text{HH}}$ 7.9 Hz, PyH), 9.30 (s, 2H, HCN)	744 $[\text{M}]^+$, 706 $[\text{M} - \text{Cl}]^+$, 669 $[\text{M} - 2\text{Cl}]^+$
2b	Yellow	1594, 1630	2.4	<i>d</i>	774 $[\text{M} - \text{Br}]^+$, 693 $[\text{M} - 2\text{Br}]^+$
3a	Brown	1592	7.0	<i>d</i>	854 $[\text{M} - \text{Cl}]^+$, 817 $[\text{M} - 2\text{Cl}]^+$
3b	Orange	1591	4.3	<i>d</i>	992 $[\text{M} - \text{Br}]^+$, 913 $[\text{M} - 2\text{Br}]^+$
3c	Yellow	1590	<i>e</i>	0.93 (d, 12H, $^3J_{\text{HH}}$ 7.0 Hz, $\text{CH}(\text{CH}_3)_2$), 1.17 (d, 12H, $^3J_{\text{HH}}$ 6.4 Hz, $\text{CH}(\text{CH}_3)_2$), 2.31 (s, 6H, CH_3CN), 3.06 (sept, 4H, $^3J_{\text{HH}}$ 6.7 Hz, $\text{CH}(\text{CH}_3)_2$), 7.12 (m, 6H, ArH), 8.08 (d, 2H, $^3J_{\text{HH}}$ 7.9 Hz, PyH), 8.24 (dd, 1H, $^3J_{\text{HH}}$ 7.9, $^3J_{\text{HH}}$ 7.6 Hz, PyH), 8.31 (dd, 2H, $^3J_{\text{HH}}$ 7.9, $^3J_{\text{HH}}$ 7.9 Hz, PyH), 8.45 (d, 2H, $^3J_{\text{HH}}$ 7.6 Hz, PyH), 8.68 (d, 2H, $^3J_{\text{HH}}$ 7.9 Hz, PyH)	872 $[\text{M} - \text{Cl}]^+$, 837 $[\text{M} - 2\text{Cl}]^+$, 734 $[\text{M} - 2\text{Cl} - \text{Zn}]^+$

^a Recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer on solid samples. ^b Recorded on an Evans Balance at room temperature. ^c Recorded in CDCl_3 solution at room temperature. ^d Broad paramagnetically shifted resonances. ^e Diamagnetic.

diamagnetic and exhibits a $^1\text{H NMR}$ spectrum (in CDCl_3 at ambient temperature) that is consistent with the molecular C_2 symmetry observed in the solid state with five signals for the pyridyl protons. In comparison with **L1**, the signals are slightly shifted with, for example, the singlet for the $\text{CH}=\text{N}$ protons in **L1** (δ 8.36) being shifted by *ca.* 1 ppm downfield in **1c** (δ 9.30). The $^1\text{H NMR}$ spectra for paramagnetic **1a** and **1b** were broad and uninformative.

(ii) Reaction of MX_2 with **L2.** The reaction of **L2** with two equivalents of MX_2 [$\text{MX}_2 = \text{FeCl}_2, (\text{DME})\text{NiBr}_2, \text{ZnCl}_2$] in *n*-butanol at elevated temperatures gave complexes $[(\text{L2})\text{M}_2\text{X}_4]$ (M = Fe, X = Cl **3a**; M = Ni, X = Br **3b**; M = Zn, X = Cl **3c**) in high yield (Scheme 2). No evidence for monometallic products was apparent under these experimental conditions nor when one equivalent of MX_2 was employed. All products have been characterised by FAB mass spectrometry, IR spectroscopy and, in the cases of **3a** and **3b**,

Table 3 Selected bond distances (Å) and angles (°) for **1a**, **1b** and **1c**

	1a (M = Fe, X = Cl)	1b (M = Ni, X = Br)	1c (M = Zn, X = Cl)
M(1)–N(2)	2.234(5)	2.110(6)	2.242(7)
M(1)–N(3)	2.073(6)	1.982(6)	2.036(8)
M(1)–N(2A)	2.234(5)	2.110(6)	2.242(7)
M(1)–X(1)	2.2889(17)	2.3919(9)	2.247(2)
M(1)–X(1A)	2.2889(17)	2.3919(9)	2.247(2)
C(13)–N(1)	1.283(8)	1.251(9)	1.278(12)
N(2)–M(1)–N(3)	75.42(13)	78.33(13)	76.16(18)
N(2)–M(1)–N(2A)	150.8(3)	156.7(3)	152.3(4)
X(1)–M(1)–X(1A)	118.03(9)	129.51(6)	119.10(14)
X(1)–M(1)–N(2)	93.50(13)	91.76(15)	93.71(18)
X(1)–M(1)–N(3)	120.99(5)	115.24(3)	120.45(7)
X(1)–M(1)–N(2A)	101.42(14)	98.15(15)	100.24(19)

Atoms with suffix A are generated by symmetry.

Fig. 3 Molecular structure of **1a**; the atoms labelled with an additional A are generated by symmetry ($1 - x, -y, z$). All hydrogen atoms, apart from H13, have been omitted for clarity.

by magnetic measurements and for **3c** by ^1H NMR spectroscopy (see Table 2 and Experimental section). In addition, crystals of **3a** and **3c** have been the subject of single-crystal X-ray diffraction studies.

Crystals of **3a** and **3c** were grown by slow cooling of hot acetonitrile solutions of the corresponding complexes. The structures of **3a** and **3c** are essentially the same and will be discussed together. A view of **3c** is depicted in Fig. 4; selected bond distances and angles are listed for both **3a** and **3c** in Table 4. The molecular structures reveal bimetallic complexes in which the two metal centres are supported on the same **L2** ligand frame and each bound terminally by two chloride ligands. One of the metal centres [M(2)] occupies a bidentate pyridylimine pocket while the other [M(1)] a tridentate dipyridylimine cavity so as to generate a tetrahedral geometry at M(2) and a distorted square pyramidal geometry at M(1). Within the ligand frame the pyridylimine and dipyridylimine moieties

are both nearly planar with each of the planes being disposed almost orthogonally to one another [torsion angles: N(3)–C(18)–C(19)–N(4) 91.5° (**3a**), 90.6° (**3c**)]. For M(1) the two M(1)–Cl bond lengths are essentially equivalent [**3a** 2.273(2) vs. 2.281(2) Å; **3c** 2.2254(12) vs. 2.2367(12) Å], while the M(1)–N distances vary with M(1)–N(2) [**3a** 2.061(6) Å; **3c** 2.064(3) Å] being shorter than the M(1)–N(1) [**3a** 2.278(6) Å; **3c** 2.270(3) Å] and the M(1)–N(3) [**3a** 2.267(5) Å; **3c** 2.285(3) Å] bond lengths. At M(2), the M(2)–N_{imine} distance is similar to the M(2)–N_{pyridyl} bond length [**3a** 2.109(5) vs. 2.102(6) Å; **3c** 2.071(3) vs. 2.056(3) Å]. There is no apparent delocalisation of the imino double bond into the adjacent pyridyl group.

Attempted crystallisation of **3b** using the conditions applied for **3a** and **3c** proved unsuccessful. However, by prolonged standing in chloroform adventitious reaction with water occurs to give [(**L2**)Ni₂Br₄(OH₂)] [**3b**(H₂O)] as orange crystals (Scheme 2). The dataset obtained for the single-crystal X-ray determination was, unfortunately, of poor quality. Nevertheless, the structure was unequivocal in revealing a bimetallic species displaying structural features similar to that observed in **3a** and **3c** (*vide supra*) but with one molecule of water additionally bound to the nickel centre [Ni(2)] occupying the bidentate cavity in **L2**. For comparison, Table 4 also contains the corresponding bond lengths and angles for **3b**(H₂O).

The FAB mass spectra for **3a–c** show fragmentation peaks corresponding to the loss of one or two halide groups from the corresponding molecular ion peak. In the IR spectra for **3a–c**, the $\nu(\text{C}=\text{N})$ bands are seen at *ca.* 1590 cm^{-1} (in both solid and solution state) and shifted to a lower wavenumber by *ca.* 52 cm^{-1} in comparison with the free ligand **L2**; supporting coordination of both imine groups. Complexes **3a** and **3b** are paramagnetic and display magnetic moments of 7.0 μ_{B} and 4.3 μ_{B} (Evans Balance at ambient temperature) which are consistent with non-spin coupled Fe(II) ($S = 2$)–Fe(II) ($S = 2$) and Ni(II) ($S = 1$)–Ni(II) ($S = 1$) systems (using $\mu^2 = \sum \mu_i^2$, where μ_i is the magnetic moment of the individual metal centres).⁹

The ^1H NMR spectrum of **3c** in CDCl_3 (at ambient temperature) indicates that the molecule has average C_2 symmetry in solution with only five resonances for the pyridyl hydrogen atoms occurring at δ 8.08, 8.24, 8.31, 8.45 and 8.68. In addition, there is only one resonance for the methyl protons on the imine groups. Attempts to lower the symmetry by recording the spectrum at lower

Table 4 Selected bond distances (Å) and angles (°) for **3a**, **3b**(H₂O) and **3c**

	3a (M = Fe, X = Cl)	3b (H ₂ O) (M = Ni, X = Br)	3c (M = Zn, X = Cl)
M(1)–N(1)	2.278(6)	2.157(17)	2.270(3)
M(1)–N(2)	2.061(6)	1.933(17)	2.064(3)
M(1)–N(3)	2.267(5)	2.192(17)	2.285(3)
M(1)–X(1)	2.273(2)	2.421(4)	2.2254(12)
M(1)–X(2)	2.281(2)	2.394(4)	2.2367(12)
M(2)–N(4)	2.102(6)	2.079(17)	2.056(3)
M(2)–N(5)	2.109(5)	2.036(17)	2.071(3)
Ni(2)–O(1) _{H₂O}	—	2.042(17)	—
M(2)–X(3)	2.221(2)	2.468(4)	2.1848(13)
M(2)–X(4)	2.237(2)	2.427(4)	2.2212(13)
C(7)–N(1)	1.269(9)	1.26(3)	1.289(5)
C(24)–N(5)	1.268(8)	1.38(2)	1.274(5)
N(1)–M(1)–N(2)	73.9(2)	78.0(7)	74.47(13)
N(1)–M(1)–N(3)	149.4(2)	154.0(6)	149.61(12)
X(1)–M(1)–N(1)	95.98(16)	99.5(4)	97.20(9)
X(2)–M(1)–N(1)	101.62(16)	94.8(4)	101.41(9)
X(1)–M(1)–X(2)	131.37(8)	110.29(13)	126.33(4)
X(1)–M(1)–N(2)	115.44(17)	96.5(5)	117.20(10)
N(4)–M(2)–N(5)	77.0(2)	79.1(7)	79.40(13)
N(4)–M(2)–X(3)	119.75(18)	172.3(5)	119.86(10)
N(4)–M(2)–X(4)	103.73(17)	89.3(5)	104.53(10)
N(4)–Ni(2)–O(1) _{H₂O}	—	85.8(7)	—
X(3)–M(2)–X(4)	118.76(9)	95.88(13)	116.80(5)

Fig. 4 Molecular structure of **3c** including the atom numbering scheme. All hydrogen atoms have been omitted for clarity.

temperature were, however, hampered by solubility problems. Scheme 3 indicates a possible fluxional process that could be operating at room temperature in solution in which the central pyridine group could be flipping between metal centre coordination. An alternative explanation may be that the central pyridine nitrogen donor is not coordinated in solution.

With the intent of synthesising monometallic complexes bound by **L2**, the reaction with MX_2 was attempted under milder conditions. Thus, when a cooled dichloromethane solution of (DME)NiBr₂ is treated with one equivalent of **L2** and left to stir overnight at room temperature, the yellow mononuclear complex [(**L2**)NiBr₂] (**2b**) can be obtained in good yield. Attempted

Scheme 3 Possible dynamic process operating for **3**.

isolation of the mononuclear zinc analogue of **2b**, [(**L2**)ZnCl₂] (**2c**), under the same reaction conditions as employed above, proved problematic with **3c** and **L2** being the main species identifiable in the ¹H NMR spectrum. Complex **2b** was characterised by FAB mass spectrometry, IR spectroscopy and by magnetic measurements (see Table 2 and Experimental section). In addition, a crystal of **2b** has been the subject of a single-crystal X-ray diffraction study.

Crystals of **2b** suitable for the X-ray determination were grown by prolonged standing in chloroform. A view of **2b** is shown in Fig. 5; selected bond distances and angles are listed in Table 5. The molecular structure consists of a single nickel atom bound by both **L2** and two terminal bromide ligands. As with its **L1**-containing counterpart, **1b**, the metal centre occupies the terpyridine cavity of the bis(imino)terpyridine ligand. In this case, however, only one of the imino groups is *exo* while the other is *endo* and forms a partial interaction with the nickel centre [Ni(1)⋯N(1) 2.537(2) Å]. The effect of the interaction in comparison with **1b** is two-fold. Firstly, an increase in the Br–Ni–Br angle from 129.51(6)° in **1b** to 172.84(2)° in **2b** occurs so that the nickel assumes a more octahedral geometry in **3b**. Secondly, the occupation of terpyridine cavity is more uneven with the nickel centre more disposed towards

one of the exterior pyridine units than the other [Ni(1)–N(2) 2.040(2) vs. Ni(1)–N(4) 2.316(2) Å], while the central pyridine remains strongly bound [Ni(1)–N(3) 1.982(2) Å]. The effect of partial coordination on the C–N double bond length in the imine is minimal.

The FAB mass spectrum for **2b** shows fragmentation peaks corresponding to the loss of one or two bromide groups from the molecular ion peak. In the IR spectra for **2b**, ν(C=N) bands at 1594 and 1630 cm^{−1} support the presence of both bound and free imino groups, respectively. As with **1b**, **2b** is paramagnetic exhibiting a magnetic moment of 2.4 μ_B (Evans Balance at ambient temperature) which is consistent with presence of two unpaired electrons.

Conversion of yellow **2b** to orange **3b** can be achieved in good yield by treating **2b** with one equivalent of (DME)NiBr₂ in *n*-butanol at 110 °C for 30 min (Scheme 2). Similarly, **2b** could be converted to **3b** on refluxing **2b** with one equivalent of (DME)NiBr₂ in dichloromethane for two days, these conditions also proving successful for the preparation of **3b** directly from **L2**.

2.3 Density functional theory calculations

The capacity of **Lx**, depending on the nature of the imino-carbon substituent, to have a selectivity for the number of metal(II) halide units it binds was unexpected. Although it could be argued that differences in electronic properties within the two ligand manifolds (*e.g.*, donor capability of the nitrogen donors within **Lx** is expected to follow the order: pyridine > ketimine > aldimine¹⁰) should be influential, such a dramatic change in binding affinity was nevertheless surprising. Therefore, a theoretical study on the relative stability of mononuclear [(**L2**)MX₂] and [(**L1**)MX₂] was carried out in order to investigate in more detail the energetic properties of these systems. Specifically, density functional calculations have been performed on ZnCl₂-containing complexes and is likely, given the similarity of the experimental results, to be representative of the other metal halide systems employed in this work.

For both **L1** and **L2**, B3LYP calculations have been undertaken on mono-zinc dichloride species in conformations **1_{Lx}** and **2_{Lx}** (Fig. 6) which are based on the conformations adopted in structurally determined **1c** and **2b**. In addition, hypothetical species **4_{Lx}** derived from the removal of one zinc dichloride unit from the bidentate pocket in bimetallic **3c** are also studied. As **1c** is the only monometallic ZnCl₂ structure characterised by X-ray diffraction, it was used to test our theoretical approach. For this configuration, theoretical (**1_{L1}**) and experimental (**1c**) structures are in good agreement with the discrepancies found being less than 0.07 Å for the bond lengths and 10° for the angles (see Tables 3 and 6). The coordinated terpyridine portion of the ligand remains planar with an out of plane displacement of 0.03 and 0.05 Å for the theoretical and experimental structures, respectively [Fig. 7(ii)]. It is likely that any discrepancies can be attributed to the vacuum conditions of the calculations. Therefore, it was viewed that this initial study demonstrated that using the B3LYP functional with our basis set is viable for studying such large systems. To extend the investigation, we have applied this theoretical approach to mono-zinc complexes that have not been characterised crystallographically.

Fig. 5 Molecular structure of **2b** including the atom numbering scheme. All hydrogen atoms have been omitted for clarity.

Table 5 Selected bond distances (Å) and angles (°) for **2b**

Ni(1)⋯N(1)	2.537(2)	Ni(1)–Br(1)	2.4827(7)
Ni(1)–N(2)	2.040(2)	Ni(1)–Br(2)	2.4780(7)
Ni(1)–N(3)	1.982(2)	N(1)–C(13)	1.269(4)
Ni(1)–N(4)	2.316(2)	N(5)–C(29)	1.277(4)
N(2)–Ni(1)–N(3)	79.76(10)	N(2)–Ni(1)–Br(1)	93.04(7)
N(3)–Ni(1)–Br(2)	92.49(7)	N(2)–Ni(1)–N(4)	156.26(9)
N(3)–Ni(1)–N(4)	76.51(9)	N(4)–Ni(1)–Br(1)	86.80(6)
N(3)–Ni(1)–Br(1)	90.81(7)	N(4)–Ni(1)–Br(2)	87.78(6)
N(2)–Ni(1)–Br(2)	93.80(7)	Br(2)–Ni(1)–Br(1)	172.84(2)

Table 6 Selected calculated bond distances (Å) and angles (°) for [(L1)ZnCl₂] and [(L2)ZnCl₂] in types-1, -2 and -4 conformations

Conformation based on 1c			Conformation based on 2b			Conformation based on 3c with one ZnCl ₂ unit removed		
	1_{L1}	1_{L2}		2_{L2}	2_{L1}		4_{L2}	4_{L1}
Zn(1)···N(1)	4.68	5.06	Zn(1)–N(1)	2.55	2.70	Zn(1)–N(1)	2.35	2.39
Zn(1)–N(2)	2.29	2.42	Zn(1)–N(2)	2.22	2.26	Zn(1)–N(2)	2.18	2.18
Zn(1)–N(3)	2.17	2.12	Zn(1)–N(3)	2.21	2.24	Zn(1)–N(3)	2.38	2.37
Zn(1)–N(2A)	2.29	2.41	Zn(1)–N(4)	2.54	2.44	Zn(1)–Cl(1)	2.35	2.35
Zn(1)···N(1A)	4.68	5.06	Zn(1)···N(5)	5.15	4.80	Zn(1)–Cl(2)	2.30	2.30
Zn(1)–Cl(1)	2.33	2.35	Zn(1)–Cl(1)	2.39	2.35	C(7)–N(1) _{imine}	1.29	1.28
Zn(1)–Cl(1A)	2.33	2.32	Zn(1)–Cl(2)	2.40	2.36	C(24)–N(5) _{imine}	1.28	1.28
C(13)–N(1) _{imine}	1.29	1.29	C(13)–N(1) _{imine}	1.29	1.28			
C(13A)–N(1A) _{imine}	1.28	1.29	C(29)–N(5) _{imine}	1.28	1.29			
N(2)–Zn(1)–N(3)	74.1	75.6	N(2)–Zn(1)–N(3)	72.8	74.2	N(1)–Zn(1)–N(2)	72.3	73.2
N(2)–Zn(1)–N(2A)	148.3	151.0	N(2)–Zn(1)–N(4)	146.0	143.7	N(1)–Zn(1)–N(3)	143.5	145.1
Cl(1)–Zn(1)–Cl(1A)	129.0	147.1	Cl(1)–Zn(1)–Cl(2)	168.9	155.0	Cl(1)–Zn(1)–N(1)	98.7	99.4
Cl(1)–Zn(1)···N(1)	78.0	94.9	Cl(1)–Zn(1)–N(1)	92.1	90.8	Cl(2)–Zn(1)–N(1)	95.6	92.3
Cl(1)–Zn(1)–N(2)	96.0	92.0	Cl(1)–Zn(1)–N(2)	92.6	95.8	Cl(1)–Zn(1)–Cl(2)	131.5	135.1
Cl(1)–Zn(1)–N(3)	116.0	94.0	Cl(1)–Zn(1)–N(3)	91.0	97.5	Cl(1)–Zn(1)–N(2)	94.5	96.7
Cl(1)–Zn(1)–N(2A)	97.5	95.7	Cl(1)–Zn(1)–N(4)	88.4	89.1			
Cl(1)–Zn(1)···N(1A)	75.1	95.9	Cl(1)–Zn(1)–N(5)	84.1	76.3			
Cl(1A)–Zn(1)–N(2)	97.5	95.4	Cl(2)–Zn(1)–N(2)	92.8	95.8			
Out of plane displacement ^a	0.03	0.31	Out of plane displacement ^a	0.21	0.37	Out of plane displacement ^b	0.21	0.19

^a Out of plane displacement of the eighteen atoms in the three pyridine moieties. ^b Out of plane displacement of the fifteen atoms in the imino-bipyridine moiety.

Fig. 6 Monometallic zinc conformations to be investigated by DFT including the atom numbering scheme (Ar = 2,6-*i*-Pr₂C₆H₃).

Firstly, **1_{L2}** has been optimised. The resulting structure exhibits a geometry substantially distorted when compared with its counterpart **1_{L1}** [Fig. 7(iii) vs. (ii)]. Inspection of the coordination sphere around zinc in **1_{L2}** indicates that N2 and N2A atoms lie further away from the metal centre [Zn(1)–N(2)/N(2A) 2.42 Å (**1_{L2}**) vs. Zn(1)–N(2)/N(2A) 2.29 Å (**1_{L1}**)] implying that the chelating ability of **L2** in this coordination mode is substantially reduced (Table 6). This observation is likely linked to the steric constraints imposed by the methyl units of the imino-carbon groups which are in close proximity in this conformation [Fig. 7(iii)]. The geometry around the metal is also altered in the fact that both chlorine atoms while equivalent in **1_{L1}** are non-equivalent in **1_{L2}** leading to a distorted structure intermediate between trigonal-bipyramidal and square-based pyramidal. The planarity of the tridentate portion of the ligand is significantly reduced in comparison with **1_{L1}** [out of plane displacement: 0.31 Å (**1_{L2}**) vs. 0.03 Å (**1_{L1}**)]. Overall, a monometallic zinc dichloride species supported by **L2** exhibits a considerable deformation when it is forced to adopt a type-1 conformation.

Secondly, a theoretical study of mono-zinc dichloride complexes bound by respectively **L2** (**2_{L2}**) or **L1** (**2_{L1}**) in conformations adopted in the structurally characterised nickel bromide complex

2b [Fig. 7(iv)], was undertaken. As a first observation, it is noted that the optimised structure of **2_{L2}** does not show any noticeable changes when compared with **2b**, apart from the expected variation in metal–nitrogen distances [Fig. 7(v) vs. (iv) and Tables 5 and 6]. Indeed, **2_{L2}** remains in a distorted octahedral geometry with its four nitrogen donor ligands from **L2** occupying the equatorial sites and the halide ligands axial. Two of the Zn–N distances are elongated [Zn(1)–N(1) 2.55 Å and Zn(1)–N(4) 2.54 Å] indicative of a weaker coordination to the metal centre. In addition, the planarity of the pyridine rings within **L2** is reduced when compared with structurally determined **2b** with an increase in the out of plane displacement evident [0.08 (**2b**) vs. 0.21 Å (**2_{L2}**)]. Nevertheless, based on these observations, it would seem that [(**L2**)ZnCl₂] when adopting a type-2 conformation is structurally possible. By contrast, the optimised structure for [(**L1**)ZnCl₂] (**2_{L1}**) indicates a more distorted geometry than in **2_{L2}** [Fig. 7(vi) vs. (v)]. Although the Zn(1)–N(4) distance is slightly shorter in this complex [2.44 (**2_{L1}**) vs. 2.54 Å (**2_{L2}**)], the Zn(1)–N(1) distance is substantially longer [2.70 Å (**2_{L1}**)] while the out of plane displacement of the pyridine rings is increased further than in **2_{L2}** [0.37 Å (**2_{L1}**) vs. 0.21 Å (**2_{L2}**)]. Indeed, the geometry at metal centre in **2_{L1}** could be

Fig. 7 Calculated structures for $[(L_x)ZnCl_2]$ (1_{Lx} , 2_{Lx} , 4_{Lx}) in conformations based on structurally determined **1c**, **2b** and **3c**. All hydrogen atoms have been omitted for clarity.

described as more five-coordinate than six-coordinate. Therefore, on comparison of the hypothetical zinc complexes 2_{L2} and 2_{L1} , it would seem that the presence of an *endo*-oriented imino group stabilises an octahedral-type conformation in the **L2** system while it leads to a significant structural rearrangement for the **L1** system.

Thirdly, to examine the possibility for equilibration of monometallic species in solution (Scheme 4, *vide supra*) and to probe potential intermediates in the formation of bimetallic species (e.g., **3c**), a hypothetical mono-zinc species has been generated by removing one $ZnCl_2$ molecule from structurally characterised **3c**. Specifically, we have focused on a conformation (4_{L2}), in which the single $ZnCl_2$ unit is bound in the tridentate iminobipyridine pocket within **L2** [N(1), N(2) and N(3)]; the corresponding 4_{L1} has also been studied [Fig. 7(viii) and (ix)]. A structural reorganisation is observed on inspection of the theoretical (4_{Lx}) and experimental structures (**3c**) and consists of a

change of the relative positions of the chloride ligands on the metal centre. This structural rearrangement is linked to a permutation in and out of the medium plane of the N(2)- and N(3)-containing pyridine rings. These changes are most likely due to the absence of a second metal centre and the isolated condition of the complex in the theoretical calculations. The most important feature though, is that both theoretical structures do not produce any noticeable structural discrepancies (see Tables 4 and 6) with a difference in bond lengths of 0.04 Å and in angles of 4.2°.

Several points emerge from inspection of the relative energies of the optimised structures established for the mono-zinc dichloride species, 1_{L1} (**1c**), 1_{L2} , 2_{L2} , 2_{L1} , 4_{L2} and 4_{L1} (Table 7). Firstly, a comparison of the $[(L1)ZnCl_2]$ structures indicates that a conformation based on type-1 is substantially preferred to the other two possible conformations [$\Delta E = 9.56$ (2_{L1}) and 8.75 kcal mol⁻¹ (4_{L1})]. Secondly, all the $[(L2)ZnCl_2]$ structures display energies

Scheme 4 Possible equilibria for $[(L_x)ZnCl_2]$ in solution (Ar = 2,6-*i*-Pr₂C₆H₃; X = halide).

Table 7 Relative potential energies (kcal.mol⁻¹) for [(L1)ZnCl₂] and [(L2)ZnCl₂] in various conformations; calculations have been performed as $\Delta E (E_y - E_{1Lx})$

y	L1	L2
1 _{Lx}	0.0	0.0
2 _{Lx}	9.56	1.21
4 _{Lx}	8.75	-1.32

that are very close to one another with a slightly more stable conformation apparent for 4_{L2} [$\Delta E = 1.21$ (2_{L2}) and -1.32 kcal mol⁻¹ (4_{L2})]. Overall, the data for these species indicate a clear preference for [(L1)ZnCl₂] to exist in a type-1 conformation, while for [(L2)ZnCl₂], the closeness in the relative energies between the different conformations (1_{L2}, 2_{L2}, 4_{L2}) suggests that an equilibrium is likely in the gas phase but with a slight preference towards 4_{L2}. It is worthy of note that for both ligands the type-2 conformation is the least stable of all although, given the accuracy of the theoretical method employed, the significance of this inference should be treated with some caution. However, the isolation and structural characterisation only in the case NiBr₂ derivative 2b suggests that the nature of the halide group may have a stabilising influence for this particular conformation. This will be the subject of further study elsewhere.

In summary, the density functional study carried out on the monometallic ZnCl₂ species with L1 and L2 as the ligand frame supports the experimental observations and indicates that the nature of the substituent on the imino-carbon moiety has a dramatic effect on the stability of the monometallic species. Several points emerge from the study. Firstly, it is apparent that the difference in the stability of species adopting conformation 1_{Lx} is mainly steric in origin which in turn directly influences the chelating properties around the metal. In the case of L1 steric interactions are minimised while good coordination within the terpyridine moiety is maximised. This stability allied with the substantial reduction of the solvent accessibility to the metal centre in this conformation would appear to suggest why 1_{L1} (1c) does not react with a further molecule of ZnCl₂ to form a bimetallic complex. Secondly, for L2, all three conformations 1_{L2}, 2_{L2} and 4_{L2} are distorted and can be considered as isoenergetic. These two points together indicate that an equilibrium could be operational in solution for L2 but not for L1 (Scheme 4). It would be expected, therefore, that further addition of a molecule of ZnCl₂ to [(L2)ZnCl₂] would drive the equilibrium towards the right hand side and allow occupation of the bidentate pocket in 4 to furnish bimetallic complex 3.

3 Conclusions

The bulky bis(imino)terpyridine ligand Lx has been used as an effective scaffold to support one or two metal(II) halide units. The nature of the imino-carbon substituent is found to have an effect on the number of metal halide units the ligand can bind with the aldimine ligand L1 showing a strong preference for a single unit while the ketimine L2 has the capacity to bind one or two metal centres. These experimental results have been further complemented by DFT calculations which reveal that a significant energy gap is apparent for L1-containing systems leading to a stabilised conformation of type-1 and also suggests that dynamic

behaviour is likely for L2-supported species leading to bimetallic formation.

4 Experimental

4.1 General

All reactions, unless otherwise stated, were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques or in a nitrogen purged glovebox. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use.¹¹ The IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer on solid samples. The ES and the FAB mass spectra were recorded using a micromass Quattro LC mass spectrometer and a Kratos Concept spectrometer with methanol or NBA as the matrix respectively. Accurate Mass FABMS were recorded on Kratos Concept spectrometer (xenon gas, 7 kV) with NBA as matrix. ¹H and ¹³C NMR spectra were recorded on a Bruker ARX spectrometer (250 or 300 MHz); chemical shifts (δ) are referred to the residual protic solvent peaks. Magnetic Susceptibility studies were performed using an Evans Balance (Johnson Matthey) at room temperature. The magnetic moments were calculated following standard methods¹² and corrections for underlying diamagnetism were applied to the data.¹³ Elemental analyses were performed at the Science Technical Support Unit, London Metropolitan University.

The metal dichlorides and (DME)NiBr₂ (DME = 1,2-dimethoxyethane) were purchased from Aldrich Chemical Co. and used without further purification while 2,6-diisopropylaniline was distilled prior to use. The compounds, 6,6'-bis-formyl-2,2':6',2''-terpyridine^{5,7} and 6,6'-bis-acetyl-2,2':6',2''-terpyridine⁵ were prepared according to previously reported procedures. All other chemicals were obtained commercially and used without further purification.

4.2 Synthesis of 6,6'-bis(iminoformyl)-2,2':6',2''-terpyridine-bis(2,6-diisopropylanil) (L1)

6,6'-Diformyl-2,2':6',2''-terpyridine (1.031 g, 3.57 mmol) was suspended in absolute ethanol (20 ml) and 2,6-diisopropylaniline (1.390 g, 7.85 mmol, 2.2 eq.) introduced along with a catalytic amount of glacial acetic acid. The mixture was stirred and heated vigorously at 60 °C for 12 h. The solution was cooled and the resulting precipitate collected by filtration and washed with ethanol (60 ml). The residue was crystallised from a dichloromethane-hexane (1 : 9) mixture at room temperature and the crystalline material filtered, washed with hexane and dried under vacuum to afford 6,6'-{(2,6-*i*-Pr₂C₆H₃)N=CH}₂-2,2':6',2''-C₁₅H₉N₃ (L1) as a pale yellow solid. Yield: 1.411 g, 65%. Anal. Calc. for C₄₁H₄₅N₃·0.5H₂O: C, 79.87; H, 7.46; N, 11.36%. Found: C, 79.62; H, 7.63; N, 10.81%. ¹H NMR (300 MHz, CDCl₃): δ 1.14 (d, ³J_{H-H} 7.0, 24H, CH(CH₃)₂), 2.92 (sept, ³J_{H-H} 7.0, 4H, CH(CH₃)₂), 7.03–7.16 (m, 6H, Ar–H), 7.91 (app. t, ³J_{H-H} 7.6, ³J_{H-H} 7.6, 1H, Py–H), 7.96 (app. t, ³J_{H-H} 7.9, ³J_{H-H} 7.9, 2H, Py–H), 8.29 (d, ³J_{H-H} 7.6, 2H, Py–H), 8.36 (s, 2H, HC=N), 8.52 (d, ³J_{H-H} 7.9, 2H, Py–H) and 8.71 (d, ³J_{H-H} 7.6, 2H, Py–H). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ 23.5 (CH₃), 28.0 (CH), 121.1 (Py), 121.4 (Py), 122.7 (Py), 122.8 (Py), 123.1 (Ar), 124.5 (Ar), 137.3 (Py), 137.6 (Py), 148.6 (Ar), 154.0 (Ar), 155.0 (Py), 156.1 (Py) and 163.5 (C=N). IR (cm⁻¹): 2952(m),

1648(m, $\nu(\text{C}=\text{N})$), 1563(s), 1434(s), 1361(w), 1190(w), 1115(s), 795(s), 786(s) and 760(s). ESI positive mass spectrum (m/z): 608 [$(\text{M} + \text{H})^+$]. Acc. Mass FABMS positive spectrum (m/z): required for ($\text{C}_{43}\text{H}_{49}\text{N}_5\text{H}^+$) 608.37532. Found 608.37532. Mp 220–222 °C.

4.3 Synthesis of 6,6''-bis(iminoacetyl)-2,2':6',2''-terpyridine-bis(2,6-diisopropylanil) (L2)

6,6''-Diacetyl-2,2':6',2''-terpyridine (1.00 g, 3.15 mmol) was suspended in absolute ethanol (16 ml) and 2,6-diisopropylaniline (1.228 g, 6.94 mmol, 2.2 eq.) introduced along with a catalytic amount of formic acid (98%). The mixture was stirred and heated vigorously at 100 °C for 36 h. The solution was cooled and the resulting precipitate collected by filtration and washed with ethanol (60 ml). The residue was crystallised from a dichloromethane–hexane (1 : 9) mixture at room temperature and the resulting crystalline material filtered, washed with hexane and dried under vacuum to afford 6,6''-{(2,6-*i*-Pr₂C₆H₃)N=CMe}₂-2,2':6',2''-C₁₅H₉N₃ (L2) as a pale yellow solid. Yield: 1.10 g, 55%. Anal. Calc. for C₄₃H₄₉N₅: C, 81.26; H, 7.72; N, 11.02%. Found: C, 81.16; H, 7.86; N, 10.92%. ¹H NMR (300 MHz, CDCl₃): δ 1.11 (d, ³J_{H-H} 6.7, 24H, CH(CH₃)₂), 2.29 (s, 6H, CH₃C=N), 2.72 (sept, ³J_{H-H} 6.7, 4H, CH(CH₃)₂), 7.0–7.1 (m, 6H, Ar-H), 7.91 (app. t, ³J_{H-H} 7.9, ³J_{H-H} 7.9, 1H, Py-H), 7.92 (app. t, ³J_{H-H} 7.9, ³J_{H-H} 7.9, 2H, Py-H), 8.37 (dd, ³J_{H-H} 7.9, ⁴J_{H-H} 0.9, 2H, Py-H), 8.54 (d, ³J_{H-H} 7.9, 2H, Py-H) and 8.71 (dd, ³J_{H-H} 7.9, ⁴J_{H-H} 0.9, 2H, Py-H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 16.3 (CH₃C=N), 21.9 (CH₃), 22.2 (CH₃), 27.3 (CH), 120.0 (Py), 120.3 (Py), 121.0 (Py), 122.0 (Ar), 122.6 (Ar), 134.8 (Ar), 136.3 (Py), 136.8 (Py), 145.5 (Py), 136.3 (Py), 136.8 (Py), 145.4 (Ar), 154.0 (Py), 154.2 (Py), 154.6 (Py) and 166.1 (C=N). IR (cm⁻¹): 2960(m), 1642(m, $\nu(\text{C}=\text{N})$), 1563(s), 1430(s), 1362(w), 1256(w), 1184(w), 1108(m), 800(s), 784(s) and 760(s). ESI positive mass spectrum (m/z): 636 [$(\text{M} + \text{H})^+$]. Mp 252–254 °C.

4.4 Synthesis of [6,6''-bis(iminoformyl)-2,2':6',2''-terpyridine-bis(2,6-diisopropylanil)]MX₂ (I)

(a) **1a**, M = Fe, X = Cl. An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous FeCl₂ (0.021 g, 0.164 mmol) in *n*-BuOH (10 ml) and the contents stirred at 110 °C until the iron salt had completely dissolved. L1 (0.100 g, 0.164 mmol, 1 eq.) was added and the mixture heated to 110 °C for a further 20 min. After cooling to room temperature, the suspension was concentrated and washed several times with hexane. The solid was dried overnight under reduced pressure to afford [6,6''-{(2,6-*i*-Pr₂C₆H₃)N=CH}₂-2,2':6',2''-C₁₅H₉N₃]FeCl₂ (1a) as a red-brown solid. Crystallisation of 1a from hot acetonitrile solution gave 1a as red needles. Yield: 0.096 g, 80%. Anal. Calc. for C₄₁H₄₅N₅FeCl₂·1.5H₂O·0.5MeCN: C, 64.49; H, 6.35; N, 9.85%. Found: C, 64.78; H, 6.06; N, 9.63%.

(b) **1b**, M = Ni, X = Br. Using an analogous procedure to that described in 4.4(a) employing (DME)NiBr₂ (0.051 g, 0.164 mmol) and L1 (0.100 g, 0.164 mmol, 1 eq.) gave [6,6''-{(2,6-*i*-Pr₂C₆H₃)N=CH}₂-2,2':6',2''-C₁₅H₉N₃]NiBr₂ (1b) as a yellow solid. Crystallisation of 1b from hot acetonitrile solution gave 1b as yellow needles. Yield: 0.108 g, 80%. Anal. Calc. for C₄₁H₄₅N₅NiBr₂: C, 59.59; H, 5.45; N, 8.48%. Found: C, 59.50; H, 5.61; N, 8.39%.

(c) **1c**, M = Zn, X = Cl. Using an analogous procedure to that described in 4.4(a) employing anhydrous ZnCl₂ (0.022 g, 0.164 mmol) and L1 (0.100 g, 0.164 mmol, 1 eq.) gave [6,6''-{(2,6-*i*-Pr₂C₆H₃)N=CH}₂-2,2':6',2''-C₁₅H₉N₃]ZnCl₂ (1c) as a yellow solid. Crystallisation of 1c from a mixture of acetonitrile/chloroform gave 1c as yellow needles. Yield: 0.085 g, 70%. Anal. Calc. for C₄₁H₄₅N₃ZnCl₂·1/3CHCl₃: C, 63.33; H, 5.79; N, 8.94%. Found: C, 62.99; H, 5.72; N, 8.91%.

4.5 Synthesis of [6,6''-bis(iminoacetyl)-2,2':6',2''-terpyridine-bis(2,6-diisopropylanil)]NiBr₂ (2b)

Under an atmosphere of nitrogen a mixture of L2 (0.178 g, 0.280 mmol) and (DME)NiBr₂ (0.086 g, 0.280 mmol, 1 eq.) were added to a Schlenk flask containing dichloromethane (10 ml) at 0 °C. The stirred reaction mixture was allowed to warm to room temperature and stirring continued for a further 12 h. The volatiles were removed under reduced pressure and the residue was washed with hexane (20 ml) to yield [6,6''-{(2,6-*i*-Pr₂C₆H₃)N=CH}₂-2,2':6',2''-C₁₅H₉N₃]NiBr₂ (2b) as a yellow solid. Crystallisation of 2b from a mixture of acetonitrile–chloroform gave 2b as yellow blocks. Yield: 0.167 g, 70%. Anal. Calc. for C₄₃H₄₉N₅NiBr₂: C, 60.39; H, 5.73; N, 8.19%. Found: C, 60.23; H, 5.92; N, 7.99%.

4.6 Synthesis of [6,6''-bis(iminoacetyl)-2,2':6',2''-terpyridine-bis(2,6-diisopropylanil)]M₂X₄ (3)

(a) **3a**, M = Fe, X = Cl. An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous FeCl₂ (0.040 g, 0.315 mmol) in *n*-BuOH (10 ml) and the contents stirred at 110 °C until the iron salt had completely dissolved. L2 (0.100 g, 0.157 mmol, 0.5 eq.) was added and the mixture heated to 110 °C for a further 20 min. After cooling to room temperature, the suspension was concentrated and washed several times with hexane. The solid was dried overnight under reduced pressure to afford [6,6''-{(2,6-*i*-Pr₂C₆H₃)N=CMe}₂-2,2':6',2''-C₁₅H₉N₃]Fe₂Cl₄ (3a) as a brown solid. Crystallisation of 3a from hot acetonitrile solution gave 3a as red blocks. Yield: 0.109 g, 78%.

(b) **3b**, M = Ni, X = Br. Using an analogous procedure to that described in 4.6(a) employing (DME)NiBr₂ (0.097 g, 0.315 mmol) and L2 (0.100 g, 0.157 mmol, 0.5 eq.) gave [6,6''-{(2,6-*i*-Pr₂C₆H₃)N=CMe}₂-2,2':6',2''-C₁₅H₉N₃]Ni₂Br₄ (3b) as an orange solid. Yield: 0.135 g, 80%. Crystallisation of 3b by prolonged standing in chloroform gave 3b(H₂O) as green needles.

(c) **3c**, M = Zn, X = Cl. Using an analogous procedure to that described in 4.6(a) employing anhydrous ZnCl₂ (0.043 g, 0.315 mmol) and L2 (0.100 g, 0.157 mmol, 0.5 eq.) gave [6,6''-{(2,6-*i*-Pr₂C₆H₃)N=CMe}₂-2,2':6',2''-C₁₅H₉N₃]Zn₂Cl₄ (3c) as a yellow solid. Crystallisation of 3c from hot acetonitrile solution gave 1b as yellow plates. Yield: 0.107 g, 75%. Anal. Calc. for C₄₃H₄₉N₅Zn₂Cl₄: C, 56.84; H, 5.40; N, 7.71%. Found: C, 56.96; H, 5.48; N, 7.68%.

4.7 Conversion of 2b to 3b

An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with (DME)NiBr₂ (0.048 g, 0.157 mmol) and *n*-BuOH (10 ml) and the suspension heated to 110 °C until the nickel

Table 8 Crystallographic and data processing parameters for **L2**, **1a–1c**, **2b**, **3a**, **3b**(H₂O) and **3c**

Complex	L2	1a	1b	1c	2b	3a	3b (H ₂ O)	3c
Formula	C ₄₃ H ₄₉ N ₅ ·CH ₂ Cl ₂	C ₄₁ H ₄₅ Cl ₂ FeN ₅ ·3H ₂ O	C ₄₁ H ₄₅ Br ₂ N ₅ Ni·MeCN	C ₄₁ H ₄₅ Cl ₂ N ₅ Zn	C ₄₃ H ₄₉ Br ₂ N ₅ Ni·2MeCN·2CHCl ₃	C ₄₃ H ₄₉ Cl ₄ Fe ₂ N ₆ ·MeCN	C ₄₃ H ₅₁ Br ₄ N ₅ Ni ₂ O·CHCl ₃ ·H ₂ O	C ₄₃ H ₄₉ Cl ₄ N ₅ Zn ₂ ·MeCN
<i>M</i>	720.80	788.62	867.40	744.09	1175.25	930.43	1229.34	949.47
Crystal size/mm	0.33 × 0.26 × 0.07	0.38 × 0.08 × 0.08	0.38 × 0.12 × 0.08	0.38 × 0.35 × 0.15	0.33 × 0.22 × 0.16	0.33 × 0.23 × 0.17	0.26 × 0.16 × 0.10	0.22 × 0.14 × 0.09
<i>T</i> /K	150(2)	160(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Tetragonal	Tetragonal	Tetragonal	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>Cc</i>	<i>P4₂-2₁-2</i>	<i>P4₂-2₁-2</i>	<i>P4₂-2₁-2</i>	<i>P</i> $\bar{1}$	<i>P2₁/c</i>	<i>Phen</i>	<i>P2₁/c</i>
<i>a</i> /Å	20.807(3)	15.1102(9)	14.9110(15)	15.044(7)	11.257(2)	17.050(6)	12.921(6)	17.026(4)
<i>b</i> /Å	11.0120(14)	15.1102(9)	14.9110(15)	15.044(7)	12.916(2)	18.307(7)	16.246(5)	18.321(4)
<i>c</i> /Å	17.781(2)	18.4635(15)	19.143(3)	18.659(12)	9.574(4)	15.606(6)	28.685(8)	15.777(3)
<i>a</i> /°	90	90	90	90	84.660(3)	90	90	90
<i>β</i> /°	94.489(2)	90	90	90	84.591(3)	110.109(6)	90	111.599(4)
<i>γ</i> /°	90	90	90	90	67.688(3)	90	90	90
<i>U</i> /Å ³	4061.6(9)	4215.6(5)	4256.3(9)	4223(4)	2615.9(8)	4574(3)	10216(5)	4575.9(17)
<i>Z</i>	4	4	4	4	2	4	8	4
<i>D_c</i> /Mg m ⁻³	1.179	1.243	1.354	1.170	1.492	1.351	1.599	1.378
<i>F</i> (000)	1536	1664	1784	1560	1200	1936	4936	1968
<i>μ</i> (Mo-Kα)/mm ⁻¹	0.196	0.526	0.740	0.246	2.246	0.906	4.062	1.320
Reflections collected	14234	32793	30818	20399	31786	31786	59878	32683
Independent reflections	6954	4162	3754	2092	10135	8049	7368	8048
<i>R</i> _{int}	0.0374	0.0592	0.0946	0.1391	0.0291	0.1585	0.2637	0.0866
Restraints/parameters	2/470	0/241	0/232	0/219	0/542	0/525	0/283	0/525
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0685 <i>wR</i> 2 = 0.1853	<i>R</i> 1 = 0.0746 <i>wR</i> 2 = 0.2266	<i>R</i> 1 = 0.0517, <i>wR</i> 2 = 0.1124	<i>R</i> 1 = 0.0807 <i>wR</i> 2 = 0.2079	<i>R</i> 1 = 0.0394 <i>wR</i> 2 = 0.0873	<i>R</i> 1 = 0.0839 <i>wR</i> 2 = 0.1675	<i>R</i> 1 = 0.1331 <i>wR</i> 2 = 0.3076	<i>R</i> 1 = 0.0473 <i>wR</i> 2 = 0.0755
All data	<i>R</i> 1 = 0.0970 <i>wR</i> 2 = 0.2148	<i>R</i> 1 = 0.0958 <i>wR</i> 2 = 0.2358	<i>R</i> 1 = 0.1095 <i>wR</i> 2 = 0.1264	<i>R</i> 1 = 0.0959 <i>wR</i> 2 = 0.2221	<i>R</i> 1 = 0.0570 <i>wR</i> 2 = 0.0909	<i>R</i> 1 = 0.1592 <i>wR</i> 2 = 0.1984	<i>R</i> 1 = 0.2179 <i>wR</i> 2 = 0.3433	<i>R</i> 1 = 0.0850 <i>wR</i> 2 = 0.0841
Goodness of fit on <i>F</i> ² (all data)	1.045	0.838	0.838	0.987	0.896	0.911	1.102	0.846

Data in common: graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å; $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$; $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2]$; $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$, where *a* is a constant adjusted by the program; goodness of fit = $[\sum (F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, where *n* is the number of reflections and *p* the number of parameters

salt had partially dissolved. **2b** (0.134 g, 0.157 mmol, 1 eq.) was added and the mixture heated to 110 °C for a further 30 min. After cooling to room temperature, the suspension was concentrated and washed several times with hexane. The solid was dried overnight under reduced pressure to afford [6,6''-{(2,6-*i*-Pr₂C₆H₃)N=CMe}₂-2,2':6',2''-C₁₅H₉N₃]Ni₂Br₄ (**3b**) as an orange solid. Yield: 0.143 g, 85%.

4.8 Density functional calculations

Quantum mechanical calculations have been carried out using the Gaussian 03 package of programs.¹⁴ The density functional theory (DFT) was applied, in particular the functional Becke's three-parameter hybrid exchange method combined with LYP correlation functional (B3LYP).¹⁵ The quasi-relativistic effective core potential (ECP) LANL2DZ was used for the metal atoms (Zn).¹⁶ The basis set for both atoms in the valence double- ζ contraction associated to this ECP.^{14,16} The valence double- ζ with polarisation 6-31 G(d)^{17,18} basis was used for N and Cl and the minimal basis STO-3G for C and H.

4.9 Crystallography

Data for **L2**, **1a–1c**, **2b**, **3a**, **3b**(H₂O) and **3c** were collected on a Bruker APEX 2000 CCD diffractometer. Details of data collection, refinement and crystal data are listed in Table 8. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections applied. Structure solution by direct methods and structure refinement on *F*² employed SHELXTL version 6.10.¹⁹ Hydrogen atoms were included in calculated positions (C–H = 0.96 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5 *U*_{eq}(C) for methyl H atoms and 1.2 *U*_{eq}(C) for all other H atoms. With the exception of **3b**(H₂O) (only Ni and Br refined anisotropically) and **1c** (all atoms apart from C21 and C9), all non-H atoms were refined with anisotropic displacement parameters. Disordered MeCN was omitted using the SQUEEZE option in PLATON for **1b** and **2b**.

CCDC reference numbers 289324–289331.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516083a

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References

- For a review, see: C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005.
- (a) E. C. Constable, S. M. Elder, P. R. Raithby and M. D. Ward, *Polyhedron*, 1991, **10**, 1395; (b) E. C. Constable, M. Neuburger, L. A. Whall and M. Zehnder, *New J. Chem.*, 1998, **22**, 219.
- (a) K. T. Potts, M. Keshavarz, K. F. S. Tham, H. D. Abruna and C. Arana, *Inorg. Chem.*, 1993, **32**, 4436; (b) E. C. Constable, M. A. M. Daniels, M. G. B. Drew, D. A. Tocher, J. V. Walker and P. D. Wood, *J. Chem. Soc., Dalton Trans.*, 1993, 1947; (c) E. C. Constable, M. D. Ward, M. G. B. Drew and G. A. Forsyth, *Polyhedron*, 1989, **8**, 2551.
- (a) K. T. Potts, M. Keshavarz-K, F. S. Tham, H. D. Abruna and C. R. Arana, *Inorg. Chem.*, 1993, **32**, 4422; (b) E. C. Constable, M. G. B. Drew and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1987, 1600; (c) M. Barley, E. C. Constable, S. A. Corr, R. C. S. McQueen, J. C. Nutkins,

- M. D. Ward and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1988, 2655; (d) K. T. Potts, M. Keshavarz-K, F. S. Tham, H. D. Abruna and C. Arana, *Inorg. Chem.*, 1993, **32**, 4436; (e) W. Dai, H. Hu, X. Wei, S. Zhu, D. Wang, K. Yu, N. K. Dalley and X. Kou, *Polyhedron*, 1997, **16**, 2059.
- 5 Y. D. M. Champouret, R. K. Chaggar, I. Dadhiwala, J. Fawcett and G. A. Solan, *Tetrahedron*, 2006, **62**, 79.
- 6 A. El-ghayouy, A. Harriman, A. De Cian, J. Fischer and R. Ziessel, *J. Am. Chem. Soc.*, 1998, **120**, 9973.
- 7 A. El-ghayoury, Z. Abdelkrim and R. Ziessel, *J. Org. Chem.*, 2000, **65**, 775.
- 8 K. T. Potts, K. A. Cheysen Raiford and M. Keshavarz-K, *J. Am. Chem. Soc.*, 1993, **115**, 2793.
- 9 A. Gerli, K. S. Hagen and L. G. Marzilli, *Inorg. Chem.*, 1991, **30**, 4673.
- 10 For use of the $\nu(\text{CO})$ stretch as a guide to relative donor capability of imines, see: (a) M. Brockmann, H. tom Dieck and J. Klaus, *J. Organomet. Chem.*, 1986, **301**, 209; (b) S. Morton and J. F. Nixon, *J. Organomet. Chem.*, 1985, **282**, 123; (c) L. Gonsalvi, J. A. Gaunt, H. Adams, A. Castro, G. J. Sunley and A. Haynes, *Organometallics*, 2003, **22**, 1047.
- 11 W. L. F. Armarego and D. D. Perrin, *Purification of Laboratory Chemicals*, Butterworth Heinemann, London, 4th edn, 1996.
- 12 F. E. Mabbs and D. J. Machin, *Magnetism and Transition Metal Complexes*, Chapman and Hall, London, 1973.
- 13 (a) C. J. O'Connor, *Prog. Inorg. Chem.*, 1982, **29**, 203; (b) *Handbook of Chemistry and Physics*, ed. R. C. Weast, CRC Press, Boca Raton, FL, 70th edn, 1990, p. E134.
- 14 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03 (Revision C.02)*, Gaussian, Inc., Wallingford, CT, 2004.
- 15 (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785; (c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
- 16 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
- 17 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.
- 18 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
- 19 G. M. Sheldrick, *SHELXTL, Version 6.10*, Bruker AXS, Inc., Madison, WI, USA, 2000.