Strong Ferromagnetic Exchange Coupling Mediated by a Bridging Tetrazine Radical in a Dinuclear Nickel Complex

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Experimental Section

Synthesis

The reagents TPMA,¹ [Ni(CH₃CN)₆](BF₄)₂,² and bmtz³ were prepared by literature procedures. Synthesis of the complex was performed in an MBRAUN dry box under an N₂ atmosphere. Cp*₂Co was purchased from Aldrich and used as received. CH₃CN was pre-dried by storage over 3 Å molecular sieves and distilled from 3Å molecular sieves prior to use. Et₂O was purified using an MBRAUN solvent purification system and then stored over 3 Å molecular sieves in the dry box. Elemental analysis was performed by Atlantic Microlabs, Inc., Norcross, GA. Magnetic measurements were conducted in the temperature range of 1.8 to 300 K using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7T superconducting magnet. The diamagnetic contribution of the plastic bag used as the sample holder was subtracted from the raw data. Core diamagnetism of the sample was accounted for using Pascal's constants.⁴

Synthesis of $[(Ni(TPMA))_2-\mu$ -bmtz[•]](BF₄)₃•3CH₃CN (1), To a pink suspension of bmtz (44.1 mg, 0.185 mmol) in CH₃CN (10 mL) was added Cp*₂Co (59.9 mg, 0.182 mmol). After stirring the reaction mixture for 30 minutes, an orange solution was obtained and $[Ni(CH_3CN)_6][BF_4]_2$ (176.1 mg, 0.368 mmol) and TPMA (106.9 mg, 0.368 mmol) in CH₃CN (10 mL) were added. The resulting brown solution was stirred for 24 h and filtered. Brown X-ray quality crystals were obtained after three days by slow diffusion of diethyl ether vapor into the filtrate. Yield: 66.0 mg (28%). Analysis calculated (found) for $[(Ni(TPMA))_2(bmtz)](BF_4)_3$ (C₄₆H₄₂N₁₆B₃F₁₂Ni₂): C: 46.17% (45.61%), H: 3.54% (3.62%), N: 18.73% (18.70%).

X-ray Crystallographic Measurements

Single crystal X-ray data for **1** were collected on a Bruker APEXII diffractometer equipped with a $Mo(K\alpha)$ sealed tube X-ray source and a CCD detector. A brown crystal of **1** was affixed to a nylon loop with Paratone oil and placed in a cold stream of $N_{2(g)}$ at 110 K. The frames were integrated with the Bruker APEXII software package⁵ and a semi-empirical absorption correction was applied using SADABS as contained within the Bruker APEXII software suite. The structure was solved using SHELXT⁶ and refined using shelXle, a graphical interface to the SHELX suite of programs.⁷ The remaining non-hydrogen atoms were located by alternating cycles of least-squares refinements and difference Fourier maps. All hydrogen atoms were placed in calculated positions. The final refinements were carried out with anisotropic thermal parameters for all non-hydrogen atoms. The tetrafluoroborate anion B2 was modeled with an idealized geometry in order to facilitate a chemically reasonable and computationally stable refinement.⁸ Thermal parameter restraints were also utilized on the disordered atoms to ensure a chemically reasonable and computationally stable refinement.

	I
Formula	$C_{52}H_{51}B_{3}F_{12}N_{19}Ni_{2}$
Molecular weight (g/mol)	1319.96
Temp (K)	110(2)
Crystal System	triclinic
Space group	<i>P</i> 1(No. 2)
<i>a</i> (Å)	9.306(1)
<i>b</i> (Å)	11.623(1)
<i>c</i> (Å)	14.654(2)
α (°)	72.159(7)
β (°)	86.534(6)
γ (°)	71.569(6)
$V(Å^3)$	1430.2(3)
Z	1
Color	brown
$ ho_{\rm calc}({\rm g/cm^3})$	1.533
$\mu (\mathrm{mm}^{-1})$	0.754
2θ range (°)	2.922 to 53.26
Reflections collected (R_{int})	30744 (0.0669)
Unique reflections	5899
Parameters/restraints	546/289
$R_{1}^{a} w R_{2}^{b} [I > 2\sigma(I)]$	0.0455, 0.1072
R_1 , ^{<i>a</i>} wR_2 ^{<i>b</i>} (all data)	0.0815, 0.1301
Goodness-of-fit ^{c} (F^2)	1.039
Largest diff. peak, hole (e Å ⁻³)	0.40, -0.56

Table S1. Crystal and structural refinement data for 1·3MeCN.

 ${}^{a}\mathbf{R} = \Sigma \left| \left| \mathbf{F}_{o} \right| - \left| \mathbf{F}_{c} \right| \right| / \Sigma \left| \mathbf{F}_{o} \right|. {}^{b}w\mathbf{R} = \left\{ \Sigma \left[w(\mathbf{F}_{o}^{2} - \mathbf{F}_{c}^{2})^{2} \right] / \Sigma w(\mathbf{F}_{o}^{2})^{2} \right\}^{1/2} \cdot \mathbf{G}$ Goodness-of-fit = $\left\{ \Sigma \left[w(\mathbf{F}_{o}^{2} - \mathbf{F}_{c}^{2})^{2} \right] / (n-p) \right\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.

 Table S2. Selected bond lengths [Å] and angles [°] for 1.

Ni(1)-N(1)	2.110(2)	
Ni(1)-N(2)	2.074(2)	
Ni(1)-N(3)	2.095(3)	
Ni(1)-N(4)	2.096(2)	
Ni(1)-N(5)	2.164(3)	
Ni(1)-N(7)	2.027(3)	
$N(7)-N(8)^{a}$	1.383(3)	
^a 2-x, -y, 2-z		
N(1)-Ni(1)-N(5)	101.20(9)	
N(2)-Ni(1)-N(1)	81.60(9)	
N(2)-Ni(1)-N(3)	86.9(1)	
N(2)-Ni(1)-N(4)	159.5(1)	
N(2)-Ni(1)-N(5)	89.45(9)	
N(3)-Ni(1)-N(1)	82.3(1)	

N(3)-Ni(1)-N(4)	95.6(1)
N(3)-Ni(1)-N(5)	174.55(9)
N(4)-Ni(1)-N(1)	78.63(9)
N(4)-Ni(1)-N(5)	89.23(9)
N(7)-Ni(1)-N(1)	171.45(9)
N(7)-Ni(1)-N(2)	106.6(1)
N(7)-Ni(1)-N(3)	100.4(1)
N(7)-Ni(1)-N(4)	93.0(1)
N(7)-Ni(1)-N(5)	76.8(1)



Figure S1. π - π stacking interactions in **1**.

EPR Experiments

X-band EPR spectra of the solution sample 1 were recorded on a Bruker ELEXYS-II E500 spectrometer equipped with an Oxford ESR910 cryostat for low-temperature measurements. The temperature was calibrated with resistors (CGR-1-1,000) from LakeShore. *SpinCount*, a Windows software package (available from www.chem.cmu.edu/groups/hendrich/facilities/index.html), was used to analyze and simulate the EPR spectra and magnetism data. Spin quantification was performed by simulation, relative to a copper ethylenediaminetetraacetate standard for which the copper concentration was accurately determined from plasma emission spectroscopy.

SQUID Magnetic Measurements

Magnetic measurements were conducted on a Quantum Design MPMS-XL SQUID magnetometer using a 7 T superconducting magnet. The diamagnetic contribution of the polypropylene bag used to hold the sample was subtracted from the raw data, and the core diamagnetic contributions of the sample were accounted for using Pascal's constants.⁴

DC susceptibility measurements for 1.3MeCN were made under 0.1 T, 1 T, and 7T applied fields, from 300 K to 2 K. Reduced magnetization measurements were performed from 2 K to 5 K at magnetic fields ranging from 1 T to 7 T. AC susceptibility measurements were made under various applied DC fields using an AC drive amplitude of 2 Oe at frequencies of 10 Hz, 100 Hz, 200 Hz, 500 Hz, 1000 Hz and 1500 Hz from 6 K to 2 K.

Analysis of EPR and Magnetic Susceptibility Data

The EPR spectra (solution sample) and the low-temperature $(T/k_B << J)$ magnetism data (solid sample) were analyzed using the S = 5/2 spin Hamiltonian for the spin coupled representation of the S = 5/2 state because the effect of exchange interaction is negligible when $T/k_B << J$.

$$\widehat{H}_{elec,5/2} = D_{5/2} \left[S_z^2 - \frac{35}{12} + {\binom{E}{D}} (S_x^2 - S_y^2) \right] + g_{iso,5/2} \beta \mathbf{B} \cdot \mathbf{S}$$
(S1)

The high temperature magnetism data (solid sample) was analyzed using the uncoupled, three-spin representation for which the Hamiltonian includes an exchange term.

$$\hat{H} = \hat{H}_{elec,Ni_1} + \hat{H}_{elec,Ni_2} + \hat{H}_{elec,rad} + \hat{H}_{exchange}$$
(S2)

Assuming that the Ni(II) sites are equivalent (an assumption supported by the crystal structure), and neglecting exchange coupling between the Ni^{II} sites, this Hamiltonian can be rewritten as:

$$\hat{H} = \sum_{i=1}^{2} \{ D_{Ni} [\boldsymbol{S}_{z,Ni,i}^{2} - 2/3 + (E/D) (\boldsymbol{S}_{x,Ni,i}^{2} - \boldsymbol{S}_{y,Ni,i}^{2})] + g_{Ni} \beta \boldsymbol{B} \cdot \boldsymbol{S}_{Ni,i} - 2J (\boldsymbol{S}_{Ni,i} \cdot \boldsymbol{S}_{rad}) \} + g_{rad} \beta \boldsymbol{B} \cdot \boldsymbol{S}_{rad}$$
(S3)

The zero field and g parameters in the coupled and the uncoupled representations are related by the following spin projection factors relate (see "EPR of Exchange Coupled Systems" by Bencini & Gatteschi)⁹

-Zero field splitting:

$$D_{5/2} = 2d_{Ni}D_{Ni} = 1/5 D_{Ni}$$

where $d_{Ni} = 1/10$

Note: anisotropic exchange is neglected

-g values:

$$g_{Ni} = \frac{g_{5/2} - c_{rad}g_{rad}}{2c_{Ni}} = \frac{1}{4} (5g_{5/2} - g_{rad})$$

where $c_{rad} = 1/5$ and $c_{Ni} = 2/5$



Figure S2. (a) χ T vs T plot for 1 at 0.1 T. The solid line is the simulation of χ T data using PHI and the experimental parameters: $J_{\text{Ni-rad}} = +96 \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.35$, $D_{\text{Ni}} = -4.7 \text{ cm}^{-1}$, and E/D = 0.25, with additional DFT computed parameters of $J_{\text{Ni-Ni}} = -0.7 \text{ cm}^{-1}$, and $zJ = -0.04 \text{ cm}^{-1}$ and (b) Simulation of χ T data at 0.1T using the PHI program and the calculated parameters: $J_{\text{Ni-rad}} = +95.8 \text{ cm}^{-1}$, $J_{\text{Ni-Ni}} = -0.7 \text{ cm}^{-1}$, $g_{\text{Ni}} = 2.31$, $D_{\text{Ni}} = -4.2 \text{ cm}^{-1}$ and $zJ = -0.04 \text{ cm}^{-1}$ (see below, Computational details for the calculated parameters).



Chart S1. Examples of N-coordinating radical ligands.¹⁰



Figure S3. Plot of χ " as a function of frequency at 1.8 K in various applied DC fields.

Electrochemistry



Figure S4. Cyclic voltammogram of 1 showing the reversible redox event of bmtz. Experiment performed in CH_3CN with 0.2 M (*n*-Bu₄)N(PF₆) supporting electrolyte, platinum auxiliary electrode, glassy carbon working electrode, and Ag/AgCl reference electrode.

Computational details

DFT calculations: We employed the B3LYP¹¹ functional with Ahlrichs¹² triple- ζ basis set as implemented in the Gaussian 09¹³ suite of programs to calculate the energies of the three spin states in Figure S5:



Figure S5. The three spin states used in the DFT calculations.

DFT State	For 1-point calculation using crystal		
	structure		
	$E_{S_{DFT}}$ (Hartree)	$\Delta E = E_{S_{DFT}} - E_{HS} (\mathrm{cm}^{-1})$	
5/2 (HS)	-5669.581502930	0	
3/2 (BS2)	-5669.578883250	575	
1/2 (BS1)	-5669.580210900	284	

Table S3. Energy of the spin states produced by the B3LYP/TZV DFT calculations.

The *J* values were computed from the energy differences between the high spin (E_{HS}) state calculated using single determinant wave functions, and the low spin (E_{BS}) state determined using the Broken Symmetry (BS) approach developed by Noodleman.¹⁴ The BS approach has a proven record of yielding good numerical estimates of *J* constants for a variety of complexes¹⁵ such as dinuclear¹⁶ and especially radical complexes¹⁷ and polynuclear complexes.^{15a, 18}

In the case of a two spin system and using the spin Hamiltonian $\mathbf{H} = -2J_{ij}\mathbf{S}_i\mathbf{S}_j$, the energy difference between the high spin and low spin state is:

$$E_{\rm HS} - E_{\rm BS} = -4J_{ij}S_iS_j$$

Considerations related to the self-interaction error in commonly used exchange functional, non-dynamic pair correlation effects, and the application of spin projection techniques to DFT calculations led to the following equation to describe the energy difference: ^{15c, 19}

 $E_{HS}^{DFT} - E_{BS}^{DFT} = -4J_{ij}(S_iS_j + S_j)$, where $S_i > S_j$.

Application of this formalism to the three-spin system of complex **1** that consists of two Ni^{II} ions bridged by the bmtz radical ligand, leads to the following expressions for the differences between the energies for the three spin states calculated by DFT methods:

$$E_{BS2} - E_{HS} = 6J_{Ni-rad}$$
$$E_{BS1} - E_{HS} = 6J_{Ni-Ni} + 3J_{Ni-rad}$$

$$J_{Ni-rad} = \frac{1}{6} (575 \ cm^{-1}) = 95.8 \ cm^{-1}$$
$$J_{Ni-Ni} = \frac{1}{6} (-3 * 95.8 \ cm^{-1} + 284 \ cm^{-1}) = -0.65 \ cm^{-1}$$

The overlap integrals (S_{ab}) of orbitals have been computed between the α (spin-up on one metal center) and β (spin-down on second metal center) using Fortran code.^{15c}

α/β	d _{xy}	d_{xz}	d_{yz}	$d_{x - y}^{2 - 2}$	d_z^2
d _{xy}	0.0123	-0.0226	0.0241	0.0131	-0.0113
d _{xz}	0.0101	0.0872	0.0173	-0.0120	-0.0017
d _{yz}	0.0116	-0.0109	-0.0430	0.0085	-0.0159
$d_{x - y}^{2 - 2}$	0.0103	0.0101	0.0061	-0.0047	0.0012
d_z^2	0.0103	-0.0011	0.0024	-0.0063	0.0091

Table S4. Overlap integral values corresponding to Ni^{II}–Ni^{II} interaction in **1**.

Ab initio calculations: The *ab initio* calculations based on wave function theory approach were performed to compute the ZFS of both Ni^{II} ions in **1** using ORCA 3.0 suite of programs.²⁰ We employed the BP86 functional along with scalar relativistic ZORA Hamiltonian and def2-TZVP basis set on the metal ions and on first coordination sphere and def2-SVP for the rest of the atoms. The RI approximation with secondary TZV/J Columbic fitting basis sets were used along with increased integration grids (Grid 5 in ORCA convention). The tight SCF convergence was used throughout the calculations (1x10⁻⁸ Eh). The SOC contributions in the *ab initio* frame work were obtained using second-order perturbation theory as well as employing the effective Hamiltonian from the *ab initio* energies and wave functions numerically. We have employed the state average-CASSCF (Complete Active Space Self-Consistent Field) method to compute the ZFS. The active space comprises of eight active electrons in five active d-orbitals (d⁸ system; CAS (8,5)). With this active space, we computed all of the 10 triplet and 15 singlet states in the configuration interaction procedure.²¹

CASSCF calculations predict the same orbital ordering as DFT methods with a small $d_{xy} - d_{xz}/d_{yz}$ energy gap and a significantly larger $d_{yz} - d_x^2 - y^2/d_z^2$ gap (See below Figure). The radical ligand in the equatorial position stabilizes the d_{xy} orbitals as compared to other orbitals. In addition to the converged CASSCF wave function, NEVPT2 calculations were performed to treat dynamic correlations.



Figure S6. CASSCF-computed metal-based d orbitals with single excitations. The image shows all possible spin-conserved excitations responsible for the D value.

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