



A cyanido-bridged trinuclear $\{\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}\}$ complex decorated with organic radicals



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ABSTRACT

Reaction of $[\text{NEt}_4][(\text{pzTp})\text{Fe}^{\text{III}}(\text{CN})_3]$, nickel(II) trifluoromethanesulfonate and 4,4,5,5-tetramethylimidazoline-1-oxyl-2-(2'-pyridyl) (IM-2Py) affords $\{[(\text{pzTp})\text{Fe}^{\text{III}}(\text{CN})_3]_2\text{Ni}^{\text{II}}(\text{IM-2Py})_2\} \cdot 2\text{DMF} \cdot \text{H}_2\text{O} \cdot 0.5\text{Et}_2\text{O}$ (**1**) as a bent cyanide-bridged trinuclear complex. As judged from simulations of the magnetic data, the magnetic exchange between the $\{\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}\}$ ($S = 2$) and both IM-2Py ($S = 1/2$) radical ligands are negligible, or in other words, each radical imparts a Curie contribution to the overall paramagnetism of the complex; the best set of parameters are $g_{\text{iso}} = 2.53(5)$, $g_{\text{rad}} = 2$ (fixed), and $J_{\text{iso}}/k_B = 3.9(1)$ K. ac susceptibility and M versus H data show that **1** does not exhibit slow relaxation of the magnetization above 1.8 K. Consistent with the magnetic data, we conclude that bent cyanide bridges, an improper alignment of the $\text{Fe}^{\text{III}}_{\text{LS}}$ anisotropy tensors, and/or small IM-2Py ring distortions conspire to bring insufficient magnetic anisotropy to the complex, and prevent observation of single-molecule magnet behavior.

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1. Introduction

Over the past decade several attempts to enhance thermal barriers to magnetization reversal for Single-Molecule Magnets (SMMs) have been explored. Among the less common approaches are those decorating known SMMs by ligands that possess spin. This so-called metal-radical approach [1] has been utilized in the construction of several classes of molecule-based magnetic materials: among these are TCNE- or TCNQ-based high T_C lattices [2], imino nitroxide-bridged Single-Chain Magnets (SCMs) [3], and transition metal-semiquinone charge transfer complexes [4]. In the aforementioned materials, the magnetically isotropic ligands effectively contribute to the overall magnetic ground state without introducing potentially disruptive magnetic anisotropy or low-lying excited states. Not surprising these attributes have been widely exploited in the construction of several SCMs [3,5] and SMMs [6–8], with the most celebrated example $[\text{Co}(\text{hfacac})_2(\text{NITPhOMe})]$, where hfacac = hexafluoroacetylacetonate and NITPhOMe = 4-methoxyphenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-2-(2'-pyridyl)-3-oxide [3a].

Among stable organic radicals imino nitroxides have received considerable attention due to the ease in which various substituted derivatives may be prepared [1,3,6–11]. Imino nitroxides can also serve as either terminal ligands for the construction of discrete high spin complexes or bridging ones that span paramagnetic ions and strongly correlate their spins; the most commonly employed chelating ligand is 4,4,5,5-tetramethyl-2-(2-pyridyl)imidazolin-1-oxyl or IM-2Py [9–13].

In these polynuclear complexes, the sign and the magnitude of the metal-radical exchange interaction is found to be strongly dependent on the symmetry of the magnetic orbitals and its coordination environment. Under ideal circumstances, large ferromagnetic metal-radical interactions ($J/k_B \sim 70$ –200 K) may be found between Ni^{II} and bidentate IM-2Py units, but structurally related complexes are also known to exhibit weak ferromagnetic or even antiferromagnetic exchange in some cases, suggesting that simplistic orbital symmetry arguments may not be straightforward [11]. Surprisingly, only two cyanide complexes containing this versatile radical ligand, $\{[\text{Ni}^{\text{II}}(\text{IM-2Py})_2]_3[\text{Fe}^{\text{III}}(\text{CN})_6]_2\}$ ($S_T = 7$) and $\{[(\text{dmbpy})_2\text{Fe}^{\text{III}}(\text{CN})_2\text{Cu}^{\text{II}}(\text{IM-2Py})_2]_2[\text{ClO}_4]_6\} \cdot 4\text{CH}_3\text{OH} \cdot 4\text{H}_2\text{O}$ ($S_T = 3$), have been reported to date, where paramagnetic Fe^{III} ($S = 1/2$), Ni^{II} ($S = 1$), and IM-2Py ($S = 1/2$) units engage in efficient ferromagnetic exchange interactions [12,13].

As part of a continuing effort to better understand how to construct SMMs, we have turned our attention towards complexes

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containing paramagnetic rather than diamagnetic ancillary ligands. Through deliberate combination of coordinatively labile complexes with those bearing terminal cyanides, a number of complexes belonging to a given structural archetype may be prepared, whose magnetic and optical properties may be systematically altered. A variety of building blocks of $[(L)M^n(CN)_x]^{n-x-1}$ stoichiometry have been utilized to prepare these SMMs, and in particular C_{3v} -symmetric tridentate and facially coordinate poly(pyrazolyl)borate tricyanide complexes, $[(Tp^R)Fe^{III}_3(CN)_3]^-$, have been widely exploited [14–42]. These complexes generally exhibit appreciable magnetic anisotropy (along their C_3 or $B \cdots Fe$ axes) arising from a degenerate spin ground state that enables first-order orbital contributions to their magnetic moments ($2.3 \leq g \leq 2.9$). These versatile and highly tunable ions can be incorporated into a variety of discrete polynuclear complexes and chains that exhibit behaviors ranging from SMM [14–26], SCM [27–29] and photomagnetic [35–42] behaviors.

By changing the numbers and locations of functional groups on the Tp^R ligands, we have demonstrated that self-assembly reactions may be controlled and selectively afford bent or linear $\{Fe^{III}_2Ni^{II}\}$ SMMs with $S_T = 2$ spin ground states [14,20]. In an effort alter the spin reversal energy barriers for these SMMs, we sought to modify the spin ground state of the complexes by substituting diamagnetic ancillary ligands (on the Ni^{II} site) for paramagnetic ones within a given structural archetype. In this contribution, we describe the synthesis, structure, and magnetic behavior of a new cyano-bridged $\{Fe^{III}_2Ni^{II}\}$ trinuclear complex, $\{[(pzTp)Fe^{III}(CN)_3]_2[Ni^{II}(IM-2Py)_2]\} \cdot 2DMF \cdot H_2O \cdot 0.5Et_2O$ (**1**) and compare its properties to structurally related $\{[(pzTp)Fe^{III}(CN)_3]_2[Ni^{II}(bpy)_2]\} \cdot 2H_2O$ (**2**) [14].

2. Experimental

2.1. General considerations

Nickel(II) trifluoromethanesulfonate $[Ni(OTf)_2]$ [43], 4,4,5,5-tetramethylimidazoline-1-oxyl-2-(2'-pyridyl) (IM-2Py) [44] and $[Net_4][(pzTp)Fe^{III}(CN)_3]$ [14] were prepared by literature methods. The IR spectra were recorded as Nujol mulls between KBr plates on a Thermo-Electron Nicolet Impact 6700 FTIR instrument in the 400–4000 cm^{-1} region. Magnetic measurements on a microcrystalline sample of **1** (19.82 mg) were performed with a Quantum Design MPMS-XL SQUID magnetometers. Alternating current (ac) susceptibility measurements were conducted using an oscillating ac field of 3 Oe with an ac frequency of 100 Hz. The magnetic data were corrected for the sample holder while diamagnetic contributions were estimated using Pascal's constants [45]. Elemental analyses were performed by Robertson Microlit Laboratories.

Caution! Although no problems were encountered during our studies cyanides are toxic and should be handled with care.

2.2. Preparation of $\{[(pzTp)Fe^{III}(CN)_3]_2[Ni^{II}(IM-2Py)_2]\} \cdot 2DMF \cdot H_2O \cdot 0.5Et_2O$ (**1**)

Treatment of $Ni(OTf)_2$ (0.073 g, 0.200 mmol) with IM-2Py (0.063 g, 0.41 mmol) in DMF (5 mL) afforded a yellow mixture which was stirred for 10 min. Addition of $[Net_4][(pzTp)Fe^{III}(CN)_3]$ (0.124 g, 0.200 mmol) in DMF (5 mL) afforded a dark red solution that was filtered and then layered with diethyl ether (30 mL). The resulting tube was allowed stand for 7 days and the dark red rectangular crystals were isolated via filtration and dried under vacuum for 2 min. at room temperature. Yield: 0.123 g (90.4%). *Anal.* Calc. for $C_{57}H_{71}N_{24}O_5B_2Fe_2Ni$ ($(1-1/2)Et_2O$): C, 52.20; H, 5.73; N, 24.77. Found: C, 52.02; H, 5.32; N, 24.65%. IR (Nujol, cm^{-1}): 2154 (s), 2127 (s).

2.3. Structure determinations and refinements

X-ray structural data for **1** were collected at 100(2) K on a Bruker X8 Proteum CCD area detector diffractometer using Cu radia-

Table 1
Crystallographic data for **1**.^{a,b,c}

Formula	$C_{62}H_{77}B_2Fe_2NiN_{30}O_{5.5}$
Formula weight	1522.75
λ (Å)	1.54178
T (K)	100(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	12.020(1)
b (Å)	16.462(1)
c (Å)	19.119(2)
α (°)	98.679(4)
β (°)	93.261(4)
γ (°)	101.246(4)
V (Å ³)	3653.2(5)
Z	2
ρ_{calcd} (mg m ⁻³)	1.384
μ (mm ⁻¹)	4.015
R_1^b	0.0743
wR_2^c	0.1871

^a $I \geq 2\sigma(I)$.

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^c $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

Table 2
Selected bond distances (Å) and angles (°) for **1**.

Fe1–C13	1.899(5)	N9–Ni1–N20	91.2(2)
Fe1–C14	1.910(7)	N9–Ni1–N23	86.6(2)
Fe1–C15	1.924(6)	N9–Ni1–N24	89.5(2)
Fe1–N1	1.983(4)	N9–Ni1–N26	94.4(2)
Fe1–N3	1.963(5)	N9–Ni1–N27	172.8(2)
Fe1–N5	1.952(4)	N23–Ni1–N24	78.8(2)
Fe2–C28	1.921(5)	N26–Ni1–N27	78.4(2)
Fe2–C29	1.906(6)	Fe1–C13–N9	174.3(5)
Fe2–C30	1.896(6)	Fe1–C14–N10	177.7(5)
Fe2–N12	1.972(4)	Fe1–C15–N11	177.3(5)
Fe2–N14	1.970(4)	Fe2–C28–N20	176.5(4)
Fe2–N16	1.958(4)	Fe2–C29–N21	178.4(6)
Ni1–N9	2.059(4)	Fe2–C30–N22	174.5(7)
Ni1–N20	2.057(4)	Ni1–N9–C13	155.1(4)
Ni1–N23	2.089(4)	Ni1–N20–C28	174.3(4)
Ni1–N24	2.075(4)	O1–N25–C36	126.1(5)
Ni1–N26	2.070(4)	O2–N28–C48	123.7(4)
Ni1–N27	2.095(4)		
N25–O1	1.271(6)		

tion ($\lambda = 1.54178$ Å). A red crystal ($0.22 \times 0.18 \times 0.12$ mm) of **1** was mounted in Paratone-N oil on a glass fiber and the structure was solved by direct methods (SHELXS97) [46,47] and completed by difference Fourier methods (SHELXL97) [47]. Refinement was performed against F^2 by weighted full-matrix least-squares (SHELXL97) [47], and empirical absorption corrections (SADABS) [48] were applied. Hydrogen atoms were found in difference maps and subsequently placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters and atomic scattering factors were taken from the *International Tables for Crystallography Vol. C* [49]. Crystal data and selected geometrical parameters appear in Tables 1 and 2.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

The infrared spectrum of **1** exhibits two strong $\bar{\nu}_{CN}$ (2154 and 2127 cm^{-1}) stretches that are shifted to higher energy relative to those seen for $[Net_4][(pzTp)Fe^{III}(CN)_3]$ (2119 cm^{-1}). The $\bar{\nu}_{CN}$ energies are in the range typically seen for compounds containing $Fe^{III}-\mu_3(CN)Ni^{II}$ units and we tentatively assign these $\bar{\nu}_{CN}$ as belonging

to bridging and terminal cyanides, respectively [14–20]. Considering that **1** belongs to the same structural archetype as $\{[(\text{pzTp})\text{Fe}^{\text{III}}(\text{CN})_3]_2[\text{Ni}^{\text{II}}(\text{bpy})_2]\} \cdot 2\text{H}_2\text{O}$ (**2**), it is surprising that the bridging $\bar{\nu}_{\text{CN}}$ stretching absorption of **2** [2162 cm^{-1}] is shifted to a significantly higher energy indicating that the electronic environments of the two complexes are remarkably different despite their structural similarities.

3.2. Crystallographic studies

Compound **1** crystallizes in the triclinic $P\bar{1}$ space group as a neutral trinuclear complex. The structure of **1** consists of two crystallographically independent $[(\text{pzTp})\text{Fe}^{\text{III}}(\text{CN})_3]^-$ anions that are linked via a single bridging cyanide to an adjacent $[\text{Ni}^{\text{II}}(\text{IM-2Py})_2]^{2+}$ unit (Ni1), leaving two terminal cyanides per Fe^{III} center (Fig. 1). The terminal cyanide Fe1–C distances [Fe1–C14, $1.910(7)$; Fe1–C15, $1.924(6)$ Å] are slightly longer than those found for Fe2 [Fe2–C29, $1.906(6)$ Å; Fe2–C30, $1.896(6)$ Å]. Within the $\text{Fe}^{\text{III}}(\mu\text{-CN})\text{Ni}^{\text{II}}$ units, the Fe–C distances [$1.899(5)$ and $1.921(5)$ Å, for Fe1–C13 and Fe2–C28] and Fe–C–N angles [$174.3(5)^\circ$ and $176.5(5)^\circ$] deviate from linearity, and likely signal that significant steric interactions exist between the pzTp and Im-2Py ligands.

The $[\text{cis-Ni}^{\text{II}}(\text{IM-2Py})_2(\mu\text{-NC})_2]$ fragment adopts a distorted NiN_6 coordination environment owing to the presence of two *cis*-cyanides and two unsymmetrical IM-2-Py ligands. The Ni1–N_{cyanide} bonds [$2.059(4)$ and $2.057(4)$ Å] are slightly shorter than the IM-2-Py ones, which range between $2.070(4)$ to $2.095(4)$ Å, for Ni1–N22 and Ni1–N21, respectively. The cyanide N9–Ni1–N20 angle [$91.2(2)^\circ$] is slightly larger than the one in structures of **2**

[$90.9(2)^\circ$], while those of involving Ni–IM-2Py units range between $78.4(2)^\circ$ [N26–Ni1–N27] and $91.5(2)^\circ$ [N24–Ni1–N27]. While the Fe–CN angles are approximately linear, those found for the Ni1–N–C units are quite different: $155.1(4)^\circ$ for Ni1–N9–C13 and $174.3(4)^\circ$ for Ni1–N20–C28. Consequently the structure of **1** is rather distorted overall and leads to two different intramolecular Fe...Ni separations of ca. $4.94(1)$ and $5.12(1)$ Å, while minimum intermolecular metal–metal contacts of ca. $7.3(1)$ Å are present. We note that close intermolecular $\text{O2} \cdots \text{N11}$ [$4.563(4)$ Å], $\text{O2} \cdots \text{pyrazole}$ [$\text{O2} \cdots \text{C2}$, $3.390(4)$ Å], and pyrazole–pyrazole [$\text{C11} \cdots \text{N19}$, $3.338(4)$ Å] contacts are also found in structures of **1**.

Complex **2** is a structurally related and ligand substituted analogue of **1**. Complex **2** crystallizes in the monoclinic $P2_1/m$ space group [14] and contains 2,2'-bipyridine ligands in place of IM-2Py. Each $[(\text{pzTp})\text{Fe}^{\text{III}}(\text{CN})_3]^-$ anion is linked via a single cyanide bridge to a central $[\text{Ni}^{\text{II}}(\text{bpy})_2]^{2+}$ unit to afford a *cis*-arrangement of $\text{Fe}^{\text{III}}(\mu\text{-CN})\text{Ni}^{\text{II}}$ linkages. The bridging cyanide Ni1–N9 distance [$2.048(4)$ Å] is slightly shorter than those in seen for **1** and the Fe–C≡N and Ni–N≡C angles are more linear, with Fe1–C13–N9 and Ni–N9–C13 angles of $176.4(4)$ and $169.8(4)^\circ$ observed, respectively; close intermolecular contacts are also found for **2** between the bpy and pyrazole rings [$3.50(5)$ Å].

3.3. Magnetic studies

The temperature dependences of the χT product collected in a static dc field of 1000 Oe for **1** and **2** are illustrated in Fig. 2. Given that **2** has been previously described [14] we will limit discussion of its magnetic properties and compare them to those found for **1**. At 300 K, the χT value for **1** [$3.6\text{ cm}^3\text{ K mol}^{-1}$] is in good agreement with the value expected [$3.35\text{ cm}^3\text{ K mol}^{-1}$] for a 2:1:2 ratio of magnetically isolated $\text{Fe}^{\text{III}}_{\text{LS}}$ ($S = 1/2$; $2.6 \leq g \leq 2.8$), Ni^{II} ($S = 1$; $2.0 \leq g \leq 2.2$), and IM-2Py ($S = 1/2$; $g = 2.0$) spin centers, if one assumes that the contribution from each fragment is ca. 0.7, 1.2, and $0.375\text{ cm}^3\text{ K mol}^{-1}$ for the $\text{Fe}^{\text{III}}_{\text{LS}}$ ($g \sim 2.7$), Ni^{II} ($g \sim 2.2$), and organic radicals ($g = 2.0$), respectively. The χT versus T data of **1** increases with decreasing temperature towards a maximum value of $4.72\text{ cm}^3\text{ K mol}^{-1}$ at 7.0 K, in agreement with the onset of ferromagnetic interactions between $\text{Fe}^{\text{III}}_{\text{LS}}$ and Ni^{II} ions, which has also been observed in **2**. At lower temperatures, the χT product decreases towards [$3.0\text{ cm}^3\text{ K mol}^{-1}$] at 1.8 K, as seen for several previously reported complexes including **2** [14,20]. As judged from the magnetic data collected for **1** and **2** (Fig. 2), it appears that the ferromagnetic interactions in **1** are qualitatively less efficient than those in **2**.

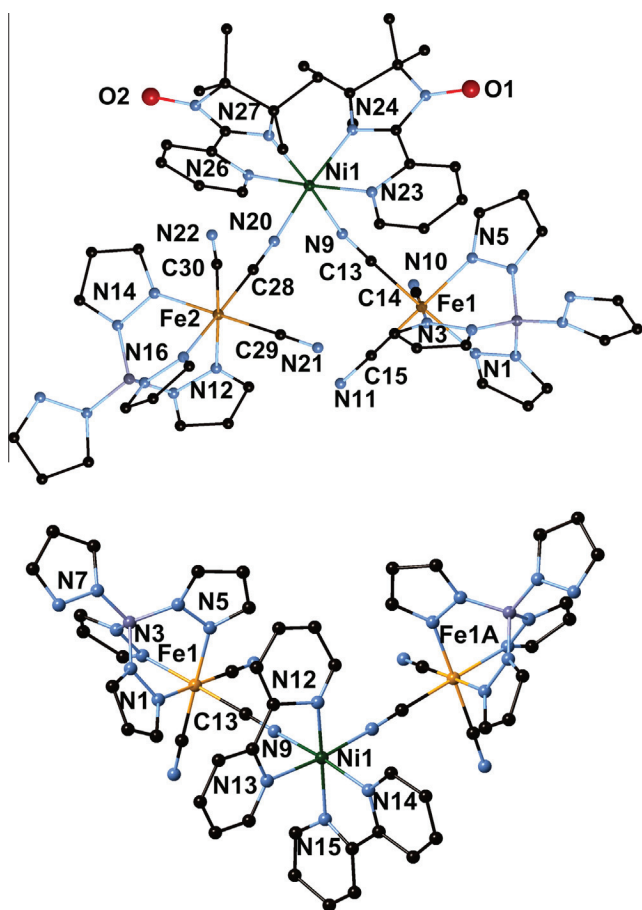


Fig. 1. X-ray structures of (top) **1** and (bottom) **2** for comparison. All lattice solvent and hydrogen atoms are eliminated for clarity.

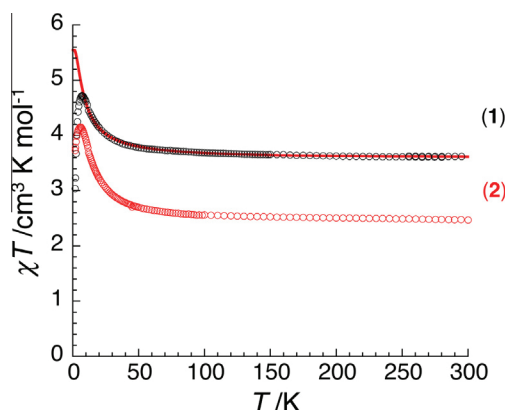


Fig. 2. Temperature dependences of the χT product (where χ is the molar magnetic susceptibility that equals M/H per complex) collected in an applied dc magnetic field of 1000 Oe for **1** (○) and **2** (○). The solid line is a best fit to the model described in the text.

Considering the distorted structure of **1**, the χT versus T data should be modeled using a minimum of three different magnetic exchange interactions: Fe–Ni (J_1 and J_2) and Ni–radical (J_3). As mentioned above, a qualitative analysis of the magnetic data [Fig. 2] suggests that ferromagnetic interactions are less efficient than those in either **2** [14] or Ni(IM-2Py)₂(NCS)₂ [11], and that the Ni–radical interactions are essentially negligible. Therefore to model the observed magnetic properties, an isotropic exchange Heisenberg Hamiltonian, $H = -2J_{\text{iso}}[S_1 \cdot (S_2 + S_3)]$, was initially used to describe the {Fe₂Ni} core, where $J_{\text{iso}} = J_1 = J_2$, J_{iso} is an average exchange interaction between paramagnetic Fe^{III} and Ni^{II} ions, and S_i is the spin operator for each ion ($S = 1/2$ for Fe^{III} and 1 for Ni^{II}, with $i = 2-3$). In this model, both organic radical ligands were considered as simple Curie contributions (i.e. $J_3 = 0$ and $g = 2$) to the magnetic properties of **1**. Considering only data above 5 K to avoid potential problems associated with magnetic anisotropy and/or weak intercomplex interactions, the deduced parameters are $J/k_B = +3.9(1)$ K and $g = 2.53(1)$ for **1**. These parameters are noticeably different from those estimated for **2** [$J/k_B = +7.0(2)$ K; $g = 2.31(1)$] [14], which is consistent with previously described infrared and X-ray structural data. On the other hand, the estimated magnetic parameters of **1** are between those found for structurally distorted $\{[(\text{pzTp})\text{Fe}^{\text{III}}(\text{CN})_3]_2[\text{Ni}^{\text{II}}(\text{L})]\} \cdot 1/2\text{MeOH}$, where $\text{L} = 1,5,8,12\text{-tetraazadodecane}$ [$J_{\text{iso}}/k_B = +1.3(1)$ K and $g_{\text{iso}} = 2.50$] and linear $\{[(\text{Tp}^{\text{Bn}})\text{Fe}^{\text{III}}(\text{CN})_3]_2[\text{Ni}^{\text{II}}(\text{DMF})_4]\} \cdot 2\text{DMF}$ [$J_{\text{iso}}/k_B = +7.1(2)$ K and $g_{\text{iso}} = 2.3(1)$] [14,20].

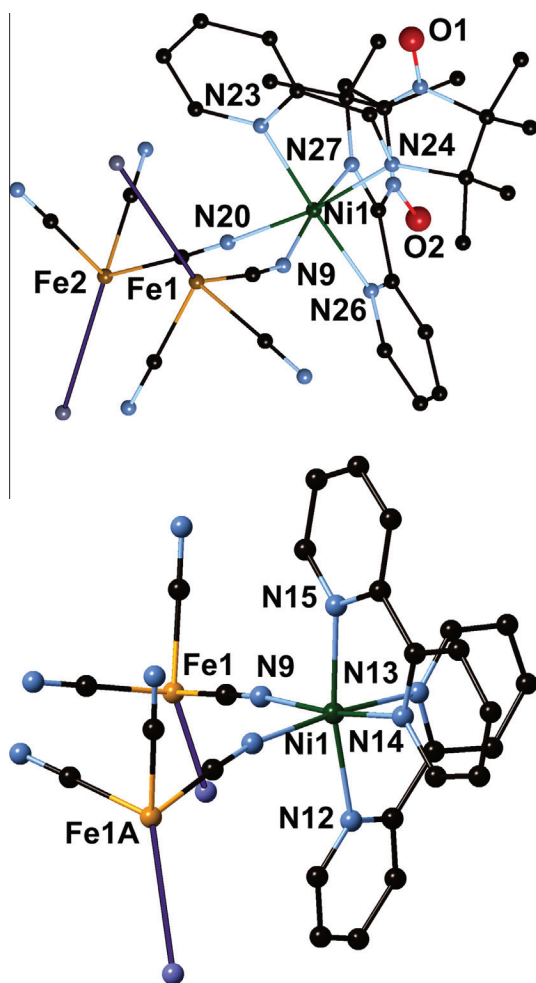


Fig. 3. Structural views showing anisotropy tensor alignment (B...Fe vectors; purple lines) in (top) **1** and (bottom) **2**.

Several attempts to simulate the magnetic data obtained for **1** with the following conditions: $J_1 \neq J_2$, $J_3 = 0$ or $J_1 \neq J_2$, $J_3 \neq 0$ were unsuccessful and systematically lead to $J_1 \approx J_2$, $J_3 \approx 0$ [50]. These results clearly suggest that it is not possible to model the χT versus T data without overparameterization, if one considers more than a single magnetic interaction parameter. Moreover, it seems that the magnetic interactions between the Ni^{II} and IM-2Py centers are extremely weak and cannot be evaluated from our experimental data. Indeed, the sign and magnitude of the metal–radical coupling constant is strongly dependent on the symmetry of the radical SOMO and those of the paramagnetic transition metal ions. Goodenough–Kanamori rules predict that ferromagnetic interactions should occur when unpaired electrons reside in orbitals that are orthogonal (e.g. Ni^{II} $d\sigma$ and radical π^* spins) to each other while antiferromagnetic exchange should be found when both orbital sets have similar symmetries [51]. As judged from the magnetic data, **1** does not exhibit measurable magnetic interactions between Ni^{II} and coordinated IM-2Py despite the presence of nearly planar rings. For example, comparable ring distortions are found in structures of $\{[\text{Ni}^{\text{II}}(\text{IM-2Py})_2]_3[\text{Fe}^{\text{III}}(\text{CN})_6]_2\}$ [12] and $\{(\text{SCN})_2\text{Ni}^{\text{II}}(\text{IM-2Py})_2\}$ [11], but in these complexes efficient Ni^{II}–radical ferromagnetic interactions are operative and magnetic ground states of $S_T = 6$ and 2 are found, respectively. We propose that slight structural distortions of the *cis*-coordinated IM-2Py ligands and low orbital symmetry of **1** likely prevents efficient ferromagnetic interactions with the Ni^{II} center.

In addition, the field dependence of the magnetization data of **1** was measured at 1.8 K [Fig. S1]. As judged from the M versus H data, the magnetization of **1** does not saturate as the experimental value is $5.0 \mu_B$ at 1.8 K and 7 T. The magnetization of **1** is far from that expected for an $S = 3$ complex and indicates that significant magnetic anisotropy is likely present. Surprisingly no slow relaxation of the magnetization was detected in ac susceptibility studies above 1.8 K [Fig. S2]. This behavior is likely due to two factors: (1) inefficient ferromagnetic interactions ($J/k_B = +3.9(1)$ K) within the non-linear $\text{Fe}^{\text{III}}(\mu\text{-CN})\text{Ni}^{\text{II}}$ units and/or (2) a non-optimum orientation of the single-ion anisotropy tensors (i.e. far from parallel) which leads to a small energy gap between the ground and excited states.

Over the past few years, we have investigated the hypothesis that the pseudo- C_3 rotation axes of $[(\text{Tp}^R)\text{Fe}^{\text{III}}(\text{CN})_3]^-$ ions within polynuclear complexes can function as structural markers for single-ion anisotropy tensor alignment [14–20]. In these $\{\text{Fe}^{\text{III}}_n\text{Ni}^{\text{II}}_m\}$ complexes, the orientation of the C_3 axes ($\text{Fe} \cdots \text{B}$ vectors) are clearly structural markers for SMM energy barriers heights, with parallel orientations generally affording the highest values. For **1**, the $\text{Fe} \cdots \text{B}$ vectors are not related via crystallographic symmetry and the C_3 axes are canted by about 136° , while for **2**, higher crystallographic symmetry (a mirror) affords a ca. 71° orientation of the $\text{Fe} \cdots \text{B}$ axes. Under the assumption that the $\text{B} \cdots \text{Fe}$ axes are collinear with their single-ion anisotropy vectors, those in **2** are closer to a parallel orientation in comparison to **1**, and a higher SMM energy barrier is expected in the former complex. Consequently, canting of the magnetic anisotropy tensors in **1** brings insufficient anisotropy to the complex while those in **2**, are better oriented so that the single-ion anisotropy of the Fe^{III} centers impart higher magnetic anisotropy to the polynuclear complex. This situation leads to a higher SMM energy barrier and the observation of slow dynamics above 1.8 K for **2** [Fig. 3].

4. Conclusions

In summary, the structures and magnetic properties of two structurally related trinuclear $\{\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}\}$ cyanometalate complexes are described. In the present case, replacement of diamagnetic bpy

ligands in favor of open shell IM-2Py ones, does not affect the magnetic ground state of the $\{\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}\}$ structural archetype as the radicals are negligibly coupled to the trinuclear core. We propose that the presence of bent cyanide bridges lead to an improper alignment of the $\text{Fe}^{\text{III}}_{\text{LS}}$ anisotropy tensors, and/or small IM-2Py ring distortions, conspire to bring insufficient magnetic anisotropy to the $S = 3$ complex. Consequently, SMM behavior is not observed for **1** but is clearly evident in structurally related complex **2**.

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Appendix A. Supplementary data

CCDC 920136 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 128 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2013.04.039>.

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