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Structure–property trends in cyanido-bridged tetranuclear Fe^{III}/Ni^{II} single-molecule magnets

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ABSTRACT

Treatment of $[NEt_4][(Tp^{*Me})Fe^{III}(CN)_3]\cdot H_2O$ with nickel(II) trifluoromethanesulfonate affords $\{[(Tp^{*Me})Fe^{III}(CN)_3]_2[Ni^{II}(DMF)_4]_2[OTf]_2\}\cdot 2DMF$ (**1**) while $\{[(Tp^{*Me})Fe^{III}(CN)_3]_2[Ni^{II}(bpy)_2]_2[ClO_4]_2\}\cdot 3MeCN\cdot 2H_2O\cdot MeOH$ (**2**) is obtained from $Ni(ClO_4)_2\cdot 6H_2O$ and 2,2′-bipyridine mixtures. In the frame of an isotropic Heisenberg model, the experimental χT versus T data were modeled well with the following best set of parameters: $J/k_B = +9.0(4)$ and $+8.5(4)$ K and $g_{av} = 2.4(1)$ and $2.5(1)$ for **1** and **2**, respectively; the first excited state ($S = 2$) for **1** and **2** are ca. 18 and 16.8 K above the $S_T = 3$ ground state. Analysis of the ac susceptibility suggests that **1** exhibits fast quantum tunneling of the magnetization above ca. 1.8 K while **2** displays slow relaxation in the range seen for many SMMs; at $H_{dc} = 2.2$ kOe an SMM energy barrier of $\Delta_{eff} = 15.7$ K is estimated for **2**. Upon prolonged standing in air, **1** is readily transformed into a new system that exhibits a respectable energy barrier ($\Delta_{eff} = 20.4$ K) suggesting that the desolvation is able to dramatically alter the dynamics and the quantum properties of the square-shaped $\{Fe^{III}_2(\mu\text{-}CN)_4Ni^{II}_2\}$SMM.

1. Introduction

Cyanometalates are an increasingly popular class of building blocks that find use in the preparation of materials, which exhibit a diverse assortment of properties such as radioactive cesium mitigation [1], room temperature magnetism [2], charge storage [3], electrochomism [4], gas separation and storage [5], and photomagnetic bistability [6,7]. Among these well-known materials are those of the three-dimensional defect solids known collectively as Prussian blues. These defect coordination networks are generally prepared using a building block synthetic approach [7] via treatment of $[M^n(CN)_x]^{n-x}$ ($x = 6, 7$, or 8) anions with a range of cationic metal ions and/or coordinatively unsaturated complexes $[M'(L)_y]^{m+}$. The ions self-assemble into a regular array of cyanido-bridged metal $M(\mu\text{-}CN)M'$ linkages, which in the presence of charge balancing alkali metal cations (A^+) and water, produce products of a generalized $A_nM(OH_2)_{6-6m}[M'(CN)_6]_m\cdot(2-n)H_2O$ formulation.

Using the concept of dimensional reduction [8], where capping ligands are used to limit the numbers of formed $M(\mu\text{-}CN)M'$ pairs during self-assembly, several low-dimensional systems such as single-molecule magnets (SMMs) [9–26,27a], single-chain magnets (SCMs) [27–33], and materials that exhibit dramatic changes in their magnetic and/or optical behavior [34–42] have been reported. These compounds are constructed from deliberate combination of $[(L)_yM(CN)_x]^{n-}$ salts with those containing substitutionally labile ligands to afford a predetermined number and geometric arrangement of $M(\mu\text{-}CN)M'$ linkages [9–42], that allows for a number of precursors containing various capping ligands to self-assemble towards a common structural archetype. Assuming that formed $M(\mu\text{-}CN)M'$ pairs are fundamentally limited by the numbers of available coordination sites and terminal cyanides present, product connectivity and stoichiometry may be predicted and controlled at the single-ion level. This strategy allows for the systematic construction of a series of structurally related polynuclear materials with tailored magnetic and optical properties [9–42].

The most common building-blocks are those of $[(Tp^R)Fe^{III}_{LS}(CN)_3]^-$ stoichiometry, where Tp^R is C_{3v}-symmetric, tridentate, and facially coordinate poly(pyrazolyl)borate ligand. These complexes find use in the construction of many SMMs owing to a favorable introduction of magnetic anisotropy via first-order orbital contributions, that appear to be collinear with their C_3 (B⋯Fe) rotation axes [14–26,31]. We previously reported that tuning of ancillary ligand steric demand affords a systematic means to direct self-assembly of various tricyanido $[(Tp^R)Fe^{III}(CN)_3]^-$ building blocks towards a variety of single-molecule magnet (SMMs)

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structural archetypes [14–26,31]. In these solids, the polypyrazolylborate (Tp^R) ligands enable coordination geometry preferences and electronic properties of derived complexes to be selectively tuned at upwards of 10 substitutable positions; this approach allows for the isolation of several tri-, tetra-, hexa-, and octanuclear complexes and one-dimensional chains that exhibit properties ranging from single-molecule magnet [9–26], photoresponsive [35–41], or single-chain magnet behavior [28–33].

As part of a continuing effort to explore new structural building units and investigate their role in directing self-assembly processes and resulting magnetic and/or optical properties of their aggregation products, we recently turned our attention towards a new building block, $[(Tp^{*Me})Fe^{III}(CN)_3]^-$, where Tp^{*Me} = tris(3,4,5-trimethylpyrazol-1-yl)borate. In comparison to Tp* analogs [Tp* = tris(3,5-dimethylpyrazol-1-yl)borate] addition of a single methyl group per pyrazolate unit affords a ligand that induces significant steric interactions with ancillary ligands residing on adjacent cyanido-bridged metal centers, while simultaneously enhancing solubility of the polynuclear complex [19,20]. These secondary interactions have enabled the construction of several SMMs that appear to favorably orient their angular momentum projections such that enhanced barriers to magnetization reversal are realized, in comparison to those containing comparatively smaller ligands. For example, owing to the steric demand of the Tp^{*Me} ligands present, a linear octanuclear $\{Fe^{III}_4Ni^{II}_4\}$ SMM was found to have a nearly parallel arrangement of anisotropy tensors and exhibits a high spin reversal energy barrier (Δ_{eff} = 33 K), in comparison to molecular boxes, which have rather small SMM energy barriers [19]. In the present contribution we report on two new and structurally related cyanido-bridged $\{Fe^{III}_2Ni^{II}_2\}$ square complexes: $\{[(Tp^{*Me})Fe^{III}(CN)_3]_2[Ni^{II}(DMF)_4]_2[OTf]\}_2\cdot 2DMF$ (**1**; OTf = trifluoromethanesulfonate, DMF = dimethylformamide) and $\{[(Tp^{*Me})Fe^{III}(CN)_3]_2[Ni^{II}(bpy)_2]_2[ClO_4]_2\}\cdot 3MeCN\cdot 2H_2O\cdot MeOH$ (**2**). Their structures and magnetic properties are discussed in the frame of other pyrazolylborate-based tetranuclear analogs.

2. Experimental

2.1. General considerations

Nickel(II) trifluoromethanesulfonate, $[Ni(OTf)_2]$ [43], and $[NEt_4][(Tp^{*Me})Fe^{III}(CN)_3]\cdot H_2O$ [19] were prepared by literature methods. 2,2′-bipyridine (bpy, Aldrich) and $Ni(ClO_4)_2\cdot 6H_2O$ (Acros) were used as received. 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 microcrystalline samples of **1** and **2** were obtained on Quantum Design MPMS-XL and PPMS-9 magnetometers. Alternating current (ac) susceptibility measurements were conducted using an oscillating ac field of 1 Oe with frequencies ranging from 10 to 10 000 Hz. The magnetic data were corrected for the sample holder while diamagnetic contributions were estimated using Pascal's constants [44]. Elemental analyses were performed by Robertson Microlit Laboratories.

Caution! Although no problems were encountered during our studies, cyanides are toxic and perchlorate salts are potentially explosive. These should be handled with great care.

2.2. Preparation of complexes

2.2.1. $\{[(Tp^{*Me})Fe^{III}(CN)_3Ni^{II}(DMF)_4][OTf]\}_2\cdot 2DMF$ (1)

Treatment of $[NEt_4][(Tp^{*Me})Fe(CN)_3]\cdot H_2O$ (0.122 g, 0.196 mmol) with $Ni(OTf)_2$ (0.107 g, 0.300 mmol) in DMF (10 mL) under an argon atmosphere afforded a red solution that allowed to stir for 1 h. The filtrate was layered with Et_2O (50 ml) and allowed to stand for 7 days. The dark red blocks were isolated via filtration and dried under vacuum for 2 min at room temperature. Yield: 0.116 g (56%). *Anal.* Calc.: C, 42.47; H, 6.07; N, 18.74. Found: C, 42.39; H, 5.78; N, 18.60%. IR (Nujol, cm^{-1}): 2549 (m), 2166 (s), 2118 (m), 1674 (vs), 1645 (vs), 1559 (w), 1516 (w), 1495 (m), 1457 (vs), 1377 (vs), 1271 (s), 1240 (s), 1224 (m), 1172 (w), 1145 (s), 1103 (s), 1059 (m), 1031 (s), 888 (s), 872 (m), 832 (s), 752 (w), 736 (m), 720 (m), 680 (s), 658 (w), 638 (s), 569 (w), 547 (m), 517 (m).

2.2.2. $\{[(Tp^{*Me})Fe^{III}(CN)_3]_2[Ni^{II}(bpy)_2]_2[ClO_4]_2\}\cdot 3MeCN\cdot 2H_2O\cdot MeOH$ (2)

Treatment of $Ni(ClO_4)_2\cdot 6H_2O$ (0.073 g, 0.20 mmol) with bpy (0.063 g, 0.41 mmol) in MeCN (5 mL) afforded a purple mixture which was stirred for 10 min. Addition of $[NEt_4][(Tp^{*Me})Fe^{III}(CN)_3]\cdot H_2O$ (0.124 g, 0.200 mmol) in methanol (10 mL) afforded a dark red solution, that was filtered, and allowed to stand for 7 days. Dark red rectangular crystals were collected via filtration and dried under vacuum for 2 min at room temperature. Yield: 0.135 g (64.9%). *Anal.* Calc.: C, 51.43; H, 5.09; N, 19.54. Found: C, 50.91; H, 5.01; N, 18.99%. IR (Nujol, cm^{-1}): 3426 (br, m), 3112 (w), 3092 (w), 3079 (w), 2555 (m), 2261 (m), 2250 (m), 2155 (vs), 2129 (m), 1644 (m), 1599 (vs), 1575 (m), 1567 (s), 1520 (s), 1490 (m), 1474 (w), 1429 (s), 1386 (m), 1360 (m), 1311 (m), 1239 (vs), 1191 (w), 1172 (m), 1154 (w), 1092 (vs), 1081 (vs), 1023 (s), 1012 (m, sh), 932 (w), 921 (w), 905 (w), 887 (w), 871 (m), 833 (m), 815 (w), 771 (vs), 738 (s), 688 (m), 667 (w), 652 (m), 623 (s), 544 (w).

2.3. Structure determinations and refinements

X-ray structural data were collected at 90.0(2) and 100.0(2) K for **1** and **2**, respectively, on Nonius Kappa CCD and Bruker APEX-II CCD diffractometers. Crystals were mounted in Paratone-N oil on glass fibers and the structures were solved by direct methods (SHELXS97) [45,46] and completed by difference Fourier methods (SHELXL97) [46]. Refinement was performed against F^2 by weighted full-matrix least-squares (SHELXL97) [46], and empirical absorption corrections (SADABS) [47] 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* [48]. Crystal data and selected details of structure determinations and geometrical parameters appear in Tables 1 and 2.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

Treatment of a 1:1 ratio of $[NEt_4][(Tp^{*Me})Fe(CN)_3]\cdot H_2O$ and $Ni(OTf)_2$ in dimethylformamide affords a mixture which contains a tetranuclear complex (**1**) and $\{[(Tp^{*Me})Fe^{III}(CN)_3]_4[Ni^{II}(DMF)_3]_2\}\cdot 4DMF\cdot H_2O$ [20] as the major and minor products, respectively; in the presence of a slight stoichiometric excess of $Ni(OTf)_2$ complex **1** is the sole crystalline product. The infrared spectrum of **1** exhibits medium intensity $\bar{\nu}_{BH}$ (2549 cm^{-1}) and $\bar{\nu}_{CN}$ (2118 cm^{-1}) stretches in addition to a more intense one (2166 cm^{-1}), that is higher in energy than those seen for $[NEt_4][(Tp^{*Me})Fe^{III}(CN)_3]\cdot H_2O$ (2119 and 2115 cm^{-1}). In **1**, we tentatively assign these $\bar{\nu}_{CN}$ stretches as bridging and terminal cyanides, respectively [20]. A second structurally related analog of **1** may also be obtained via combination of a 1:1:2 ratio of $[NEt_4][(Tp^{*Me})Fe(CN)_3]\cdot H_2O$, $Ni(ClO_4)_2\cdot 6H_2O$ and 2,2′-bipyridine in acetonitrile/methanol mixtures. The infrared spectrum of the bipridine-substituted complex,