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Communication

Single-Molecule Magnets Constructed from Cyanometalates: $\{[Tp^*Fe^{III}(CN)_3M^{II}(DMF)_4]_2[OTf]_2\}\cdot 2DMF$ ($M^{II} = Co, Ni$)

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Treatment of several divalent transition-metal trifluoromethanesulfonates [$M^{II}(OTf)_2$; M^{II} = Mn, Co, Ni] with $[NEt_4][Tp^*Fe^{III}(CN)_3]$ [Tp* = hydridotris(3,5-dimethylpyrazol-1-yl)borate] in DMF affords three isostructural rectangular clusters of $\{[Tp^*Fe^{III}(CN)_3M^{II}(DMF)_4]_2[OTf]_2\}\cdot 2DMF$ (M^{II} = Mn, **3**; Co, **4**; Ni, **5**) stoichiometry. Magnetic studies of **3**–**5** indicate that the $Tp^*Fe(CN)_3^-$ centers are highly anisotropic and exhibit antiferromagnetic (**3** and **4**) and ferromagnetic (**5**) exchange to afford $S = 4$, 2, and 3 spin ground states, respectively. ac susceptibility measurements suggest that **4** and **5** exhibit incipient single-molecule magnetic behavior below 2 K.

The systematic preparation of cyanometalate networks and clusters has celebrated a resurgence of activity over the past decade.[1] Of these, many species exhibit unusual properties such as room-temperature magnetism,[2] electro-[3] and photomagnetism,[4] single-molecule magnetism (SMM),[5] charge-transfer-induced spin transitions,[6] compensation behavior,[7] and single-chain magnetism (SCM).[8] Cyanometalates are excellent building blocks for constructing molecule-based clusters and networks because cyanides generally form linear μ-CN linkages between two metal centers, stabilize a variety of transition-metal centers and oxidation states, and efficiently communicate spin density information.[1]

Of known cyanometalate clusters, the dominant structural building block contains *fac*-$LM(CN)_3^{n-}$ centers where cyanides link adjacent transition-metal centers and L is a facially coordinate tripodal ligand.[9,10] Surprisingly, despite the prevalence of poly(pyrazolyl)borates in inorganic chemistry, only tris(pyrazolyl)borate iron(III) tricyanide and a few derived clusters and networks have been described.[5e,8c,10]

As part of a continuing effort to prepare such materials, we have turned our attention toward molecular species that can be systematically substituted via a building block approach, to afford compounds that exhibit tunable magnetic, electrical, and optical properties. Through such a synthetic strategy, we hope to incorporate a series of aniosotropic centers to systematically prepare several SMM and SCM materials that

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exhibit high-spin ground states, large and negative axial zero-field splittings, and high blocking temperatures.[5,8−11]

In the present communication, we report the synthetic, magnetic, structural, and spectroscopic details of three isostructural molecular rectangles that are derived from hydridotris(3,5-dimethylpyrazol-1yl)borate tricyanoferrate(III) and divalent transition-metal centers. Treatment of $[NEt_4][Tp^*Fe^{III}(CN)_3]\cdot H_2O$ (**1**) or $[NEt_4][Tp^*Fe^{III}(CN)_3]$ (**2**) with several divalent transition-metal trifluoromethanesulfonates in DMF readily affords clusters of $\{[Tp^*Fe^{III}(CN)_3M^{II}(DMF)_4]_2[OTf]_2\}\cdot 2DMF$ (M^{II} = Mn, **3**; Co, **4**; Ni, **5**; OTf = O_3SCF_3) stoichiometry in 80−92% yields. The infrared spectra of **3**−**5** exhibit strong ν_{BH} absorptions at 2543, 2545, and 2547 cm^{-1}, while the ν_{CN} stretching absorptions are found at 2158, 2150, and 2119 cm^{-1} for **3**, 2163, 2156, and 2120 cm^{-1} for **4**, and 2170, 2163, and 2120 cm^{-1} for **5**. The majority of the cyanide stretching absorptions are shifted to higher energies relative to **1** (2119 cm^{-1}) and **2** (2115 cm^{-1}), suggesting that bridging cyanides are present in **3**−**5**. The highest energy ν_{CN} absorptions appear to increase as a function of M^{II} electronegativity, while the lowest energy absorptions are close to those in **2**; these cyanide absorptions are tentatively assigned to bridging and terminal cyanides, respectively.[12]

Compounds **3**−**5** crystallize in the monoclinic $P2_1/m$ (**3**) and $P2_1/n$ (**4** and **5**) space groups.[13] The Fe^{III} and M^{II} centers reside in alternate corners of the rectangular clusters and are linked via cyanides (Figure 1).[10a] A third terminal cyanide per $Tp^*Fe(CN)_3^-$ center remains, and these are related by an inversion center, in an *anti* orientation relative to the Fe_2M_2 plane. A single methyl group per Tp* ligand projects perpendicular to and above (ca. 3.65 Å) the Fe_2M_2 plane, located opposite the terminal cyanides; the closest contacts between pyrazole rings are *ca.* 4.42 Å. The $M^{II}{}_1$−N bond distances are 2.195(4) Å for **3**, 2.083(3) Å for **4**, and 2.041 (4) Å for **5**, scaling as a function of increasing M^{II} electronegativity.

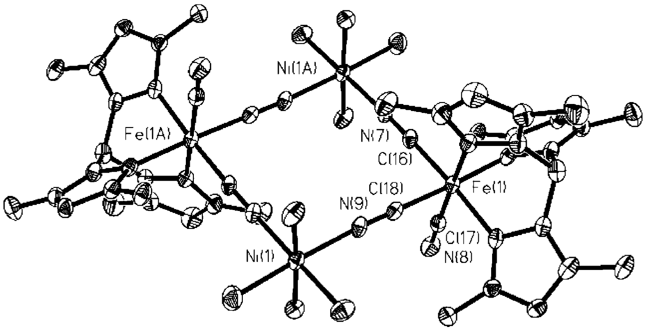

Figure 1. Partial X-ray structure of **5**. Ellipsoids are at the 50% level, all hydrogen atoms are eliminated, and only DMF oxygen atoms are illustrated for clarity. Selected bond distances (Å) and angles (deg): Fe(1)−C(16) 1.928(5), Fe(1)−C(18) 1.927(5), Ni(1)−N(9) 2.039(4), Fe(1)···Fe(1A) 7.461(1), and Ni(1)···Ni(1A) 6.972(1) Å; C(16)−Fe(1)−C(17) 86.84(18), C(16)−Fe(1)−C(18) 85.41(18), and N(7A)−M(1)−N(9) 92.34 (14)°.

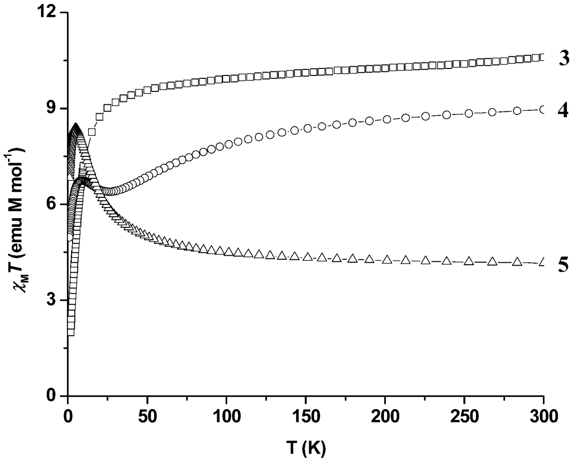

Figure 2. Temperature dependence of χT for **3** (□), **4** (○), and **5** (△) in an applied dc field of 1 kG.

In each rectangle, the carbon-bound cyanides give rise to low-spin Fe^{III} ($S = {}^1/_2$), which is expected to exhibit an orbital contribution to the magnetic moment.[5d,9a,11a,14] Consequently, spin-only formulas are not expected to be relevant. If we assume that the Mn^{II} centers in **3** are high-spin and that g_{Mn} is 2, we calculate (from the χT data, crushed crystals) a g_{Fe} value of 2.92. Further assuming that this value of g_{Fe} does not change for **4** and **5**, we conclude that g_{Co} and g_{Ni} are 2.84 and 2.38, respectively.

The temperature dependence of χT for **3** suggests that the Fe^{III} and Mn^{II} centers couple antiferromagnetically (Figure 2). Between 300 and 35 K, the χT values gradually decrease from 10.60 to 9.63 emu K mol^{-1} and then more abruptly below *ca.* 10 K, reaching a minimum value of 1.99 emu K mol^{-1} at 1.8 K; similar behavior has been reported for clusters of $[TpFe(CN)_3]_2[Mn(MeOH)_4]$ and $[TpFe(CN)_3]_2[Mn(bpy)_4]_2[ClO_4]_2$ stoichiometry [Tp = tris(pyrazol-1-yl)borate].[10a] We propose that zero-field splitting of the $S = 4$ ground state at low temperatures affords lower than expected χT values, rather than intercluster antiferromagnetic interactions, because the closest pyrazole-ring contacts between clusters are *ca.* 5.434(4) Å.[19]

The temperature dependence of χT for **4** appears to be dominated by spin−orbit coupling effects exhibited by the cobalt(II) centers present (Figure 2). Between 300 and 22 K, χT gradually decreases from 8.90 to 6.55, and this is probably due to depopulation of thermally populated low-lying excited states for the $S = {}^3/_2$ Co^{II} centers. Below 22 K, the χT product increases to a maximum value of 6.65 emu K mol^{-1} at 10 K and then decreases further to 4.80

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(13) Crystal and structure refinement parameters. **3**: $C_{68}H_{114}B_2F_6Fe_2Mn_2N_{28}O_{16}S_2$, $P2_1/m$, $Z = 2$, $a = 15.295(3)$ Å, $b = 13.194(3)$ Å, $c = 24.321(5)$ Å, $\beta = 107.09(3)°$, $V = 4691.3(16)$ Å^3, R1 = 0.0655, wR2 = 0.1811. **4**: $C_{68}H_{114}B_2F_6Fe_2Co_2N_{28}O_{16}S_2$, $P2_1/n$, $Z = 2$, $a = 15.3587(2)$ Å, $b = 13.1573(2)$ Å, $c = 24.1959(4)$ Å, $b = 108.3940(7)°$, $V = 4639.67(12)$ Å^3, R1 = 0.0492, wR2 = 0.0938. **5**: $C_{68}H_{114}B_2F_6Fe_2Ni_2N_{28}O_{16}S_2$, $P2_1/n$, $a = 15.3227(2)$ Å, $b = 13.13430(10)$ Å, $c = 24.0570(3)$ Å, $b = 108.1414(5)°$, $V = 4600.87(9)$ Å^3, R1 = 0.0636, wR2 = 0.1740. All data were collected on a Nonius Kappa CCD diffractometer at 90.0(2) K using Mo Kα ($\lambda = 0.710\,73$ Å) radiation. Structures were solved by direct methods and refined against all data using SHELXL 97.

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emu K mol^{-1} at 2 K;[11e] ac susceptibility measurements suggest that intramolecular coupling of Co^{II} and Fe^{III} centers occurs at low temperatures.

For **5**, the χT product gradually increases between 300 and 165 K. At lower temperatures, the χT rapidly increases to 8.27 emu K mol^{-1} at 7 K, suggesting a ferromagnetically coupled $S = 3$ ground state; below 7 K, the χT product decreases further to 6.71 emu K mol^{-1} at 2 K.[18]

Goodenough and Kanamori describe that superexchange between low-spin Fe(III) and the divalent centers should be either antiferromagnetic or ferromagnetic, depending on spin state and orbital symmetry considerations. Assuming, for simplicity, that the Mn^{II}($t_{2g}^3e_g^2$), Co^{II}($t_{2g}^5e_g^2$), and Ni^{II}($t_{2g}^6e_g^2$) centers are octahedral, then the low-spin Fe^{III}(t_{2g}^5) centers should couple antiferromagnetically to Mn^{II} and Co^{II} (**3** and **4**) and ferromagnetically to Ni^{II} (**5**).[11e] However, the clusters are actually of lower symmetry (C_2) and the t_{2g} and e_g orbitals become nondegenerate, thus complicating simple orbital orthogonality arguments.

Fitting of the magnetic data using the Curie−Weiss equation suggests that antiferromagnetic coupling occurs between cyanide-bridged Fe^{III}, Mn^{II}, and Co^{II} centers while ferromagnetic exchange is present between Fe^{III} and Ni^{II}. Simulations of the χT versus T data using MAGPACK[21] allowed for estimations of g(M^{II}) and J_{iso}; the calculated values are 2.1 and −2.1 cm^{-1} for **3**, 2.7 and −10 cm^{-1} for **4**, and 2.2 and 5.3 cm^{-1} for **5**.[18] The sign and relative magnitudes of θ in **3**−**5** (−8.80, −9.61, and 4.18 K) are comparable to those of hexacyanoferrate(III) networks of $\{Mn(OH_2)_2[Mn(bpym)(OH_2)]_2[Fe(CN)_6]_2\}_\infty$ ($\theta = -12.8$ K),[15] $Co^{II}_3[Fe^{III}(CN)_6]_2\cdot 6H_2O$ ($\theta = -15$ K),[16] and $\{[Ni^{II}(tn)_2]_5[Fe^{III}(CN)_6]_3]_n[ClO_4]_n\cdot 2.5nH_2O\}$ ($\theta = 7.45$ K)[17] stoichiometry.

The field dependence of the magnetization for **3**−**5** suggests that nonlinear magnetization versus applied field effects that grow faster than the Brillouin functions are operative.[11,18] At 1.8 K, the magnetization values for **3**−**5** are 7.0, 6.6, and 6.11 μ_B, suggesting spin ground states (S) of 4, 2, and 3 for **3**−**5**, respectively. Assuming $S = 2$ and 3 ground states for **4** and **5**, fits of the magnetization data using ANISOFIT[20] for $T \leq 5$ K afford zero-field splitting parameters $D = -3.04$ and -3.98 cm^{-1} and g(cluster) = 3.49 and 2.44 (Figure 3).[18] Assuming that the sign and magnitude of D are correct, the spin reversal barrier energies should be $U = |D|S_T^2 = 12.2$ and 35.8 cm^{-1} for **4** and **5**, respectively.[18]

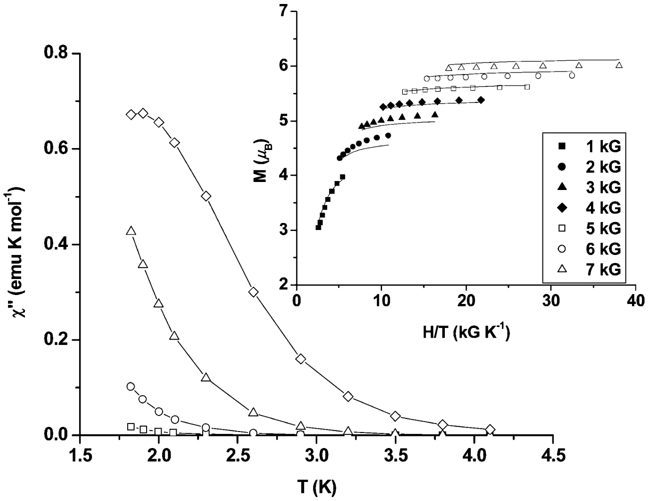

Figure 3. Temperature dependence of the imaginary component (χ'') of the ac susceptibility for **5** ($H_{dc} = 0$ G and $H_{ac} = 2.5$ G) at 1 (□), 9 (○), 100 (△), and 997 (◇) Hz. Inset: Plot of reduced magnetization vs H/T between 1.8 and 5 K. Solid lines represent a least-squares fitting of the data.

ac susceptibility measurements indicate that χ'' is frequency-independent for **3** and frequency-dependent for **4** and **5**. The frequency dependence of χ'' for **4** and **5** suggests that the blocking temperatures lie below 1.8 K because frequency-dependent shoulders are readily apparent (Figure 3);[18] such slow magnetic relaxation effects have been previously described for several SMM and SCM derivatives.[5,11d] The frequency dependence of χ'' exhibits Arrhenius behavior for **5** because plots of ln τ vs $1/T$ are linear; least-squares fitting indicates that the relaxation time is $\tau = 7 \times 10^{-7}$ s for **5**. We propose that **5**, and possibly **4**, exhibits incipient single-molecule magnetic behavior below 1.8 K.[18]

In summary, we have described the preparation of three molecular clusters, of which two are likely single-molecule magnets. We anticipate that systematic insertion of paramagnetic transition-metal centers exhibiting greater single ion anisotropy (such as 4d and 5d centers) into this structural archetype will afford additional analogues that exhibit higher spin ground states and blocking temperatures relative to **4** and **5**.[20,22]

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Supporting Information Available: X-ray crystallographic data (CIF format, **3**−**5**), synthetic details, and additional magnetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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