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First Structurally Characterized Tricyanomanganate(III) and its Magnetic $\{Mn^{III}_2M^{II}_2\}$ Complexes (M^{II} = Mn, Ni)

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Treatment of tris(3-cyano-2,4-pentanedionato)manganese(III) with KTp*, followed by $[NEt_4]CN$ affords $[NEt_4][(Tp^*)Mn^{III}(CN)_3]$ (**1**); subsequent treatment of **1** with divalent triflates (OTf) and 2,2′-bipyridine (bpy) affords $\{Mn^{III}_2M^{II}_2\}$ complexes (M^{II} = Mn, **2**; Ni, **3**). Magnetic measurements show that **1**−**3** exhibit S_T = 1, 3, and 4 spin ground states, respectively.

Cyanometalates find extensive use as reagents for the rational construction of polynuclear complexes that exhibit superparamagnetism like behavior,[1] spin crossover,[2a] and optically responsive materials.[2b,c] Using a synthetic strategy known as a building block approach, molecular precursors are allowed to self-assemble with intact structures into a common structural archetype. The most common units for constructing polynuclear cyanometalate complexes are those containing tripodal ligands, L, with generalized [*fac*-$LM^n(CN)_m$] stoichiometry.[1,2a−c]

Over the last five years, we have systematically investigated the use of poly(pyrazolyl)borates as platforms for tuning the magnetic and optical behavior of several structurally related tri-, tetra-, and octanuclear complexes. Tricyano- building blocks such as $[(Tp^R)Fe^{III}(CN)_3]^-$ (Tp^R = pzTp, Tp, Tp*) exhibit substantial orbital contributions to their $S_T = {}^1/_2$ ground state that are crucial for engineering polynuclear complexes that exhibit slow relaxation of the magnetization (i.e., single-molecule magnets, SMMs).[1d−i]

In oxo-carboxylate complex chemistry, high spin (S = 2) manganese(III) ions are used extensively as a source of single-ion magnetic anisotropy in the design of SMMs.[2d] However, surprisingly few cyanomanganate analogues have been described with the best characterized example being a pentanuclear complex containing $[Mn^{II}(tmphen)]^{2+}$ (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) and hexacyanomanganate(III) ions in a 3:2 ratio;[1b,2a] this trigonal bipyramidal complex exhibits slow dynamics below 1.8 K (for a time scale of 1 s). Surprisingly, however, no tricyano- analogues have been reported to date. In the present Communication, we describe the synthesis of the first tricyanomanganate(III) complex and its self-assembly into well-defined $\{Mn^{III}_2M^{II}_2\}$ complexes.

Treatment of tris(3-cyano-2,4-pentanedionato)manganese(III) with KTp* followed by three equivalents of $[NEt_4]CN$ in methanol affords $[NEt_4][(Tp^*)Mn(CN)_3]$ (**1**) as yellow crystals.[3] The infrared spectrum of **1** contains intense $\tilde{\nu}_{BH}$

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(3) (a) See the Supporting Information. (b) Crystal data for **1**: $C_{26}H_{42}BMnN_{10}$, $P3_2$, Z = 3, a = 9.8102(1) Å, b = 9.8102(1) Å, c = 26.2483(4) Å, V = 2187.70(5) Å^3, R1 = 0.0427, wR2 = 0.0800. Crystal data for **2**: $C_{78}H_{78}B_2Mn_4N_{26}O_7S_2$, $P\bar{1}$, Z = 2, a = 13.431(1) Å, b = 18.332(2) Å, c = 19.943(2) Å, α = 88.878(5)°, β = 89.742(5)°, γ = 74.204(5)°, V = 4724.1(8) Å^3, R1 = 0.0977, wR2 = 0.1886.

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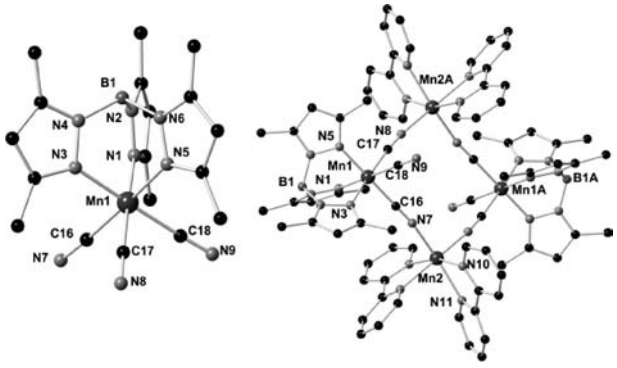

Figure 1. X-ray structures of **1** (left) and **2** (right). All cations, anions, lattice solvents, and hydrogen atoms are eliminated for clarity.

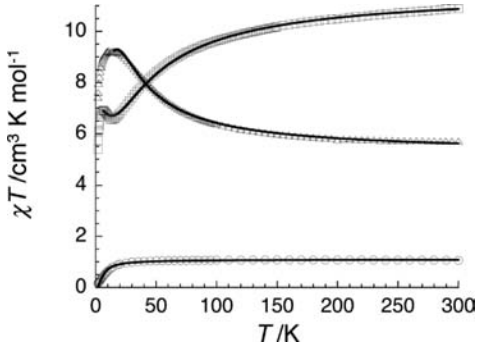

Figure 2. χT vs T plots for **1** (○), **2** (□), and **3** (△) at H_{dc} = 1000 Oe (χ being the magnetic susceptibility defined as M/H per complex). The solid black lines are the best fit and simulations obtained (see text).

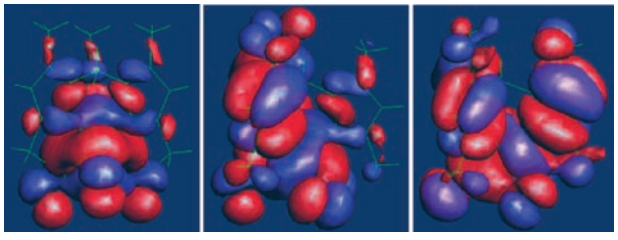

Figure 3. Shapes of the three lowest energy orbitals of **1** obtained from EHTB calculations: (left) $d(z^2)$, (middle) $d(xz)$, and (right) $d(yz)$ orbitals.

and $\tilde{\nu}_{CN}$ stretches [2552 and 2113 cm^{-1}] that are shifted to higher energies relative to KTp* (2436 cm^{-1}) and $[NEt_4]CN$ (2056 cm^{-1}), respectively.[4a,b] For **1**, the $\tilde{\nu}_{CN}$ stretch is higher in energy than those seen for $[Mn^{II}(CN)_2(bpy)_2]\cdot 3H_2O$ (2114 cm^{-1}), $[NEt_4]_2[Mn^{II}(CN)_4]$ (2120 and 2078 cm^{-1}), $K_3[Mn^{III}(CN)_6]\cdot H_2O$ (2112 and 2121 cm^{-1}), $[NEt_4]_3[Mn^{III}(CN)_6]\cdot H_2O$ (2094 cm^{-1}), and $[PPN]_3[Mn^{III}(CN)_6]$ (2096 cm^{-1}), suggesting that charge delocalization (via π-back bonding) is less efficient.[3a,4b−g,5a]

Treatment of **1** with a 1:2 ratio of $Mn(OTf)_2$ and bpy or $[Ni(bpy)_2(OH_2)_2](OTf)_2$ in acetonitrile readily affords $[(Tp^*)Mn^{III}(CN)_3]_2[M^{II}(bpy)_2]_2(OTf)_2\cdot nH_2O$ (M^{II} = Mn, **2**; Ni, **3**). The energies of the $\tilde{\nu}_{CN}$ stretches in **2** and **3** are similar to those reported for $\{Mn^{III}_2Mn^{II}_3\}$ [2068−2138 cm^{-1}] and $Ni^{II}_3[Mn^{III}(CN)_6]\cdot 12H_2O$ [2164 cm^{-1}], while intense $\tilde{\nu}_{BH}$ [2551 and 2552 cm^{-1}] absorptions are comparable to those found in infrared spectra of **1**. We conclude that $Mn^{III}(\mu\text{-}CN)M^{II}$ linkages are present in **2** and **3**.[3a,4c,5a]

Compound **1** crystallizes in the trigonal $P3_2$ space group.[3b] The C_{3v}-symmetric anions have Mn−C and Mn−N distances that range between 1.976(3) and 1.985(3) Å and 2.019(2) and 2.036(2) Å, respectively, indicating that no Jahn−Teller distortions are present (Figure 1 and Supporting Information Figure S2). In **1**, the average Mn−C distances [1.976(3) Å] are comparable to those in $K_3[Mn^{III}(CN)_6]$ [1.978(2) Å] and $[PPN]_3[Mn(CN)_6]$ [2.020(2) Å], while the C−Mn−C angles are between 85.8(1)° [C17−Mn1−C18] and 91.7(1)° [C16−Mn1−C18]; the N−Mn−N angles are between 87.56(8)° [N3−Mn1−N5] and 89.65(9)° [N1−Mn1−N5].[3a,5a,5b] Close Tp*−Tp* methyl [3.596(3) Å] and cyanide-methyl contacts [3.452(3) Å] are also present in structures of **1** (Supporting Information Figures S3−S4).[3a]

Crystals of **2** are found in the $P\bar{1}$ space group and its tetranuclear core consists of alternating di- and trivalent manganese ions linked by cyanides.[3a,b] The Mn^{III} centers (Mn1 and Mn1A) contain terminal cyanides (C18−N9) that are related via inversion centers and adopt an anti orientation relative to the $\{Mn^{III}_2(\mu\text{-}CN)_4Mn^{II}_2\}$ plane (Figure 1 and Supporting Information Figures S5−S7). Complex **2** is structurally related to $\{Fe^{III}_2M^{II}_2\}$ and $\{[V^{IV}O]_2Mn^{II}_2\}$ analogues where a Tp* methyl projects toward the rectangular face that is opposite to the terminal cyanide.[5c,d] The $\{Mn^{III}_2Mn^{II}_2\}$ core is slightly larger than the corresponding Fe^{III} analogues due to longer average Mn1−C [1.970(6) Å] and Mn2−N [2.154(5) Å] bonds; close bpy-Tp* ring contacts [3.185(3) Å] are also present.[3a]

At 300 K, the χT product of **1** is 1.1 cm^3 K mol^{-1}, which is in good agreement with the expected value (1.0 cm^3 K mol^{-1}) for a complex containing a magnetically isolated Mn^{III} ion with two unpaired electrons (Figure 2). On the other hand, the experimental χT value is far from those seen for either $[PPN]_2[Mn^{II}(CN)_4]$ or $[PPN]_3[Mn^{III}(CN)_6]$ (4.49 and 1.98 cm^3 K mol^{-1}), suggesting that trivalent ions are present and that orbital contributions to the spin ground state are nearly absent in **1**.[3a,4d−g] At low temperatures, the χT product follows Curie behavior down to 100 K and then decreases toward a minimum value of 0.15 cm^3 K mol^{-1} at 1.8 K. To reproduce this thermal behavior, an anisotropic Heisenberg Hamiltonian ($H = DS_{Mn}^2$) was utilized; the calculated values for g and D/k_B are 2.09(2) and +9.4(2) K, respectively (Figure 2 and Supporting Information Figure S8).[3a] The surprisingly large value of D must be considered with caution as antiferromagnetic intercomplex interactions probably act to artificially enhance the estimated value. This assumption is qualitatively supported by the M versus H data (below 8 K, Supporting Information Figure S9) in that the same D value was not reproduced using an anisotropic Heisenberg model.[3a]

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Extended Hückel tight-binding (EHTB) calculations[6] for **1** suggest that it adopts an $S_T = 1$ spin ground state, because the $d(xz)$ and $d(yz)$ orbitals lie close to the $d(z^2)$ orbital (225 and 267 meV above, respectively). The shapes of these orbitals (Figure 3) show that significant π-type spin density is delocalized into the Tp* and cyanide ligands. Furthermore, short H···H and H···NC-Mn contacts (ca. 2.4 and 2.7 Å) are found between adjacent $[(Tp^*)Mn(CN)_3]^-$ anions in **1**. Below ca. 20 K these short contacts may allow for intercomplex antiferromagnetic interactions that are, as suspected (vide supra), partially responsible for the low temperature behavior of the χT data seen for **1**.

For **2**, the room temperature χT value, 10.9 cm^3 K mol^{-1}, is close to that expected (10.75 cm^3 K mol^{-1}) for a $\{Mn^{III}{}_2Mn^{II}{}_2\}$ complex containing noninteracting Mn^{III} [$S = 1$, $C = 1.0$ cm^3 K mol^{-1}] and Mn^{II} [$S = {}^5/_2$, $C = 4.375$ cm^3 K mol^{-1}] spins (Figure 2 and Supporting Information S10). At lower temperatures the χT values slowly decrease toward a minimum of 6.5 cm^3 K mol^{-1} at 14 K and below this temperature, χT increases, reaching a maximum of 6.9 cm^3 K mol^{-1} at 6 K. This thermal behavior indicates that antiferromagnetic interactions are dominant within the tetranuclear complex between adjacent $S = 1$ Mn^{III} and $S = {}^5/_2$ Mn^{II} spins. At lower temperatures, the χT value decreases and reaches 5.2 cm^3 K mol^{-1} at 1.85 K, suggesting the presence of magnetic anisotropy and/or intercomplex antiferromagnetic interactions. On the basis of the molecular structure of **2**, the magnetic data were first modeled using an isotropic spin Hamiltonian [$H = -2J(S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_4 \cdot S_1]$ (eq 1), where J is the average exchange constant in the tetranuclear unit and S_i are the spin operators for the respective manganese ions [$S_1 = S_3 = S_{Mn(III)} = 1$; $S_2 = S_4 = S_{Mn(II)} = {}^5/_2$].[5e] MAGPACK[5f] simulation of the experimental data above 6 K gave a rough estimation of J/k_B at −4.8(1) K with $g(Mn^{II}) = 2.10(2)$ and $g(Mn^{III}) = 1.98(2)$ (Figure 2 and Supporting Information Figure S10), and this simple model leads to an energy difference between the $S_T = 3$ ground and $S_T = 2$ first excited states of ca. 19.2 K. Attempts to model the magnetic data with more parameters such as magnetic anisotropic or/and intercomplex interactions were not able to improve significantly the fit of the experimental data below 6 K. The M versus H data support an $S_T = 3$ ground state for **2** as the magnetization is almost saturated at 7 T and 1.8 K and reaches 6.3 μ_B (Supporting Information Figure S11).[3a] Additionally, **2** does not exhibit slow relaxation of its magnetization above 1.8 K, as judged from the lack of hysteresis in the M versus H (Supporting Information Figure S10) and frequency-independent ac susceptibility data in stark contrast to many reports on $S = 2$ Mn^{III}-based SMMs. We infer that the tricyanomanganate(III) ions do not bring enough magnetic anisotropy to complex **2** for the observation of SMM behavior.

The χT product at 300 K of **3** is equal to 5.4 cm^3 K mol^{-1} (Figure 2 and Supporting Information Figure S12). This value is greater than the value anticipated for isolated Mn^{III} and Ni^{II} spins (4 cm^3 K mol^{-1} with $g = 2.0$). With decreasing temperature, the experimental χT product increases monotonically approaching a maximum of 9.2 cm^3 K mol^{-1} at 14 K. The large room temperature χT product and its thermal behavior indicate that ferromagnetic interactions are present in **3**. Below 14 K, the χT values decrease toward a minimum of 7.4 cm^3 K mol^{-1} at 1.85 K (Figure 2),[3a] suggesting that additional antiferromagnetic intercomplex interactions or/and magnetic anisotropy are present.

The magnetic data for **3** were also modeled using the Heisenberg Hamiltonian given in eq 1 with $S_i = S_{Mn(III)} = S_{Ni(II)} = 1$. The susceptibility was derived from application of the van Vleck equation to the Kambe vector coupling method.[5e,f] The data fitted well to ca. 25 K with $J/k_B = +6.8(5)$ K, and $g = 2.3(1)$. Alternative models have been tried and additional intercomplex interactions treated in terms of the mean field theory were added to the Heisenberg tetranuclear model. Above 12 K, a good fit of the data is obtained and values of $J/k_B = +9.0(2)$ K, $zJ'/k_B = -0.38(5)$ K and $g = 2.3(1)$ are found (Figure 2 and Supporting Information S12);[3a] introduction of an anisotropic term, $2D(S^2{}_z(Ni) + S^2{}_z(Mn))$, into the Heisenberg Hamiltonian (eq 1) was also tried and the susceptibility was calculated using the MAGPACK program.[5g] Simulations of the χT versus T data between 1.8 and 300 K have been unsuccessful, suggesting that magnetic anisotropy and intercomplex antiferromagnetic interactions are likely present in **3**. Nevertheless, the χT versus T data demonstrate the presence of ferromagnetic interactions between $S = 1$ Mn^{III} and $S = 1$ Ni^{II} spins suggesting that **3** exhibits an $S_T = 4$ ground state. At 1.8 K and $H_{dc} = 7$ T, the magnetization value (7.1 μ_B) approaches that expected for an $S_T = 4$ ground state (8 μ_B) (Supporting Information Figure S13). Evidence for slow relaxation of the magnetization in **3** was absent in the M versus H and ac susceptibility data above 1.8 K, suggesting misalignment of anisotropy tensors is operative in **3**.[3a]

In summary we have described the preparation, crystal structures, and magnetic properties of a new paramagnetic tricyanomanganate(III) and two of its tetranuclear $\{Mn^{III}{}_2M^{II}{}_2\}$ complexes. We have shown that the $[(Tp^*)Mn^{III}(CN)_3]^-$ unit possesses an $S_T = 1$ spin state that antiferromagnetically and ferromagnetically interacts with $S = {}^5/_2$ Mn^{II} and $S = 1$ Ni^{II} spin centers, respectively. While slow dynamics are seen for Fe^{III} analogues of **3**, $[(Tp^*)Fe^{III}(CN)_3]_2[Ni^{II}(bpy)_2]_2[OTf]_2 \cdot 2H_2O$,[5d] the weaker magnetic anisotropy of the $[(Tp^*)Mn^{III}(CN)_3]^-$ unit leads to $S_T = 3$ and $S_T = 4$ complexes without SMM properties.

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Supporting Information Available: Synthetic details ($[NEt_4]_3[Mn(CN)_6]$, **1**−**3**) and X-ray crystallographic (CIF format, **1**,**2**) and additional magnetic data (Figures S1−S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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