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A Nontwisted, Ferromagnetically Coupled $Mn^{III}{}_3O$ Triangular Complex from the Use of 2,6-Bis(hydroxymethyl)-*p*-cresol

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The reaction between $Mn(O_2CMe)_2 \cdot 4H_2O$ and $hmcH_3$ [$hmcH_3$ = 2,6-bis(hydroxymethyl)-*p*-cresol] in CH_2Cl_2 in the presence of NEt_3 affords the $Mn^{III}{}_3$ complex $[NEt_3(CH_2Cl)]_2[Mn_3O(hmcH)_3(hmcH_2)_3]$ (**1**). The anion of **1** contains a $[Mn^{III}{}_3(\mu_3\text{-}O)]^{7+}$ triangular core, with the central O^{2-} ion lying above the Mn_3 plane. The complex is ferromagnetically coupled with a resulting $S = 6$ ground state.

Polynuclear clusters of paramagnetic 3d metal ions are of interest for a variety of reasons, one of which is their often unusual magnetic properties. A major development in the latter direction was the realization that certain individual molecules can exhibit superparamagnetic properties, i.e., the phenomenon of single-molecule magnetism. Single-molecule magnets (SMMs) combine a large spin ground state with a significant magnetoanisotropy of the easy-axis or Ising type (negative axial zero-field splitting (zfs) parameter, *D*), resulting in the observation of hysteresis in magnetization versus applied field studies, as well as quantum tunneling of magnetization (QTM).[1,2]

The $[Mn_{12}O_{12}(O_2CR)_{16}(L)_4]$ family (R = various, L = H_2O or MeOH) of SMMs is by far the most extensively studied and has been enlarged with some new high-symmetry members, as well as with one-, two-, and three-electron-reduced versions.[3] In addition, there are now many different Mn_x structural types of SMMs, with nuclearities (x) up to the giant Mn_{84} torus,[4] and one of the newest members to be identified has been the family of cationic, oxide-centered, $[Mn^{III}{}_3O(O_2CR)_3(mpko)_3]^+$ triangular SMMs with mixed oximato/carboxylato ligation.[5a] These and related[5b] oximato complexes are ferromagnetically coupled with an $S = 6$ ground state, and they exhibit magnetization hysteresis loops. We have been seeking additional examples of ferromagnetically coupled triangular $Mn^{III}{}_3$ complexes for further study and herein report the synthesis and characterization of a new example of this type. It has been prepared by a reaction that employs 2,6-bis(hydroxymethyl)-*p*-cresol ($hmcH_3$), which has been used only sparingly to date in manganese cluster chemistry.[6] This takes advantage of the known ability of groups with multiple alcohol groups to foster the formation of metal clusters.[7−9] 2,6-Bis(hydroxymethyl)-*p*-cresol used in the present work incorporates both aromatic and aliphatic alcohol groups, namely, one phenol and two hydroxymethyl groups.

The reaction of $hmcH_3$ and NEt_3 with $Mn(O_2CMe)_2 \cdot 4H_2O$ in a 1:3:1 molar ratio in CH_2Cl_2 resulted in a dark-brown solution upon stirring for 20 min. The solution was filtered, and from the filtrate slowly grew large brown crystals of $[NEt_3(CH_2Cl)]_2[Mn_3O(hmcH)_3(hmcH_2)_3] \cdot 3CH_2Cl_2$ ($\mathbf{1} \cdot 3CH_2Cl_2$) in ~40% yield based on manganese.[10] The unusual $[NEt_3(CH_2Cl)]^+$ cation can be attributed to attack by NEt_3 on CH_2Cl_2 solvent molecules. There are two crystallographically independent Mn_3 anions in the unit cell, but they are structurally very similar, and thus only the one containing atoms Mn1−Mn3 will be discussed in detail.

The structure of the anion of **1** (Figure 1) consists of a near-equilateral $Mn^{III}{}_3$ triangle capped by $\mu_3\text{-}O^{2-}$ ion O19.

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(10) Anal. Calcd (found) for dried **1** (solvent-free): C, 55.10 (55.22); H, 6.60 (6.65); N, 1.89 (1.89). Crystal structure data for $\mathbf{1} \cdot 6CH_2Cl_2$: $C_{142}H_{206}Cl_{16}Mn_6N_4O_{38}$, 3473.95 g mol^{-1}, monoclinic, *Cc*, $a = 26.38(5)$ Å, $b = 29.954(6)$ Å, $c = 19.741(4)$ Å, $\beta = 93.56(4)°$, $Z = 4$, $V = 15569(5)$ Å^3, $d_{calc} = 1.422$ g cm^{-3}, $T = 173(2)$ K. Final R1 = 5.37% and wR2 = 10.82%.

10.1021/ic802084h CCC: $40.75

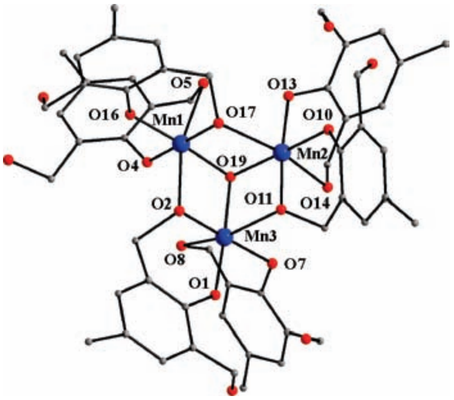

Figure 1. Partially labeled structure of the anion of complex **1**. Color code: Mn^{III}, blue; O, red; C, gray. Selected bond angles (deg): Mn1−O19−Mn2 = 103.4(6), Mn1−O19−Mn3 = 103.4(6), Mn2−O19−Mn3 = 107.9(6), Mn1−O17−Mn2 = 92.9(5), Mn1−O2−Mn3 = 93.7(5), Mn2−O11−Mn3 = 96.2(5).

Each edge is bridged by the deprotonated alkoxide arm (O2, O11, or O17) of an $\eta^1:\eta^2:\mu$-hmcH^{2-} group, whose phenoxide O atom (O1, O10, or O16) is bound terminally and whose other alcohol arm stays protonated and unbound. Octahedral coordination at each manganese is completed by a chelating $\eta^1:\eta^1$-hmcH$_2^-$ group, which is bound through its deprotonated phenoxide O atom (O4, O7, or O13) and one of its protonated alcohol arms (O5, O8, or O14), with the other protonated arm again remaining unbound. The central oxide ion, atom O19, lies 0.765 Å above the Mn_3 plane. The Mn•••Mn separations are within a small range [3.006(4)−3.035(4) Å], almost equivalent within the usual 3σ convention, but the Mn_3 triangle is, nevertheless, best described as isosceles on the basis of the distinctly different central Mn−O^{2-} bonds [Mn1−O19 = 2.001(12) Å; Mn2−O19 = 1.860(11) Å; Mn3−O19 = 1.859(12) Å] and Mn−O19−Mn angles (Figure 1, caption). The Mn^{III} oxidation states were established by charge-balance considerations and inspection of the Mn−O bond distances and confirmed quantitatively by bond valence sum (BVS) calculations.[11] The Mn^{III} atoms are near-octahedral, exhibiting Jahn−Teller (JT) axial elongations, as expected for high-spin d^4 ions in this geometry; the JT axes are O2−Mn1−O5, O14−Mn2−O17, and O8−Mn3−O11.

Solid-state, direct-current (dc) magnetic susceptibility (χ_M) data for dried complex **1** were collected in the temperature range 5.0−300 K in an applied field of 0.1 T. $\chi_M T$ steadily increases from 9.95 cm^3 K mol^{-1} at 300 K to a maximum of 18.85 cm^3 K mol^{-1} at 8.0 K before dropping slightly to 18.69 cm^3 K mol^{-1} at 5.0 K (Figure 2). This behavior is indicative of ferromagnetic exchange between the metal centers and a resulting $S = 6$ ground state, with the low temperature decrease assigned to zfs, Zeeman effects, and/or weak intermolecular antiferromagnetic interactions. The spin-only ($g = 2$) $\chi_M T$ for an $S = 6$ state is 21 cm^3 K mol^{-1}, close to the experimental value at 8.0 K. The data were fit to the theoretical expression for a Mn^{III}_3 isosceles triangle, using the 2J model of Figure 2 (inset).[5a] The fit (solid line in Figure 2) gave fit parameter values ($H = -2J\hat{S}_i\cdot\hat{S}_j$ convention) of $J = +8.7(1)$ cm^{-1}, $J' = +1.2(2)$ cm^{-1}, and $g = 1.90(1)$,[12a] indicating an $S = 6$ ground state and an $S = 5$ first excited state at 44.4 cm^{-1} higher in energy.

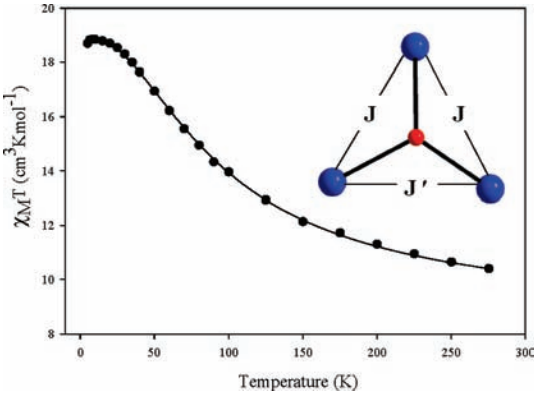

Figure 2. $\chi_M T$ vs T plot for **1**. The solid line is the fit of the data; see the text for the fit parameters.

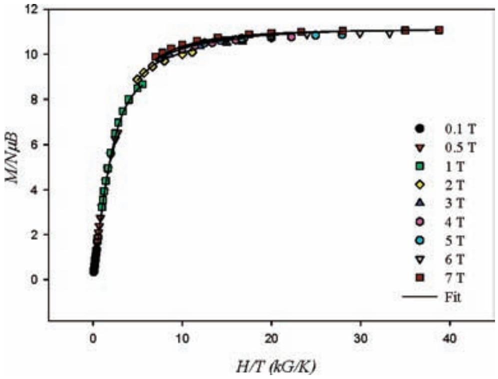

Figure 3. Plot of the reduced magnetization, $M/N\mu_B$, vs H/T for complex **1** at the indicated fields. The solid lines are the fit of the data; see the text for the fit parameters.

In order to confirm the ground state of **1**, as well as to obtain an estimate of the axial zfs parameter, D, magnetization data were collected in the 1−70 kOe and 1.8−10.0 K ranges, and these are plotted as reduced magnetization ($M/N\mu_B$) vs H/T in Figure 3. The data were fit by matrix diagonalization to a model that assumes that only the ground state is populated, includes axial zfs ($D\hat{S}_z^2$) and the Zeeman interaction, and carries out a full powder average.[12b] The best fit (solid lines in Figure 3) gave $S = 6$, $D = -0.11(3)$ cm^{-1}, and $g = 1.86(5)$; the lower-than-expected latter value is no doubt due to the assumption of axial symmetry, the inherent uncertainties in obtaining g from fits of bulk magnetization data, and other experimental errors.

Alternating-current (ac) magnetic susceptibility studies were also performed on a dried sample of **1** in the temperature range 1.8−15 K, using a 3.5 Oe ac field oscillating at frequencies in the 50−1000 Hz range. The resulting data are plotted as $\chi_M'T$ vs T in Figure S1 in the Supporting Information, where χ_M' is the in-phase component of the ac susceptibility. $\chi_M'T$ is essentially constant with

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[11] Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102. BVS for the Mn^{3+} and O^{2-} ions were 2.80−3.27 and 1.93, respectively.

[12] (a) Because **1**·6CH_2Cl_2 consists of two crystallographically independent (but structurally very similar) trinuclear molecules, the values for the fit parameters may be considered as the average. (b) Davidson, E. *MAGNET*; Indiana University: Bloomington, IN, 1999.

decreasing temperature below 15 K at a value of ~20 cm^3 K mol^{-1}, indicating an $S = 6$ ground state (with $g \sim 1.95$) that is well isolated from the nearest excited state. This is in agreement with the conclusions from the dc fits. The ac data thus further confirm an $S = 6$ ground state for the complex. No out-of-phase, χ_M'', ac signals were observed for **1** (Figure S2 in the Supporting Information), indicating the absence of slow magnetization relaxation.

It is of interest to compare **1** with other complexes with a $[Mn^{III}_3(\mu_3\text{-}O)]^{7+}$ triangular core. The latter is not uncommon in Mn^{III} chemistry:[5,13] there are antiferromagnetically coupled complexes of the general formula $[Mn_3O(O_2CR)_6L_3]^+$ (L = monodentate ligand) and recently the $[Mn^{III}_3O(O_2CR)_3(mpko)_3]^+$ family of carboxylato/oximato complexes that are ferromagnetically coupled, like **1**, and are SMMs.[5a] The central $\mu_3\text{-}O^{2-}$ ion in the former lies in the Mn^{III}_3 plane and contains essentially planar Mn−O−C−O−Mn units, whereas the $\mu_3\text{-}O^{2-}$ ion in the latter is displaced out of the plane and the edges are bridged by a combination of carboxylate and oximato ligands; the latter cause a significant Mn−N−O−Mn torsion angle ("twist"). Complex **1** is distinctively different from both of these two classes of compounds because (i) the central $\mu_3\text{-}O^{2-}$ ion lies far above the Mn_3 plane [0.765 Å in **1** vs ~0.3 Å in the $[Mn^{III}_3O(O_2CR)_3(mpko)_3]^+$ complexes], (ii) the complex is carboxylate-free, and (iii) there is no "twist" in **1** because there are only monatomic bridges on each Mn_3 edge.

There is one other carboxylate-free triangular Mn^{III}_3 complex with monatomic bridges on the edges, $[Mn_3O(5\text{-}Br\text{-}sap)_3(H_2O)_3]Cl$ (**2**), in which the central O^{2-} ion lies ~0.8 Å above the Mn_3 plane, giving the same type of $[Mn^{III}_3(\mu_3\text{-}O)(\mu\text{-}OR)_3]^{4+}$ core as that in **1**.[13f] However, small structural differences between **1** and **2**, such as larger Mn−μ-OR−Mn angles,[9d,14] are obviously enough to make this compound antiferromagnetically coupled, in contrast to **1**.

Although **1** has an $S = 6$ ground state, its low $D = -0.11$ cm^{-1} value gives an upper limit to the relaxation barrier of only 3.96 cm^{-1}, with the true barrier being even smaller because of QTM, and this is consistent with the absence of an ac out-of-phase signal (down to 1.8 K at least). The small D is consistent with the propeller-like arrangement of the Mn^{III} JT axes and their relatively small angle with the Mn_3 plane ($\theta = 19.9-37.2°$). This is distinctly different from the $[Mn^{III}_3O(O_2CR)_3(mpko)_3]^+$ complexes, which also have $S = 6$ but a larger D (~ -0.35 cm^{-1}; $\theta_{av} \sim 60°$) and which are thus SMMs.[5a]

Complex **1** thus demonstrates for the first time that it is not necessary to have oximate bridging groups on the edges of a Mn^{III}_3 triangular compound in order to have ferromagnetic coupling. While such "twists", when present, no doubt serve to increase the exact magnitude of the observed ferromagnetic exchange parameters,[15] their presence appears not to be essential to obtain ferromagnetic Mn^{III}_3 complexes; i.e., the presence of significant Mn−N−O−Mn torsion angles ("twists") is not a sine qua non for seeing ferromagnetic coupling in such species. Instead, as we have argued elsewhere,[5a] a major contributor to the ferromagnetic coupling in $[Mn^{III}_3O(O_2CR)_3(mpko)_3]^+$ and **1** is very likely the displacement of the $\mu_3\text{-}O^{2-}$ ion from the Mn_3 plane, which will weaken the $Mn-O^{2-}-Mn$ $d_\pi-p_\pi-d_\pi$ antiferromagnetic pathways/contributions to the net exchange coupling parameters, leading to net ferromagnetic coupling. This is due, of course, to the fact that an observed J value (J_{obs}) is the net sum of antiferro- and ferromagnetic contributions, J_{AF} and J_F, respectively (eq 1).

$$J_{obs} = J_{AF} + J_F \qquad (1)$$

In our opinion, the ferromagnetic coupling in triangular $[Mn_3O(bamen)_3]^+$ [$bamenH_2$ = 1,2-bis(biacetylmonoxime-imino)ethane] does not argue against this conclusion: this complex is bridged by oximate groups along the edges of the Mn^{III}_3 triangle, and its $\mu_3\text{-}O^{2-}$ ion is *in* the Mn_3 plane,[13e] which might at first glance suggest that the oxime twists are the sole cause of the ferromagnetic coupling. However, this complex contains seven-coordinate Mn^{III}: thus, (i) the symmetries and energies of the magnetic orbitals will differ from those in the other Mn^{III}_3 complexes (which contain near-octahedral Mn^{III}), and (ii) the $Mn^{III}-O^{2-}$ bonds are slightly longer on average, as expected for an increased coordination number. Thus, the $d_\pi-p_\pi-d_\pi$ overlaps will again be weakened, and antiferromagnetic contributions to the net coupling will be decreased. The $[Mn_3O(bamen)_3]^+$ complex, therefore, is to be taken, in our opinion, as merely indicating that anything that affects the antiferromagnetic interactions through the $\mu_3\text{-}O^{2-}$ ion will contribute to switching of the coupling to ferromagnetic, whether in addition to oximate "twists" or without them, and that these possibilities include displacement of the $\mu_3\text{-}O^{2-}$ ion from the Mn_3 plane, $Mn-O^{2-}$ bond lengthening, increased Mn/O $d_\pi-p_\pi$ orbital energy mismatch, or combinations thereof. All of these will weaken antiferromagnetic contributions to the net exchange coupling via the $Mn-O^{2-}-Mn$ pathways.

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Supporting Information Available: Crystallographic data (CIF format) for **1** and magnetism figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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