A Nontwisted, Ferromagnetically Coupled Mn$^{III}_3$O Triangular Complex from the Use of 2,6-Bis(hydroxymethyl)-p-cresol

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Received October 30, 2008

The reaction between Mn(O$_2$CMe)$_2$·4H$_2$O and hmcH$_3$ [hmcH$_3$ = 2,6-bis(hydroxymethyl)p-cresol] in CH$_2$Cl$_2$ in the presence of NEt$_3$ affords the Mn$^{III}_3$ complex [NEt$_3$(CH$_2$Cl)]$_2$[Mn$_3$O(hmcH)$_3$(hmcH$_2$)$_3$] (1). The anion of 1 contains a [Mn$^{III}_3$(µ$_3$-O)]$^{4+}$ 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. These and related oximato/carboxylato ligations$^5$ combine magnetization (QTM)$^1,2$ applied field studies, as well as quantum tunneling of magnetization versus hysteresis in magnetization versus magnetic field. SMMs combine a large spin ground state with a significant magnetoanisotropy of the easy-axis or Ising type. The unusual [NEt$_3$(CH$_2$Cl)]$^{4+}$ cation can be attributed to attack by NEt$_3$ on CH$_2$Cl$_2$ 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 µ$_3$-O$^{2-}$ ion O19.

(10) Anal. Calcd (found) for dried I (solvent-free): C, 55.10 (55.22); H, 6.60 (6.65); N, 1.89 (1.89). Crystal structure data for I·6CH$_2$Cl$_2$: C$_{14}$H$_{26}$O$_8$Mn$_3$N$_x$O$_y$: 3473.95 g mol$^{-1}$, monoclinic, $C_c$; $a = 26.38(5)$ Å; $b = 29.954(6)$ Å; $c = 19.741(4)$ Å; $β = 93.56(4)^o$; 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%.
Each edge is bridged by the deprotonated alkoxide arm (O2, O11, or O17) of an \( \eta^1: \eta^1 \)-hmch2 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 \( \eta^1: \eta^1 \)-hmch2 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, atom O19, lies 0.765 Å above the Mn3 plane. The protonated arm again remaining unbound. The central oxide 

\[ \text{Mn}^{III} - \text{Mn}^{III} - \text{Mn}^{III} \]

protons were 2.80 Å. 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 Mn3 triangle is, nevertheless, best described as isosceles. 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 Mn3 triangle is, nevertheless, best described as isosceles. 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 Mn3 triangle is, nevertheless, best described as isosceles. 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 Mn3 triangle is, nevertheless, best described as isosceles. 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 Mn3 triangle is, nevertheless, best described as isosceles.

Solid-state, direct-current (dc) magnetic susceptibility (\( \chi_M \)) 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 cm³ K mol⁻¹ at 300 K to a maximum of 18.85 cm³ K mol⁻¹ at 8.0 K before dropping slightly to 18.69 cm³ 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 cm³ K mol⁻¹, close to the experimental value at 8.0 K. The data were fit to the theoretical expression for a Mn\(^{III} \) 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.

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/\( N_{Hb} \)) 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\( \hat{S}_z \)) 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 \( \chi_M \) is the in-phase component of the ac susceptibility. \( \chi_M T \) is essentially constant with

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\( \text{(11)} \) Liu, W.; Thorp, H. H. Inorg. Chem. 1993, 32, 4102. BVS for the Mn\(^{III} \) and O\(^{2-} \) ions were 2.80–3.27 and 1.93, respectively.

\( \text{(12)} (\text{a}) \) Because 1‧6CH2Cl2 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 ~ 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″ 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 [MnIII₃(µ₃-O)₇]⁺⁺ triangular core. The latter is not uncommon in MnIII chemistry;⁵,¹³ there are antiferromagnetically coupled complexes of the general formula [Mn₃₋₁O₂ClBr₂L₃]⁺⁺ (L = monodentate ligand) and recently the [Mn₃₋₁O₂Cr₂(mpko)₃]⁺ family of carboxyato/oximate complexes that are ferromagnetically coupled, like 1, and are SMMs.⁵ᵃ The central µ₃-O²⁻ ion in the former lies in the Mn₃ plane and contains essentially planar Mn—O—C—O—Mn units, whereas the µ₃-O²⁻ ion in the latter is displaced out of the plane and the edges are bridged by a combination of carboxylato and oximate ligands; the latter cause a significant Mn—N—O—Mn torsion angle (“twist”). Complex 1 is distinctly different from both of these two classes of compounds because (i) the central µ₃-O²⁻ ion lies far above the Mn₃ plane (0.765 Å in 1 vs ~0.3 Å in the [Mn₃₋₁O₂Cr₂(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 Mn₃ edge.

There is one other carboxylate-free triangular Mn₃ complex with monatomic bridges on the edges, [Mn₃(O5-Br-sap)(H₂O)₃]Cl (2), in which the central O²⁻ ion lies ~0.8 Å above the Mn₃ plane, giving the same type of [Mn₃₋₁(µ₃-O)(µ-OR)]⁺⁺ core as that in 1.¹³ 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 Mn₃ JT axes and their relatively small angle with the Mn₃ plane (θ = 19.9°–37.2°). This is distinctly different from the [Mn₃₋₁O₂Cr₂(mpko)₃]⁺ complexes, which also have S = 6 but a larger D (~0.35 cm⁻¹; θav ~ 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 Mn₃⁺⁺ 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 Mn₃⁺⁺ 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 [Mn₃₋₁O₂Cr₂(mpko)₃]⁺ and 1 is very likely the displacement of the µ₃-O²⁻ ion from the Mn₃ plane, which will weaken the Mn—O²⁻—Mn d₃—pₓ—d₅ 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 (Jobs) is the net sum of antiferro- and ferromagnetic contributions, JAF and JF, respectively (eq 1).

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J_{obs} = J_{AF} + J_F
\]

In our opinion, the ferromagnetic coupling in triangular [Mn₃O(bamen)]⁺⁺ [bamenH₂ = 1,2-bis(biacetylmonoxime- imino)ethane] does not argue against this conclusion: this complex is bridged by oximate groups along the edges of the Mn₃ triangle, and its µ₃-O²⁻ ion is in the Mn₃ 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 MnIII; thus, (i) the symmetries and energies of the magnetic orbitals will differ from those in the other Mn₃⁺⁺ complexes (which contain near-octahedral MnIII), and (ii) the Mn—O—O bonds are slightly longer on average, as expected for an increased coordination number. Thus, the d₃—pₓ—d₅ overlaps will again be weakened, and antiferromagnetic contributions to the net coupling will be decreased. The [Mn₂O(bamen)]⁺⁺ complex, therefore, is to be taken, in our opinion, as merely indicating that anything that affects the antiferromagnetic interactions through the µ₃-O²⁻ 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 µ₃-O²⁻ ion from the Mn₃ plane, Mn—O²⁻ bond lengthening, increased Mn/O d₃—pₓ orbital energy mismatch, or combinations thereof. All of these will weaken antiferromagnetic contributions to the net exchange coupling via the Mn—O²⁻—Mn pathways.

**Acknowledgment.** This work was supported by NSF Grant CHE-0414555.

**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.

IC802084H

