

High Nuclearity Molecular Species Exhibiting Spin Frustration: Fusion of Two $\text{Mn}^{\text{III}}\text{O}_2$ Butterfly Complexes to yield an Intermediate Spin Ground State $\text{Mn}^{\text{III}}_7\text{O}_4$ Complex

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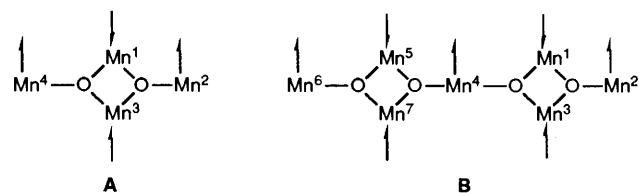
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The preparation and characterization of $(\text{NEt}_4)[\text{Mn}_7\text{O}_4(\text{OAc})_{10}(\text{dbm})_4] \cdot 3\text{CH}_2\text{Cl}_2 \cdot 2\text{C}_6\text{H}_{14}$ ($1 \cdot 3\text{CH}_2\text{Cl}_2 \cdot 2\text{C}_6\text{H}_{14}$) (H dbm = dibenzoylmethane) are reported; the $\text{Mn}^{\text{III}}_7\text{O}_4$ core of **1** consists of two Mn_4O_2 butterfly units fused together by sharing of one wing-tip manganese atom and it is shown using magnetization data that complex **1** has either an $S = 3$ or $S = 4$ ground state.

Three different types of transition metal-containing molecular ferromagnets have recently been reported: organometallic ferromagnets^{1,2} that consist of metallocene cations and radical organic anions; ferrimagnetic Cu^{II} -bridge- Mn^{II} compounds;³ and ferrimagnetic chains⁴ consisting of metal complexes with paramagnetic nitroxide ligands. High-spin organic⁵ and transition metal⁶ molecules should serve as good building blocks for molecular magnetic materials.⁷ One major problem in constructing a molecule-based ferromagnet concerns the engineering of intermolecular interactions so that they are appreciable and lead to a net ferromagnetic ordering. Recently, we suggested⁸ that polynuclear metal complexes, which have relatively high-spin ground states as a result of spin frustration, may be good building blocks for molecular magnets. A number of discrete oxide-bridged Fe^{III}_x and Mn^{III}_x complexes⁹⁻¹¹ have been shown to exhibit spin frustration. In the case of $\text{Mn}^{\text{III}}_4\text{O}_2$ butterfly complexes an $S = 3$ ground state results (**A**) because the $\text{Mn}^{\text{I}}-\text{Mn}^{\text{III}}$ body-body antiferromagnetic exchange interaction ($J_{1,3}$ parameter for $-2J\hat{S}_i \cdot \hat{S}_j$ Hamiltonian) dominates the antiferromagnetic $\text{Mn}(\text{body})-\text{Mn}(\text{wing tip})$ (*i.e.* $J_{1,2} = J_{2,3} = J_{3,4} = J_{1,4}$) interactions. Thus, the $S = 2$

spins on the Mn^{I} and Mn^{III} ions almost spin pair and this frustrates the spins on the two wing-tip Mn^{II} ions in **A**. In this communication we show how spin frustration can lead to appreciable numbers of unpaired electrons in a complex whose core is derived by the fusion of two Mn_4O_2 butterfly units, suggesting that extrapolation of this effect to polymeric systems might be a viable means to ferromagnetic solids.

A brown solution of $[\text{Mn}_4\text{O}_2(\text{OAc})_6(\text{py})_2(\text{dbm})_2]^{12}$ **2** (H dbm = dibenzoylmethane; py = pyridine) in CH_2Cl_2 was treated with 1 equiv. of $\text{NEt}_4\text{Cl} \cdot x\text{H}_2\text{O}$. After *ca.* 6 h and with no noticeable colour change having occurred, the solution was layered with Et_2O -hexane (2:1) and stored at 0 °C. After several days, large essentially black crystals had formed in 55–60% isolated yield. Crystallographic studies[†] indicated the formulation $(\text{NEt}_4)[\text{Mn}_7\text{O}_4(\text{OAc})_{10}(\text{dbm})_4] \cdot 3\text{CH}_2\text{Cl}_2 \cdot 2\text{C}_6\text{H}_{14}$, ($1 \cdot 3\text{CH}_2\text{Cl}_2 \cdot 2\text{C}_6\text{H}_{14}$), but isolated crystals lose sol-



[†] Crystallographic data at -155 °C: triclinic, space group $P\bar{1}$; $a = 18.422(3)$, $b = 22.162(4)$, $c = 14.794(3)$ Å, $\alpha = 90.04(1)$, $\beta = 96.18(1)$, $\gamma = 113.02(1)^\circ$, $Z = 2$; $R = 0.0873$, $R_w = 0.0908$ using 7157 reflections with $F > 3.00\sigma(F)$. The structure was solved by a combination of direct methods (MULTAN) and Fourier techniques. All non-hydrogen atoms were readily located. Owing to the large number of atoms in the structure, no attempt was made to include hydrogen atoms. Three well defined CH_2Cl_2 solvate molecules were located; however, the hexane solvate molecules are disordered. Only the Mn and Cl atoms were refined with anisotropic thermal parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, issue No. 1.

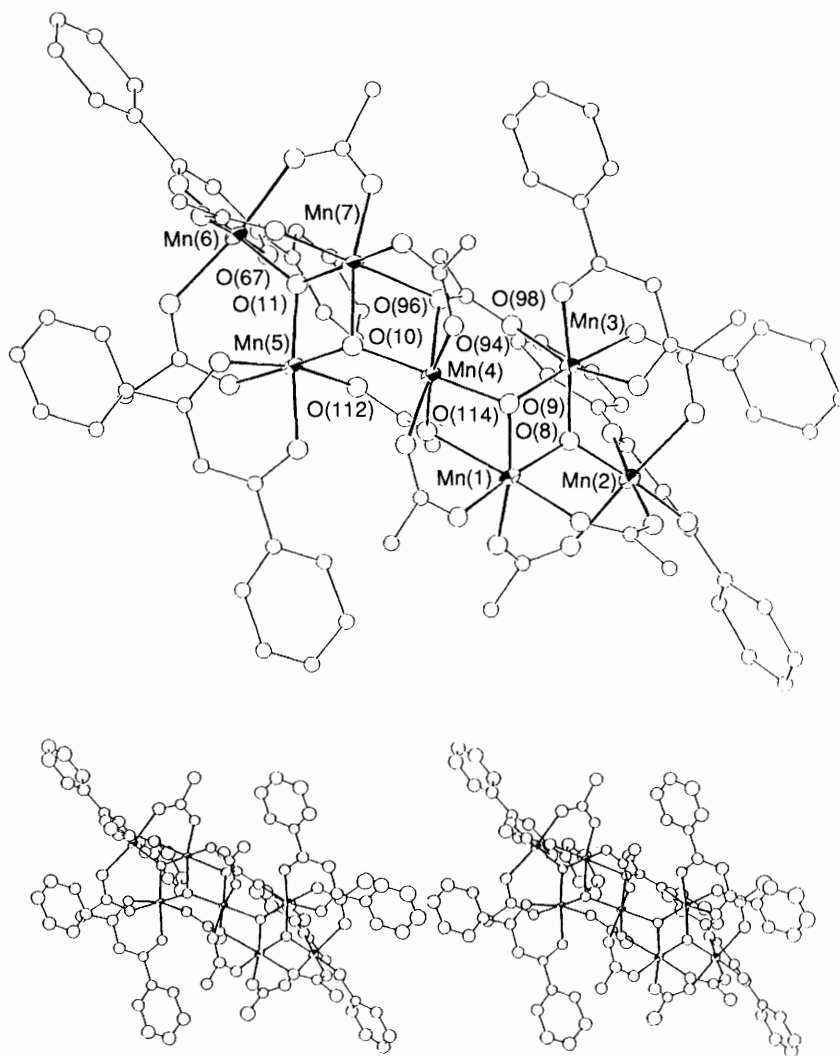


Fig. 1 Labeled structure and stereoview of the anion of complex **1**. Large circles represent oxygen, small circles carbon. Selected distances (Å) and angles (°): Mn(1)···Mn(2), 3.338(3); Mn(1)···Mn(3), 2.862(4), Mn(1)···Mn(4), 3.079(3); Mn(2)···Mn(3), 3.380(3); Mn(3)···Mn(4), 3.347(4); Mn(4)···Mn(5), 3.332(6); Mn(4)···Mn(7), 3.089(3); Mn(5)···Mn(6), 3.374(3); Mn(5)···Mn(7), 2.849(4); Mn(6)···Mn(7), 3.324(4); Mn(1)–O(8), 1.896(10); Mn(1)–O(9), 1.902(9); Mn(2)–O(8), 1.855(10); Mn(3)–O(8), 1.889(10); Mn(3)–O(9), 1.911(10); Mn(4)–O(9), 1.905(10); Mn(4)–O(10), 1.888(10); Mn(5)–O(10), 1.933(10); Mn(5)–O(11), 1.884(10); Mn(6)–O(11), 1.868(9); Mn(7)–O(10), 1.911(10); Mn(7)–O(11), 1.864(10); O(8)–Mn(1)–O(9), 82.3(4); O(8)–Mn(3)–O(9), 82.2(4); O(9)–Mn(4)–O(10), 178.8(4); Mn(1)–O(8)–Mn(2), 125.7(5); Mn(1)–O(8)–Mn(3), 98.2(5); Mn(2)–O(8)–Mn(3), 129.1(5); Mn(1)–O(9)–Mn(3), 97.3(4); Mn(1)–O(9)–Mn(4), 108.0(1); Mn(3)–O(9)–Mn(4), 122.6(5).

vent *extremely* rapidly.‡ The structure of the anion of **1** (Fig. 1) consists of a $[\text{Mn}_7(\mu_3\text{-O})_4]^{13+}$ core peripherally ligated by ten bridging acetate and four chelating dbm[−] groups. Eight acetates are in the familiar μ_2 bridging mode whereas the remaining two [O(96), O(98); O(112), O(114)] are in the rarer μ_3 mode.¹³ Based on charge considerations and metric parameters, the metals are all Mn^{III}. The Mn₇O₄ core of **1** can be considered as two Mn₄O₂ butterfly units fused together by sharing of one wing-tip Mn atom [Mn(4)]. Such wing-tip-sharing structural units are extremely rare but not unknown, with one previous example in Mn chemistry.¹⁴ Two of the $\mu_3\text{-O}^{2-}$ ions [O(9) and O(10)] are pyramidal, as in **2**, whereas the remaining two [O(8) and O(11)] are almost trigonal planar; oxygen atoms O(9) and O(10) are *ca.* 0.64 Å above their Mn₃ planes, in contrast to only *ca.* 0.28 Å for O(8) and O(11).

Magnetic susceptibility data were measured for a polycrystalline sample of complex **1** at 10 kG (1 G = 10^{−4} T) in the range 5.01 to 260.0 K. Fig. 2 shows that the effective magnetic

moment (μ_{eff}) per molecule at 260.0 K is 10.06 μ_{B} and gradually decreases with decreasing temperature to 8.17 μ_{B} at 40.0 K, whereupon it decreases more rapidly to 6.04 μ_{B} at 5.01 K. The shape of the 40.0–260.0 K μ_{eff} vs. temperature curve of complex **1** (Fig. 2) is similar to those reported¹¹ for Mn^{III}₄O₂ butterfly complexes. Furthermore, the value of μ_{eff} /molecule for complex **1** in this temperature range is proportionately larger than μ_{eff} /molecule values for Mn^{III}₄O₂ complexes. Thus, the two Mn^{III}₄O₂ butterfly complexes have been fused together to form the anion in complex **1** in such a way that there is still an appreciable number of unpaired electrons.

The reduced magnetization, $M/(N\mu_{\text{B}})$ (N is Avogadro's number and μ_{B} is the Bohr magneton), was determined at 50.0 kG for a sample of complex **1** in the temperature range of 2.0–30.0 K. The 50.0 kG magnetization data in Fig. 2, together with preliminary magnetization data at other fields, indicate that complex **1** has either an $S = 3$ or $S = 4$ ground state. There may be appreciable zero-field splitting and/or low-lying excited states as found¹¹ for the Mn^{III}₄O₂ complexes. Considerable additional magnetization data and detailed fittings to theoretical models will be necessary to specify the spins of low-energy states in complex **1**.

‡ Dried solid is also hygroscopic. Satisfactory elemental analyses were obtained for $1 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2 \cdot \frac{1}{2}\text{C}_6\text{H}_{14} \cdot \text{H}_2\text{O}$.

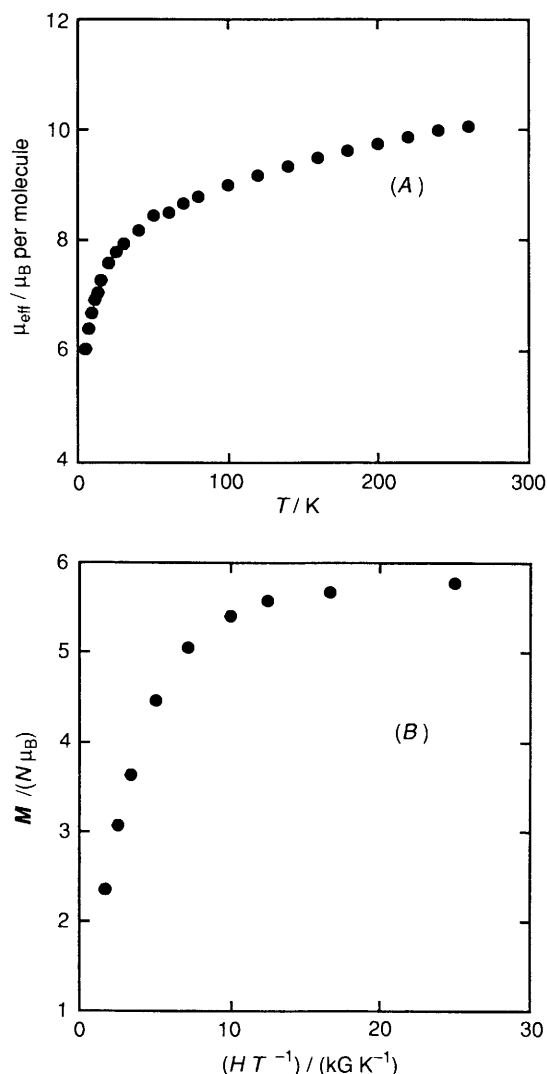
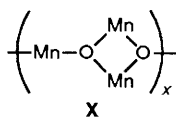


Fig. 2 Panel (A) shows a plot of the effective magnetic moment per molecule vs. temperature for a polycrystalline sample of complex **1** maintained at 10.0 kG. Panel (B) shows a plot of the reduced magnetization, $M/N\mu_B$, vs. temperature for a polycrystalline sample of complex **1**. The magnetization data were collected at a field of 50.0 kG in the 2.00–30.0 K range.

An $S = 4$ or $S = 3$ ground state for the anion in complex **1** clearly establishes the presence of spin frustration in this fused butterfly complex (see drawing **B**). The antiferromagnetic couplings in the two body pairs (Mn^1-Mn^3 and Mn^5-Mn^7) will dominate to give a resultant $S = 1$ (or 0) for each pair. The $S = 2$ spins on each of the three wing-tip ions (Mn^2 , Mn^4 and Mn^6) are frustrated and cannot pair their spins totally with neighbouring body manganese ions. If each body pair has $S = 1$, then the antiferromagnetic interactions between body pairs and wing-tip ions would give a ground state with $S = 4$ for complex **1**. Further, these arguments suggest that extension of the Mn_4O_2 'chain' should result in yet higher nuclearity spin-frustrated systems. Thus, it is clear that retention of spin frustration effects within polymeric units **X** is a potential



means of access to materials possessing a large number of unpaired electrons, *i.e.* ferromagnetic solids.

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