High Nuclearity Molecular Species Exhibiting Spin Frustration: Fusion of Two MnIII2O2 Butterfly Complexes to yield an Intermediate Spin Ground State MnIII7O4 Complex

Sheyi Wang, Hui-Lien Tsai, William E. Streib, George Christou* and David N. Hendrickson

Department of Chemistry and the Molecular Structure Center, Indiana University, Bloomington, Indiana 47405, USA
Department of Chemistry 0506, University of California at San Diego, La Jolla, California 92093-0506, USA

The preparation and characterization of \((\text{NET}_4)_2[\text{Mn}_7\text{O}_4(\text{OAc})_{10}(\text{dbm})_4].3\text{CH}_2\text{Cl}_2.2\text{C}_6\text{H}_14\) (1.3CH2Cl2.2C6H14) (H dbm = dibenzoylmethane) are reported; the MnIII7O4 core of 1 consists of two Mn4O2 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\(^1\) that consist of metallocene cations and radical organic anions; ferrimagnetic CuII-bridge-MnIII compounds\(^3\); and ferrimagnetic chains\(^4\) consisting of metal complexes with paramagnetic nitroxide ligands. High-spin organic\(^5\) and transition metal\(^6\) 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 suggested\(^8\) 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 FeIII\(_x\) and MnIII\(_x\) complexes\(^9\)-\(^11\) have been shown to exhibit spin frustration. In the case of MnIII4O2 butterfly complexes an \(S = 3\) ground state results (A) because the MnI-MnI body-body antiferromagnetic exchange interaction \((J_{1,3} \text{ parameter for } -2J_{S,S}S\) Hamiltonian) dominates the antiferromagnetic Mn(body)-Mn(wing tip) \((i.e. J_{1,3} = J_{2,4} = J_{3,4} = J_{1,4})\) interactions. Thus, the \(S = 2\) spins on the MnI and MnI\(_3\) ions almost spin pair and this frustrates the spins on the two wing-tip MnIII 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 Mn4O2 butterfly units, suggesting that extrapolation of this effect to polymeric systems might be a viable means to ferromagnetic solids.

A brown solution of \([\text{Mn}_4\text{O}_2(\text{OAc})_6(\text{py})_2(\text{dbm})_2]_2(\text{H-dbml = dibenzoylmethane; py = pyridine})\) in CH2Cl2 was treated with 1 equiv. of NET4Cl-xH2O. After ca. 6 h and with no noticeable colour change having occurred, the solution was layered with Et2O-hexane (2:1) and stored at 0°C. After several days, large essentially black crystals had formed in 55-60% isolated yield. Crystallographic studies\(^\dagger\) indicated the formulation \((\text{NET}_4)_2[\text{Mn}_7\text{O}_4(\text{OAc})_{10}(\text{dbm})_4].3\text{CH}_2\text{Cl}_2.2\text{C}_6\text{H}_14\), but isolated crystals lose solvate molecules on heating.

\(\dagger\) Crystallographic data at -155 °C: triclinic, space group P\(\bar{1}\); \(a = 18.422(3), b = 22.162(4), c = 14.794(3)\) \(\AA, \alpha = 90.04(1), \beta = 96.18(1), \gamma = 113.02(1)\); \(Z = 2; R = 0.0873, R_w = 0.0908\) using 7157 reflections with \(F > 3.00o(F)\). 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 CH2Cl2 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.
vent extremely rapidly. The structure of the anion of I (Fig. 1) consists of a [Mn7(μ3-O)4]13+ core peripherally ligated by ten bridging acetate and four chelating dbm− groups. Eight acetates are in the familiar μ2 bridging mode whereas the remaining two [O(96), O(98); O(112), O(114)] are in the rarer μ3 mode.13 Based on charge considerations and metric parameters, the metals are all MnI+. The Mn7O4 core of I 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 only previous example in Mn chemistry.14 Two of the μ3-O2− 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 I at 10 K (1 G = 10−4 T) in the range 5.01 to 260.0 K. Fig. 2 shows that the effective magnetic moment (μeff) per molecule at 260.0 K is 10.06 μB and gradually decreases with decreasing temperature to 8.17 μB at 40.0 K, whereupon it decreases more rapidly to 6.04 μB at 5.01 K. The shape of the 40.0–260.0 K μeff vs. temperature curve of complex I (Fig. 2) is similar to those reported11 for MnII14O2 butterfly complexes. Furthermore, the value of μeff/molecule for complex I in this temperature range is proportionately larger than μeff/molecule values for MnII14O2 complexes. Thus, the two MnII14O2 butterfly complexes have been fused together to form the anion in complex I in such a way that there is still an appreciable number of unpaired electrons.

The reduced magnetization, M/(NμB) (N is Avogadro’s number and μB is the Bohr magneton), was determined at 50.0 kG for a sample of complex I 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 I 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 MnII14O2 complexes. Considerable additional magnetization data and detailed fittings to theoretical models will be necessary to specify the spins of low-energy states in complex I.

† Dried solid is also hygroscopic. Satisfactory elemental analyses were obtained for 1·CH2Cl2·IC6H4·H2O.
The Mn402 ‘chain’ should result in yet higher nuclearity than the antiferromagnetic interactions between body pairs are frustrated and cannot pair their spins totally with spins on each of the three wing-tip ions (Mn2, Mn4 and Mn6) and wing-tip ions would give a ground state with butterfly complex (see drawing). Neighbouring body manganese ions. If each body pair has dominate to give a resultant couplings in the two body pairs (Mn \textsuperscript{1}-Mn\textsuperscript{3} and Mn\textsuperscript{7}-Mn\textsuperscript{8}) will frustration effects within polymeric units spin-frustrated systems. Thus, it is clear that retention of spin means of access to materials possessing a large number of unpaired electrons, i.e. ferromagnetic solids.

This work was supported by the National Institutes of Health and the National Science Foundation. We thank the Dreyfus Foundation for a Teacher-Scholar Grant (G. C.)

Received, 3rd January 1992; Corn. 200015F

Fig. 2 Panel (A) shows a plot of the effective magnetic moment per molecule vs. temperature for a polycrystalline sample of complex I maintained at 10.0 kG. Panel (B) shows a plot of the reduced magnetization, M/NH\textsubscript{A}, vs. temperature for a polycrystalline sample of complex I. The magnetization data were collected at a field of 50.0 kG. The antiferromagnetic couplings in the two body pairs (Mn\textsuperscript{1}-Mn\textsuperscript{3} and Mn\textsuperscript{7}-Mn\textsuperscript{8}) 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\textsuperscript{2}, Mn\textsuperscript{4} and Mn\textsuperscript{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 I. Further, these arguments suggest that extension of the Mn\textsubscript{2}O\textsubscript{4} ‘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

$\left( \frac{H T^{-1}}{(kG^{-1})} \right)$

$T/K$

$M/(\mu B)$

$\left( \frac{H T^{-1}}{(kG^{-1})} \right)$

$\mu_B/\mu_B$ per molecule

References

13. See also: A. R. Schake, J. B. Vincent, Q. Li, P. D. W. Boyd, K. Folting, J. C. Huffman, D. N. Hendrickson and G. Christou, Inorg. Chem., 1989, 28, 1915. Since the Mn(1)-O(114) and Mn(7)-O(96) distances are quite long (ca. 2.3 Å), it is expected that these two unusual acetate groups would not provide very viable magnetic exchange pathways.