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Supercubane Mixed-Valence Tridecanuclear Manganese Complex

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Molecules with a large number of unpaired electrons are potential building blocks for magnetic materials.[1−5] In a related active area of research the focus has been on nanoscale magnetic materials.[6−8] Nanoscale magnets have been prepared by fragmenting bulk ferromagnets or ferrimagnets; however, this gives a material with a range of particle sizes. Only one class (four examples) of molecules has been characterized that behaves as a single-molecule magnet.[9−15] These molecules have 12 manganese ions and exhibit magnetization hysteresis loops below 3 K. Here we report the synthesis, X-ray structure, and magnetochemical properties of a Mn_{13} complex that has a novel supercubane $[Mn^{IV}Mn^{III}_6Mn^{II}_6(\mu_5\text{-}O)_6(\mu_3\text{-}O)_2(\mu_3\text{-}OEt)_6]^{12+}$ core. This core is structurally similar to a piece of a cubic metal oxide extended lattice. A $S = {}^{15}/_{2}$ ground state (15 unpaired electrons) is found for the complex, a ground state that is explicable in terms of two interpenetrating spin sublattices. The complex is, in essence, a piece of an extended metal−oxide antiferromagnet.

A 25 wt % solution of $[Me_4N]OH$ (0.213 g, 2.34 mmol) in methanol (1 mL) was added dropwise to a methanol−tetrahydrofuran (1:1) solution of $Mn(O_2CPh)_2{\cdot}2H_2O$ (1.0 g, 2.71 mmol) and 2,2′-biphenol (0.10 g, 0.54 mmol). The resulting solution was stirred for 10 min and then heated to boiling for 1 h. Evaporation to dryness, followed by washing with methanol, gave a red-brown crystalline product. Crystals of $[Mn_{13}(\mu_5\text{-}O)_6(\mu_3\text{-}O)_2(\mu_3\text{-}OEt)_6(O_2CPh)_{12}]$ (**1**) were obtained by dissolving some of the product in THF/EtOH and layering this solution with CH_2Cl_2. A single-crystal X-ray diffraction study[16] showed that complex **1** at 192 K is monoclinic with space group $C2/c$ (unit-cell constants $a = 24.936(13)$ Å, $b = 15.129(8)$ Å, $c = 29.015(14)$ Å, $V = 10688(10)$ Å^3, $Z = 4$, $d_{calc} = 1.595$ g cm^{-3}, $\mu = 1.559$ mm^{-1}, 9608 reflections collected, 7309 observed ($F > 4.0\sigma(F)$), $R = 4.22\%$ and $R_w = 5.70\%$).

An ORTEP drawing of complex **1** is shown in Figure 1, where the $[Mn^{IV}Mn^{III}_6Mn^{II}_6(\mu_5\text{-}O)_6(\mu_3\text{-}O)_2(\mu_3\text{-}OEt)_6]^{12+}$ core is also shown. It can be seen that the 13 manganese, six $\mu_5\text{-}O^{2-}$, two $\mu_3\text{-}O^{2-}$, and six $\mu_3\text{-}OEt^-$ ions are arranged in a distorted supercubane $[Mn_{13}O_8(OEt)_6]^{12+}$ core. Eight of the oxygen atoms are located at the vertices of the cube and the other six oxygen atoms ($\mu_5\text{-}O^{2-}$) are found near the face centers. Twelve of the manganese ions are found at the centers of edges, and one is at the body center of the supercubane. Every manganese ion is six-coordinate with six oxygen atom ligands. Each of the 12 benzoate ligands symmetrically bridges between two Mn ions. In addition to the novel supercubane structure, two other features of complex **1** are unusual: $\mu_5\text{-}O^{2-}$ ions are very rare; and a Mn^{IV}, Mn^{III}, Mn^{II} mixed-valence composition with three oxidation states is very unusual. As far as we know, there is only one other example of a $\mu_5\text{-}O^{2-}$ bridge found in $[(C_5H_5)_5Y_5(\mu\text{-}OCH_3)_4(\mu_3\text{-}OCH_3)_4(\mu_5\text{-}O)]$.[17] A bond valence sum analysis[18] confirms that the central manganese ion Mn(7) is Mn^{IV} and is interacting with six Mn^{III} and six Mn^{II} ions. It is extremely rare to have a molecule form spontaneously that has a metal ion present in three different oxidation states. The manganese ions labeled Mn(1), Mn(1a), Mn(2), Mn(2a), Mn(3), and Mn(3a) are the Mn^{III} ions, as substantiated by the tetragonally elongated Jahn-Teller distortion present at each of these Mn^{III} ions.

In view of the fact that the core of complex **1** bears a strong resemblance to a piece of an extended metal oxide lattice, it was of interest to characterize the magnetochemistry of complex **1**. Variable-temperature (2−320 K) magnetic susceptibility data were determined for a polycrystalline sample in a 10.0 kG dc magnetic field employing a SQUID susceptometer. In the inset of Figure 2 is shown a plot of the effective magnetic moment (μ_{eff}) per molecule versus temperature. The value of μ_{eff} increases with decreasing temperature from 18.6 μ_B at 320 K to a maximum of 18.9 μ_B at ∼180 K, below which μ_{eff} decreases to become eventually 9.05 μ_B at 2.00 K. Curiously, there is a region of almost linear decrease in μ_{eff} in the 80−10 K range.

Variable-field (10.0−50.0 kG) magnetization data run in the 2−30 K range are shown in Figure 2. The data are plotted as reduced magnetization, $M/N\mu_B$ (where M is magnetization, N is Avogadro's number and μ_B is the Bohr magneton), versus

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(16) A brown-black single crystal (0.35 × 0.50 × 0.70 mm) was mounted on a glass fiber coated with silicone grease. Data were collected on a Siemens R 3m/V diffractometer equipped with a graphite monochromater and Mo Kα radiation at $\lambda = 0.71073$Å using the $\omega-2\theta$ scan (3.0−50.0°). Of the 9608 reflections collected, 9417 were unique ($R_{int} = 1.63\%$). The structure was solved by direct methods by using the Siemens SHELXTL PLUS (PC version) computer program. Refinement was carried out by full-matrix least-squares methods, with all non-hydrogen atoms assigned anisotropic thermal parameters. Two of the three independent ethoxy ligands were disordered, and all three were described as idealized rigid bodies. The disorder was described with two at O5 (80% and 20% occupancy), two at O7 (60% and 40% occupancy), and a single ligand at O6. In the last cycles, we used independent 100% O5, O6, and O7 atoms with the bonded carbon atoms and their hydrogen atoms as aggregated rigid bodies. Hydrogen atoms were included with fixed isotropic thermal parameters. A total of 664 parameters were refined. Some 7309 observed [$F > 4.0\sigma(F)$] reflections gave $R = 4.22\%$ and $R_w = 5.70\%$.

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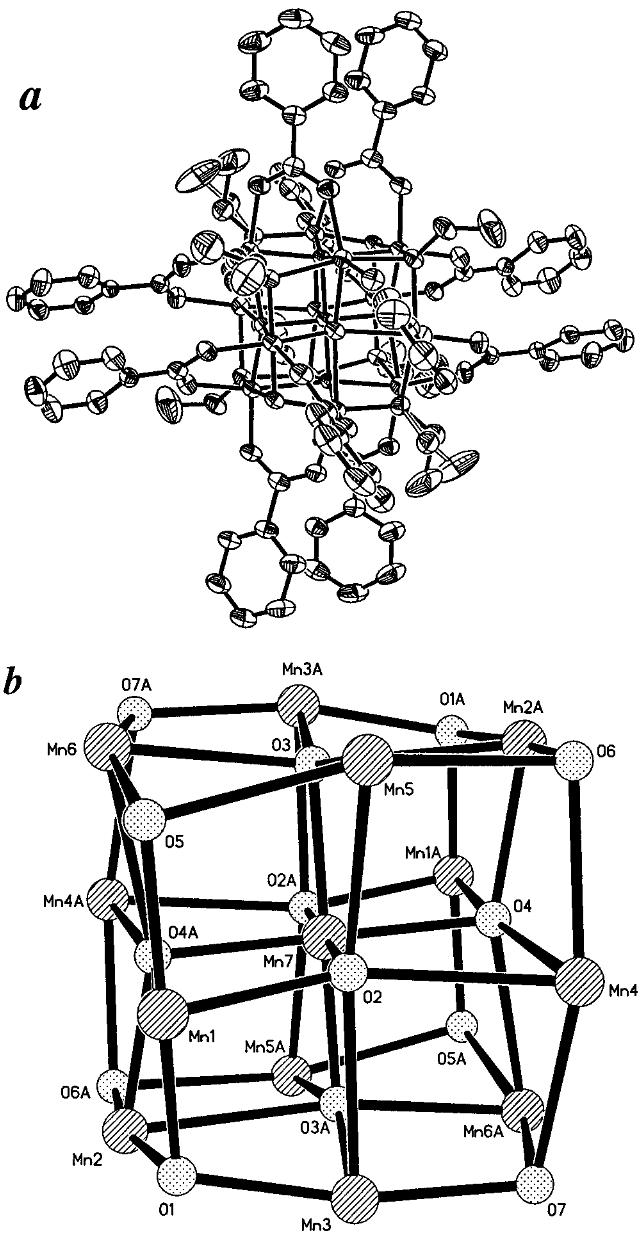

Figure 1. (a) The structural framework and (b) the supercubane $[Mn^{IV}Mn^{III}_6Mn^{II}_6(\mu_5\text{-}O)_6(\mu_3\text{-}O)_2(\mu_3\text{-}OEt)_6]^{12+}$ core of $[Mn_{13}(\mu_5\text{-}O)_6(\mu_3\text{-}O)_2(\mu_3\text{-}OEt)_6(O_2CPh)_{12}]$ (**1**) with the atom numbering scheme. The hydrogen atoms of the benzoate groups were omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

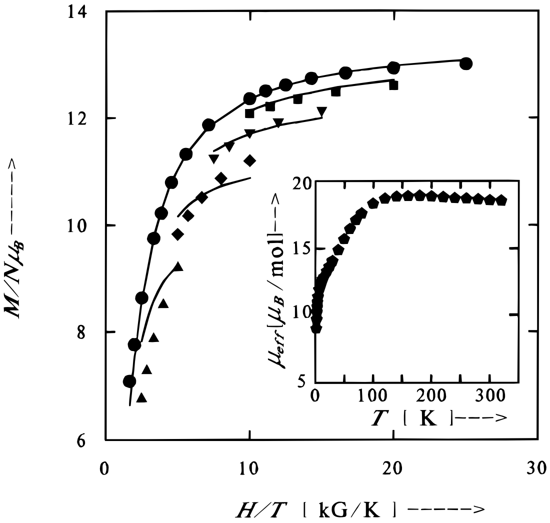

Figure 2. Plot of reduced magnetization, $M/N\mu_B$, versus the ratio of the magnetic field to the absolute temperature, H/T, for complex **1**. M is magnetization, N is Avogadro's number, μ_B is the Bohr magneton, H is the magnetic field, and T is the temperature. Data were measured in the 2.0−4.0 K range for the magnetic fields of (▲) 10.0 kG, (◆) 20.0 kG, (▼) 30.0 kG, and (■) 40.0 kG and in the 2.0−30.0 K range at (●) 50.0 kG. The solid lines result from least-squares fitting the data to the spin Hamiltonian and the best fit[19] was found with a $S = {}^{15}/_2$ ground state with $D = 0.33$ cm^{-1} and $g = 1.87$. The inset shows a plot of the effective magnetic moment (μ_{eff}) per molecule versus temperature measured for a polycrystalline sample of complex **1** in a 10.0 kG field.

the ratio of the magnetic field H divided by the absolute temperature T. In a field of 50.0 kG the value of $M/N\mu_B$ approaches saturation at a value of 13.0. Least-squares fitting of the data[19] (solid lines) indicate that complex **1** has a $S = {}^{15}/_2$ ground state. The poorer fit of reduced magnetization data at the lower fields could reflect the situation that the ground state is not the only state populated at low temperatures in a relatively small field. This is an intriguing result, for it can be rationalized by assuming that the magnetic properties of complex **1** can be explained in analogy to those for extended metal oxides. For such a metal oxide that is an antiferromagnet the long-range ordering of spins generally results from two interpenetrating sublattices.[20] Half of the metal ions are found in sublattice A; each metal ion in sublattice A usually has as its nearest neighbors metal ions in sublattice B. Thus, in one type of ordering in an extended antiferromagnet there are alternating layers of ions in the two different sublattices. The $S = {}^{15}/_2$ ground state of complex **1** can be rationalized analogously. If the 13 Mn ions in the core (see Figure 1b) are assumed to be grouped in three layers, then the $S = {}^{15}/_2$ ground state can be explained. In the top layer there are two Mn^{III} and two Mn^{II} ions [Mn(2a), Mn(3a), Mn(5) and Mn(6)], which if all ions had their spins aligned would give $S = {}^5/_2 + {}^5/_2 + {}^4/_2 + {}^4/_2 = {}^{18}/_2$. The middle layer has one Mn^{IV}, two Mn^{III}, and two Mn^{II} ions to give $S = {}^{21}/_2$ if all spins are aligned for this layer. Thus, the first and third layers each have $S = {}^{18}/_2$, whereas the middle layer has $S = {}^{21}/_2$. If the spins are aligned "up", "down", and "up" from the first to the second to the third layer, then complex **1** would have a ground state with $S = {}^{15}/_2$.

It will be interesting to confirm the spin alignment suggested above for complex **1** to see that it is magnetically behaving as a small piece of an extended metal−oxide antiferromagnet. Efforts are underway to try to generalize the synthesis of complex **1** to see if other pieces of extended metal oxides of larger size can be prepared.

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Supporting Information Available: Tables of crystallographic details, atomic coordinates, complete bond distances and angles, anisotropic thermal parameters and hydrogen atom coordinates and isotropic thermal parameters for $[Mn_{13}(\mu_5\text{-}O)_6(\mu_3\text{-}O)_2(\mu_3\text{-}OEt)_6(O_2CPh)_{12}]$ (**1**) (17 pages). Ordering information is given on any current masthead page.

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(19) In the least-squares fitting procedure for the reduced magnetization data, it is assumed that a ground state of spin S is the only state populated in the 2.0−4.0 K range and the magnetization is calculated with eq 1. In this equation $\delta E_i/\delta H$ is the change in energy of the ith

$$M = N\sum_{i=1}^{p}\left(\frac{\delta E_i}{\delta H}\right)\exp\left(\frac{-E_i}{kT}\right)\Bigg/\sum_{i=1}^{p}\exp\left(\frac{-E_i}{kT}\right) \qquad (1)$$

level in response to a change in the magnetic field. The energies of various sublevels of the ground state are obtained by diagonalization on each iteration of the spin Hamiltonian matrix that includes the Zeeman and axial zero-field $D\hat{S}_z^2$ interactions.

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