

Hexanuclear Manganese(III) Single-Molecule Magnets**

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Single-molecule magnets (SMMs)^[1,2] are molecular species that can retain magnetization in the absence of a magnetic field below a blocking temperature. They represent the smallest possible magnetic storage device, which retains information in a single molecule rather than in a magnetic particle or array of particles. Furthermore, such molecules straddle the classical/quantum interface in also displaying quantum tunneling of magnetization and quantum phase interference. The SMM behavior derives from the intrinsic intramolecular properties of a high-spin ground state, and large and negative (easy axis type) magnetoanisotropy.^[1,2] Experimentally, a SMM exhibits both a frequency-dependent out-of-phase alternating current (ac) magnetic susceptibility (χ'') signal and hysteresis loops in magnetization versus direct current (dc) field studies.^[1] To date, the best and most extensively studied SMMs are the class of the dodecanuclear species $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_x]^{n-}$ ($n=0, 1, 2$; $x=3, 4$; $\text{Mn}^{\text{III}}_8\text{Mn}^{\text{IV}}_4$ for $n=0$) and their derivatives,^[1,2] but there are a number of other examples of SMMs containing manganese (at the oxidation states II/III, III/IV or II/III/IV), iron, cobalt, nickel, and vanadium.^[1–3] Important to the future of the field of SMMs is the development of new synthetic schemes that can yield molecules with a large spin and/or anisotropy. Herein we report access to the first members of a new class of manganese-based SMMs consisting exclusively of Mn^{III} ions with T_B (T_B = blocking temperature) greater than 2 K.

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Reaction of $\text{Mn}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ with salicylaldoxime (H_2salox , 1:1 molar ratio) in EtOH at room temperature led to a deep green solution from which the hexanuclear complex **1**·4EtOH was isolated. The presence of the dianionic form of



the ligand (salox^{2-}) is a consequence of the 2:1 $\text{MeCO}_2^-:\text{H}_2\text{salox}$ ratio used in the reaction.

Another route to good yields of pure **1** involves a comproportionation reaction between $n\text{Bu}_4\text{NMnO}_4$ and $\text{Mn}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ in the presence of H_2salox (3:1:3 molar ratio) in EtOH at room temperature.

In the crystal structure (Figure 1),^[4] **1** lies on an inversion center and has a novel $[\text{Mn}^{\text{III}}_6(\mu_3\text{-O})_2(\mu_2\text{-OR})_2]^{12+}$ core, whose topology consists of six Mn ions arranged as two $\{\text{Mn}_3(\mu_3\text{-O})\}$

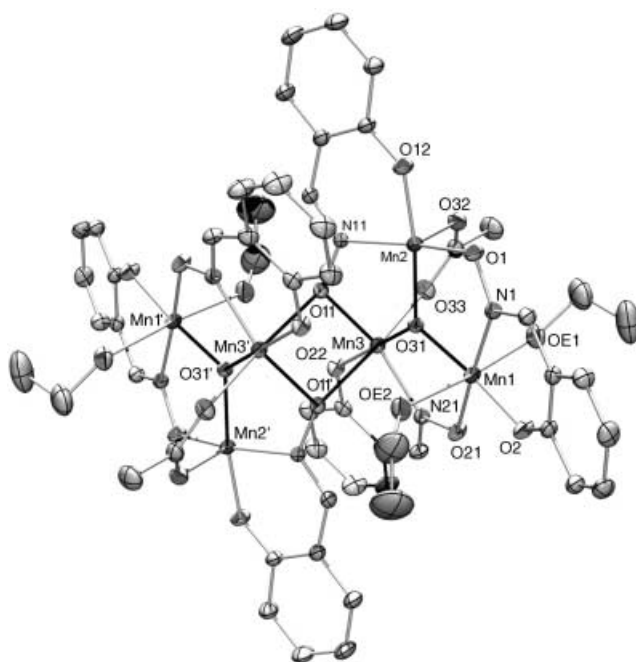
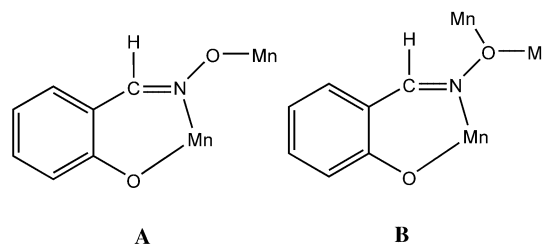


Figure 1. ORTEP plot of the molecular structure of **1** (the thermal ellipsoids are set at 20% probability). Primed and unprimed atoms are related by the crystallographic inversion center, OE1 and OE2 are the oxygen atoms of the crystallographically independent ethanol ligands.

subunits bridged by two oximate oxygen atoms (O11, O11'). The $\text{Mn}2\cdots\text{Mn}3$ moiety is further bridged by one *syn, syn*- μ_2 : $\eta^1:\eta^1$: MeCO_2^- group. Four of the salox^{2-} ligands show the common $\mu_2:\eta^1:\eta^1:\eta^1$ coordination mode (**A**), while the other



two adopt the rare^[5] $\mu_3:\eta^1:\eta^2:\eta^1$ (**B**) mode. The two crystallographically independent EtOH ligands complete the six-coordination at Mn1. Ions Mn1 and Mn3 are bound to an O₅N set of donor atoms and display Jahn–Teller elongation, as expected for high-spin 3d⁴ ions in near octahedral geometry; the Jahn–Teller axes are OE1–Mn1–OE2 and O33–Mn3–O11'. Mn2 has a distorted square-pyramidal geometry, with the acetate oxygen O32 at the apical position. Complex **1** joins a very small family of Mn^{III}₆ clusters^[6] and has a remarkably similar structure to [Cr₆O₂(O₂CET)₂(salox)₆(H₂O)₂·(EtCN)₂].^[7]

Complex [Mn₆O₂(O₂CPh)₂(salox)₆(EtOH)₄]·EtOH (**2**·EtOH) was prepared in a fashion very similar to that for **1** by using Mn(O₂CPh)₂·2H₂O. Disregarding the difference in RCO₂[−] ligand and the fact that the structure of the benzoate cluster^[4] contains two almost identical hexanuclear molecules, compounds **1** and **2** display similar molecular structures.

Solid-state dc magnetic susceptibility measurements were performed in the range 2.0–200 K under a field of 0.1 T (Figure 2). The data were fitted using a full-diagonalization treatment^[8] based on the interaction pattern shown in Figure 3 and on the corresponding Hamiltonian [Eq. (1)].

$$\mathcal{H} = -2J_1(S_3 \cdot S_3') - 2J_2(S_2 \cdot S_3 + S_2' \cdot S_3') - 2J_3(S_1 \cdot S_2 + S_1' \cdot S_3 + S_1' \cdot S_2' + S_1' \cdot S_3') - 2J_4(S_2 \cdot S_3' + S_2' \cdot S_3) \quad (1)$$

Measurements below 15 K were omitted in the fitting because zero-field effects are likely to influence the data in this temperature range. The best fitting parameters obtained are $J_1 = +12.4 \text{ cm}^{-1}$, $J_2 = -3.5 \text{ cm}^{-1}$, $J_3 = -12.6 \text{ cm}^{-1}$, $J_4 = -0.45 \text{ cm}^{-1}$, $g = 2.00$ ($R = 2.1 \times 10^{-4}$, $R = \sum(\chi_M^{\text{calcd}} - \chi_M^{\text{exp}})^2 / \sum(\chi_M^{\text{exp}})^2$). Interaction through the oximate bridges indicate antiferromagnetic (AF) coupling as usually observed for this

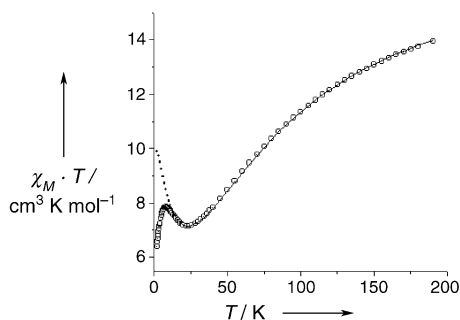


Figure 2. Plot of the $\chi_M T$ versus T for a solvated form of complex **1**. Solid line is a fit of the data down to 15 K. The dotted line below 15 K indicates the spin-only behavior that tends to reach a $\chi_M T$ value of $10 \text{ cm}^3 \text{ K mol}^{-1}$ ($S = 4$).

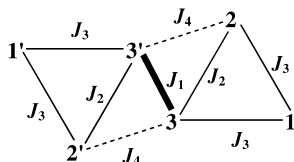


Figure 3. The exchange-interaction pattern for complex **1**. The numbering scheme used for the spin carriers is the same as that used in Figure 1.

kind of ligand and the positive J_1 value obtained is in agreement with magnetostructural correlations found in dinuclear Mn^{III} units containing the $\{\text{Mn}_2^{\text{III}}(\mu_2\text{-OR})_2\}^{4+}$ sub-core.^[9] The system may be envisaged as two ferromagnetically coupled AF triangles. The competitive interactions (J_2 and J_3) and the fact that $J_3 \gg J_2$, clearly stabilize a local $S = 2$ ground state in each triangular unit.^[10] The dominant ferromagnetic J_1 pathway (versus the very weak J_4 one) leads to an $S = 4$ ground state for the hexanuclear cluster.

A crucial requirement for the SMM response is parallel alignment of the anisotropy axes which generates a bulk cluster anisotropy. As has been pointed out,^[2] anisotropic ions are a necessary (but not sufficient) condition to generate SMMs; an adequate topological arrangement of the local anisotropy tensors is also required. Compounds **1** and **2** with an $S = 4$ ground state, local anisotropic ions, and an adequate global topology (all the elongation axes are parallel), are good candidates to be SMMs. Thus, ac susceptibility experiments were performed to determine whether these complexes would exhibit a slow magnetization-relaxation phenomenon. The in-phase χ_M' signal of a solvated form of **1** shows a frequency-dependent decrease at $T < 6 \text{ K}$ indicative of the onset of slow relaxation. This was confirmed by the concomitant appearance of an out-of-phase (χ_M'') signal (Figure 4) arising from

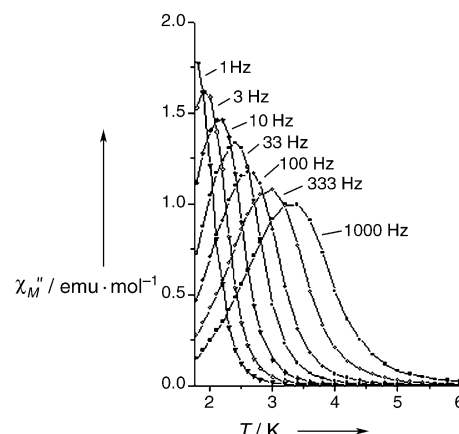


Figure 4. Plot of the out-of-phase (χ_M'') signal in ac susceptibility studies versus T under a field oscillating at the frequencies indicated for a solvated form of compound **1**.

the inability of **1** to relax sufficiently rapidly, at these temperatures, to keep up with the oscillating field. For the ac frequency range 1–1000 Hz, the χ_M'' peaks of solvated **1** occur between 1.96–3.30 K. The presence of an out-of-phase signal establishes^[1–3] that **1** is a SMM. The magnetization relaxation rate data obtained from the ac data were fitted to the Arrhenius equation $\tau = \tau_0 e^{-U_{\text{eff}}/(kT)}$, where τ is the relaxation time, U_{eff} is the energy barrier for the relaxation of the magnetization, k is Boltzmann's constant and τ_0 is the preexponential factor. From the fit, U_{eff} was found to be 28.0 K with $\tau_0 = 3.6 \times 10^{-8} \text{ s}$. For an integer spin system, the barrier to thermally activated magnetization relaxation is $S^2|D|$, where D is the axial zero-field splitting (ZFS) parameter. Thus, the experimentally determined kinetic

energy barrier of 28.0 K (19.5 cm^{-1}) implies a minimum value of D of -1.22 cm^{-1} . In spite of the relatively large $|D|$ value and that τ_0 is comparable to that of manganese SMMs with higher nuclearities,^[1,2] the relaxation is still fast at 2 K, owing to the moderate S value of the ground state. Further studies at lower temperatures are planned to investigate magnetization hysteresis loops (expected at $T < 1 \text{ K}$) and the possible presence of quantum tunneling of the magnetization. Preliminary results show that **2** exhibits a comparable SMM response with τ_0 , U_{eff} , and $|D|$ values of $2.3 \times 10^{-8} \text{ s}$, 19.4 cm^{-1} , and 1.21 cm^{-1} , respectively.

Simulation of the reduced magnetization dependence upon H/T for solvated **1**, assuming the D value to be -1.22 cm^{-1} for $S = 4$ and $g = 2.00$, shows excellent agreement with the experimental data, which gives an independent confirmation of the ground state of the system and the energy-barrier value (Figure 5).

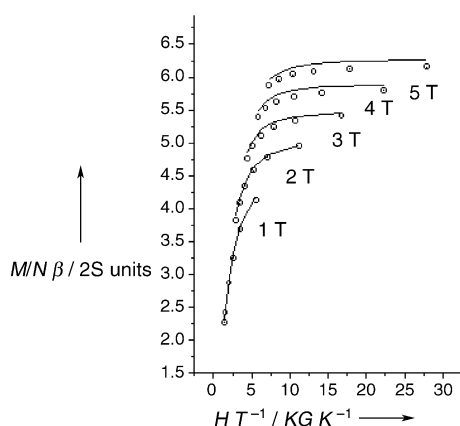


Figure 5. Plot of the reduced magnetization versus H/T for solvated **1** at 1, 2, 3, 4, and 5 T. The solid lines correspond to the simulation using the D and S values obtained from ac and dc independent measurements.

Work in progress reveals that substitution of the benzoate ligands present in **2** by various chlorobenzoates leads to products with similar structures and SMM properties. A full magnetic analysis of this potentially large family of SMMs will be reported elsewhere.^[11]

Experimental Section

Treatment of a stirred colorless solution of $\text{Mn}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ (0.073 g, 0.30 mmol) in EtOH (25 mL) with $n\text{Bu}_4\text{NMnO}_4$ (0.036 g, 0.10 mmol) resulted in a dark red-brown solution. Solid H_2salox (0.041 g, 0.30 mmol) was slowly added to this solution and soon dissolved to give a dark green solution. This solution was stirred for a further 30 min, filtered, and the filtrate layered with $\text{Et}_2\text{O}/n$ -hexane (40 mL, 1:1 v/v) to give X-ray quality, dark red-green crystals of the product, which were collected by filtration, washed with EtOH, and dried in air; the formulation **1**·4EtOH was determined crystallographically, but the dried solid was analyzed as solvate EtOH-free. Yield 40–50%, elemental analysis (%) calcd for $\text{C}_{54}\text{H}_{60}\text{Mn}_6\text{N}_6\text{O}_{22}$: C 43.97, H 4.04, N 5.70; found for dried sample: C 44.27, H 4.11, N 5.61; selected IR data (KBr pellet): $\tilde{\nu} = 3424$ (br, m), 1598 (s), 1540 (m),

1472 (m), 1440 (s), 1282 (s), 1044 (s), 1028 (s), 918 (s), 754 (m), 680 (s), 652 (m), 476 cm^{-1} (m).

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