

Magnetic Clusters

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Linking Centered Manganese Triangles into Larger Clusters: A $\{\text{Mn}_{32}\}$ Truncated Cube**

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Single-molecule magnets (SMMs) have many potential applications including high-density information storage, in which each bit of information is stored as the magnetization orientation of an individual molecule, and as qubits for quantum computation, in which the required arbitrary superposition of quantum states with opposite projections of spin can be produced by either quantum tunneling of the magnetization, intermolecular exchange, or multifrequency EPR pulses.^[1–4] The fundamental requirements for a molecule to behave as an SMM are a) a relatively large spin ground state (S) and b) a large and negative zero-field splitting (zfs) of that ground state (as measured by the zfs parameter D). The upper limit of the barrier to the reorientation of the magnetization is given by $S^2 |D|$ for integer spins and $(S^2 - 1/4) |D|$ for half-integer spins.

To make large molecular clusters, two successful, but somewhat opposing, synthetic strategies have generally been employed. The first is the use of rigid bridging ligands, for example, cyanide, that impose the geometry on the resultant cluster,^[5] and the second is the use of flexible ligands, for example, carboxylates, that impose little or no geometry.^[6] Both approaches have produced molecules with extremely

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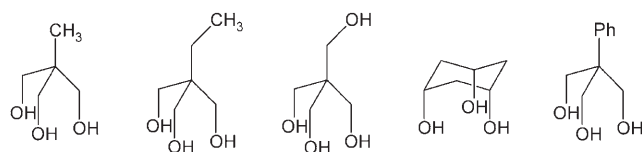
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large spin ground states: $S = 39/2$ for the former^[7] and $S \geq 23$ and $S = 51/2 \pm 1$ for the latter.^[8]

We have been exploring the reactivity of tripodal alcohol ligands (Scheme 1) in the synthesis of 3d transition metal



Scheme 1. The tripodal ligands (from left to right) 1,1,1-tris(hydroxymethyl)ethane (H₃thme), 1,1,1-tris(hydroxymethyl)propane (H₃tmp), pentaerythritol (H₄peol), *cis,cis*-1,3,5-cyclohexanetriol (H₃cht), and 1',1',1'-tris(hydroxymethyl)toluene (H₃thmt).

SMMs. The basic principle here is that paramagnetic metal ions linked together in triangular arrays may lead to molecules with large spin ground states. If these arrays consist of simple {M₃} equilateral triangles then the resultant competing exchange interactions or spin frustration may stabilize a nonzero spin ground state. If the arrays consist of {M₄} centered triangles or “metal stars”, in which the three peripheral ions are connected only to the central ion and not to each other, then the antiferromagnetic interaction between these ions may stabilize a large spin state. If these high-spin triangular units can then be linked together by using bridging ligands that promote ferromagnetic exchange then the resultant complexes could well be characterized by extremely large spin ground states.

The cation [Mn₃₂(thme)₁₆(bpy)₂₄(N₃)₁₂(OAc)₁₂]⁸⁺ (Figure 1; bpy = bipyridine) consists of eight such {M₄} centered triangles linked together to form a truncated cube. Each [Mn₄(thme)₂]⁴⁺ corner unit consists of a central Mn⁴⁺ ion and three peripheral Mn²⁺ ions. The Mn²⁺ ions are linked to the Mn⁴⁺ ion through the μ₂-oxygen arms of two thme³⁻ ligands, which sit directly above and below the [Mn^{IV}Mn^{II}]₃ plane. The coordination of the peripheral Mn²⁺ ions is completed by one chelating bpy ligand, one acetate group and one azide function. The CH₃CO₂⁻ and N₃⁻ ligands bridge the Mn²⁺ ions in neighboring corner units along each edge of the cube (Figure 2). The charge balance of the complex is completed by the presence of eleven ClO₄⁻ ions and one and a half [Mn(bpy)₃]²⁺ molecules, thus giving the complex the overall formula {Mn(bpy)₃}_{1.5}[Mn₃₂(thme)₁₆(bpy)₂₄(N₃)₁₂(OAc)₁₂](ClO₄)₁₁ (**1**). The oxidation states of the Mn ions were confirmed by BVS (bond-valence-sum) calculations and bond-length considerations.

To probe the magnetic properties of **1**, susceptibility measurements were performed on powdered crystalline samples in the ranges 1.8–300 K and 0–7 T, and on single crystals at temperatures down to 40 mK. Direct current (dc) susceptibility measurements were carried out in a 0.1-T dc field in the temperature range 1.8–300 K, with the sample restrained in eicosane to prevent torquing. The calculated ($g = 2$) contribution from the 1.5 [Mn(bpy)₃]²⁺ cations per [Mn₃₂] was subtracted from the measured data. The room temperature $\chi_M T$ value of approximately 78.8 cm³ K mol⁻¹

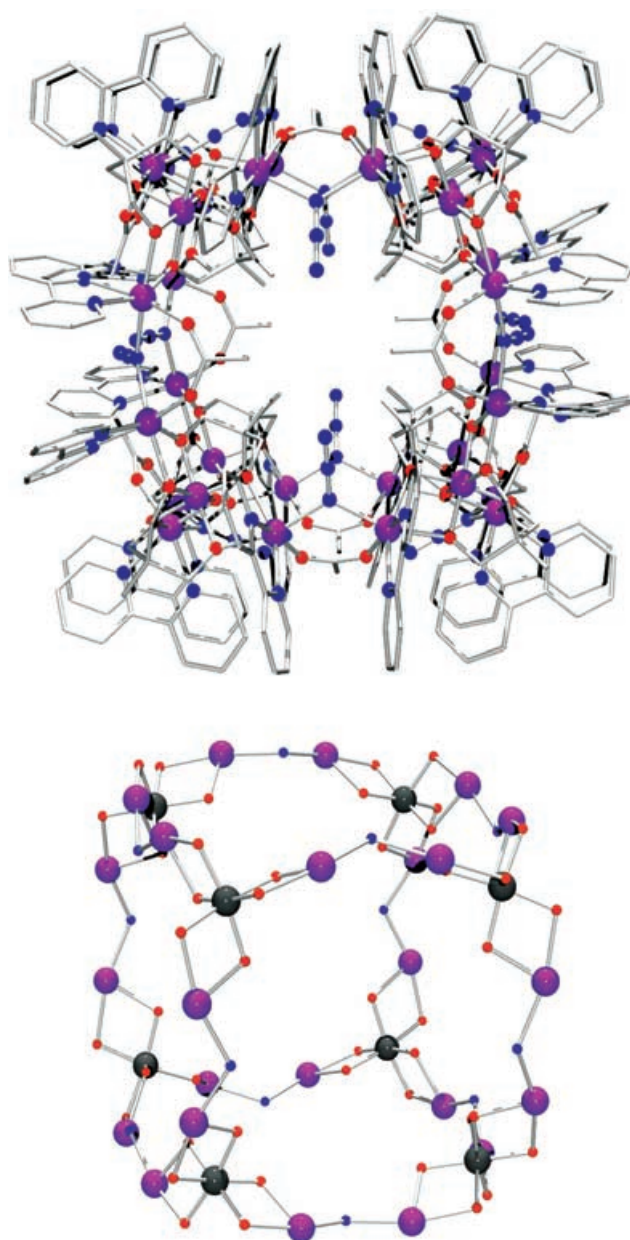


Figure 1. The structure of the [Mn₃₂]⁸⁺ cation (top) and its core (bottom). In the lower picture the eight corner Mn⁴⁺ ions of an ideal cube are highlighted in black.

slowly increases upon cooling to a maximum of approximately 86.2 cm³ K mol⁻¹ at 90 K, and then decreases rapidly to a value of approximately 37.8 cm³ K mol⁻¹ at 2 K. This behavior is indicative of dominant antiferromagnetic exchange between the metal centers with the value at 2 K in the region expected for an $S = 9$ ground state (spin-only ($g = 2$) value of 45 cm³ K mol⁻¹).

In alternating current (ac) susceptibility experiments, a weak field (typically 1–5 G) oscillating at a particular frequency (ν) is applied to a sample to probe the dynamics of the magnetization (magnetic-moment) relaxation. The ac susceptibility measurements, which avoid Zeeman and other effects of an applied dc field, are an excellent complementary

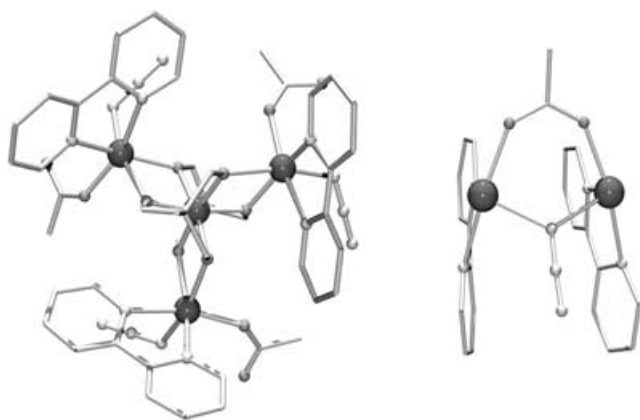


Figure 2. The building blocks of complex **1**: the $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{II}}_3]$ “corner” unit (left) and the $[\text{Mn}^{\text{II}}]$ “edge” (right).

tool for the estimation of S as the presence of a temperature-independent (in-phase) χ_M/T versus T signal would indicate a well-isolated ground state, whereas a sloping χ_M/T vs T signal would indicate the population of a number of low-lying excited states.^[9] In-phase ac susceptibility measurements for complex **1** taken in the temperature range 1.8–10 K are shown in Figure 3. The steeply sloping lines observed show a rapid decrease in χ_M/T with decreasing temperature and therefore suggest the population of many excited states with larger S values. This is a common feature in many Mn clusters that are either a) of high nuclearity and thus exhibit a large density of spin states or b) contain multiple Mn^{2+} ions that typically promote weak exchange. Extrapolation of the χ_M/T signal from values above about 3 K (to avoid decreases due to effects such as intermolecular interactions at lower temperatures) to 0 K gives a value of 42–43 $\text{cm}^3\text{K mol}^{-1}$, which suggests a spin ground state of $S=9$ (or 10), consistent with the dc data.

Magnetization measurements also confirm the presence of many excited states. Studies on a single crystal of complex **1** at temperatures down to 40 mK and in fields of up to 1.4 T performed on a micro-SQUID setup show curves that do not reach saturation (Figure 3). At all temperatures studied, the magnetization continues to rise sharply with increasing field strength. This is as expected for field-induced stabilization of M_S levels of excited states with S values greater than that of the ground state; approach to and crossing of excited-state M_S levels with those of the ground state lead to increases in the measured magnetization. Thus, for example, the magnitude of the magnetization at 40 mK in an applied field of 1 T is suggestive of $S \geq 25$. Similarly, magnetization measurements (Figure 3) carried out on a powdered crystalline sample at temperatures below 10 K in fields of up to 7 T saturate at a value of $M/N\mu_B \approx 85$, a value consistent with the stabilization of an $S \geq 43$ spin state (with $g=2.0$). However, when smaller applied fields are used, the magnitude of $M/N\mu_B$ decreases and does not saturate. Again this is indicative of a field-induced stabilization of excited states with larger S values than that of the ground state.

If we were to assume the interaction between the central Mn^{4+} ion and the three peripheral Mn^{2+} ions within an

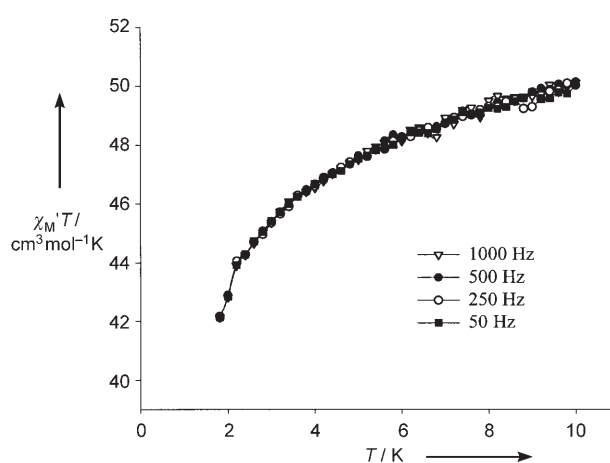
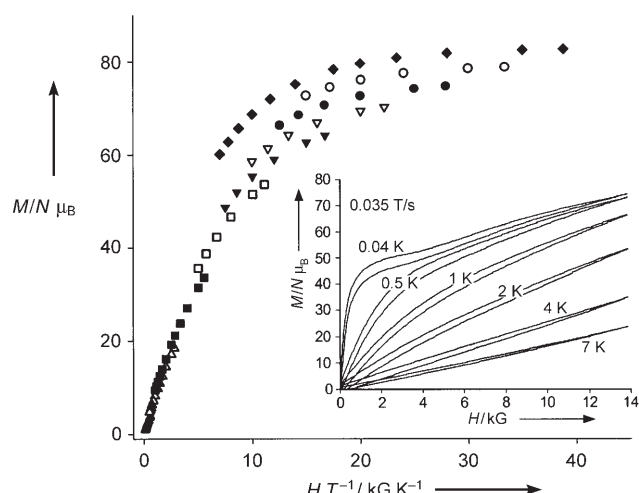


Figure 3. Top: Magnetization data for **1** plotted as reduced magnetization ($M/N\mu_B$) versus H/T in the temperature range 1.8–10 K and in fields of 0.1 T (\blacktriangle), 0.5 T (\triangle), 1 T (\blacksquare), 2 T (\square), 3 T (\blacktriangledown), 4 T (\triangledown), 5 T (\bullet), 6 T (\circ), and 7 T (\blacklozenge). Inset: Magnetization measurements performed on single crystals of complex **1** by using an array of micro-SQUIDs (SQUID = superconducting quantum interference device) at the indicated sweep rate and temperature range. Bottom: In-phase ac susceptibility (χ_M/T) measurements of complex **1** measured below 10 K at the indicated frequencies.

isolated $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{II}}_3]$ unit to be antiferromagnetic, then we would expect a spin ground state of $S=6$ for this unit. Between each of these corner units, the *syn, syn* $\mu\text{-CH}_3\text{CO}_2^-$ ligands are likely to promote antiferromagnetic exchange, but the end-on N_3^- ligands are likely to promote ferromagnetic exchange. If the antiferromagnetic interactions were to dominate, then we might expect to observe an overall spin ground state of $S=0$, but if the ferromagnetic interactions were to dominate then a ground state with $S=48$ could result. However, there are a total of 24 Mn^{2+} ions present in the $[\text{Mn}_{32}]^{8+}$ cation and these are known to promote weak exchange between the metal centers, the result of which is likely to be a large number of S states with comparable energies to the ground state. This “problem” is then further compounded by the fact the $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{II}}_3]$ units are linked

together by two different ligands—one azide and one carboxylate—and this countercomplementarity will likely lead to an interaction that is either weakly ferro- or weakly antiferromagnetic, but in either case near 0 cm^{-1} . Weak intermolecular interactions—if comparable in magnitude to the intracluster exchange—will also complicate the analysis. Essentially all of the above means that an accurate quantitative analysis is impossible.

In conclusion, the use of the tripodal ligand H_3thme has again been shown to stabilize elaborate triangular arrays of Mn ions. In the studies described herein, these “high-spin” building blocks have self-assembled in the presence of end-on-bridging azide ligands to form a $\{\text{Mn}_{32}\}$ truncated cube. This is the second largest Mn cluster reported to date.^[10] Initial magnetic studies revealed that the complex has a spin ground state of $S = 9$ (or 10), but the presence of multiple Mn^{2+} ions, ligand countercomplementarity, and possible weak intermolecular interactions precludes a more accurate analysis. Application of strong magnetic fields effectively overcomes weak antiferromagnetic exchange, thus stabilizing spin states with larger values of S .

However, the combination of tripodal alcohol ligands and end-on bridging azides may be an excellent, yet simple, route to clusters with potentially extremely large spin ground states and promises many more exciting compounds.

Experimental Section

1: NaOAc (1 equiv) and NaN_3 (1 equiv) were added with stirring to a solution of $[\text{Mn}_2(\text{Hthme})_2(\text{bpy})_4](\text{ClO}_4)_2$ ^[11] (1 equiv) in MeCN. After 30 min the solution was filtered and layered with diethyl ether. Black crystals grew during one week. Elemental analysis (%): calcd for $\text{C}_{411}\text{H}_{465}\text{Cl}_{11}\text{Mn}_{33.5}\text{N}_{104}\text{O}_{128}$: C 44.31, H 4.21, N 13.08, Mn 16.52; found: C 44.62, H 3.93, N 12.94, Mn 16.73. Crystallographic details for **1**: $\text{C}_{412}\text{H}_{545.50}\text{Cl}_{11}\text{Mn}_{33.50}\text{N}_{104.50}\text{O}_{127.50}$, crystal size: $0.41 \times 0.38 \times 0.27\text{ mm}^3$, triclinic, $P\bar{1}$, $a = 25.9460(6)$, $b = 26.1225(6)$, $c = 40.5498(9)\text{ Å}$, $\alpha = 91.2630(10)$, $\beta = 93.3990(10)$, $\gamma = 97.4450(10)^\circ$, $V = 27191.7(11)\text{ Å}^3$, $T = 150(2)\text{ K}$, $Z = 2$, $\rho_{\text{calcd}} = 1.372\text{ g cm}^{-3}$, $\mu(\lambda = 0.71073\text{ Å}) = 1.574\text{ mm}^{-1}$, 364332 reflections collected, 78020 unique ($R_{\text{int}} = 0.0959$), $R1 = 0.1068$ and $wR2 = 0.2973$ using 55631 reflections with $I > 4\sigma(I)$. CCDC-273452 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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