Making 'wheels' and 'cubes' from triangles†

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[$Mn^{IV}Mn^{II}_3$] triangular units directed by the presence of tripodal alcohols self-assemble in the presence of azide and acetate ligands to form either a [Mn_{24}] 'wheel' or a [Mn_{32}] 'cube'.

The design of polymetallic paramagnetic cluster compounds ranges from (i) the use of rigid bridging ligands such as cyanide,[1] or polytopic ligands based on diazines, pyridines and alkoxo-(*etc*) fragments,[2] in which the known coordination mode of the ligand in combination with the predictable geometry and electronic structure of specific transition metals, sometimes allows the structures of products to be predicted, to (ii) more flexible ligands such as carboxylates, alkoxides and phosphonates *etc*,[3–6] in which the exact structure of the product is extremely difficult to predict. Both approaches have led to a plethora of beautiful complexes with nuclearities up to eighty-four and spin ground states $S > 20$.[7]

We have been investigating the reactions of tripodal alcohols with 3d transition metals on the basis that paramagnetic metal ions linked together into triangular-based arrays may lead to the isolation of molecules displaying non-zero spin ground states and single-molecule magnetism behaviour.[4] While the structures of the products obtained from the reactions of metal salts or complexes with H_3thme (1,1,1-tris(hydroxymethyl)ethane), H_3tmp (1,1,1-tris(hydroxymethyl)propane) and their analogues (Fig. 1) are extremely hard to predict, their metal topologies are always based on [M_3] triangles when the tripodal ligand is in its fully deprotonated tripod^{3-} form. These can be 'simple' [M_3] or [M_4] (centred) triangles; rod-like complexes describing 'one-dimensional' arrays of edge-sharing triangles; planar disc-like complexes describing 'two-dimensional' arrays of edge-sharing triangles; or more complicated 'three-dimensional' arrays commonly based on tetrahedra, octahedra and icosahedra.[4] Here we describe how the simple change between using H_3thme and H_3tmp in an otherwise identical reaction leads to the formation of either a [Mn_{24}] 'wheel' or a [Mn_{32}] 'cube' containing identical building blocks.

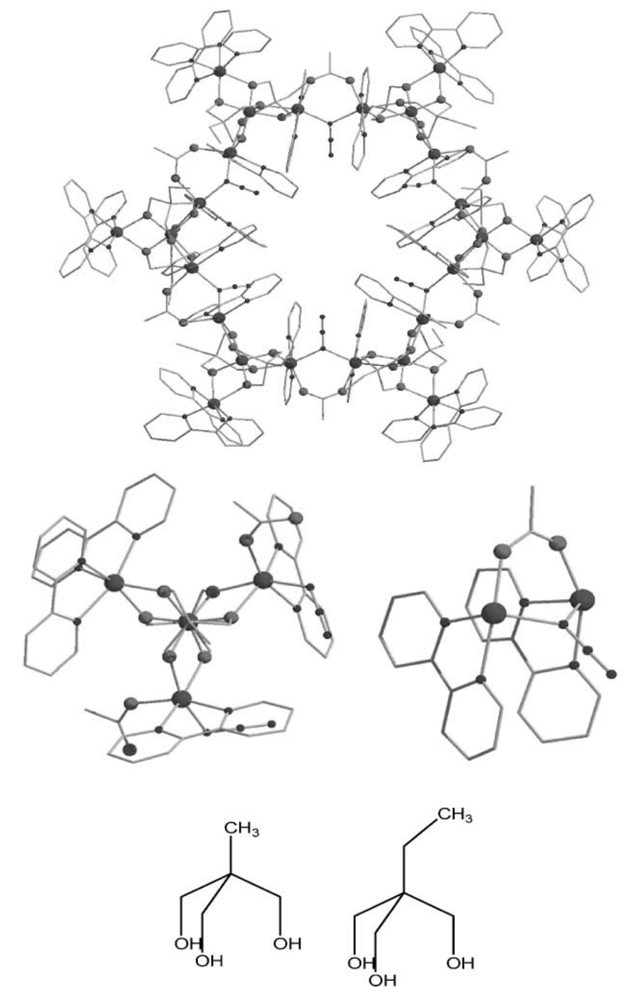

Fig. 1 The molecular structure of complex **1** (top); the building blocks of complex **1**: the [$Mn^{IV}Mn^{II}_3$] 'corner' unit (middle, left) and the [Mn^{II}_2] 'edge' (middle, right); the structures of H_3thme (bottom, left) and H_3tmp (bottom, right).

Reaction of 1 equivalent of NaN_3 and NaOAc with [$Mn_2(Htmp)_2(bpy)_4](ClO_4)_2$[8] in MeCN leads to the formation of a red–brown solution and a light brown precipitate. Removal of the precipitate and subsequent layering of the solution with Et_2O leads to the formation of crystalline [$Mn_{24}(tmp)_{12}(bpy)_{24}(N_3)_6(OAc)_6](ClO_4)_{12}\cdot 20MeCN$ (**1**·20MeCN) after approximately 1 week in 15% yield.‡ The complex crystallises in the monoclinic space group $P2_1/c$. The [$Mn_{24}(tmp)_{12}(bpy)_{24}(N_3)_6(OAc)_6]^{12+}$ cation (Fig. 1) consists of six [$Mn^{IV}Mn^{II}_3$] centered triangles (or 'metal stars') linked together to form a 'hexagonal loop' or 'wheel' with approximate sixfold symmetry perpendicular to the metal plane. Each [$Mn_4(tmp)_2]^{4+}$ 'corner unit' consists of a central Mn^{4+} ion and three peripheral Mn^{2+} ions. The Mn^{2+} ions are linked to the Mn^{4+} ion *via* the μ-oxygen arms of two tmp^{3-} ligands, which sit directly above and below the [$Mn^{IV}Mn^{II}_3$] plane. The coordination of the two 'inner' Mn^{2+} ions is completed by one chelating bpy

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† The HTML version of this article has been enhanced with colour images.

ligand, one acetate and one azide (Fig. 1). The $CH_3CO_2^-$ and N_3^- ligands bridge between the Mn^{2+} ions in neighbouring corner units along each edge of the loop creating a single-stranded $[Mn_{18}]$ hexagonal wheel. The Mn–N–Mn bridging angles all fall within the range ~115–119°. The remaining 'outer' Mn^{2+} ion is chelated by two bpy molecules. The oxidation states of the Mn ions were confirmed by a combination of charge balance and bond length considerations, and BVS calculations.[9]

Remarkably, the building blocks present in complex **1** are identical to those found in the cation $[Mn_{32}(thme)_{16}(bpy)_{24}(N_3)_{12}(OAc)_{12}]^{8+}$ (**2**, Fig. 2):[10] both contain $[Mn^{IV}Mn^{II}_3]$ centered triangles linked together *via syn,syn*, μ-acetates and end-on azides. In **2** there are eight such $[Mn^{IV}Mn^{II}_3]$ triangles that self-assemble to form a truncated cube (Fig. 2). Both are made from identical reactions, with the only difference being the identity of the tripodal alcohol: $thme^{3-}$ in **1** and tmp^{3-} in **2**, and clearly this directs a dramatic change in the nature of the crystallised product.

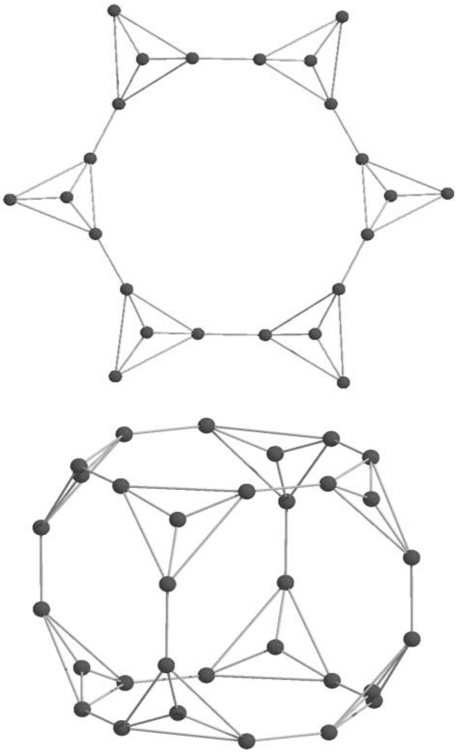

Fig. 2 The metallic skeletons for complexes **1** (top) and **2** (bottom).

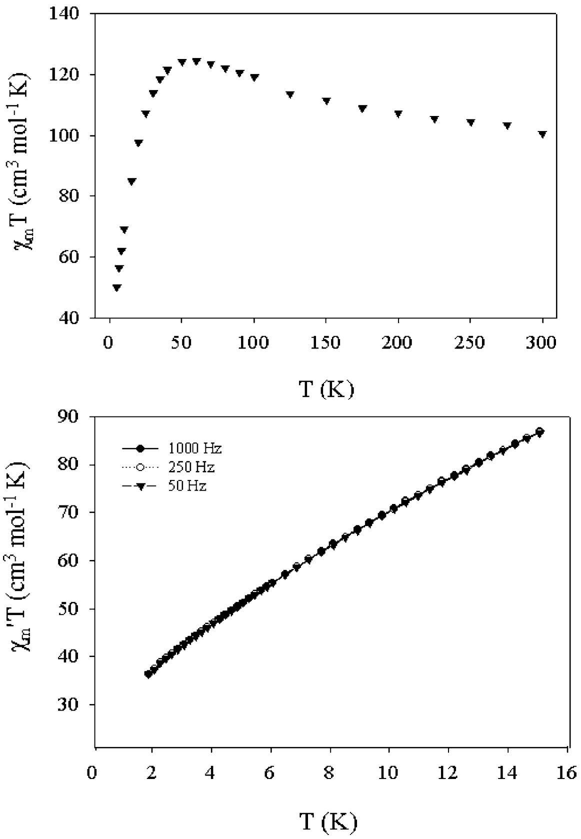

Fig. 3 Plot of $\chi_m T$ *vs.* T for **1** in the 300–5 K temperature range in an applied field of 0.1 T (top); $\chi'_m T$ *vs.* T for **1** in the 16–1.8 K temperature range, using a 3.5 G ac field oscillating at the indicated frequencies (bottom).

In order to probe the magnetic properties of **1**, susceptibility measurements were performed on powdered crystalline samples in the ranges 5–300 K and 0–7 T, and on single crystals in temperatures down to 40 mK. Dc susceptibility measurements (Fig. 3) were carried out in a 0.1 T dc field in the temperature range 5–300 K, with the sample restrained in eicosane to prevent torquing. The room temperature $\chi_M T$ value of approximately 100.5 cm^3 K mol^{-1} slowly increases upon cooling to a maximum of approximately 124.7 cm^3 K mol^{-1} at 60 K, and then decreases rapidly to a value of approximately 50.2 cm^3 K mol^{-1} at 5 K. This behaviour is indicative of dominant antiferromagnetic exchange between the metal centers with the value at 5 K in the region expected for an $S = 9 \pm 1$ ground state. Ac measurements, which avoid Zeeman and other effects of an applied dc field, are an excellent complementary tool for the estimation of S since the presence of a temperature independent (in-phase) $\chi_M'T$ *vs.* T signal would indicate a well isolated ground state, while a sloping $\chi_M'T$ *vs.* T signal would indicate the population of a number of low-lying excited states. In-phase ac susceptibility measurements for complex **1** taken in the temperature range 1.8–15 K are shown in Fig. 3. The observed steeply sloping lines showing a rapid decrease in $\chi_M'T$ with decreasing temperature therefore suggest the population of many excited states with larger S values. This is a common feature in many Mn clusters that are either of high nuclearity and thus possess a large density of spin states, or those that contain multiple Mn^{2+} ions (as here) that typically promote rather weak exchange. Extrapolation of the $\chi_M'T$ signal from values above ~5 K (to avoid decreases due to such effects as intermolecular interactions at lower temperatures) to 0 K gives a value of approximately 35 cm^3 K mol^{-1}, suggesting a spin ground state of $S \approx 8$, consistent with the dc data.

Magnetisation measurements on a single crystal of complex **1** at temperatures down to 40 mK and in fields up to 1.4 T, performed on a micro-SQUID set-up (Fig. 4), show the absence of significant anisotropy. For all measured low-temperature curves at different directions of the applied field, the magnetisation continues to rise sharply with increasing field strength. Field sweep-rate studies show no significant hysteresis effects which agrees with the finding of small anisotropy. Similarly, magnetisation measurements (Fig. 4) carried out on a powdered crystalline

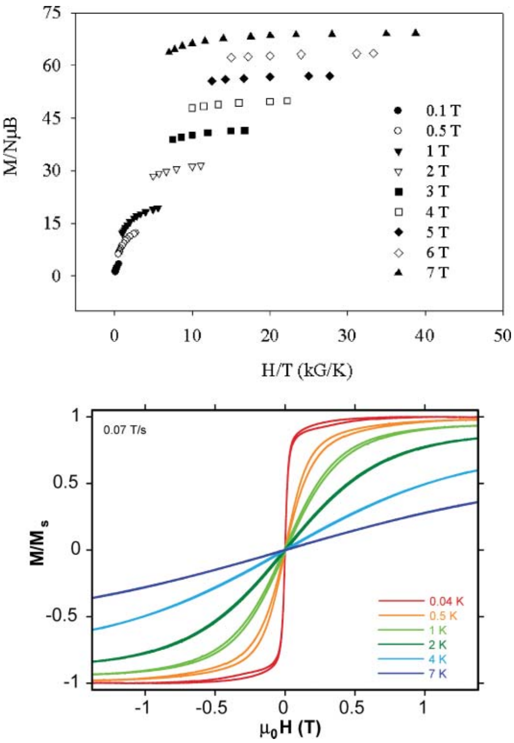

Fig. 4 Plot of $M/N\mu_B$ *vs.* H/T for complex **1** at the indicated temperatures and fields (top); Magnetisation measurements performed on single crystals of complex **1** using an array of micro-SQUIDS at the indicated sweep rate and temperature range (bottom); the magnetisation is normalised to its saturation value.

sample in temperatures below 10 K in fields up to 7 T plateau at a maximum value of $M/N\mu_B = 72$, consistent with the stabilisation of an $S = 36$ spin state (assuming $g = 2$). When smaller applied fields are used the magnitude of $M/N\mu_B$ decreases and does not saturate. This is as expected for field-induced stabilisation of M_S levels of excited states with S values greater than that of the ground state: the crossing of these excited state M_S levels with those of the ground state will lead to increases in the measured magnetisation.

If we assume the interaction between the central Mn^{4+} ion and the three peripheral Mn^{2+} ions within an 'isolated' $[Mn^{IV}Mn^{II}_3]$ unit to be antiferromagnetic, then we would expect a spin ground state of $S = 6$. Between each of these corner units the *syn,syn* μ-$CH_3CO_2^-$ ligands are likely to promote antiferromagnetic exchange, but the end-on N_3^- ligands ferromagnetic exchange.[11] 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 an $S = 36$ ground state would result. However, there are a total of eighteen Mn^{2+} ions present in the $[Mn_{24}]^{12+}$ cation and the result is likely to be a large number of S states with comparable energies to the ground state since these are known to promote weak exchange between the metal centres. This 'problem' is then further compounded by the fact the $[Mn^{IV}Mn^{II}_3]$ units are linked together by two different ligands—one azide and one carboxylate—and this counter-complementarity will likely lead to an interaction that is either weakly ferro- or weakly antiferromagnetic, but in either case, near 0 cm^{-1}. This behaviour is analogous to that seen for **2**, which also possesses an $S \approx 9$ ground state, but where the application of strong magnetic fields leads to the stabilisation of an $S = 48$ spin state.[10]

In conclusion, a dramatic change in the nature of the product is observed when performing identical reactions with H_3thme and H_3tmp—a $[Mn_{24}]$ 'wheel' and a $[Mn_{32}]$ 'cube'. Despite the major topological differences between the two compounds, the building blocks of each are identical. Both have spin ground states of $S \approx 9$, but upon application of much stronger fields spin states as large as $S = 36$ and $S = 48$ can be stabilised.

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Notes and references

‡ Complex **1** analysed (C, H, N) as **1**·3MeCN, expected (found): C, 46.24 (46.45); H, 4.09 (4.26); N, 11.28 (11.35%). Diffraction data were collected with Cu-Kα radiation ($\lambda = 1.54184$ Å) on an Oxford Diffraction Xcalibur PX Ultra diffractometer. Crystal data:[12] $C_{364}H_{402}Cl_{12}Mn_{24}N_{86}O_{96}$, $M = 9261.68$, red block, monoclinic, $P2_1/c$, $a = 29.7460(9)$, $b = 17.8290(6)$, $c = 46.7650(15)$ Å, $\beta = 106.019(3)°$, $V = 23838.4(13)$ Å^3, 67966 reflections collected of which 17179 were independent ($R_{int} = 0.0424$), 1150 parameters and 5507 restraints, $R1 = 0.1097$ [based on $F > 4\sigma(F)$], $wR2 = 0.3506$ (based on F^2 and all data). CCDC 605514. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607822m

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