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Chiral single-molecule magnets: a partial Mn(III) supertetrahedron from achiral components†

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A [Mn(III)$_9$] partial supertetrahedron is a Single-Molecule Magnet (SMM) with an energy barrier to magnetisation reversal of ~ 30 K and represents the first chiral SMM obtained from achiral starting materials.

Chirality, innately connected with the Natural selection of one enantiomer over another, means that a molecule has a non-superimposable mirror image.[1–3] The uniqueness of the absolute configuration of each of the two enantiomers of a chiral molecule implies that they will be differently recognised by their surroundings.[1–5] This uniqueness is also reflected in the interaction of the two enantiomers with light, since they are able to rotate the plane of polarised light in different directions.[1–5] A chiral object displaying an additional property or function is a promising candidate for applications in materials science.[4,5] Consequently, there is great interest in developing methods to obtain chiral materials.[4,5]

Restricting further discussion to coordination compounds we can recognise two general synthetic strategies employed to obtain chiral complexes.[5,6–15] The first involves the use of enantiopure ligands to introduce chirality; and the second relies on the use of achiral ligands that upon coordination result in spontaneously resolved chiral complexes[6–14] or due to the distortion applied by coordination to the metal ion.[7] When paramagnetic metal ions are involved, which may result in magnetically ordered solids, an opportunity arises to obtain materials that combine chirality with magnetism.[15] In a chiral magnetic material the breaking of the parity-reversal symmetry which is related to the chirality coexists with the breaking of the time-reversal symmetry which is related to the magnetism, leading to manifestation of the magnetochiral

effect.[2,15,16] When a chiral magnetic material enters into the ferromagnetic phase, the resulting large internal magnetic field induces an amplification of the magnetochiral effect.[15,16] So far, due to the difficulty of obtaining chiral magnetic materials, such an enhanced magnetochiral effect has only been observed in chiral chromium–manganese oxalate layers.[15,16] In principle, a chiral molecular material which is able to manifest magnetic ordering [such as a spin-polarised Single-Molecule Magnet (SMM)] could deliver the same magnetochiral effect under certain conditions.

For some time we have been exploiting the coordination chemistry of salicylaldoxime (saoH$_2$) and its derivatives (R-saoH$_2$) for the formation of Mn^{III}-based Single-Molecule Magnets; in particular families of hexanuclear (*i.e.* [Mn$^{III}_6$])[17] and trinuclear (*i.e.* [Mn$^{III}_3$])[18] SMMs. We have noticed, over several years and several thousand reactions, that the products obtained from reactions performed in alcohol are *always* based on the triangle [Mn$_3$O(R-sao)$_3$]$^{1+}$ or its dimer [Mn$_6$O$_2$-(R-sao)$_6$]$^{2+}$. In a deliberate effort to change this we began a program of reactions designed to discover the conditions and ingredients required to produce molecules of different topologies; the purpose of the "new" ingredients being twofold: (a) to act as co-ligands that can compete/dominate R-sao^{2-} coordination; or (b) to *not* be incorporated into the structure of the final product, but simply to enforce changes in the self-assembly process by their mere presence in the reaction mixture.

In fact the complex [Mn$_9$O$_4$(OMe)$_4$(OAc)$_3$(Me-sao)$_6$-(H$_2$O)$_2$]·1.5H$_2$O (**1**·1.5H$_2$O) can be made successfully (and completely serendipitously) by adding a huge variety of highly charged anions or cations to a solution of Mn(O$_2$CMe)$_2$·4H$_2$O, Me-saoH$_2$ and NEt$_3$ in MeOH.‡ The equivalent reaction without the presence of these anions/cations affords the known complex [Mn$_6$O$_2$(R-sao)$_6$(O$_2$CMe)$_2$(MeOH)$_4$]. The core of **1** (Fig. 1) describes a partial Mn(III) supertetrahedron in which the upper vertex is missing (as drawn in Fig. 1). The [Mn$_6$] basal plane of the supertetrahedron (Mn1, Mn2 and symmetry equivalents (s.e.)) is linked to the upper [Mn$_3$] plane *via* three μ_4-O^{2-} ions (O123). The upper [Mn$_3$] (Mn3 and s.e.) triangle contains a central μ_3-O^{2-} (O333) ion with its edges comprising the –N–O– oximate moieties of the Me-sao^{2-} ligands and its upper face capped by a disordered combination of MeO$^-$ and H$_2$O molecules (Mn–O = 2.138 Å).‡ The phenoxide O-atoms (O1C) of the upper Me-sao^{2-} ligands form the exterior edges of the supertetrahedron linking the

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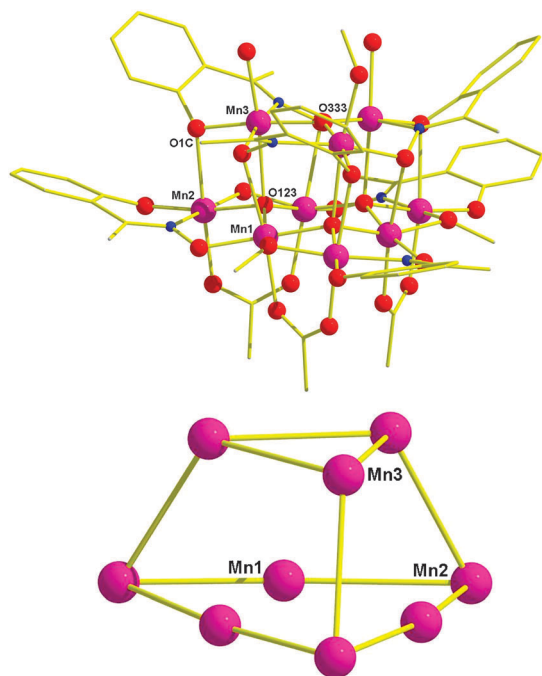
Fig. 1 The molecular structure of **1** (top) and its metallic skeleton describing the partial [Mn(III)$_9$] supertetrahedron (bottom). Colour code: Mn, purple; O, red; N, blue; C, gold.

[Mn$_3$] and [Mn$_6$] planes. The equatorial edges of the [Mn$_6$] unit are bridged alternately by oximate and methoxide ligands with the lower face capped by three μ-bridging OAc$^-$ ligands. The [Mn$_3$] and [Mn$_6$] planes are parallel and separated by 2.825 Å. A three fold axis passes through the μ_3-O^{2-} (O333) ion and is perpendicular to the [Mn$_3$] and [Mn$_6$] planes. The Mn ions are all in the 3+ oxidation state (as checked by bond length and charge balance considerations, and BVS calculations) and in Jahn–Teller (JT) distorted octahedral coordination geometries as expected for high spin d^4 ions. The JT axes are approximately co-parallel, lying perpendicular to the [Mn$_6$] and [Mn$_3$] planes. The Mn–N–O–Mn torsion angles are of two types: those in the upper [Mn$_3$] triangle are rather puckered at $\sim 45°$, while those in the lower [Mn$_6$] unit are much more planar at $\sim 27°$. Although quite rare, a number of [Mn$_{10}$] supertetrahedra have been reported recently—although they are all of [Mn(III)$_6$Mn(II)$_4$] oxidation state distribution with the Mn(II) ions at the four vertices.[19]

1 crystallises in the cubic space group *I*23 which is one of the 65 space groups containing only symmetry operations of the first kind (rotations and translations) and accommodates chiral molecules.[20] In effect, the [Mn$_9$] cluster exists in two enantiopure forms one of which is present in the crystals of **1**. The non-superimposable mirror image of the [Mn$_9$] enantiomer (Fig. S1, ESI†), reproduced by applying the space reversal parity operator ($\hat{P}$), confirms the enantiopure form of the [Mn$_9$].[2] Nevertheless, in order to prove that the bulk material is chiral further experiments are needed.[5,21] Circular dichroism experiments on bulk **1**·1.5H$_2$O gave no signal indicating that it is a conglomerate (a racemic mixture of crystals each of which contains one enantiomer).[5] Although we did not manage to obtain a CD spectrum from a conglomerate single-crystal due to their small size, we can exclude the possibility of a false conglomerate[22] by carefully comparing all eight ($Z = 8$) [Mn$_9$] clusters present in the unit cell of **1**·1.5H$_2$O with the mirror image (see above) of the crystallographically independent [Mn$_9$]. To the best of our knowledge complex **1** is only the third chiral SMM and the first chiral SMM built from achiral starting materials.[12–14]

In the crystal the [Mn$_9$] clusters interact with six neighbours through six (one unique) C–H···O interactions [$\angle$ C24–H24E···O21A ($1/2 - x$, $3/2 - y$, $1/2 + z$) 156.0°, C···O 3.395(7) Å and H···O 2.48 Å] to create a 6-connected three-dimensional (3D) hydrogen-bonded network that conforms to the **pcu** net (Fig. S2, ESI†).

Solid state dc magnetisation measurements were performed on **1** in the range 300–5 K in a field of 0.1 T. The $\chi_M T$ value (Fig. S3, ESI†) of ~ 22 cm^3 K mol^{-1} at 300 K is below the spin-only ($g = 2.00$) value expected for nine non-interacting Mn(III) ions of 27 cm^3 K mol^{-1}. The value decreases with decreasing temperature to a minimum value of ~ 16.7 cm^3 K mol^{-1} at 40 K before rising again to a value of ~ 18 cm^3 K mol^{-1} at 5 K. The behaviour is indicative of the presence of competing ferro- and antiferromagnetic exchange interactions with the low temperature value suggestive of an $S = 6 \pm 1$ spin ground state.

In order to determine the ground state spin, magnetisation data were collected in the ranges 1.8–7 K and 1–7 T. The data were fit (Fig. 2) to a Zeeman plus axial zero-field splitting Hamiltonian (eqn (1)),

$$H = D(\hat{S}_z^2 - S(S + 1)/3) + \mu_B g B \hat{S} \tag{1}$$

assuming only the ground state is populated, affording the parameters $S = 6$, $g = 1.98$ and $D = -0.60$ cm^{-1}. From a cartoon perspective one may consider that the ground state results from either of two combinations: (a) the metal ions in the [Mn$_6$] unit coupled antiferromagnetically to each other giving an $S = 0$ moiety, with the Mn ions in the upper [Mn$_3$] triangle being ferromagnetically coupled giving an $S = 6$ moiety; (b) the Mn ions in the [Mn$_6$] unit being AF coupled to those in the [Mn$_3$] triangle. The former is consistent with trends seen in oximato-based [Mn$_6$] and [Mn$_3$] clusters where F exchange is observed for Mn–N–O–Mn torsion angles greater than $\sim 31°$.[17,18]

Ac magnetisation measurements were performed on **1** in the 1.8–10 K range in a 3.5 G ac field oscillating at 50–1000 Hz. The in-phase (plotted as $\chi_M' T$ in Fig. S4, ESI†) and out-of-phase (χ_M'' in Fig. S5, ESI†) signals show frequency-dependent behaviour below $T \approx 4$ K indicative of the onset of slow magnetic relaxation. The out-of-phase signal shows a peak at *ca.* 2.5 K at a frequency of 1000 Hz. The presence of an out-of-phase signal is diagnostic of single-molecule magnetism behaviour and is caused by the inability of **1** to relax quickly enough, at these temperatures, to keep up with the oscillating field. This establishes that **1** is an SMM and is confirmed by temperature and sweep rate dependent hysteresis loops in single crystal magnetisation *versus* field studies (Fig. 2) with the field applied along the easy axis of magnetisation.[23] Data obtained by varying the frequency of oscillation of the ac field combined with single crystal dc relaxation data were fit to the Arrhenius equation (Fig. S6, ESI†) to obtain the effective energy barrier (U_{eff}) for the relaxation of magnetisation. The slope of the Arrhenius plot gives $U_{eff} = 30$ K, in good agreement with the theoretical upper limit of $S^2|D| = 31$ K.
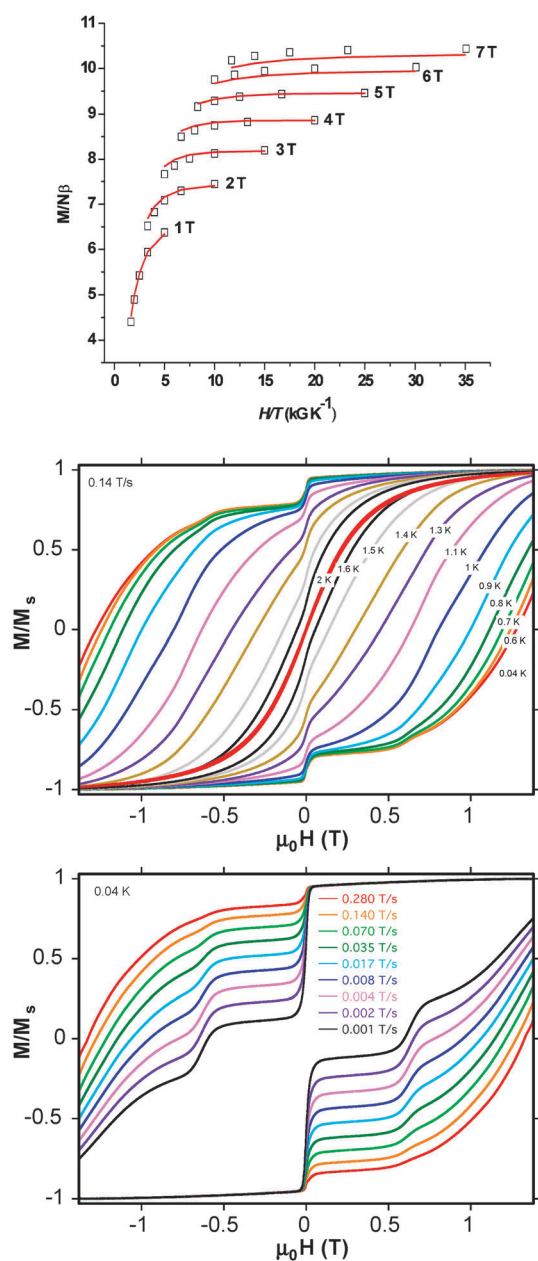
Fig. 2 Plot of reduced magnetisation ($M/N\beta$) *versus* H/T in the indicated field ranges (top). The solid lines are a fit of the experimental data to the Hamiltonian in eqn (1). Temperature (middle) and sweep-rate (bottom) dependent hysteresis loops measured on single crystals of **1**, M is normalised to its saturation value.

To conclude, we have serendipitously isolated a [Mn₉] cluster which is an SMM with an energy barrier to magnetisation reversal of ~30 K. The topology of the nine Mn^III ions conforms to a supertetrahedron missing one vertex while the [Mn₉] clusters interact *via* C–H···O contacts to create a 3D hydrogen-bonded network that conforms to the **pcu** net. The cluster has crystallised in a space group that is compatible with chiral crystal structures and forms a conglomerate. To the best of our knowledge this is the first chiral SMM built from achiral starting materials and as such opens a door to a new family of chiral SMMs.

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