A rare ferromagnetic manganese(III) 'cube'

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A $\{Mn^{III}_4\}$ distorted cube has been synthesized that possesses an $S = 8$ ground state and single-molecule magnetism behaviour.

Recent years have witnessed great research activity in tetranuclear manganese complexes, partly because of their relevance to the $\{Mn_4\}$ cluster at the water oxidation center of photosystem II,[1] and partly because some of them are single-molecule magnets (SMMs)[2]—the latter having potential uses in information storage and quantum computation. There are very few polynuclear $\{Mn^{III}_n\}$ ($n \geqslant 4$) complexes (almost all are mixed-valent) and the majority of the tetrametallic Mn^{III} complexes possess a *planar-diamond* or '*butterfly*'-like $\{Mn_4O_2\}^{8+}$ core. From a detailed search of the CCDC database, it appears there are now over one hundred cube-like[3] $\{Mn_4\}$ complexes reported, but only one of these is a $\{Mn^{III}_4\}$ cube—the complex $[Mn^{III}_4O_4(O_2PPh)_4]$ which displays a diamagnetic $S = 0$ ground state.[4] Herein we report the synthesis, structure and magnetic properties of the first ferromagnetic $\{Mn^{III}_4\}$ cube built using the ligand 2-hydroxyphenylethanone oxime, Me-saoH$_2$. This belongs to the family of phenolic oximes[5] and can be easily prepared *via* the reaction of 2-hydroxyphenylethanone with hydroxylamine and sodium acetate in EtOH.[6]

$Mn(O_2CMe)_2{\cdot}4H_2O$ (1.0 mmol, 245 mg) and Me-saoH$_2$ (1.0 mmol, 151 mg) were stirred in MeCN (20 ml) for a period of 20 min. The solution was then filtered and allowed to stand. Green–black crystals of $[Mn^{III}_4(Me\text{-}sao)_4(Me\text{-}saoH)_4]$ (**1**) crystallised in the monoclinic space group $P2_1/c$ over 3 days in approximately 40% yield.† The preparation of the complex is summarized in the balanced chemical eqn (1).

$$4\ Mn^{II}(O_2CMe)_2{\cdot}4H_2O + 8\ Me-saoH_2 + O_2 \xrightarrow{MeCN} [Mn_4^{III}(Me-sao)_4(Me-saoH)_4] + 8\ MeCO_2H + 18\ H_2O \qquad (1)$$

The central core (Fig. 1) consists of a tetrahedron of Mn^{III} ions linked together by four fully deprotonated Me-sao^{2-} ligands in a η^2:η^1:η^1:μ_3 fashion to form a distorted $[Mn_4(NO)_4]^{8+}$ cube comprising alternate single (O) and double (N–O) atom edges. The four remaining Me-saoH^{1-} ligands each chelate a Mn^{III} ion with the protonated phenolic arm H-bonded to an oximate oxygen on a neighbouring Mn^{III} ion. The dimensions of the metallic tetrahedron are in the range 3.549(1)–4.001(1) Å with the shortest distance between Mn2 and Mn4, and the longest between Mn2 and Mn3. The oxidation states of the Mn ions were confirmed by a combination of bond length considerations (the presence of Jahn–Teller axes), charge balance and BVS calculations. To the best of our knowledge this is the first example of any polynuclear cluster complex stabilised with the Me-saoH$_2$ ligand. The molecules in the crystal lattice stack upon each other in an off-set manner, forming sheets with the closest intermolecular (H···H) distances being ~3.2 Å. No intermolecular H-bonds are present.

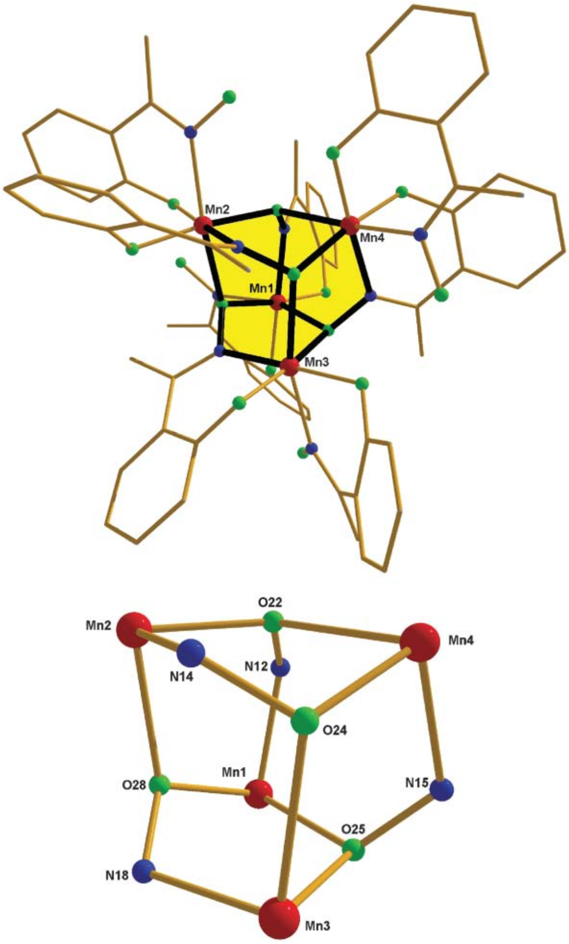

Fig. 1 The molecular structure of complex **1** (top); its $[Mn_4(NO)_4]^{8+}$ core (bottom). Colour code: Mn = red; O = green; N = blue; C = yellow.

It should be mentioned at this point that the 1 : 1 reactions between $Mn(O_2CMe)_2{\cdot}4H_2O$ and the unsubstituted derivative of Me-saoH$_2$, *i.e.* salicylaldoxime (saoH$_2$) using alcohols as solvents give the hexanuclear clusters $[Mn^{III}_6O_2(O_2CMe)_2(sao)_6(ROH)_4]$ as products,[7] illustrating the important role of a number of synthetic

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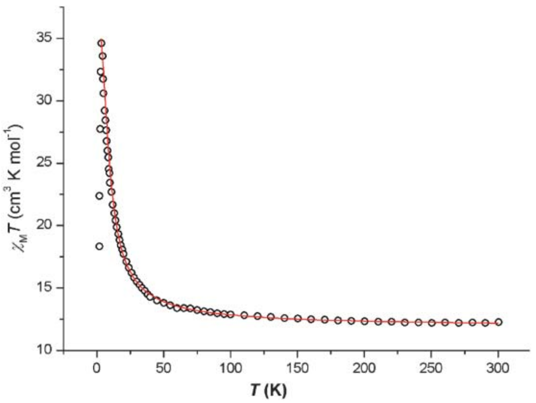

Fig. 2 Plot of $\chi_M T$ *vs.* T for complex **1**·3.5CH$_3$CN. The solid line represents a fit of the data in the temperature range 300–5 K (see text for details).

parameters (solvent, substituents on the ligands *etc.*) on the identity of the products in cluster synthesis.

Variable temperature dc magnetic susceptibility data were collected for complex **1**·3.5CH$_3$CN in the temperature range 5.0–300 K under an applied field of 0.1 T and are plotted as $\chi_M T$ *vs.* T in Fig. 2. The $\chi_M T$ value of 12.11 cm^3 K mol^{-1} at 300 K is very close to the spin-only (g = 2) value of 12 cm^3 K mol^{-1} expected for four high-spin non-interacting Mn^{III} ions. The value rises gradually upon cooling until *ca.* 50 K when it increases rapidly to a value of 34.8 cm^3 K mol^{-1} at 5 K. This behaviour is consistent with dominant ferromagnetic interactions and an S = 8 ground state. Inspection of the molecular structure reveals that there are two exchange pathways between the metal centres mediated by the η^2:η^1:μ_3-NO group of the Me-sao^{2-} ligands. Each Mn^{III} ion interacts with two Mn^{III} ions through one μ_3-diatomic oximate group and one μ_2-O atom, and with a third *via* two μ_3-diatomic oximate groups. The variable-temperature susceptibility data were fit using such a 2J-model. However, employing a model in which we assume only one interaction between the metal centres (Fig. 3) provided an equally good fit of the data. Indeed a range of values in the 2J-model were found to all satisfactorily reproduce the experimental curve. Using the program MAGPACK[8] and employing the spin Hamiltonian in eqn (2), yielded the parameters J = +0.45 cm^{-1} and g = 1.98. The ground state of the complex was found to be S = 8 with S = 7 and S = 6 excited states 8 and 14 cm^{-1} above this, respectively.

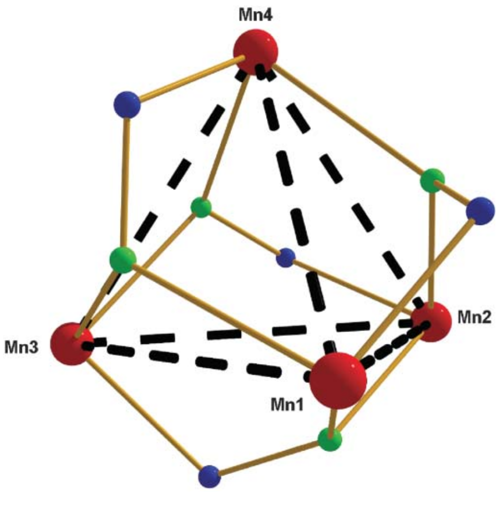

Fig. 3 The magnetic exchange interaction scheme adopted for the Mn$_4$ tetrahedron of **1** (see text for details).

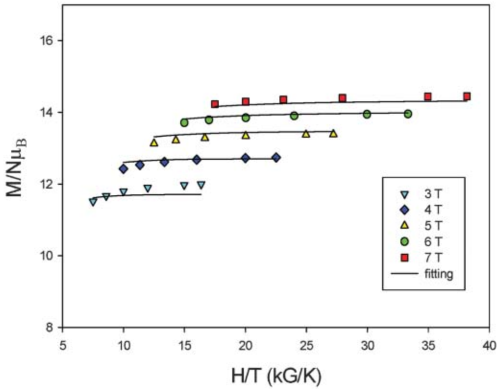

Fig. 4 Plot of reduced magnetization ($M/N\mu_B$) *vs.* H/T for **1**·3.5CH$_3$CN in fields 3–7 T and temperatures 1.8–10 K.

$$\hat{H} = -2J(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_1\cdot\hat{S}_3 + \hat{S}_1\cdot\hat{S}_4 + \hat{S}_2\cdot\hat{S}_3 + \hat{S}_2\cdot\hat{S}_4 + \hat{S}_3\cdot\hat{S}_4) \quad (2)$$

In order to verify the nature of the ground state, magnetization data were collected in the ranges 3–7 T and 1.8–10 K and these are plotted as reduced magnetization ($M/N\mu_B$) *vs.* H/T in Fig. 4. The data were fit by a matrix diagonalization method to a model that assumes only the ground state is populated, includes axial zero-field splitting ($D\hat{S}_z^2$) and the Zeeman interaction, and carries out a full powder average. The corresponding Hamiltonian is given by eqn (3), where D is the axial anisotropy, μ_B is the Bohr magneton, μ_0 is the vacuum permeability, $\hat{S}_z$ is the easy-axis spin operator, and H is the applied field. The best fit gave S = 8, g = 1.91 and D = −0.34 cm^{-1}.

$$\hat{H} = D\hat{S}_z^2 + g\mu_B\mu_0\hat{S}\cdot H \quad (3)$$

Ac magnetic susceptibility measurements, measured in the 1.8–5 K range in a 3.5 G ac field oscillating at 50–1000 Hz, show frequency-dependent out-of-phase (χ_M'') signals below 2.5 K, but no peaks are seen (Fig. 5). The in-phase $\chi_M'T$ signal increases

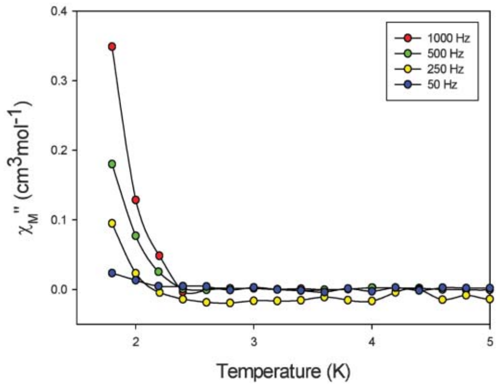

Fig. 5 Plots of the out-of-phase (χ_M'') signals for **1**·3.5CH$_3$CN in ac susceptibility studies *vs.* T in a 3.5 G oscillating ac field.

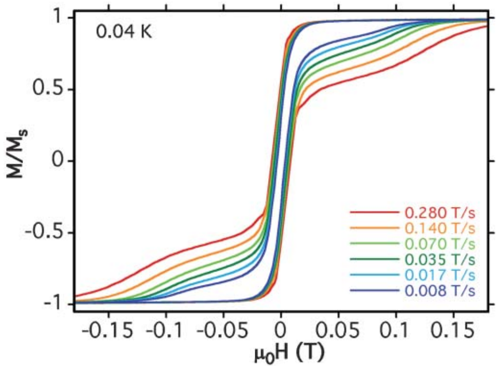

Fig. 6 Single-crystal magnetization (*M*) *vs.* applied field for **1** at 0.04 K. Hysteresis loops are shown at different field sweep-rates. *M* is normalised to its saturation value.

upon cooling suggesting the presence of low-lying excited states with smaller *S* values than the ground state, in agreement with the dc data. The *S* and *D* values obtained for $\mathbf{1}\cdot3.5CH_3CN$ suggest an upper limit to the potential energy barrier (*U*) to magnetization reversal ($U = S^2|D|$) of $\sim$31 K. This suggests that it may exhibit single-molecule magnetism behaviour. This was confirmed by single crystal hysteresis loop measurements performed using a micro-SQUID setup.[9] Studies of the magnetization performed at very low temperature show that **1** behaves as an SMM. Magnetization (*M*) *vs.* applied dc field measurements reveal hysteresis loops whose coercivity is temperature and sweep-rate dependent, increasing with decreasing temperature and increasing field sweep rate, as expected for the superparamagnetic-like behaviour of an SMM. The data obtained at 40 mK (Fig. 6) show hysteresis loops with a very large step at zero field. A step indicates a surge in the magnetization relaxation rate due to quantum tunnelling of the magnetization through the barrier, occurring at a field position where there is an avoided level crossing. At $H = -1$ T all the molecules are in the $M_S = +8$ state. When the field is swept in a positive direction there is resonance between the +8 and -8 M_S levels at $H = 0$, and some of the molecules tunnel. The height of the step, in this case, indicates that the tunnelling process is fast, and for species with relatively large tunnel splittings a direct relaxation process between the ground state M_S levels becomes possible. The space group $P2_1/c$ allows for large transverse terms in the Hamiltonian, and thus to large tunnel splittings and fast tunnelling at $H = 0$. When the same experiment is carried out at higher field sweep rates (Fig. 6) the number of molecules tunnelling at zero field decreases and the hysteresis loop is larger. In the variable temperature experiment hysteresis loops appear below *ca.* $T = 0.3$ K indicating that below this temperature the magnetization is blocked. At higher temperatures there is no hysteresis and the loops appear more '*S-shaped*' indicative of the presence of intermolecular interactions—consistent with the packing of the molecules in the crystal.

In conclusion, the use of Me-saoH$_2$ has led to the formation of a new tetranuclear Mn cluster—the first example of a ferromagnetically coupled Mn^{III} cube. It possesses an $S = 8$ ground state and displays SMM behaviour. Electrochemical and multifrequency EPR studies are underway and will be reported in a full paper.

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Notes and references

† The complex analysed as (C, H, N) $\mathbf{1}\cdot3.5CH_3CN$, expected (found): C, 54.50 (54.37); H, 4.80 (4.94); N, 10.29 (10.33)%. Diffraction data were collected with Mo-Kα radiation (λ = 0.71073 Å) on a Bruker Smart Apex CCD Diffractometer. Crystal data:[10] $C_{71}H_{74.5}Mn_4N_{11.5}O_{16}$, $M = 1563.1$, dark brown block, monoclinic, $P2_1/c$, $a = 13.6720(4)$, $b = 19.6080(6)$, $c = 27.9570(9)$ Å, $\beta = 103.6350(10)^\circ$, $V = 7283.5(4)$ Å^3, $T = 150$ K, 71 703 reflections collected of which 22 020 were independent ($R_{int} = 0.054$), 829 parameters and 0 restraints, $R1 = 0.0465$ [based on $F > 4\sigma(F)$], $wR2 = 0.0475$ (based on *F* and all data). CCDC 616497. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611174b

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