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# Synthesis, structure and magnetism of a new manganese carboxylate cluster: $[Mn_{16}O_{16}(OMe)_6(OAc)_{16}(MeOH)_3(H_2O)_3]\cdot 6H_2O$

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***Received (in Cambridge, UK) 18th December 2001, Accepted 25th February 2002***
***First published as an Advance Article on the web 12th March 2002***

**A new manganese(III/IV) carboxylate cluster $[Mn_{16}O_{16}(OMe)_6(OAc)_{16}(MeOH)_3(H_2O)_3]\cdot 6H_2O$ has been structurally characterised and shown to display net antiferromagnetic coupling with preliminary evidence for single-molecule magnetic behaviour.**

The synthetic and physicochemical studies made by Christou and Hendrickson *et al.*,[1] Gatteschi and Sessoli *et al.*,[2] and Powell *et al.*[3] on high nuclearity manganese and iron oxo/carboxylato cluster complexes have led to significant advances being made in the understanding of nanoscale magnets termed 'single molecule magnets' (SMMs). In the case of manganese, the nuclearities known to date to display SMM behaviour include $Mn_4$, $Mn_{12}$ and $Mn_{30}$.[4] Other nuclearities such as $Mn_3$, $Mn_6$, $Mn_7$, $Mn_8$, $Mn_9$, $Mn_{10}$, $Mn_{13}$, $Mn_{18}$ do not, even though some have high-spin ground states, one of the prerequisites for being a SMM. Another key prerequisite for SMM behaviour is a negative anisotropy in the axial zero-field splitting term $D$, which in the Mn clusters is introduced into the cluster ground state by $Mn^{III}$ single-ion centres.

The archetypal cluster, $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]\cdot 2HOAc\cdot 4H_2O$ ('$Mn_{12}$-acetate'), contains a central cubane $Mn^{IV}{}_4O_4$ core, bridged to an outer belt of eight $Mn^{III}$ ions by $\mu_3$-$O^{2-}$ bridges, the eight $Mn^{III}$ being bridged by $OAc^-$ ligands.

We report here details of a new manganese carboxylate cluster, $[Mn_{16}O_{16}(OMe)_6(OAc)_{16}(MeOH)_3(H_2O)_3]\cdot 6H_2O$ (**1**). This complex was first obtained accidentally when attempting to expand our dicyanamide (dca$^-$, $N(CN)_2{}^-$) molecule-based magnet work into networks of $Mn_3$ or $Mn_4$ clusters bridged by dca$^-$ ligands.[5] It was subsequently found that dca$^-$ was not necessary for its formation. Thus, addition of solid $n$-$Bu_4NMnO_4$ to a stirred solution of $Mn(NO_3)_2\cdot 4H_2O$ in a mixture of methanol and acetic acid yielded a dark brown solution which was allowed to stand for several weeks, with the formation of black block-like crystals of **1**.† If Na(dca) and $Me_4NBr$ are included in the reaction, **1** is formed first followed by small red crystals, identified as a triply-bridged linear chain complex $[Mn^{III}(OMe)(OAc)_2]_n$, which will be described elsewhere.[6] The presence of alkoxide bridges in **1** is rare in Mn clusters and probably responsible for the nuclearity obtained.[7]

In the structure of **1**,‡ the cluster lies on an inversion centre relating one half of the cluster to the other. The asymmetric unit contains half of the molecule and three lattice water molecules. The cluster consists of six $Mn^{IV}$ and ten $Mn^{III}$ ions[8] held together by fourteen $\mu_3$-$O^{2-}$, two $\mu$-$O^{2-}$, four $\mu$-$OMe^-$ and two $\mu$-$OAc^-$ groups to give a roughly elliptical planar $[Mn_{16}O_{16}(OMe)_4(OAc)_2]^{18+}$ core (Fig. 1). Peripheral ligation consists of the remaining fourteen $\mu$-$OAc^-$, two $\mu$-$OMe^-$ groups and three axial water and methanol molecules.

The $Mn_{16}$ core can be divided into two sub-units, a central $[Mn^{IV}{}_6O_6(OMe)_4]^{8+}$ unit connected to an outer perimeter of ten $Mn^{III}$ ions by ten $\mu_3$-$O^{2-}$ ions in the plane of the molecule and two $\mu$-$OAc^-$ groups perpendicular (above and below) to the plane of the molecule. The central unit contains six $Mn^{IV}$ ions in two rows of three (Mn(1), Mn(2), Mn(3) and the symmetry related Mn(1′), Mn(2′), Mn(3′)) lying in a plane that is sandwiched between two planes of oxygen atoms. Each plane contains two $\mu_3$-$O^{2-}$, one $\mu$-$O^{2-}$ and two $\mu$-$OMe^-$ ions. One oxygen plane contains O(1) and O(3) ($\mu_3$-$O^{2-}$), O(2′) ($\mu$-$O^{2-}$), and O(4′) and O(6′) ($\mu$-$OMe^-$). The other oxygen plane

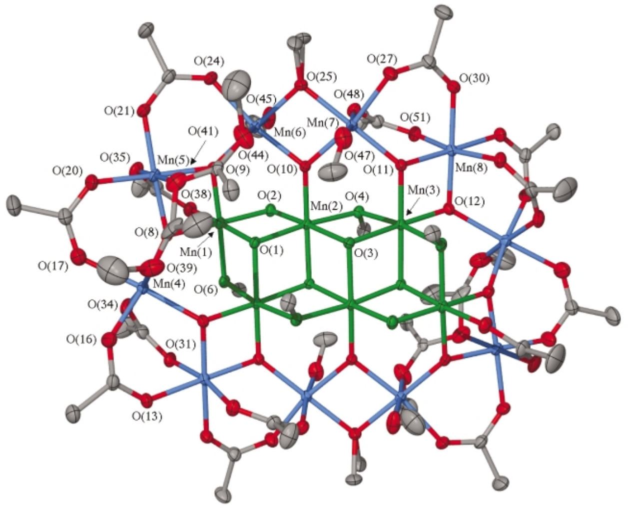

**Fig. 1** $[Mn_{16}O_{16}(OMe)_6(OAc)_{16}(MeOH)_3(H_2O)_3]\cdot 6H_2O$ with atom labelling scheme of manganese and oxygen atoms only (hydrogen atoms have been omitted for clarity). The central $[Mn^{IV}{}_6O_6(OMe)_4]^{8+}$ sub-unit is highlighted in green.

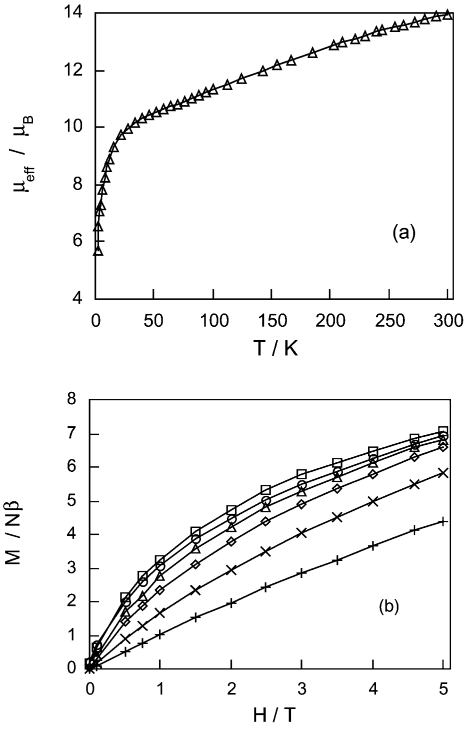

**Fig. 2** (a) Plot of $\mu_{eff}$ *vs.* temperature at 1 T and (b) Plots of magnetization, $M$ (in units $N\beta$) *vs.* applied field at various temperatures: (□) 2 K, (○) 3 K, (Δ) 4 K, (◇) 5.5 K (×) 10 K, (+) 20 K. Solid lines are not fits.

DOI: 10.1039/b111404b

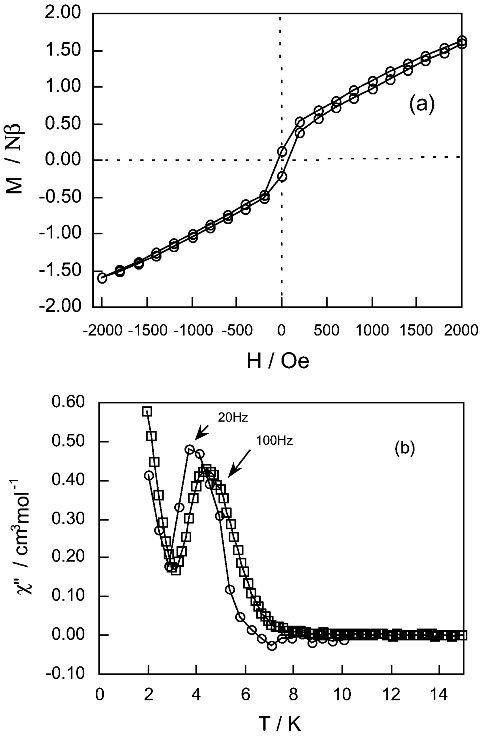

**Fig. 3** (a) Hysteresis plot of a powder sample dispersed in vaseline, at 2 K and (b) out of phase AC $\chi''$ plots with $H = 3.5$ Oe.

contains O(1′) and O(3′) (μ$_3$-O$^{2-}$), O(2) (μ-O$^{2-}$), and O(4) and O(6) (μ-OMe$^-$). The $Mn^{IV}$ ions occupy distorted octahedral sites between these two hexagonal close-packed O layers, in the manner seen in manganese oxide minerals,[9] and within two related $Fe_{17}$ and $Fe_{19}$ oxyhydroxide clusters.[10] Thus **1** could be thought of as a captured portion of a layered manganese oxide mineral. Such is not the case in $Mn_{12}$-acetate.

Peripheral ligation around the $Mn^{III}_{10}$ perimeter contains eight equatorial μ-OAc$^-$ groups, six axial μ-OAc$^-$ groups (three each on either side of the cluster in an alternating up-down-up fashion) and two μ-OMe$^-$ ligands (bridging Mn(6) and Mn(7)). Eight of the ten perimeter $Mn^{III}$ ions experience Jahn–Teller (JT) axial elongation in the direction perpendicular to the plane of the cluster. The remaining two (Mn(4) and Mn(4′)) experience JT axial compression roughly parallel to the plane of the cluster in the direction of a μ-OAc$^-$ and a core μ$_3$-O$^{2-}$. This may be important in regard to AC $\chi''$ behaviour.[11] Hydrogen bonding from an axial disordered water/methanol and an axial μ-OAc$^-$ *via* two lattice water molecules between each cluster links them into chains that propagate parallel to the *c*-axis direction.

Variable temperature magnetic susceptibilities were measured on freshly isolated samples of **1** in a field of 1 T over the range 2–300 K (Fig. 2(a)). The same results were obtained on neat powders and on vaseline mulls. The effective magnetic moment, per $Mn_{16}$, decreases gradually from 14.0 $\mu_B$ at 300 K to *ca.* 10.5 $\mu_B$, then more rapidly, reaching 5.7 $\mu_B$ at 2 K and still decreasing. The value of $\mu_{eff}$ at 300 K compares to the value of 18.16 $\mu_B$ calculated for six uncoupled $Mn^{IV}$ ($S = 3/2$) and ten $Mn^{III}$ ($S = 4/2$) and is thus indicative of overall antiferromagnetic coupling. To try to identify the ground spin state of **1**, magnetization ($M$) measurements were made in the ranges of $H = 0$–5 T and temperature = 2–20 K (Fig. 2(b)). It can be seen that, at 2 K, the $M$ values increase in a gradual curved fashion between 0 and 5 T to reach *ca.* 7 $N\beta$ in the 5 T field. The $M$ values are still increasing and saturation is not achieved. This is most likely due to thermal population of the ground-state and of other low lying spin-states occurring even at 2 K. Zero-field splitting and Zeeman effects will also influence the shape and size of the $M$ *vs.* $H$ plots. Cluster–cluster interactions, *via* hydrogen bonding pathways, may also play a part. It is therefore not possible, without fitting of the $M/H$ data, to unambiguously assign the ground state spin. A hysteresis loop (±0.2 T) at 2 K shows a rapid increase in $M$ in the ±250 Oe region (Fig. 3(a)). Preliminary AC $\chi''$ susceptibility measurements made in the range 2–15 K, at two frequencies (20 and 100 Hz) and $H = 3.5$ Oe, show a clear maximum which moves from 3.9 K at 20 Hz to 4.6 K at 100 Hz (Fig. 3(b)). This frequency dependence of $\chi''_{max}$ is one of the key experimental criteria for SMM behaviour and we are presently confirming this at different frequencies.

This work was supported by a Large Grant (to K. S. M.) and a Fellowship (to S. R. B.) from the Australian Research Council.

## Notes and references

† *Typical synthetic procedure*: to a stirred methanolic solution (120 mL) of $Mn(NO_3)_2 \cdot 4H_2O$ (11.57 mmol, 2.90 g), and glacial acetic acid (10 mL), *n*-$Bu_4NMnO_4$ (3.15 mmol, 1.14 g) was added in small portions over a period of 30 min. The solution was then left to stand. After several weeks a small amount of block-like black crystals of $Mn_{16}$-acetate formed. The solution was decanted and the crystals collected (0.20 g, 8% based on total Mn). $\nu$(OH) 3387 cm$^{-1}$ (br), $\nu$(C=O) 1558 cm$^{-1}$.

In reactions which also had Na(dca) (25.0 mmol, 2.23 g) and $Me_4NBr$ (25.0 mmol, 3.85 g) added, black crystals of $Mn_{16}$-acetate, **1**, formed first, followed by smaller red crystals of $[Mn^{III}(OMe)(OAc)_2]_n$, the latter in higher yield.[6] $\nu$(C=O) 1568 cm$^{-1}$.

Many repeats of the reaction show that crystals of **1** decompose with time to yield species containing low content of carbon and poor diffraction quality despite a good external morphology. Presumably slow hydrolysis of OMe$^-$ and OAc$^-$ groups occurs in the solid state. Analysis of a fresh sample, found: C, 18.8; H, 3.8. Calc. for $C_{41}H_{96}Mn_{16}O_{66}$: C, 19.6; H, 3.5%.

‡ *Crystal data* for $C_{41}H_{96}Mn_{16}O_{66}$, $M = 2524.22$, triclinic, space group $P\bar{1}$, $a = 12.8547(2)$, $b = 14.4366(2)$, $c = 14.4590(2)$ Å, $\alpha = 108.276(1)$, $\beta = 116.273(1)$, $\gamma = 96.900(1)°$, $U = 2176.49(5)$ Å$^3$, $T = 123(2)$ K, $Z = 1$, $F(000) = 1270$, $D_c = 1.926$ g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 2.343 mm$^{-1}$, $2\theta_{max} = 56.6°$. A black block (0.2 × 0.15 × 0.15 mm). 37016 total reflections, 10573 independent reflections ($R_{int} = 0.0609$), of which 8648 were observed [$I > 2\sigma(I)$]. At final convergence $R_1$ [$I > 2\sigma(I)$] = 0.0424, $wR_2$ (all data) = 0.1101 for 669 parameters, $S = 1.051$. CCDC reference number 176429. See http://www.rsc.org/suppdata/cc/b1/b111404b/ for crystallographic data in CIF or other electronic format.

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8 The oxidation states were so assigned for the following reasons. The central $Mn^{IV}$ ions have bond lengths comparable to those seen in the central $[Mn^{IV}_4O_4]^{8+}$ cubane of $Mn_{12}$-acetate (T. Lis, *Acta Crystallogr., Sect. B*, 1980, **36**, 2042) and lack the Jahn–Teller distortion common for $Mn^{III}$ *e.g.* α-$Mn^{III}O(OH)$ (T. Kohler, T. Armbruster and E. Libowitzky, *J. Solid State Chem.*, 1997, **133**, 486). In contrast, the perimeter $Mn^{III}$ ions did show significant Jahn–Teller distortion. This oxidation state assignment therefore requires the pyramidal oxygen atoms to be O$^{2-}$ rather than OH$^-$, again consistent with $Mn_{12}$-acetate.

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