



Synthesis, characterization and magnetic properties of $[\text{Mn}_{30}\text{O}_{24}(\text{OH})_8(\text{O}_2\text{CCH}_2\text{C}(\text{CH}_3)_3)_{32}(\text{H}_2\text{O})_2(\text{CH}_3\text{NO}_2)_4]$: the largest manganese carboxylate cluster

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Abstract

We report the synthesis, structure and magnetic properties of a new member of the family of high nuclearity Mn clusters. The complex $[\text{Mn}_{30}\text{O}_{24}(\text{OH})_8(\text{O}_2\text{CCH}_2\text{C}(\text{CH}_3)_3)_{32}(\text{H}_2\text{O})_2(\text{CH}_3\text{NO}_2)_4]$ (**1**), is the highest nuclearity manganese cluster to date. Complex **1** was obtained from the comproportionation reaction between $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and KMnO_4 , followed by ligand substitution with $\text{Me}_3\text{CCH}_2\text{CO}_2\text{H}$. It is mixed-valent with a trapped-valence 3Mn^{II} , 26Mn^{III} , Mn^{IV} oxidation state description. Dc magnetic susceptibility studies indicate an $S = 7$ ground state, and ac susceptibility studies show an out-of-phase susceptibility signal below 3 K, indicating complex **1** to display the slow magnetization relaxation diagnostic of a single-molecule magnet. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Manganese; Crystal structure; High nuclearity cluster; Single-molecule magnets

1. Introduction

Over the last decade, a strong interest has developed in our group in 3d metal carboxylate clusters because they represent a large family of high-nuclearity products with interesting structural, spectroscopic and magnetic properties. The majority of our efforts has been concentrated in polynuclear manganese complexes and has led to a large variety of clusters, such as Mn_4 [1–3], Mn_6 [4,5], Mn_7 [6,7], Mn_8 [8–11], Mn_9 [9,12,13], Mn_{10} [14–17], Mn_{11} [18,19], Mn_{12} [20,21], Mn_{13} [22], Mn_{18} [23–26] species. Magnetic studies have shown that they often possess a large number of unpaired electrons. In combination with a sufficiently large magnetic anisotropy, this has led some of them to display the new magnetic phenomenon of single-molecule magnetism (SMM).

The largest manganese clusters studied to date are the Mn_{18} complexes [23–26], possessing three different

types of structure and different kinds of magnetic behavior. We have now been able to synthesize an even larger Mn cluster, $[\text{Mn}_{30}\text{O}_{24}(\text{OH})_8(\text{O}_2\text{CCH}_2\text{C}(\text{CH}_3)_3)_{32}(\text{H}_2\text{O})_2(\text{CH}_3\text{NO}_2)_4]$ (**1**) from a multistep reaction employing $\text{Mn}(\text{O}_2\text{CCH}_3)_2 \cdot 4\text{H}_2\text{O}$ and KMnO_4 , followed by addition of *tert*-butylacetic acid [27]. This compound has been characterized using IR, EA, magnetic studies and crystallography. In this paper we describe the crystal structure and magnetic properties of this new compound, showing that it is a new example of a single-molecule magnet.

2. X-ray crystallography

$[\text{Mn}_{30}\text{O}_{24}(\text{OH})_8(\text{O}_2\text{CCH}_2\text{C}(\text{CH}_3)_3)_{32}(\text{H}_2\text{O})_2(\text{CH}_3\text{NO}_2)_4]$ -solvent (**1**) crystallizes in the monoclinic space group $C2/c$. The asymmetric unit contains half of a Mn_{30} complex located on a twofold axis, which passes through four manganese ions (Mn1, Mn2, Mn6 and Mn7). In addition to the main molecule of interest, the asymmetric unit contains some unidentified solvent.

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Fig. 1 shows an ORTEP representation of complex **1** with only the manganese and oxygen atoms. Selected interatomic distances are collected in Table 1.

The complex comprises 30 manganese ions held together by 24 oxide and eight hydroxide ions to give an $[\text{Mn}_{30}\text{O}_{24}(\text{OH})_8]^{32+}$ core, with peripheral ligation provided by 32 *tert*-butylacetate ligands, four nitromethane molecules and two terminal H_2O molecules. The oxidation states of the manganese ions can best be described as trapped valence $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}]$, where Mn2, Mn10 and Mn10' are Mn^{II} ions, Mn1 is an Mn^{IV} ion and the rest are Mn^{III} ions. The oxidation states have been assigned based on relative Mn–O bond distances, bond valence sum calculations [28] and the presence of a Jahn–Teller axial elongation on all the 26 Mn^{III} sites. One peculiarity is two longer distances Mn– O^{2-} (Mn2–O21 and Mn2–O21') of ~ 2.423 Å, indicating very distorted octahedral geometry at this site. The 24 bridging oxide ions are separated into two types: 18 are μ_3 - O^{2-} and six μ_4 - O^{2-} . The *tert*-butylacetate groups show three types of binding mode: 24 are bridging two manganese ions in the familiar syn,syn-bridging mode, six are bridging three manganese ions in the syn,syn,anti-bridging mode, and two of them, related by symmetry, are monodentate to Mn10 or Mn10', which are Mn^{II} ions. Two of the four nitromethane molecules (O171–N172–O173 and the symmetrically related partner) are chelating Mn10 and Mn10'. The other two nitromethane molecules (O123–N124–O125 and partner) are bridging Mn14, Mn3 and Mn16 in a syn,syn,anti-bridging mode on the Jahn–Teller elongation axes of the manganese ions. Finally, the two terminal H_2O molecules (O34, O34') are both bound to Mn6 on the Jahn–Teller elongation axis. Fig. 2 shows

the ORTEP representation of the entire molecule, emphasizing the positions of the nitromethane molecules, the monodentate carboxylate groups and the two water molecules.

3. Magnetism studies

A variable-temperature magnetic susceptibility study was performed on complex **1** in a 10.0 kG field and in the 2.0–300.0 K range (Fig. 3). The effective magnetic moment decreases from $22 \mu_{\text{B}}$ at 300 K to around $10 \mu_{\text{B}}$ at 10 K. In order to determine the ground state, magnetization data for complex **1** were collected in the 10.0–70.0 kG and 1.8–25 K ranges. Fitting of the obtained $M/N\mu_{\text{B}}$ versus H/T data gave best-fit parameters of $S = 7$, $D = -0.79 \text{ cm}^{-1}$, $E = -0.19 \text{ cm}^{-1}$ and $g = 1.97$. However, the theoretical model for the fitting assumes that the spin ground state is well isolated, which does not seem to be the case here, as commonly observed in high nuclearity systems, especially those containing Mn^{II} for which exchange interactions are weak.

Ac magnetic susceptibility studies at zero dc field and 3.5 G ac field were also carried out. In the ac susceptibility experiment, the ac magnetic field is oscillating at a particular frequency and a peak in the out-of-phase χ''_{M} versus T plot is observed when the magnetic moment of the molecule cannot relax (reorient) fast enough to keep in-phase with the oscillating field. Fig. 4 shows the in-phase component of the ac susceptibility $\chi'_{\text{M}}T$ versus T and the out-of-phase susceptibility χ''_{M} versus T for complex **1**. As can be seen in the upper plot, the $\chi'_{\text{M}}T$ is not constant in the 3–10 K range,



Fig. 1. ORTEP representation of complex **1** showing 50% probability ellipsoids. Only manganese and oxygen atoms are shown, and only the former are labeled.

Table 1
Selected bond distances

A	B	Distance (Å)	A	B	Distance (Å)
Mn(1)	Mn(6)	2.849(3)	Mn(10)	O(30)	2.154(6)
Mn(3)	Mn(14)	2.795(2)	Mn(10)	O(77)	2.099(9)
Mn(4)	Mn(11)	2.760(2)	Mn(10)	O(83)	2.165(9)
Mn(6)	Mn(7)	2.873(3)	Mn(10)	O(163)	2.233(10)
Mn(1)	O(18)	1.947(6)	Mn(10)	O(171)	2.299(10)
Mn(1)	O(19)	1.917(6)	Mn(10)	O(173)	2.332(10)
Mn(1)	O(20)	1.854(6)	Mn(11)	O(26)	1.888(7)
Mn(2)	O(18)	2.227(6)	Mn(11)	O(27)	1.848(7)
Mn(2)	O(21)	2.423(7)	Mn(11)	O(30)	1.985(7)
Mn(2)	O(22)	2.120(7)	Mn(11)	O(33)	2.308(7)
Mn(3)	O(18)	1.915(6)	Mn(11)	O(85)	2.280(7)
Mn(3)	O(19)	2.310(6)	Mn(11)	O(91)	1.977(7)
Mn(3)	O(21)	1.946(7)	Mn(12)	O(26)	1.890(7)
Mn(3)	O(23)	1.882(6)	Mn(12)	O(31)	1.835(6)
Mn(3)	O(24)	1.881(7)	Mn(12)	O(93)	1.956(8)
Mn(3)	O(125)	2.359(7)	Mn(12)	O(99)	1.948(7)
Mn(4)	O(18')	1.964(6)	Mn(12)	O(107)	2.081(8)
Mn(4)	O(19)	2.279(6)	Mn(13)	O(24)	1.874(7)
Mn(4)	O(25)	1.918(7)	Mn(13)	O(31)	1.827(7)
Mn(4)	O(26)	1.891(6)	Mn(13)	O(101)	1.937(7)
Mn(4)	O(27)	1.857(7)	Mn(13)	O(109)	2.051(8)
Mn(4)	O(32)	2.433(7)	Mn(13)	O(115)	1.939(8)
Mn(5)	O(20)	1.938(6)	Mn(14)	O(23)	1.857(7)
Mn(5)	O(23)	1.862(7)	Mn(14)	O(24)	1.880(7)
Mn(5)	O(27')	2.085(7)	Mn(14)	O(37)	1.965(7)
Mn(5)	O(28)	1.900(7)	Mn(14)	O(45)	2.086(8)
Mn(5)	O(35)	2.008(6)	Mn(14)	O(117)	1.962(8)
Mn(5)	O(43)	2.288(7)	Mn(14)	O(123)	2.342(8)
Mn(6)	O(20)	1.906(6)	Mn(15)	O(21)	1.892(6)
Mn(6)	O(29)	1.928(6)	Mn(15)	O(25)	1.855(7)
Mn(6)	O(34)	2.290(7)	Mn(15)	O(31)	2.148(7)
Mn(7)	O(29)	1.869(6)	Mn(15)	O(127)	1.956(8)
Mn(7)	O(51)	2.205(8)	Mn(15)	O(139)	2.021(7)
Mn(7)	O(59)	1.950(8)	Mn(15)	O(157)	2.269(8)
Mn(8)	O(28)	1.884(7)	Mn(16)	O(21)	1.924(7)
Mn(8)	O(29)	1.879(6)	Mn(16)	O(22)	1.819(7)
Mn(8)	O(43)	2.226(7)	Mn(16)	O(125)	2.352(8)
Mn(8)	O(53)	2.247(8)	Mn(16)	O(129)	1.957(8)
Mn(8)	O(61)	1.951(7)	Mn(16)	O(147)	1.976(8)
Mn(8)	O(67)	1.976(7)	Mn(16)	O(155)	2.136(9)
Mn(9)	O(28)	1.892(6)	Mn(17)	O(22)	1.820(7)
Mn(9)	O(30')	2.204(7)	Mn(17)	O(25)	1.902(7)
Mn(9)	O(33')	1.905(7)	Mn(17)	O(32)	2.253(7)
Mn(9)	O(53)	2.354(8)	Mn(17)	O(141)	1.979(8)
Mn(9)	O(69)	1.948(8)	Mn(17)	O(149)	1.927(9)
Mn(9)	O(75)	1.921(7)	Mn(17)	O(157)	2.247(8)
O(123)	N(124)	1.213(12)	O(171)	N(172)	1.249(15)
O(125)	N(124)	1.321(12)	O(173)	N(172)	1.262(15)

indicating that it is not only the ground state that is populated at these temperatures. Below 3 K, there is a frequency-dependent drop in the in-phase signal paralleling the appearance of an out-of-phase (χ''_M) signal, whose peak lies at temperatures below the operating limit of the instrument (1.7 K). Lower temperature studies will be reported in due course.

4. Conclusion

We have prepared the largest manganese cluster ever synthesized. A close inspection of the structure shows the manganese ions to span three oxidation states from Mn^{II} – Mn^{IV} . The metal ions are bridged by a combination of O^{2-} and OH^- , and the coordination

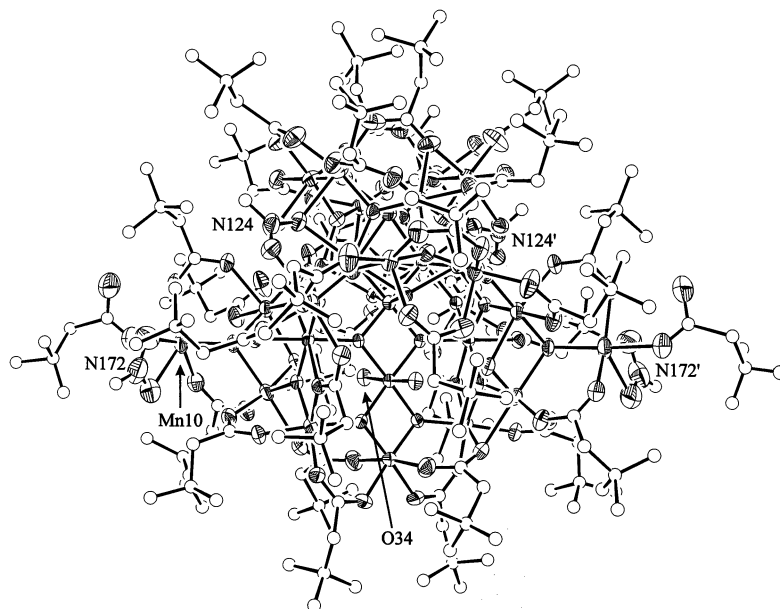


Fig. 2. ORTEP representation of complete complex **1** showing 50% probability ellipsoids; only nitrogen atoms from nitromethane and oxygen atoms from H₂O molecules are labeled.

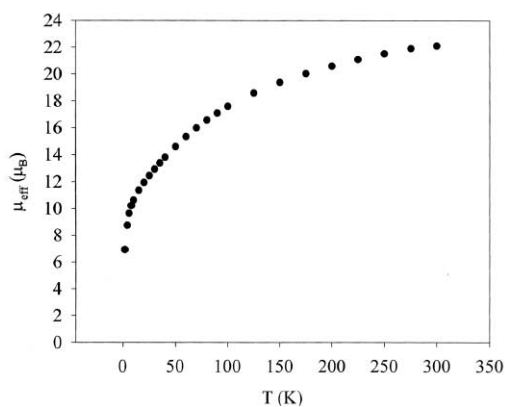


Fig. 3. Plot of the effective magnetic moment μ_{eff} versus temperature for complex **1**.

is terminated by terminal, bridging and chelating ligands.

Preliminary magnetic studies show that the molecule exhibits frequency-dependent out-of-phase ac susceptibility signals characteristic of single-molecule magnets. The fitting of the reduced magnetization suggests $S = 7$ and an appreciable magnetoanisotropy; together, these yield the SMM properties.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 152687. Copies of this infor-

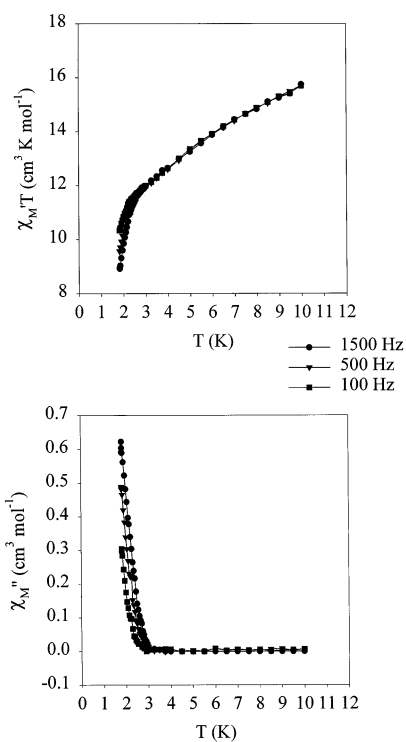


Fig. 4. Plots of the in-phase (χ'_M) and out-of-phase (χ''_M) ac magnetic susceptibility for complex **1** in a 3.5 G AC field at the indicated oscillation frequencies of the applied field.

mation may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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