1,1,1-Tris(hydroxymethyl)propane in manganese carboxylate chemistry: synthesis, structure and magnetic properties of a mixed-valence [Mn$^{III}_4$Mn$^{II}_4$] cluster featuring the novel [Mn$^{III}_4$Mn$^{II}_4$(μ_3-OR)$_6$(μ_2-OR)$_8$]$^{6+}$ core†

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The reaction between MnBr$_2$·4H$_2$O with H$_3$tmp (1,1,1-tris(hydroxymethyl)propane) in MeCN in the presence of Na(O$_2$CCMe$_3$) and NBu$_4$Br produces the complex [Mn$_8$(O$_2$CCMe$_3$)$_2$(tmp)$_2$(Htmp)$_4$Br$_4$-(H$_2$O)$_2$]·2MeCN (1·2MeCN) in good yield. The centrosymmetric octanuclear molecule consists of four Mn^{III} and four Mn^{II} ions assembled together by fourteen alkoxo bridges to give a [Mn$^{III}_4$Mn$^{II}_4$(μ_3-OR)$_6$(μ_2-OR)$_8$]$^{6+}$ rod-like core in which the metal centres are arranged in a planar zigzag fashion. Peripheral ligation is provided by a combination of bridging pivalate ions, terminal bromides and water molecules. Dc magnetic susceptibility measurements reveal the presence of dominant antiferromagnetic interactions leading to a spin ground state of $S = 0$. A rationalization of this result is attempted by structural comparison with previously reported tetranuclear manganese complexes containing the [Mn$^{III}_2$Mn$^{II}_2$(μ_3-OR)$_2$(μ_2-OR)$_4$] core in which the magnetic interactions are ferromagnetic.

Introduction

Polynuclear manganese carboxylate chemistry is a field of research that has attracted scientists from multi-disciplinary areas, including synthetic inorganic chemistry, biology, material science, magnetochemistry and physics. In particular, the discovery of a tetranuclear mixed-valence manganese complex at the active site of the oxygen-evolving complex in photosystem II[1] led to the attempted synthesis of many model complexes that would exhibit the same structural and/or spectroscopic characteristics and functions.[2] In molecular magnetism an increasing number of polynuclear manganese carboxylate complexes have been found to possess large spin ground states and some have also been shown to display the phenomenon of single-molecule magnetism in which single molecules can function as single-domain magnetic particles at low temperatures-exhibiting both slow relaxation of the magnetization and quantum tunnelling of the magnetization.[3]

Discovering new preparative routes towards the synthesis of high nuclearity Mn complexes is thus of great interest not only for the discovery of completely new complexes but also as a means of building up families of related species so that structure-property relations can be developed. Although the use of the tripodal alcohol ligand 1,1,1-tris(hydroxymethyl)propane (H$_3$tmp) (Scheme 1) has been investigated widely in oxo-vanadium chemistry,[4a–g] its use in manganese chemistry is confined to four examples: a [Mn$_{10}$] compound with a decametallate-type structure;[4h] a wheel-like [Mn$_{22}$] single-molecule magnet (SMM);[4i] a hexanuclear mixed-
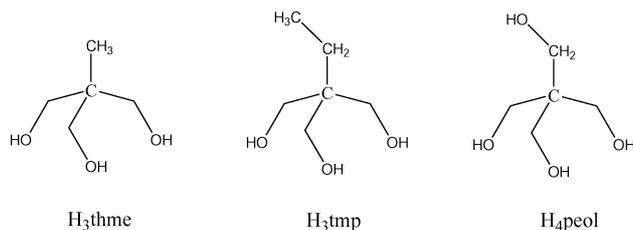
Scheme 1 The tripodal ligands 1,1,1-tris(hydroxymethyl)ethane (H$_3$thme), 1,1,1-tris(hydroxymethyl)propane (H$_3$tmp) and pentaerythritol (H$_4$peol).

valent [Mn$_6$] rod-like complex;[4j] and a tetranuclear mixed-metal [Mn$_2$Dy$_2$] rhomb-like SMM.[4k] The majority of these complexes have been made using the well known oxo-centred triangles of general formula [Mn$_3$O(O$_2$CR)$_6$L$_3$]$^{0/+}$ (L = py, MeCN etc.). In the present work we describe the synthesis, structure and magnetic properties of a new octanuclear Mn cluster made from the reaction of a simple Mn^{II} source (MnBr$_2$·4H$_2$O) with H$_3$tmp in the presence of sodium pivalate and tetrabutylammonium bromide.

Experimental

Syntheses

All manipulations were performed under aerobic conditions using solvents and reagents as received. 1,1,1-tris(hydroxymethyl)-propane is commercially available.

[Mn$_8$(O$_2$CCMe$_3$)$_2$(tmp)$_2$(Htmp)$_4$Br$_4$(H$_2$O)$_2$]·2MeCN (1·2MeCN). A pale yellow suspension of MnBr$_2$·4H$_2$O (0.286 g, 1 mmol), H$_3$tmp (0.134 g, 1 mmol), Na(O$_2$CCMe$_3$) (0.124 g, 1 mmol) and NBu$_4$Br (0.322 g, 1 mmol) in MeCN (25 ml) was kept under stirring for 12 h during which time it changed colour to dark orange/brown. The suspension was filtered and the remaining solution left

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† This paper is dedicated to the memory of Prof. Ian P. Rothwell (1955–2004).

undisturbed to evaporate slowly. X-Ray quality brown crystals were formed during two weeks. The crystals were collected by filtration, washed with Et_2O and dried *in vacuo*. The yield was approximately 45%. The dried sample analyzed as $\mathbf{1}\cdot0.5MeCN$. Found (calc.%) $C_{46}H_{88}Br_4Mn_8O_{24}\cdot0.5\ CH_3CN$; C 30.95 (31.28), H 4.97 (5.00), N 0.40 (0.39). IR data (KBr pellet; cm^{-1}): 1636s, 1539vs, 1482s, 1414m, 1359w, 1223w, 1112m, 1049vs, 943s, 583m.

X-Ray crystallography

Diffraction data were collected at 150 K on a Bruker Smart Apex CCD diffractometer equipped with an Oxford Cryosystems LT device. The structure was solved by direct methods (Shelxs) and refined by full-matrix least squares against F^2 (CRYSTALS).[5]

The complex resides on a crystallographic inversion centre. The H-atoms in the aquo-ligand were found in a difference map and refined subject to distance restraints; other H-atoms were included in calculated positions. The methyl group of the MeCN of solvation solvent molecule was disordered over two sites; the occupancies refined to 0.46(3) and 0.54(3), displacement parameters being modelled at the isotropic level. Bond distances from the disordered C-sites to the adjacent carbon atom were refined subject to a similarity restraint. In the ʻBu-ligands two out of the three methyl C-atoms developed elongated displacement ellipsoids; a disorder model for these regions was tested, but the refinement residuals are hardly better than the ordered model presented here [$R1 = 4.89\ vs.\ 4.83\%$]. The high thermal motion and/or disorder is modelled with the adps. The ʻBu groups were refined subject to similarity restraints which impose local three-fold symmetry.[5] Crystallographic data for complex $\mathbf{1}\cdot2MeCN$ are summarised in Table 1.

CCDC reference number 280380

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511258c

Table 1 Crystallographic data for complex $\mathbf{1}\cdot2MeCN$

	$\mathbf{1}\cdot2MeCN$
Formula[a]	$C_{50}H_{94}Br_4Mn_8N_2O_{24}$
M_r	1866.64
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	11.4048(2)
b/Å	12.8147(3)
c/Å	14.1353(3)
α/°	108.2590(10)
β/°	97.2100(10)
γ/°	110.7390(10)
V/Å³	1768.50(7)
Z	1
T/K	150
λ[b]/Å	0.71073
D_c/g cm⁻³	1.752
μ(Mo-Kα)/mm⁻¹	3.710
Meas./indep. refl. (R_{int})	36443/9899 (0.032)
Obs. refl. [$I > 4\sigma(I)$]	5761
$wR2$[c,d]	0.1667
$R1$[d,e]	0.0483
Goodness of fit on F^2	1.0035
$\Delta\rho_{max,\ min}$/e Å⁻³	2.51, −1.01

[a] Including solvate molecules. [b] Mo-Kα radiation, graphite monochromator. [c] $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$. [d] For observed data. [e] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

Physical measurements

Elemental analyses (C, H, N) were performed by the University of Edinburgh microanalysis service. IR spectra (4400–450 cm^{-1}) were recorded as KBr pellets on a JASCO FT/IR-410 spectrophotometer. Variable-temperature, solid-state direct current (dc) magnetic susceptibility data down to 1.80 K were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T DC magnet at the University of Florida. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants.

Results and discussion

Synthesis

The reaction between $MnBr_2\cdot4H_2O$ and H_3tmp in the presence of $Na(O_2CCMe_3)$ and NBu_4Br in MeCN gives the complex $[Mn_8(O_2CCMe_3)_2(tmp)_4(Htmp)_2Br_4(H_2O)_2]\cdot(\mathbf{1})$ which was crystallographically identified as $\mathbf{1}\cdot2MeCN$. The complex is a mixed-valent species containing four Mn^{III} and four Mn^{II} ions. Given that the starting manganese source contains only Mn^{II} ions it is clear that the Mn^{III} ions are formed by aerial oxidation upon stirring, as observed by the colour change from pale-yellow to dark orange/brown. Complex $\mathbf{1}$ is neutral and its structure contains no additional cations (NBu_4^+) or anions (Br^-). The question arose therefore as to whether NBu_4Br was essential for the formation of the product. The same synthetic procedure was thus repeated without the presence of NBu_4Br, but this led to the precipitation of an insoluble yellow non-crystalline powder (indicative of the presence of only Mn^{II} ions) with a different IR spectrum to that of $\mathbf{1}\cdot2MeCN$. We therefore believe that the use of NBu_4Br is essential for the formation of complex $\mathbf{1}$ and it may indeed have a dual role in (a) enabling the more rapid oxidation of the Mn^{II} ions in solution, and (b) providing additional Br^- ions to act as terminal ligands in the product. No isolable product was obtained when we replaced NBu_4Br with $NBu_4(NO_3)$. However, as is almost always the case in Mn cluster chemistry the actual mechanism of formation is likely to be extremely complicated, involving the protonation/deprotonation, oxidation/reduction and structural rearrangement of several species in solution, and thus a detailed mechanistic description remains impossible. With the identity of compound $\mathbf{1}$ established we also tried similar reactions but employing different carboxylates (*e.g.* $MeCO_2^-$, $PhCO_2^-$ *etc.*) as a means of obtaining a number of structural analogues. However, our attempts yielded only non-crystalline materials.

We have previously reported the synthesis and magnetic properties of a number of rod-like Mn clusters containing tripodal alcohols ranging in nuclearity from six to twelve.[6] In each case the product was formed upon the reaction of the appropriate oxo-centered metal triangle $[Mn_3O(O_2CR)_6(py)_3]^{0/+}$ with $H_3tripod$ in MeCN and the only one of these complexes to contain tmp^{3-} was the hexanuclear rod $[Mn_6(O_2CCMe_3)_8(tmp)_2(py)_2]$.[6] Because of the lack of a 'simple' or 'convenient' source of Mn^{III} these $[Mn_3O(O_2CR)_6(py)_3]^{0/+}$ triangles have proven to be remarkably successful starting materials, but here we show that structurally similar complexes containing Mn ions in different oxidation levels can also be made from simple Mn^{II} salts such as $MnBr_2\cdot4H_2O$.

Table 2 Selected interatomic distances (Å) and angles (°) for complex **1**·2MeCN[a]

Mn(1)–O(21)	2.110(3)	Mn(2)–O(32)	1.866(4)
Mn(1)–O(33′)	2.146(3)	Mn(2)–O(21)	1.900(4)
Mn(1)–O(22)	2.198(4)	Mn(2)–O(12)	1.950(3)
Mn(1)–O(41′)	2.199(3)	Mn(2)–O(22)	1.960(3)
Mn(1)–O(41)	2.337(4)	Mn(2)–O(31)	2.221(4)
Mn(1)–Br(1)	2.679(2)	Mn(2)–O(42)	2.223(5)
Mn(3)–O(43)	1.876(4)	Mn(4)–O(32)	2.182(4)
Mn(3)–O(33)	1.893(3)	Mn(4)–O(43)	2.183(3)
Mn(3)–O(31)	1.916(3)	Mn(4)–O(1)	2.185(5)
Mn(3)–O(41)	1.948(4)	Mn(4)–O(31)	2.243(3)
Mn(3)–O(23)	2.260(5)	Mn(4)–O(14)	2.245(3)
Mn(3)–O(22)	2.308(4)	Mn(4)–Br(4)	2.550(1)
Mn(4)–O(31)–Mn(3)	100.9(1)	Mn(1)–O(33′)–Mn(3′)	100.7(1)
Mn(4)–O(43)–Mn(3)	104.4(1)	Mn(1)–O(41′)–Mn(3′)	97.1(1)
Mn(4)–O(32)–Mn(2)	100.5(1)		
Mn(4)–O(31)–Mn(2)	88.6(1)		
Mn(2)–O(31)–Mn(3)	98.4(1)	Mn(4)···Mn(2)···Mn(1)···Mn(3)	−0.1(1)
Mn(2)–O(22)–Mn(1)	98.4(1)	Mn(2)···Mn(1)···Mn(1′)···Mn(3)	−3.0(1)
Mn(2)–O(21)–Mn(1)	103.4(1)	Mn(3)···Mn(3)···Mn(3′)···Mn(1′)	0.0(1)
Mn(3)–O(22)–Mn(1)	95.7(1)	Mn(1)···Mn(1′)···Mn(2′)···Mn(3′)	3.0(1)
Mn(3)–O(41)–Mn(1)	102.2(1)	Mn(1′)···Mn(3′)···Mn(4′)···Mn(2)	0.1(1)
Mn(3)–O(41)–Mn(1′)	97.1(1)	Mn(1)–O(41)–Mn(1′)–O(41′)	0.0(1)
Mn(3)–O(33)–Mn(1′)	100.7(1)		
Mn(1′)–O(41′)–Mn(1)	100.3(1)		

[a] Symmetry code (′) = −x + 1, −y + 1, −z + 1.
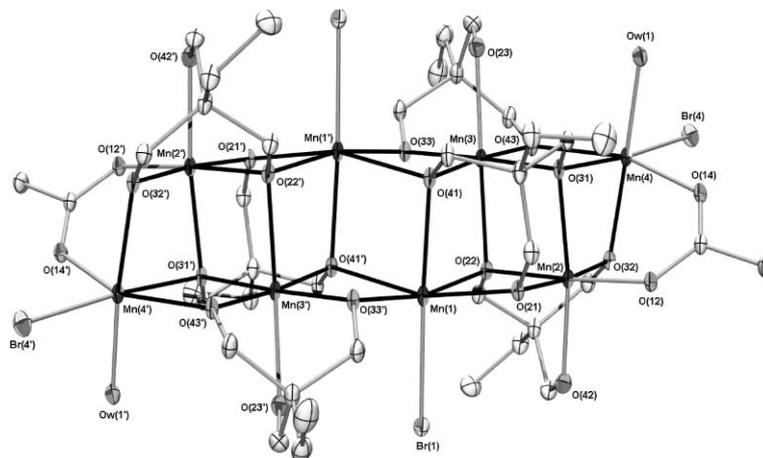
Fig. 1 ORTEP representation of complex **1**. Only the *ipso* carbon atoms of the pivalate anions are shown. Hydrogen atoms have been omitted for clarity; the core of the molecule is outlined in bold.

Description of structure

An ORTEP representation of complex **1** is shown in Fig. 1 and selected interatomic distances and angles given in Table 2. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with the molecule lying on an inversion centre. The complex consists of a planar rod-like $[Mn^{III}_4Mn^{II}_4(\mu_3\text{-OR})_6(\mu_2\text{-OR})_8]^{6+}$ unit (Fig. 2). The core is trapped-valence with Mn2 and Mn3 (and symmetry equivalents) being the Mn^{III} ions, and can be described as consisting of six edge-sharing $[Mn_3O]$ triangles or three edge-sharing $[Mn_4O_2]$ butterfly units. An alternative view is that of two fused '*planar diamond*' $[Mn^{III}_2Mn^{II}_2(\mu_3\text{-OR})_2(\mu_2\text{-OR})_4]^{4+}$ fragments (*i.e.* that containing Mn1–Mn4 and symmetry equivalents). All eight Mn ions are in distorted octahedral geometries with the Mn^{III} ions displaying the expected Jahn–Teller elongations—these are co-parallel lying approximately perpendicular the $[Mn_8]$ plane
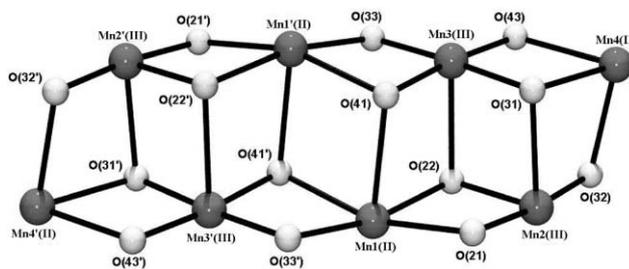
Fig. 2 The $[Mn^{III}_4Mn^{II}_4(\mu_3\text{-OR})_6(\mu_2\text{-OR})_8]^{6+}$ core of complex **1**.

(O31–Mn2–O42; O23–Mn3–O22 and symmetry equivalents). The two fully deprotonated tmp[3−] ligands sit directly above and below the $[Mn_8]$ plane each bonding in a $\eta^2,\eta^3,\eta^3,\mu_5$-fashion (*e.g.* O(21), O(31), O(41)) directing the formation of a pentanuclear metal

fragment comprising three edge-sharing [Mn₃O] triangles (*e.g.* Mn(1)–Mn(4), Mn(1'); Fig. 3(A)). The four doubly deprotonated Htmp²⁻ ligands are located around the edges of the 'rod' and coordinate in two distinct ways: two in a $\eta^1,\eta^2,\eta^3,\mu_4$-fashion (*e.g.* O(42), O(32), O(22) and symmetry equivalents) and two in a $\eta^1,\eta^2,\eta^2,\mu_3$-fashion (*e.g.* O(23), O(43), O(33) and symmetry equivalent). This directs the formation of a tetranuclear metal fragment describing two edge-sharing [Mn₃O] triangles (*e.g.* Mn(1)–Mn(4); Fig. 3(B)) and a linear trinuclear metal fragment (*e.g.* Mn(1), Mn(3'), Mn(4'); Fig. 3(C)), respectively. The coordination spheres of the eight six-coordinate Mn ions are completed by two Me₃CCO₂⁻ ligands that bridge in their usual η^1,η^1,μ-fashion (*e.g.* O(12), O(14) and O(12'), O(14')), four terminal Br⁻ ions and two terminal H₂O molecules (Ow(1) and Ow(1')). Thus Mn(1) and Mn(4) are bound to an {O₅Br} set of donor atoms and Mn(2) and Mn(3) to an {O₆} set of donor atoms.
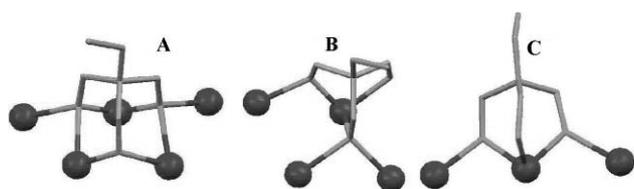
Fig. 3 The three coordination modes of the tripodal ligand found in complex **1**: (A) $\eta^2,\eta^3,\eta^3,\mu_5$; (B) $\eta^1,\eta^2,\eta^3,\mu_4$ and C: $\eta^1,\eta^2,\eta^2,\mu_3$.

The oxidation states of the Mn ions were determined from a combination of charge balance, bond length considerations and bond valence sum (BVS) calculations.[7] These are summarised in Table 3. The oxidation states of the metal ions requires the presence of two fully and four doubly deprotonated tripodal ligands given the presence of two Me₃CCO₂⁻ and four Br⁻ ions. Although no hydrogen atoms were crystallographically located at bonding distances from any of the tripodal oxygen atoms they are easily assigned to the tripods bearing O(23), O(42) (and symmetry equivalents) based on (a) their monocoordinate bonding; (b) their long bond lengths (*e.g.* O(23)–Mn(3), 2.260(5) Å); (c) their preference for occupying the JT elongation axes of the Mn^{III} ions and (d) the presence of a H-bond to the terminal Br⁻ ions located on Mn(1) and Mn(1') (O–H···Br, 3.156–3.227 Å). In the crystal the molecules stack directly upon each other forming sheets with the solvent molecules sitting in between these sheets.

The planar diamond [Mn^{III}₂Mn^{II}₂(μ₃-OR)₂(μ₂-OR)₄] moiety seen twice in complex **1** has been reported previously in the tetranuclear complexes [Mn^{III}₂Mn^{II}₂(hmp)₆(NO₃)₂(MeCN)₂]²⁺ (**2**), [Mn^{III}₂Mn^{II}₂(hmp)₆(NO₃)₄] (**3**), [Mn^{III}₂Mn^{II}₂(hmp)₄(acac)₂(MeO)₂]²⁺ (**4**),[8] [Mn^{III}₂Mn^{II}₂(O₂CMe)₂(pdmH)₆]²⁺ (**5**),[9] [Mn^{III}₂Mn^{II}₂Br₂-(hmp)₆(H₂O)₂]²⁺ (**6**),[10] [Mn^{III}₂Mn^{II}₂(O₂CMe)₂(LH)₂(LH₂)₂(H₂O)₂]²⁺ (**7**),[11] [Mn^{III}₂Mn^{II}₂(O₂CPh)₂(LH)₂(LH₂)₂(H₂O)₂]²⁺ (**8**),[11] and [Mn^{III}₂Mn^{II}₂(O₂CEt)₂(LH)₂(LH₂)₂(H₂O)₂]²⁺ (**9**)[11] (where hmpH = 2-hydroxymethylpyridine; pdmH₂ = pyridine-2,6-dimethanol;

Table 3 Bond valence sum calculations for complex **1**

Atom	Mn²⁺	Mn³⁺	Mn⁴⁺	Assignment
Mn(1)	1.79	1.64	1.61	2+
Mn(2)	3.45	3.19	3.13	3+
Mn(3)	3.44	3.17	3.11	3+
Mn(4)	1.75	1.61	1.58	2+

LH₃ = triethanolamine). However the [Mn^{III}₄Mn^{II}₄(μ₃-OR)₆(μ₂-OR)₈]⁶⁺ topology of complex **1** is observed for the first time, to the best of our knowledge, either in a discrete molecule or as a fragment of a higher nuclearity complex. It is however structurally related to the core seen in the rod-like complex [Mn₈O₄(O₂CCMe₃)₁₀(thme)₂(py)₂], but here the core consists of a homovalent [Mn^{III}₈(μ₃-O)₄(μ₃-OR)₂(μ₂-OR)₄]¹⁰⁺ unit.[6] Octanuclear manganese clusters are quite common but complex **1** is only the third member of the [Mn^{III}₄Mn^{II}₄] sub-family after the complexes [Mn₈O₂(OH)₂(O₂CPh)₁₀{(ph)(2-py)CNO}₄] and [Mn₈(O₂CCH₂tBu)₁₂(teaH)₄] (where (ph)(2-py)CO is phenyl 2-pyridyl ketone and teaH₃ is triethanolamine).[12]

Magnetic properties

Solid-state dc magnetic susceptibility (χ_M) measurements were performed on a polycrystalline sample of **1** in 0.01, 0.1 and 1 T applied magnetic fields in the 2.00–300 K temperature range. The results are plotted as $\chi_M T$ *vs.* T in Fig. 4. The room temperature $\chi_M T$ value of approximately 29 cm³ mol⁻¹ K (0.1 T) is slightly lower than that expected for a complex comprising four Mn^{III} and four Mn^{II} ions (29.5 cm³ K mol⁻¹ with $g = 2$). The value of $\chi_M T$ remains almost constant as the temperature is decreased until *ca.* 50 K where it then decreases rapidly to a value of approximately 2 cm³ K mol⁻¹ at 2.0 K. This behaviour is indicative of dominant antiferromagnetic exchange between the metal centres with the low temperature value suggesting a small, probably $S = 0$, spin ground state. In-phase ac susceptibility measurements performed in the temperature range 1.8–10 K support this assignment: extrapolation of the $\chi_M' T$ signal from values above ~3 K (to avoid decreases due to such effects as intermolecular interactions at lower temperatures) to 0 K gives a value of ~1 cm³ K mol⁻¹. The slope of the $\chi_M' T$ *vs.* T plot also decreases rapidly with decreasing temperature revealing the presence of several spin-states of larger S values lying very close to the ground-state. This is to be expected for a molecule containing multiple Mn^{II} ions that are known to promote weak exchange interactions—the result of which is likely to be a large number of S states with comparable energies to the ground state.
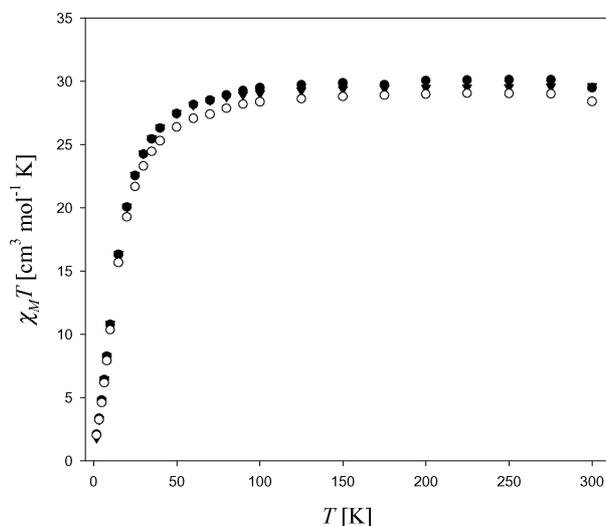
Fig. 4 Plot of $\chi_M T$ *vs.* T for complex **1**; filled circles = 0.1 T, filled triangles = 1 T and open circles = 0.01 T.

Table 4 Exchange interactions calculated for complexes **2–9**

Complex	$J_{wb}(Mn^{III}–Mn^{II})/cm^{-1}$	$J_{bb}(Mn^{III}–Mn^{III})/cm^{-1}$
2	+1.0	+9.9
3	+4.2	+6.3
4	+0.78	+5.3
5	+0.4	+8.1
6	+0.9	+9.0
7	+1.7	+6.5
8	+0.4	+6.6
9	+0.22	+10.9

Due to the low symmetry of the molecule it is impossible to apply the Kambe method[13] in order to calculate the various individual pairwise J_{ij} exchange interactions between Mn_iMn_j pairs (since there are five different exchange interactions present), but an attempt to rationalize the $S = 0$ ground-state of **1** can be carried out on the basis of the well-known magnetic behaviour of the planar diamond $[Mn^{III}_2Mn^{II}_2(\mu_3\text{-}OR)_2(\mu_2\text{-}OR)_4]^{4+}$ unit present in complexes **2–9**. In all of these tetranuclear complexes this topology has led to ferromagnetic exchange between the metal centres resulting in a spin ground-state of $S = 9^{8\text{–}11}$ (or $S = 8$ depending on the degree of solvation of the cluster).[9] In Fig. 5 (top) we show the metal–oxygen core common to complexes **2–9** and the two magnetic exchange pathways employed to fit the experimental data. In each case only two main exchange pathways were considered: one (J_{wb}) between the peripheral Mn^{II} ions and the central Mn^{III} ions; and one (J_{bb}) between the two central Mn^{III} ions. The results of these fits are summarized in Table 4 and suggest that all the interactions are ferromagnetic, but weak with J_{wb} falling in the range 0.40–4.2 cm^{-1} and J_{bb} falling in the range 5.3–10.9 cm^{-1}.
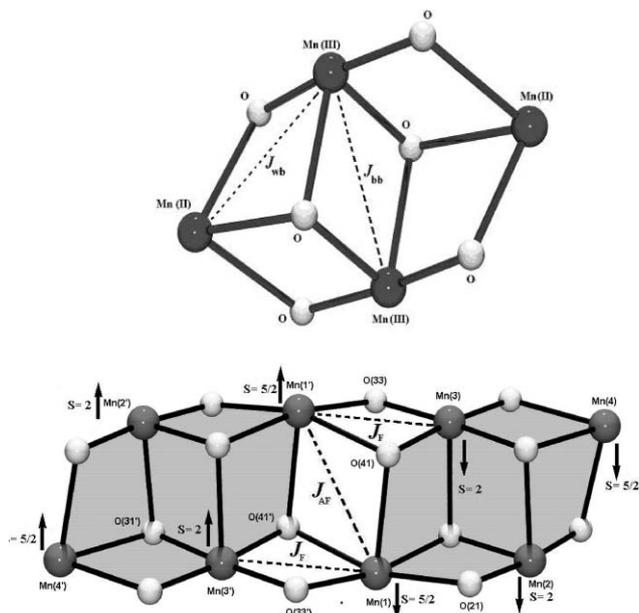
Fig. 5 The $[Mn^{III}_2Mn^{II}_2(\mu_3\text{-}OR)_2(\mu_2\text{-}OR)_4]^{4+}$ core common to complexes **2–9** and the two exchange pathways used to fit the experimental $\chi_M T$ vs. T data (top). A speculative interaction scheme for complex **1**; J_{AF} and J_F represent the antiferro- and ferromagnetic interactions, respectively, between the two $[Mn^{III}_2Mn^{II}_2]$ fragments of the core (highlighted in grey).

Complex **1** consists of two identical planar diamond units (Fig. 5, bottom) which are connected at the two central Mn^{II} ions (Mn1, Mn1′) via two μ_3-OR (O(41) and O(41′)) bridges. Previous experimental evidence suggests that this interaction is likely to be weak and antiferromagnetic.[14] DFT calculations on Mn^{II}–O–Mn^{II} dimers also suggest an antiferromagnetic interaction with a strong dependence of the strength of coupling as function of the Mn–O–Mn angle. Below angles of ~98° the interaction is weak and antiferromagnetic but becoming increasingly strong (and antiferromagnetic) for angles in the 98–110° range.[15] In **1** the Mn(1)–O(41)–Mn(1′) angle is 100.3(1)° and thus we might expect a reasonably '*strong*' antiferromagnetic exchange between Mn(1) and Mn(1′). If we assume that each 'isolated' $[Mn^{III}_2Mn^{II}_2]$ unit (shaded in grey in Fig. 5) remains ferromagnetically coupled then we are left with two possibilities: (a) the central Mn^{II}–Mn^{II} antiferromagnetic interaction is stronger than the ferromagnetic interaction between Mn(1) and Mn(3′) (i.e. $|J|_{Mn^{II}-Mn^{II}} > |J|_{Mn^{III}-Mn^{II}} = |J|_{AF} > |J|_{wb} = |J|_F$) resulting in an $S = 0$ ground state; or (b) the central Mn^{II}–Mn^{II} antiferromagnetic interaction is weaker than the ferromagnetic interaction between Mn(1) and Mn(3′) (i.e. $|J|_{Mn^{II}-Mn^{II}} > |J|_{Mn^{III}-Mn^{II}} = |J|_{AF} > |J|_{wb} = J_F$)) resulting in an $S = 18$ ground state. For complex **1**, and in accordance with both experimental and theoretical evidence, the former appears to be true.

Conclusions

All previously characterised Mn rod-like complexes were obtained from reactions involving the oxo-centred metal triangles $[Mn_3O(O_2CR)_6L_3]^{0/+}$. These complexes all consist of rod-like arrays of edge-sharing $[Mn_3]$ triangles. The present work shows that structurally similar complexes but with different levels of oxidation can be made from simple Mn^{II} salts. By synthesising families of related compounds and studying their magnetic properties we can build up an understanding of the correlation between structural and magnetic data which may help us design complexes with predictable and sought-after magnetic properties.

Although complex **1** possesses a $S = 0$ ground state it is clear that only a very small change in the magnitude of one J-value could have produced a cluster with a (potentially) $S = 18$ ground state. We hope that chemical/electrochemical oxidation of some of the Mn^{II} ions in **1** will allow us to isolate clusters with larger spin ground states. This work is currently in progress.

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