New octa- and dodecametallic mixed-valent Mn rods

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Abstract

The combination of $MnBr_2 \cdot 4H_2O$ with tripodal alcohols results in the formation of new octa- and dodecametallic $[Mn_4^{III}Mn_4^{II}]$ and $[Mn_6^{III}Mn_6^{II}]$ clusters. Their structures describe 'one-dimensional' rod-like arrays of six and ten edge-sharing triangles, respectively. Both complexes display $S \approx 0$ spin ground states.
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We have been investigating the reactions of tripodal alcohols such as 1,1,1-tris(hydroxymethyl)ethane (H_3thme), 1,1,1-tris(hydroxymethyl)propanane (H_3tmp) and their analogues with 3d transition metals [1]. When fully deprotonated the disposition of the three alkoxide arms of the tri-anion generally directs the formation of triangular $[M_3]$ units where each arm of the ligand bridges one edge of the triangle. In the presence of co-ligands such as carboxylates or β-diketonates, these smaller units can combine in diverse ways to produce elaborate polymetallic '1D' rods, '2D' sheets or '3D' complexes based on tetrahedra, octahedra and icosahedra *etc*. We previously reported a family of '1D' Mn rod-like complexes with nuclearities ranging from 6 to 12 [2], each of which was made from the reaction of the oxo-centred triangles $[Mn_3O(O_2CR)_6L_3]^{n+}$ (R = Me, Ph, CMe_3; L = py, *etc.*) with the appropriate tripodal alcohol in MeCN. Here, we show that structurally similar complexes – but in different oxidation levels – can be made from simple Mn(II) salts such as $MnBr_2 \cdot 4H_2O$.

The reaction between $MnBr_2 \cdot 4H_2O$, NaO_2CCMe_3, H_3tmp and NBu_4Br in MeCN results in the formation of $[Mn_8(O_2CCMe_3)_2(tmp)_2(Htmp)_4Br_4(H_2O)_2]$ (**1**) (Fig. 1) which crystallizes in the triclinic space group $P\bar{1}$. The complex consists of a planar rod-like $[Mn_4^{III}Mn_4^{II}(\mu_3\text{-}OR)_6(\mu_2\text{-}OR)_8]^{6+}$ unit with a trapped-valent core (Fig. 2) that 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' $[Mn_2^{III}Mn_2^{II}(OR)_6]^{4+}$ fragments. 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. The two fully deprotonated tmp^{3-} ligands sit directly above and below the $[Mn_8]$ plane each bonding in a $\eta^2:\eta^3:\mu_5$-fashion, directing the formation of a pentanuclear metal fragment comprising three edge-sharing $[Mn_3O]$ triangles. The four doubly deprotonated $Htmp^{2-}$ 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 and two in a $\eta^1:\eta^2:\eta^2:\mu_3$-fashion This directs the formation of a tetranuclear metal fragment describing two edge-sharing $[Mn_3O]$ triangles and a linear trinuclear metal fragment, respectively. The coordination spheres of the eight six coordinate Mn ions are completed by two $Me_3CCO_2^-$ ligands that bridge in their usual $\eta^1:\eta^1:\mu_2$-fashion, four terminal Br^- ions and two terminal H_2O molecules.

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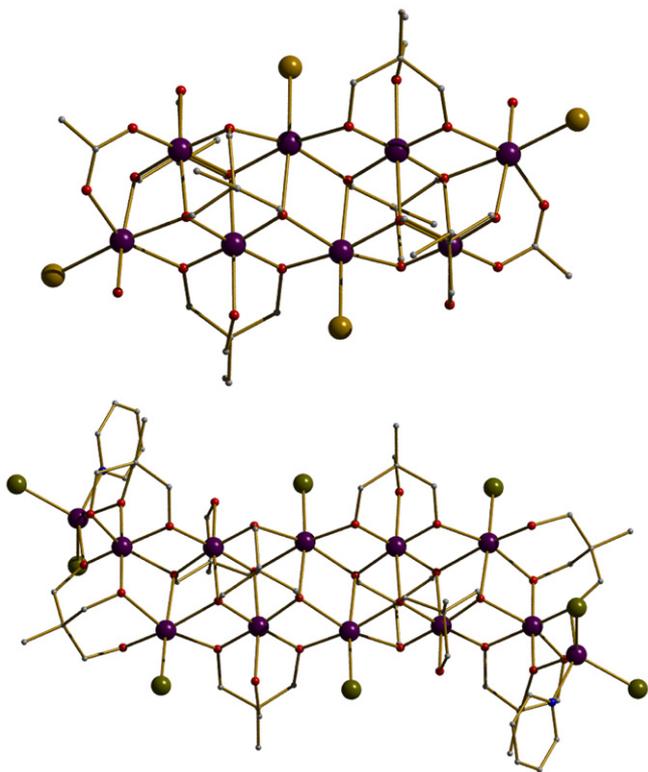*E-mail address:* ebrechin@staffmail.ed.ac.uk (E.K. Brechin).

Fig. 1. Molecular structures of complexes **1** (top) and **2** (bottom). Colour code: Mn, purple; O, red; Br, green; C, grey. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
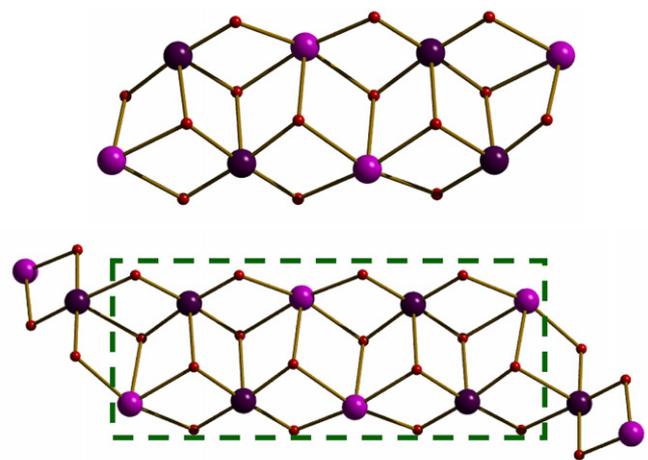

Fig. 2. The Mn–O cores of **1** (top) and **2** (bottom). Colour code: Mn(III), purple; Mn(II), pink; O, red. The $[Mn_4^{III}Mn_4^{II}(\mu_3\text{-}OR)_6(\mu_2\text{-}OR)_8]^{6+}$ unit common to both is highlighted in green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The core of complex **2** $[Mn_{12}(Hthme)_8(thme)_2(py)_2Br_8]$ is remarkably similar (Figs. 1 and 2). The molecule, made from the reaction of $MnBr_2 \cdot 4H_2O$, H_3thme and H_3tea (triethanolamine) in MeCN/py, consists of a non-planar $[Mn_6^{III}Mn_6^{II}(\mu_2\text{-}OR)_{14}(\mu_3\text{-}OR)_8]^{8+}$ unit, with a trapped-valent core that can be described as consisting of eight

edge-sharing $[Mn_3O]$ triangles, or four edge-sharing $[Mn_4O_2]$ butterfly ('planar diamond') units. The 10 central metals this describes are planar with the two outermost (pentagonal bipyramidal) Mn(II) ions above and below that plane, respectively.

The six Mn(III) display Jahn–Teller elongations, all of which are approximately co-parallel at an angle of $\sim70°$ with respect to Mn_{10} plane. The two fully deprotonated $thme^{3-}$, ligands are located directly above and below the Mn_{10} plane bridging in a $\eta^3{:}\eta^3{:}\eta^2{:}\mu_5$-fashion to five metal centres that describe three edge-sharing triangles. The other eight tripodal ligands are doubly deprotonated ($Hthme^{2-}$) and coordinate in two different ways: two in a $\eta^3{:}\eta^3{:}\eta^1{:}\mu_5$-fashion linking five metals into three edge-sharing triangles; and six in a $\eta^1{:}\eta^2{:}\eta^2{:}\mu_3$-fashion linking three metals in a near-linear array. Four of the eight bromides are coordinated terminally to the Mn(II) ions in the central Mn_{10} plane, with the remaining four bonded to the peripheral five coordinate Mn(II) ions. The coordination sphere of these ions is completed by two terminal pyridines.

The two complexes are clearly related with the $[Mn_4^{III}Mn_4^{II}(\mu_3\text{-}OR)_6(\mu_2\text{-}OR)_8]^{6+}$ unit present in **1** being replicated exactly in the central section of complex **2** (Fig. 2). The planar diamond $[Mn_2^{III}Mn_2^{II}(\mu_3\text{-}OR)_2(\mu_2\text{-}OR)_4]$ moiety seen twice in both complex **1** and complex **2** is well known and has been reported previously in the tetranuclear complexes $[Mn_2^{III}Mn_2^{II}(hmp)_6(NO_3)_2(MeCN)_2]^{2+}$ (**3**), $[Mn_2^{III}Mn_2^{II}(hmp)_6(NO_3)_4]$ (**4**), $[Mn_2^{III}Mn_2^{II}(hmp)_4\text{-}(acac)_2(MeO)_2]^{2+}$ (**5**), $[Mn_2^{III}Mn_2^{II}(O_2CMe)_2(pdmH)_6]^{2+}$ (**6**), $[Mn_2^{III}Mn_2^{II}Br_2(hmp)_6(H_2O)_2]^{2+}$ (**7**), $[Mn_2^{III}Mn_2^{II}(O_2\text{-}CMe)_2(teaH)_2(teaH_2)_2(H_2O)_2]^{2+}$ (**8**), $[Mn_2^{III}Mn_2^{II}(O_2CPh)_2\text{-}(teaH)_2(teaH_2)_2(H_2O)_2]^{2+}$ (**9**), and $[Mn_2^{III}Mn_2^{II}(O_2 CEt)_2\text{-}(teaH)_2(teaH_2)_2(H_2 O)_2]^{2+}$ (**10**) (where hmpH = 2-hydroxymethylpyridine; $pdmH_2$ = pyridine-2,6-dimethanol; $teaH_3$ = triethanolamine) [3–6]. Three 'reverse' rhomboidal clusters with $[Mn_2^{II}Mn_3^{III}(OR)_6]$ cores in which the metal ions have *swapped* places, i.e. the Mn(III) ions are the 'wing-tips' and the Mn(II) ions are the 'body-ions', have also been reported: $[Mn_2^{III}Mn_2^{II}(O_2CPh)_4(teaH)_2(acac)_2]$ (**11**); $[Mn_2^{III}Mn_2^{II}(teaH)_2(acac)_4(MeOH)_2](ClO_4)_2$ (**12**); $[Mn_2^{III}\text{-}Mn_2^{II}(bheapH)_2(acac)_4(MeOH)_2](ClO_4)_2$ (**13**) (bheapH_3 = 1-[N,N-bis(2-hydroxyethyl)amino]-2-propanol) [7]. This 'reversed' $[Mn_2^{II}Mn_2^{III}]$ distribution is also found in the hexanuclear cluster $[Mn_2^{III}Mn_4^{II}(teaH)_2(teaH_2)_2(O_2CCH\text{-}Ph_2)_8]$ (**14**) [8].

Both structures are also related to the octa- and dodecanuclear Mn rods $[Mn_8O_4(O_2CCMe)_{10}(py)_2]$ (**15**) and $[Mn_{12}O_4(OH)_2(PhCOO)_{12}(thme)_4(py)_2]$ (**16**) we previously described [2], but here the cores contain bridging O^{2-} ions, and are in different oxidation levels, consisting of a homovalent $[Mn_8^{III}(\mu_3\text{-}O)_4(\mu_3\text{-}OR)_2(\mu_2\text{-}OR)_4]^{10+}$ unit and a $[Mn_{10}^{III}Mn_2^{II}O_4(OH)_2]^{24+}$ unit, respectively.

Solid-state dc magnetic susceptibility (χ_M) measurements were performed on polycrystalline samples of **1** and **2** in a 0.1 T applied dc magnetic field in the 5.00–300 K temperature range. The results are plotted as $\chi_M T$ versus T in Fig. 3. For **1**, the room temperature $\chi_M T$ value
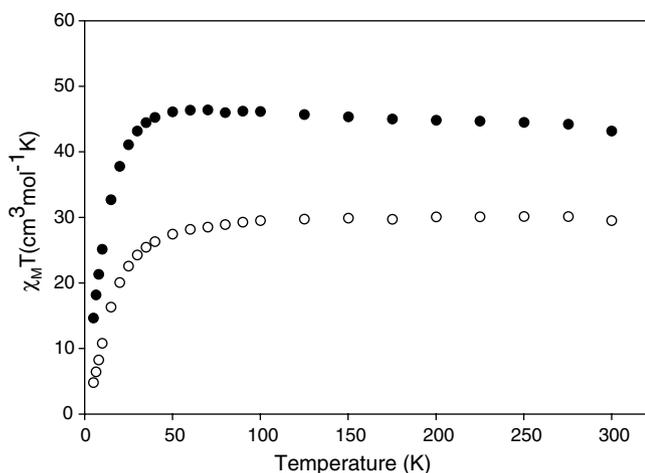
Fig. 3. Plot of $\chi_M T$ versus T for **1** (○) and **2** (●) in an applied field of 0.1 T and the temperature range 300–5 K.

of approximately 29 cm^3 K mol^{-1} (0.1 T) is slightly lower than that expected for a complex comprising four Mn(III) and four Mn(II) ions (29.5 cm^3 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 cm^3 K mol^{-1} at 5.0 K. For **2** the behaviour is rather similar: the room temperature $\chi_M T$ value of approximately 43 cm^3 K mol^{-1} (spin only = ~46 cm^3 K mol^{-1}) remains essentially unchanged until *ca.* 50 K where it drops rapidly to a value of 14.6 cm^3 K mol^{-1} at 5 K. This is indicative of dominant (weak) antiferromagnetic exchange between the metal centres with the low temperature values suggesting small spin ground states for both complexes.

In-phase ac susceptibility measurements performed in the temperature range 1.8–10 K support the above assignments: 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 values of 1 ± 1 cm^3 K mol^{-1} for both. In each case the slope of the $\chi'_M T$ versus T plot 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 molecules 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. This behaviour is consistent with other Mn(III)–Mn(II) systems [3–8].

An attempt to rationalize the $S = 0$ or $S = 1$ ground-states of **1** and **2** (although clearly very difficult) can be made on the basis of the well-known magnetic behaviour of complexes **3–13**. The planar diamond $[\text{Mn}_2^{\text{III}}\text{Mn}_4^{\text{II}}$-$(\text{OR})_6]$ unit present in complexes **3–10** in which the Mn(III) ions occupy the central body positions gives rise to ferromagnetic exchange and $S = 9$ spin ground states. The $[\text{Mn}_2^{\text{II}}\text{Mn}_2^{\text{III}}(\text{OR})_6]$ unit in **11–13** in which the Mn ions have 'swapped' positions is characterized by antiferromagnetic

exchange and results in small ($S = 0$ or 1) spin ground states. The calculated exchange interactions for all are given in Table 1. The majority of the Mn(III)–Mn(III) and Mn(III)–Mn(II) interactions appear to be ferromagnetic (with only J_{wb} in **12** and **13** antiferromagnetic) – but in all cases the interactions are very weak. Both **1** and **2** are linked at their centres by two Mn(II) ions *via* two μ_3-OR bridges. Previous experimental evidence suggests that this interaction is likely to be weak and antiferromagnetic [9–12]. 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 [13,14]. The Mn(II)–O–Mn(II) angle is 100.3(1)° in **1** and 99.9(1)° in **2** and thus we might expect a reasonably 'strong' antiferromagnetic exchange for both. If we assume that each 'isolated' $[\text{Mn}_2^{\text{III}}\text{Mn}_2^{\text{II}}]$ diamond on either side of this central Mn(II)–Mn(II) unit remains ferromagnetically coupled then we can imagine that for complex **1** the two 'halves' of the molecules are "spin-up" and "spin-down" respectively, leading to an $S = 0$ ground state. For **2** we can then simply assume that the two remaining Mn(III)–Mn(II) *dimers* (Mn–O–Mn = ~103–104°) at each end of the same $[\text{Mn}_8]$ core 'cancel each other out' either *via* a local antiferromagnetic interaction or one *ferromagnetic dimer* being "spin-up" and the other "spin-down".

All previously characterized Mn rod-like complexes were obtained from reactions involving the oxo-centred metal triangles $[\text{Mn}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3]^{0/+}$. The present work shows that structurally similar complexes but with different levels of oxidation can be made from simple Mn(II) salts like MnBr$_2 \cdot 4\text{H}_2\text{O}$. Although both complexes **1** and **2** possesses $S = 0$ or $S = 1$ ground states, the magnitude of the exchange interactions present in these types of species suggest that only a very small change in the magnitude of one J-value (e.g. that between the two central Mn(II) ions) could have a pronounced effect on the nature of the ground state. Of course it remains extremely difficult to predict the magnitude and sign of such interactions in complicated molecules, but by synthesizing families of related

Table 1
Exchange interactions calculated for complexes **3–13**

Complex	Mn$^{\text{III}}$–Mn$^{\text{II}}$, J_{wb} (cm^{-1})	Mn$^{\text{III}}$–Mn$^{\text{III}}$, J_{bb} (cm^{-1})
3	+1.0	+9.9
4	+4.2	+6.3
5	+0.78	+5.3
6	+0.4	+8.1
7	+0.9	+9.0
8	+1.7	+6.5
9	+0.4	+6.6
10	+0.22	+10.9
11	N/A	N/A
12	−0.7	+0.7
13	−0.8	+2.1

compounds and studying their magnetic properties we can build up some understanding of the correlation between structural and magnetic data which may help us design complexes with predictable, sought-after properties. We hope that chemical/electrochemical oxidation of some of the Mn(II) ions in both **1** and **2** will allow us to further this idea.

1. Supplementary material

CCDC 280380 contains the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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