Novel octanuclear and enneanuclear manganese clusters with carboxylate and pyrimidine ligands

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The syntheses, structures and initial magnetic properties of three new high nuclearity manganese clusters containing new topologies of metal ions are reported.

The synthesis of high nuclearity metal clusters with large numbers of unpaired electrons has been the focus of much attention since it was discovered that such molecules could act as nanoscale magnets.¹ In order to function as a single-molecule magnet (SMM) a molecule must have a combination of a large spin ground state (S) and large and negative magnetoanisotropy (as gauged by the zero field splitting parameter D). This combination, however, is rare and found more often in clusters of manganese than for any other metal.² The synthesis of such molecules is difficult and relies on the self-assembly of metal ions with organic bridging ligands. Thus the control of nuclearity and therefore properties of these metal clusters remains difficult.³ Nevertheless the number of reported SMMs has increased in the past few years.⁴ We herein report the synthesis, structures and initial magnetic properties of three new manganese carboxylate clusters: one octanuclear and two enneanuclear clusters which feature new topologies of metal ions and demonstrate how simple changes in geometry can alter the magnetic properties of a cluster.

Reaction of mixed-valent [Mn₄O(OAc)₄(py)] (1 equivalent) with 2,4-dimethyl-6-hydroxypyrimidine (DMHP, 1 equivalent) in MeCN affords the octanuclear species [Mn₈O₄(OAc)₄(OH)₂(OAc)₄(DMHP)₂(py)] (Fig. 1), in good yield after 2 days. I crystallises in the triclinic space group P1. The centrosymmetric core of I consists of two [Mn₂O₃] butterfly units linked by two µ-OH ligands (O3). Each butterfly contains three Mn³⁺ ions, one Mn²⁺ (Mn3) ion and two µ-O₂⁻ ions (O1, O2). The Mn ions all have distorted octahedral geometries with the Mn³⁺ ions displaying the usual Jahn–Teller elongations. The [Mn₈O₄(OH)₄]²⁺ core is non-planar and best described as Z-shaped with Mn3 and Mn3A above and below the plane described by the six Mn³⁺ ions. The AcO⁻ ligands are of two types: either bridging in the usual µ-manner between Mn ions both within and between each butterfly unit, or µ-y with one O-atom bridging two metals. The pyridine and DMHP ligands are both monodentate, bound to the two Mn²⁺ ions at the periphery of the structure. The nitrogen of the pyrimidine is protonated and H-bonded to an oxide in the [Mn₉O₃]⁷⁺ unit (O1–N82, 2.785 Å). Changing the carboxylate from AcO⁻ to PhCO⁻ produces a related enneanuclear cluster. Reaction of [Mn₈O₄(OAc)₄(py)](H₂O) (1 equivalent) with DMHP (1 equivalent) in MeCN produces a precipitate that can be crystallised from CH₂Cl₂ to give the species [Mn₈O₄(PhCO)₄]⁺ (DMHP)₂ (Fig. 1), in good yield after 2 days. Complex 2 crystallises in the monoclinic space group C2/c and contains a [Mn₉O₃]⁷⁺ core that can be described as two fused [Mn₉O₃] butterflies (Mn1, Mn2, Mn3, Mn5) sharing one Mn atom.

Fig. 1 The structure of I (top). The structure (middle) and core (bottom) of 2.

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No peaks were observed in out-of-phase ac susceptibility studies for complexes 1–4 in the 1.8–10 K and 10–70 K range. This observation is consistent with the non-alignment of Jahn–Teller axes in the two structural types and the resultant small magnetic anisotropy present in 1–4. Low temperature single-crystal studies to discover whether 1 acts as a SMM are currently underway.

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Notes and references
† Satisfactory elemental analyses (C, H, N) were obtained for all compounds.

For 1: Mn$_2$C$_9$H$_{13}$NO$_{12}$. Calc. (%) C, 33.41; H, 3.87; N, 3.39. Found: C, 33.37; H, 3.92; N, 3.64.

For 2: Mn$_2$C$_9$H$_{13}$NO$_{12}$. Calc. (%) C, 50.93; H, 3.34; N, 2.31. Found: C, 51.00; H, 3.23; N, 2.55.

For 3: H$_2$O·Mn$_2$C$_9$H$_{13}$NO$_{12}$. Calc. (%) C, 50.78; H, 3.28; N, 1.09. Found: C, 50.8; H, 3.40; N, 1.09.

For 4: Mn$_2$C$_9$H$_{13}$NO$_{12}$. Calc. (%) C, 51.54; H, 3.29; N, 1.17. Found: C, 51.50; H, 3.56; N, 1.40.

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Solid state dc magnetisation measurements have been performed on complexes 1–4 in the temperature range 1.8–300 K in a field of 5 kG. For 1, the $\chi_M T$ value of 18.1 cm$^3$ K mol$^{-1}$ at 300 K decreases slowly to approximately 12 cm$^3$ K mol$^{-1}$ at 50 K before falling rapidly to approximately 6 cm$^3$ K mol$^{-1}$ at 1.8 K. This is indicative of antiferromagnetic exchange between the metal centres. In order to determine the ground state spin, magnetisation data were collected in the ranges 1.8–10 K and 10–70 K. The data saturate at a value consistent with a S = 4 or 5 ground state but no satisfactory fit could be obtained. This is very likely due to the existence of weakly coupled Mn$^{2+}$ ions and thus the presence of low lying excited states. Complexes 2–4 have similar cores but their magnetic behaviour is different. Complex 3 has been studied in detail and reported previously. The value of $\chi_M T$ for 3 declines from a room temperature value of approximately 10.5 cm$^3$ K mol$^{-1}$ to 8.5 cm$^3$ K mol$^{-1}$ at 1.8 K. This is indicative of antiferromagnetic exchange between the Mn$^{3+}$ ions with a non-zero ground state. Reduced magnetisation data for 3 taken at 2–4 K in fields of 0.5–20.0 kG were least squares fit to give a $S = 4$ ground state with $g = 1.94$ and $D = -0.25$ cm$^{-1}$. Data were also collected in the 30–50 K and 2–4 K range but when included resulted in a poorer fit than obtained with the lower field data alone, suggesting the presence of low lying excited states. For 2 and 4 the room temperature $\chi_M T$ value of approximately 20 cm$^3$ K mol$^{-1}$ remains constant to 150 K, before declining steadily to a value of 3 cm$^3$ K mol$^{-1}$ at 1.8 K. Reduced magnetisation data taken in the range 1.8–10 K and 10–70 K G, saturate at a value consistent with a $S = 2$ ground state, although no satisfactory fit was obtained. Again this is most likely due to the existence of low lying excited states. Clearly this behaviour is not the same as that observed for 3, and must arise from the change in geometry at the basal [Mn$_2$O$_3$] unit.


