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 nano-scale 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 $[Mn_3O(OAc)_6(py)_3]$ (1 equivalent) with 2,4-dimethyl-6-hydroxypyrimidine (DMHP, 1 equivalent) in MeCN affords the octanuclear species $[Mn_6^{III}Mn_2^{II}O_4(OH)_2(OAc)_{12}(DMHP)_2(py)_2]$ **1** (Fig. 1), in good yield after 2 days. **1**†‡ crystallises in the triclinic space group $P\bar{1}$. The centrosymmetric core of **1** consists of two $[Mn_4O_2]^{7+}$ butterfly units linked by two μ-OH ligands (O3). Each butterfly contains three Mn^{3+} ions, one Mn^{2+} (Mn3) ion and two μ_3-O^{2-} ions (O1, O2). The Mn ions all have distorted octahedral geometries with the Mn^{3+} ions displaying the usual Jahn–Teller elongations. The $[Mn_8O_4(OH)_2]^{12+}$ core is non-planar and best described as Z-shaped with Mn3 and Mn3A above and below the plane described by the six Mn^{3+} 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_3- with one O-atom bridging two metals. The pyridine and DMHP ligands are both monodentate, bound to the two Mn^{2+} ions at the periphery of the structure. The nitrogen of the pyrimidine is protonated and H-bonded to an oxide in the $[Mn_4O_2]^{7+}$ unit (O1–N82, 2.785 Å). Changing the carboxylate from AcO⁻ to $PhCO_2^-$ produces a related enneanuclear cluster. Reaction of $[Mn_3O(O_2CPh)_6(py)_2(H_2O)]$ (1 equivalent) with DMHP (1 equivalent) in MeCN produces a precipitate that can be crystallised from CH_2Cl_2 to give the species $[Mn_9^{III}O_7(PhCO_2)_{13}(DMHP)_2]$ **2**, in good yield after 2 days. Complex **2**†‡ (Fig. 1) crystallises in the monoclinic space group $C2/c$ and contains a $[Mn_9O_7]^{13+}$ core that can be described as two fused $[Mn_4O_2]$ butterflies (Mn1, Mn2, Mn3, Mn5) sharing one Mn atom
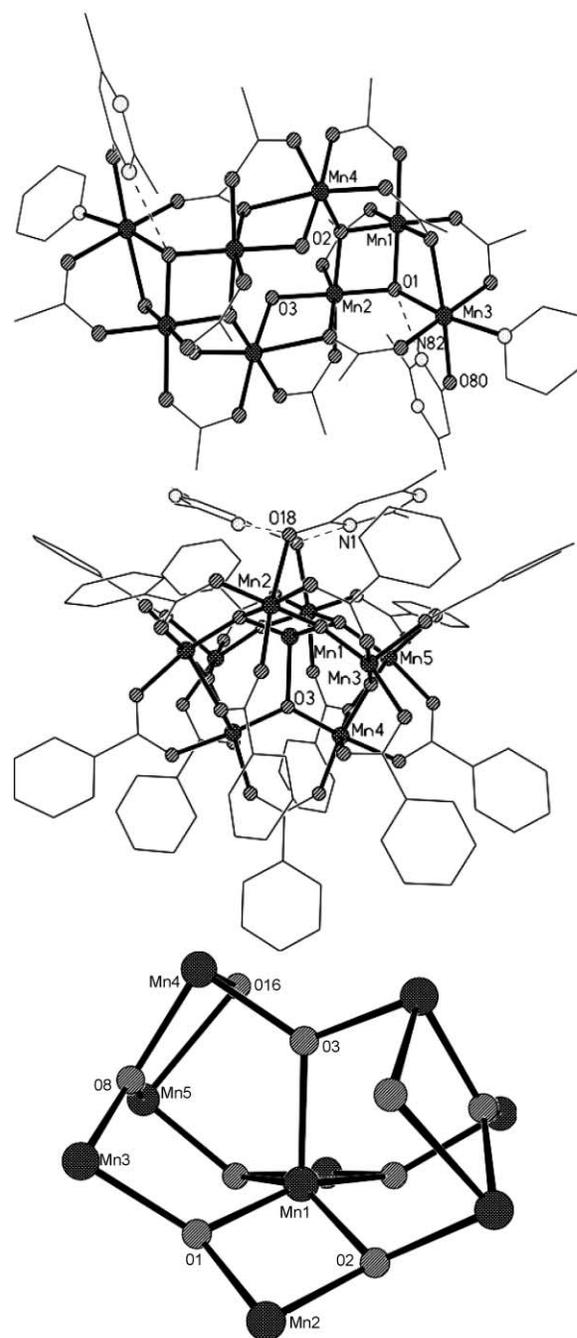
Fig. 1 The structure of **1** (top). The structure (middle) and core (bottom) of **2**.

(Mn1, which lies on a two-fold axis). The remaining two Mn ions (Mn4) are connected to the fused butterfly unit through an O^{2-} ion (O3) forming a $[Mn_3O]$ triangle with Mn1. The $[Mn_3O_4]$ base of this unit (Mn1, Mn2 and Mn2A) is non-planar with the Mn2–Mn1–Mn2A angle approximately 145°. The metal ions are all Mn^{3+} but display differing geometries. Mn1 and Mn3 are five-coordinate and square pyramidal whilst the remaining Mn ions are all in distorted octahedral geometries and display axial Jahn–Teller elongations. For Mn1 and Mn3, the axial Mn–O bond [2.141(4)–2.057(3) Å] is longer than the basal Mn–O bonds [1.862(3)–1.974(3) Å]. Again the carboxylate adopts two binding modes: eleven $PhCO_2^-$ ligands adopt their normal μ-bridging mode and two the rarer μ₃-mode, with one oxygen bridging two metals. The two DMHP ligands are terminally bound to Mn2 and are protonated, hydrogen-bonding to each other (N1–O18, 2.785 Å).

Compounds with similar cores to **2** have been reported containing Na ions, $[Mn_9Na_2(PhCO_2)_{15}(MeCN)_2]$ **3**, and terminal pyridines.[5,6] The terminal pyrimidines in **2** can in fact be replaced with other terminal ligands. For example, addition of an excess of 2-hydroxy-6-methylpyridine (Hmhp) gives the compound $[Mn_9^{III}O_7(PhCO_2)_{13}(Hmhp)_2]$ **4**. Complex **4**†‡ crystallises in the triclinic space group $P\bar{1}$ and is analogous to **2** with Hmhp ligands replacing the pyrimidines. There are two main structural differences between **3**, and **2** and **4**. One is the replacement of the $[Na_2(PhCO_2)_2(MeCN)_2]$ fragment in **3** with either DMHP or Hmhp ligands. This changes the $[Mn_3O_4]$ basal angle from 140° in **3** to approximately 145° in **2** and **4**. The second difference is the bridging modes of the $PhCO_2^-$ groups. Of the thirteen $PhCO_2^-$ groups in **2** and **4**, eleven are μ and two are μ₃; of the fifteen $PhCO_2^-$ groups in **3**, nine are μ and six are μ₃. For each compound, oxidation states were assigned using a combination of charge balance, bond lengths and BVS calculations.

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 cm³ K mol⁻¹ at 300 K decreases slowly to approximately 12 cm³ K mol⁻¹ at 50 K before falling rapidly to approximately 6 cm³ 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 kG. 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.[5] The value of $\chi_M T$ for **3** declines from a room temperature value of approximately 10.5 cm³ K mol⁻¹ to 8.5 cm³ 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 kG 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 cm³ K mol⁻¹ remains constant to 150 K, before declining steadily to a value of 3 cm³ K mol⁻¹ at 1.8 K. Reduced magnetisation data taken in the range 1.8–10 K and 10–70 kG, saturate at a value consistent with a $S = 2$ ground state, although no satisfactory fit was obtained. 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 $[Mn_3O_4]$ unit.

No peaks were observed in out-of-phase ac susceptibility studies for complexes **1**–**4** in the 1.8–10 K and 10–70 kG 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.

Notes and references

† Satisfactory elemental analyses (C, H, N) were obtained for all compounds.
    For **1**: $Mn_8C_{46}H_{64}N_6O_{32}$. Calc. (%) C, 33.41; H, 3.87; N, 3.39. Found: C, 33.37; H, 3.92; N, 3.64.
    For **2**: $Mn_9C_{103}H_{81}N_4O_{35}$. Calc. (%) C, 50.93; H, 3.34; N, 2.31. Found: C, 51.0; H, 3.25; N, 2.55.
    For **3·1.5H₂O**: $Mn_9C_{109}H_{84}N_2O_{38.5}$. Calc. (%) C, 50.78, H, 3.28; N, 1.09. Found: C, 50.8; H, 3.40; N, 1.09.
    For **4**: $Mn_9C_{103}H_{79}N_2O_{35}$. Calc. (%) C, 51.54; H, 3.29; N, 1.17. Found: C, 51.50; H, 3.56; N, 1.40.
‡ Crystal data for **1**: $C_{52}H_{76}Cl_{12}Mn_8N_6O_{32}$, $M = 2162.10$, triclinic, $P\bar{1}$, $a = 10.3843(8)$, $b = 15.5276(12)$, $c = 15.7421(12)$ Å, $\alpha = 61.988(2)$, $\beta = 71.912(2)$, $\gamma = 79.640(2)°$, $U = 2128.4(3)$ Å³, $Z = 1$, $D_c = 1.687$ g cm⁻³, $\mu = 1.602$ mm⁻¹ (SRS station 9.8, $\lambda = 0.6881$ Å), $T = 150(2)$ K, 17147 measured, 8620 unique data ($R_{int} = 0.0428$), of which 6430 $I > 2\sigma(I)$. R [$I > 2\sigma(I)$] = 0.0757, $wR2$ (on F^2, all data) = 0.2363 with 512 refined parameters, Goodness-of-fit = 1.065.
    For **2**: $C_{52.50}H_{41.50}Cl_2Mn_{4.50}N_2O_{17.50}$, $M = 1298.51$, monoclinic, $C2/c$, $a = 17.691(5)$, $b = 24.076(6)$, $c = 25.499(7)$ Å, $\beta = 93.060(6)°$, $U = 10845(5)$ Å³, $Z = 8$, $D_c = 1.591$ g cm⁻³, $\mu = 1.194$ mm⁻¹ (Mo-Kα, $\lambda = 0.71073$ Å), $T = 150$ K, 33870 reflections measured, 12691 unique data ($R_{int} = 0.1521$), of which 4639 have $I > 2\sigma(I)$. R [$I > 2\sigma(I)$] = 0.0557, $wR2$ (on F^2, all data) = 0.1082 with 703 refined parameters, Goodness-of-fit = 0.654.
    For **4**: $C_{113}H_{101}Cl_4Mn_9N_2O_{37}$, $M = 2715.22$, triclinic, $P\bar{1}$, $a = 16.999(5)$, $b = 17.190(5)$, $c = 20.444(6)$ Å, $\alpha = 82.629(7)$, $\beta = 78.476(6)$, $\gamma = 79.163(6)°$, $U = 5723(3)$ Å³, $Z = 2$, $D_c = 1.576$ g cm⁻³, $\mu = 1.136$ mm⁻¹ (Mo-Kα, $\lambda = 0.71073$ Å), $T = 100(2)$ K, 29874 reflections measured, 19870 unique data ($R_{int} = 0.1382$), of which 6641 have $I > 2\sigma(I)$. R [$I > 2\sigma(I)$] = 0.0806, $wR2$ (on F^2, all data) = 0.1782, Goodness-of-fit = 0.763. Programs: standard Bruker AXS control and integration software and SHELXTL. CCDC reference numbers 199944–199946. See http://www.rsc.org/suppdata/dt/b2/b212347a/ for crystallographic data in CIF or other electronic format.

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