Dodecanuclear and octanuclear manganese rods

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The reaction of the neutral triangle \([\text{Mn}_3\text{O}(\text{O}_2\text{O}_2\text{CR})_3\text{O}(\text{O})_3]^{2+}\) with 1,1,1-tris(hydroxymethyl)ethane (H\text{thme}) affords novel dodecanuclear and octanuclear manganese complexes with unusual ladder-like cores built from edge-sharing triangles.

The synthesis of polynuclear transition metal clusters has recently been driven by the discovery that molecules with large numbers of unpaired electrons can function as nanoscale magnets.\(^1\) The first single-molecule magnet (SMM) \([\text{Mn}_3\text{O}(\text{acac})_6\text{py}](\text{H}_2\text{O})]^{2+}\) was discovered in 1993 and since then the vast majority of SMMs reported have contained either manganese or iron.\(^2\) Each of these SMMs has been synthesised using an appropriate metal and coordinatively flexible organic ligands such as carboxylates, \(\beta\)-diketonates and alkoxides. The tripodal ligand 1,1,1-tris(hydroxymethyl)ethane (H\text{thme}) has been used extensively in the synthesis of oxovanadium and o xo molybdenum clusters\(^3\) but has been sparingly used with other metals.\(^4\) Following our initially encouraging results using this ligand with manganese and iron,\(^5,6\) we herein report the synthesis, structure and initial magnetic properties of new dodecanuclear and octanuclear manganese rods based on a series of edge-sharing Mn\text{thme} units.

The reaction of the triangular Mn\text{thme} complex \([\text{Mn}(\text{PhCO}_2\text{})(\text{spiv})(\text{thme})_2\text{py}][\text{H}_2\text{O}])\) with 1 equivalent of H\text{thme} in MeCN gives the mixed-valent complex \([\text{Mn}_{12}\text{O}_4\text{OH}_{2}\text{PhCO}_2\text{thme}_3\text{py}][\text{H}_2\text{O}])\). In this case the core consists of ten edge-sharing \([\text{Mn}_3\text{O}]\) triangles or butterfly units. All twelve Mn ions are in distorted octahedral geometries with the ten Mn\text{thme} ions displaying the expected Jahn-Teller elongations. The four thme\text{thme} ligands are fully deprotonated, sitting directly above and below the \([\text{Mn}_3\text{O}_2\text{OH}]^{2+}\) plane, and are of two types: two use two of their arms in a \(\mu_2\)-fashion with the third arm acting as a \(\mu_3\)-bridge; the reverse situation applies for the other two thme\text{thme} ligands which have two \(\mu_2\)-arms and one \(\mu_3\)-arm. The PhCO\text{thme} ligands bridge in their usual \(\mu_3\)-manner with the remaining coordination sites occupied by two pyridines. The four \(\text{O}_2\text{Ph}\) (O1, O18, O22, O34) and two \(\text{OH}^{−}\) ions (O19, O23) ligands are \(\mu_2\)-bridging respectively.

Solid-state dc magnetization measurements were performed on 1 in the range 5–300 K in a field of 5.0 kG. The \(\chi_T\) value of approximately 30 cm\(^3\) K mol\(^−1\) at 300 K remains constant as the temperature is decreased until ca. 150 K when it begins to decrease to a value of ca. 23 cm\(^3\) K mol\(^−1\) at 8 K, suggesting that the molecule has a high spin ground state. In order to determine the ground state spin, magnetization data were collected in the ranges 1.8–10 K and 10.0–4.0 T. The data were fit giving \(S = 7\), \(g = 1.98\) and \(D = −0.13\) K. When fields up to 7 T were employed the best fit gave \(S = 10\), \(g = 1.78\) and \(D = −0.30\) K, but this was of poorer quality than the low field data. This behaviour is characteristic of low-lying excited states with \(S\) values greater than the ground state of \(S = 7\). Low-lying excited states are a common problem when Mn\text{thme} ions are present since they exhibit weak exchange coupling. The use of only low-field data in the fits can avoid this problem and provide more reliable results.
For complex 2, the $\chi_M T$ value at 300 K of approximately 24 cm$^3$ K mol$^{-1}$ drops slowly as the temperature is decreased until ca. 20 K where it then increases to a value of ca. 18 cm$^3$ K mol$^{-1}$ at 8 K. Again this suggests that the molecule has a high spin ground state. Magnetization data (Fig. 2) collected in the ranges 1.8–10 K and 0.10–4.0 T gave a best fit of $S = 6$, $g = 1.81$ and $D = -0.36$ K. The large spin ground states for both complexes presumably arise from the triangular [Mn$_3$] building blocks in each cluster and thus the presence of a number of competing exchange interactions.

Ac magnetization measurements were performed on 1 and 2 in the 1.8–10 K range in a 3.5 G ac field oscillating at 50–1000 Hz. For both complexes frequency dependent ac signals are seen below approximately 3 K but no peaks are observed.

Quantum tunnelling of magnetization (QTM) studies were performed on 1 by magnetization measurements on single crystals using an array of micro-SQUIDs. Relaxation data were collected in the 1.8–20 K where it then increases to a value of $D = 0.16$ K indicative of QTM. Single crystal studies of 2 are currently under way and will be reported at a later date.

In summary compounds 1 and 2 represent new structural types in manganese carboxylate chemistry and 1 is an important new addition to the small family of SMMs. It also suggests that the use of triangular building blocks is an excellent way to make large metal clusters with non-zero spin ground states.

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Notes and references

1 Complex 1 analysed satisfactorily (C, H, N) as 1-McCN-Et$_2$O. Complex 2 analysed satisfactorily (C, H, N) as 2-McCN-Et$_2$O. Crystals were kept in contact with mother liquor to avoid solvent loss and were crystallographically identified as E=2.25Et$_2$O and 2-McCN-H$_2$O.  

Crystal data for 1: $a = 18.4232(10)$, $b = 28.2896(15)$, $c = 26.5871(14)$ Å, $\alpha = 90$, $\beta = 90.085(2)$, $\gamma = 90$, $V = 13861.2(13)$ Å$^3$, $Z = 4$, $T = 150(2)$ K, $\mu = 1.132$ mm$^{-1}$. Synchrotron radiation (CLRC Daresbury Laboratory, Station 9.8 $\lambda = 0.6687$ Å). 10618 reflections collected, 19860 unique, (Rint = 0.0492) $2\theta_{max} = 44.83^\circ$, R1 = 0.0372 [3320 data with $I > 2(\sigma(I))]$, wR2 = 0.2086 for 1815 parameters. Crystal data for 2: $a = 12.552(2)$, $b = 25.289(3)$ Å, $\alpha = 90$, $\beta = 108.264(4)$, $\gamma = 90$, $V = 5203(12)$ Å$^3$, $Z = 2122.42$, Z = 2, $T = 150(2)$ K, $\mu = 1.012$ mm$^{-1}$. Synchrotron radiation (CLRC Daresbury Laboratory, Station 9.8 $\lambda = 0.6685$ Å), 7735 reflections collected, 5119 unique, (Rint = 0.0359) $2\theta_{max} = 40^\circ$, R1 = 0.0572 [3639 data with $I > 2(\sigma(I))]$, wR2 = 0.1574 for 533 parameters. Data collection, structure solution and refinement used programs SMART, SAINT and SHELXL. See http://www.rsc.org/suppdata/cc/b3/b302057f/ for crystallographic data in cif or other electronic format.


