New routes to manganese higher-nuclearity topologies: synthesis of the cluster [Mn$_8$(μ$_4$-O)$_4$(phpz)$_8$(thf)$_4$]

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Reaction of Mn(ClO$_4$)$_2$·6H$_2$O with 3(5)-methyl-5(3)-(2-hydroxyphenyl)pyrazole (H$_2$phpz) affords a highly asymmetric octanuclear manganese(III) cluster resulting from the different bridging coordination modes of the ligand H$_2$phpz.

The search for high-nuclearity manganese clusters is presently driven by their potential to act as single-molecule magnets (SMM).[1–4] While manganese carboxylate chemistry has been largely developed affording various nuclearities and metal oxidation levels,[5–10] the chemistry and the magnetic properties of pyrazolato-bridged manganese compounds have been less explored.[11,12] Recently, we have shown that 3(5)-methyl-5(3)-(2-hydroxyphenyl)pyrazole (H$_2$phpz) is capable of binding to iron(III) in a didentate chelating coordination mode (Scheme 1, I) and the availability of the acidic N–H group for hydrogen bonding interactions allows new structural features.[13] Herein, we report that H$_2$phpz is capable of losing H$^+$ from both the OH and NH groups, providing new coordination modes (Scheme 1, II and III) and an original route to high-nuclearity manganese cluster compounds.
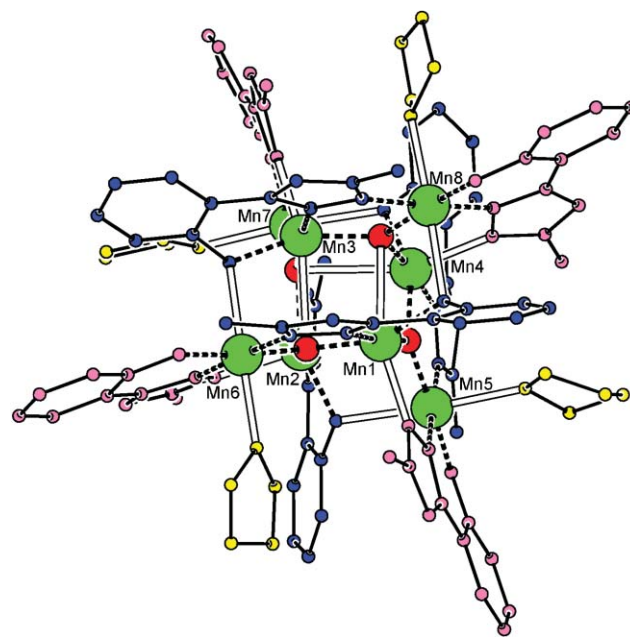
The reaction of Mn(ClO$_4$)$_2$·6H$_2$O (0.14 mmol) with H$_2$phpz (0.28 mmol) in tetrahydrofuran (thf) in the presence of triethylamine (0.56 mmol) followed by the diffusion of pentane affords a dark brown crystalline product, **1**, in 86% yield.[14] Crystals were obtained by diffusion of diethyl ether into a dichloromethane solution of **1**. Studies of the cluster formation reaction have shown that the compound is formed in 70–86% yield, irrespective of the nature of the used manganese salt.

A single crystal X-ray analysis of **1** revealed the identity of the product as [Mn$_8$(μ$_4$-O)$_4$(phpz)$_8$(thf)$_4$] (Fig. 1).[15] The complex has local, non crystallographic S$_4$ symmetry. The oxo anions (O1, O2, O3 and O4) and four of the manganese(III) ions (Mn1, Mn2, Mn3 and Mn4) are arranged in a rectangular antiprism which forms the core of the complex (Fig. 2). The sides of this antiprism are trapezoids; the top and the bottom plane are rectangles, the long

axes of which are rotated 90° with respect to each other. The four remaining manganese(III) ions are attached to the μ$_4$-oxo anions; the Mn–(μ$_4$-O)–Mn angles span a wide range: 86.88–124.19°. Such topology has been encountered only rarely in cluster coordination chemistry, involving Fe,[16] Cr,[17] and Co,[18] respectively; their metal ions and the μ$_4$-oxo anions are arranged as in **1**, but simple pyrazolato (for Fe) or carboxylato (for Cr and Co) ions are bridging between a peripheral and a central metal ion. All metals in **1** are octahedrally coordinated and their oxidation state has been assigned based on the presence of Jahn–Teller (JT) axial elongation, as expected for Mn(III), and from charge balance considerations. Thus, the Mn–O bond distances are divided into two groups, axially elongated and equatorial, as are the Mn–N bonds (see caption to Fig. 1). The JT elongation is different for the central metal ions than for the peripheral metal ions. The Mn(III) ions in the antiprism show four equatorial Mn–O bonds of *ca.* 1.9 Å, one axial Mn–N bond of *ca.* 2.1 Å and one axial Mn–O bond of *ca.* 2.7 Å. The peripheral Mn(III) ions show more

Fig. 1 Pluton projection of [Mn$_8$(μ$_4$-O)$_4$(phpz)$_8$(thf)$_4$], emphasizing the JT axes of the Mn(III) atoms. Hydrogen atoms were omitted for clarity. Green, Mn; Red, O; Pink, side ligands (II); Blue, top ligands (III); Yellow, thf molecules. Interatomic distances ranges [Å]: Mn–O(eq), 1.840(2)–1.9305(19); Mn–O(ax), 2.2998(19)–2.7221(19); Mn–N(eq), 1.959(3)–1.9739(2), Mn–N(ax), 2.024(2)–2.185(2).
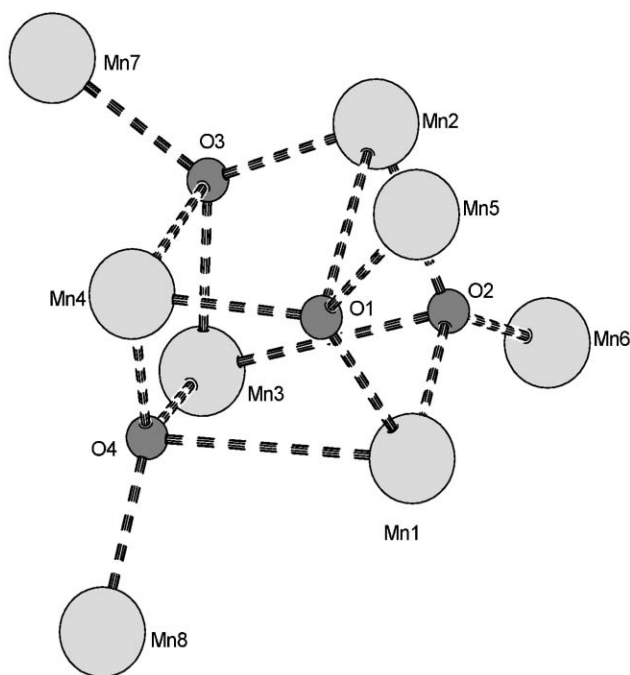

Scheme 1 The coordination modes of Hphpz$^-$ (I) and phpz^{2-} (II and III).

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Fig. 2 Pluton projection of the $Mn_8(\mu_4\text{-}O)_4$ in **1**.

Fig. 3 Plot of χ_mT vs. T for **1** in the range 1.8 to 300 K in 1 T field.

symmetric JT axes (Mn–O *ca.* 2.3 Å) and more variety in the equatorial distances (Mn–N,O *ca.* 1.8–2.1 Å). Four phpz^{2-} ligands coordinate to the Mn(III) in the binding mode II; they are arranged along the sides of the antiprism, linking the metal ion pairs {Mn1, Mn5}, {Mn2, Mn6}, {Mn3, Mn7} and {Mn4, Mn8} *via* N–N pyrazolato-bridges. The phenolate oxygen is also bound to peripheral metal ions already coordinated by a nitrogen of the same ligand (Mn5, Mn6, Mn7 and Mn8, respectively). On both rectangular ends of the antiprism two ligands are coordinated along both short sides, in the binding mode III. These ligands also link a peripheral and a cubane metal ion through pyrazolato bridges (Mn1 with Mn6, Mn2 with Mn7, Mn3 with Mn8, Mn4 with Mn5, with average Mn⋯Mn separation of 3.365 Å). In contrast to the "side-ligands", the phenolate-oxygens of these "top-ligands" form bridges between the pairs of metal ions {Mn1, Mn8}, {Mn2, Mn5}, {Mn3, Mn6} and {Mn4, Mn7}. As a result, the "top-ligands" are more deviated from planarity (angles between five- and six-membered ligand rings are in the range 16.68(17)–24.44(15)°) than the "side-ligands" (angles in the range 6.56(16)–13.88(15)°). The remaining coordination sites of the four peripheral metal ions Mn5 to Mn8 are occupied by thf molecules, three of which show conformational disorder. First-neighbour Mn⋯Mn separations are in the range 3.3195(8)–3.3387(8) Å. The coordination of the phpz^{2-} ligands in the outer part of the cluster provides a hydrophobic surface, which is responsible for the high solubility of **1** in non-polar solvents.

The magnetic susceptibility of compound **1** was examined under 1 T field in the 2–300 K temperature range. The χ_mT value per cluster at 300 K is 18.44 cm^3 K mol^{-1}, corresponding to the spin-only value (24 cm^3 K mol^{-1}) expected for eight non-interacting Mn(III) ions. Upon cooling, the χ_mT product gradually decreases to 0.54 cm^3 K mol^{-1} at 2 K (Fig. 3). These features indicate that the cluster molecule possesses an overall intramolecular antiferro-magnetic interaction. Owing to the size and the low symmetry of
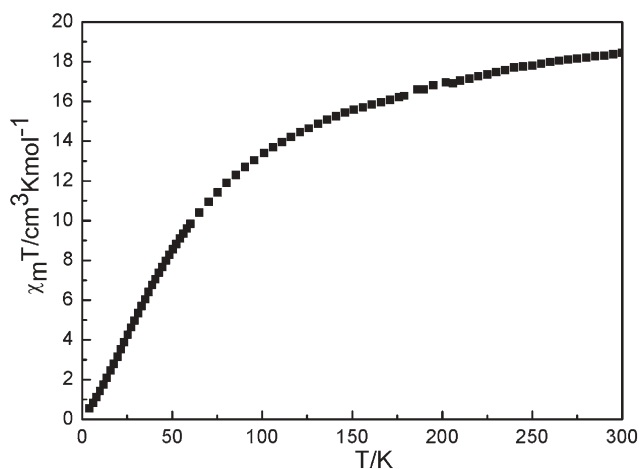
the molecule, it is not possible to apply the Kambe vector-coupling method and to evaluate the exchange parameters between the individual Mn(III) ions. However, the measured value of χ_mT at 2 K (0.54 cm^3 K mol^{-1}) is consistent with a small ground state spin value, probably $S = 0$, with very low-lying excited states that are even populated at 2 K.

In conclusion, we have shown that the versatile H$_2$phpz ligand has provided access to a new octanuclear manganese cluster with topology not seen in manganese carboxylate chemistry. Various reactions of **1** are currently being explored, including those with monodentate ligands and mononuclear Mn(III) species to replace the labile thf molecules from the complex and identify synthetically attainable higher-nuclearity topologies and their properties.

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14 Elemental analysis for **1**: $C_{96}H_{96}Mn_8N_{16}O_{16}$. Calc. (%) C, 53.15; H, 4.46; N, 10.33. Found: C, 52.81; H, 4.80; N, 10.63.
15 Crystal data for **1**: $C_{96}H_{96}Mn_8N_{16}O_{16} \cdot 2C_4H_8O$, 2313.63 g mol^{-1}, triclinic, P-1 (No. 2), $a = 16.078(2)$, $b = 16.328(2)$, $c = 19.889(3)$ Å, $\alpha = 81.583(12)$, $\beta = 82.687(10)$, $\gamma = 77.143(10)°$, $Z = 2$, $V = 5011.2(12)$ Å^3, $D_{calc} = 1.533$ g cm^{-3}, μ(Mo-Kα) = 1.1 mm^{-1}, $T = 150$ K, 115873 reflections, 22731 unique ($R_{int} = 0.100$). The structure was solved by automated direct methods using SHELXS-97 and was refined on F^2 by least-squares procedures using SHELXS-97. Two of the coordinated thf molecules are described with a two-site disorder model. The disordered atoms are refined with isotropic displacement parameters. The unit cell contains two uncoordinated disordered thf molecules. Their contribution to the structure factors was ascertained using the PLATON/SQUEEZE procedure. The total volume of disordered uncoordinated solvent in the unit cell is 636 Å^3 and contains 123 e. No coordinates are available for these solvent molecules. The contributions of the squeezed solvent to D_{calc}, μ, $F(000)$, Mr and formulae are included in the values reported here. The final residuals are $R_1 = 0.047$ [15199 $F_{obs} > 4\sigma(F_{obs})$] and $wR_2 = 0.117$ (all data). CCDC 267864. See http://www.rsc.org/suppdata/cc/b5/b504215a/ for crystallographic data in CIF or other electronic format.
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