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Synthesis and studies of a tetradecanuclear manganese(II)/(III) cage

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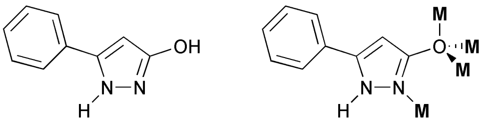
A novel Mn_{14} cluster is reported; this is a new nuclearity for manganese cages and highly unusual in that the ligands are not exclusively oxygen donors.

Much of the current interest in the magnetism of polymetallic cage complexes is based on observations originally made on manganese cages. The first 'single molecule magnet'[1] (SMM) discovered was a $\{Mn_{12}\}$ cage, and this metal features in the majority of SMMs known to this date.[2] Given the excitement of this chemistry the range of ligands reported to stabilise Mn cages is surprisingly small, and dominated by oxygen donor ligands such as carboxylates or β-diketonates.[3,4] A rare exception is a $\{Mn_8\}$ cage featuring amino-pyrimidine ligands.[5] Here we report studies of a new manganese cage which has an unusual nuclearity and structure, and which features a new bridging ligand.

The ligand used is the anion of 3-phenyl-3-pyrazolin-5-one (Hppo, see Scheme 1). Hppo is itself straightforwardly made from reaction of ethyl benzoylacetate (22 g, 0.114 mmol) with 62% hydrazine hydrate solution (9 mL, 0.114 mmol) in refluxing ethanol (100 mL). The yield of Hppo is 67%, and no further purification steps are necessary.† Deprotonation of Hppo (320 mg, 2 mmol) with NBu_4OH (2 mL of a 1 M methanolic solution, 2 mmol) in the presence of hydrated $Mn(NO_3)_2$ (500 mg, 2 mmol) in MeCN (40 mL) led to a brown solution that produced crystals of the title compound in *ca*. 25% yield upon diffusion of Et_2O into the reaction mixture. These crystals were suited for X-ray diffraction experiments using a synchrotron source.



Scheme 1 Hppo (left) and ppo in its 4.31 coordination mode (right).

The unit cell contains two independent $\{Mn_{14}\}$ cages, with almost identical structures.‡ Each is centro-symmetric, with the formula $[Mn_{14}O_2(OH)_4(ppo)_{18}(Hppo)_4(NO_3)_4(MeCN)_4]$ **1** (Fig. 1). The molecule is mixed-valent, containing two Mn(III) and twelve Mn(II) centres. A possible description of the core (Fig. 2) is based on $\{Mn_7\}$ fragments, two of which are found in the asymmetric unit. Each fragment contains a $\{Mn_3O_4\}$ distorted incomplete cubane, lacking one Mn site (Fig. 2). Two of the O-centres within this unit are hydroxide [O(2), O(3)], and each of these is bound to one further Mn(II) site [Mn(7) and Mn(5), respectively]. A single O-atom of the $\{Mn_3O_4\}$ is part of a ppo ligand [O(31)], and it also bridges to one further Mn(II) [Mn(4)]. The last O-atom [O(1)] is an oxide, and this is capped by two Mn(III) sites [Mn(1) and Mn(1a)]. These two Mn(III) sites form the shared edge of a bitetrahedron and serve to link the two $\{Mn_3O_4\}$ distorted cubanes. Hexanuclear Mn bitetrahedra have been reported previously.[6]

The coordination geometries of the Mn sites vary. Mn(1) is clearly a Mn(III) site, with a Jahn–Teller elongated octahedral geometry and an O_5N coordination sphere. Five of the six

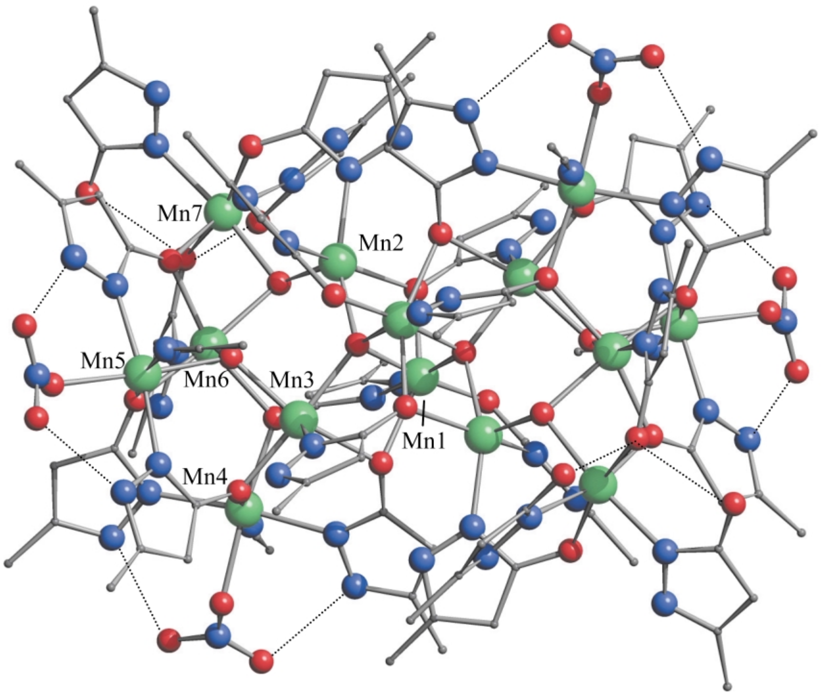


Fig. 1 SCHAKAL representation of **1** showing the intramolecular hydrogen bondings. Only the *ipso* carbon atoms of the phenyl rings are shown. Colours: C, grey; N, blue; O, red; Mn, green.

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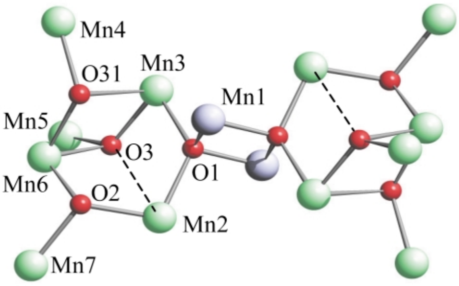

Fig. 2 SCHAKAL representation of the core of **1**, showing Mn^{III} in purple and Mn^{II} in green. The dashed line is a guide to the eye.

Mn(II) sites are six coordinate, with O_5N, O_4N_2, and O_3N_3 donor sets. The final site is five coordinate, bound to three O- and two N-donors. The bond lengths and geometries are consistent with the oxidation states required for charge balance.

In each of the fragments there are nine ppo and two Hppo ligands. The former, which have been deprotonated at the hydroxy group, show three distinct bridging modes which differ in the number of Mn-centres bound to the oxygen (Scheme 1). One ppo ligand shows the 4.31 mode (Harris notation);[10] five show the 3.21 and three the 2.11 mode. The two Hppo ligands are bound *via* an N-atom, and form a H-bond through their protonated O-atom to an O-atom of a deprotonated ppo ligand. What differentiates the two independent molecules in the lattice is that in one (Fig. 1), both N-atoms of the Hppo groups are hydrogen bonded to the same oxygen atom, whereas in the other they H-bond to oxygen atoms from different ligands.

There are two terminal nitrate ions per asymmetric unit. Each shows an unusual orientation as the Mn–O bond is approximately 34° to the plane of the nitrate, rather than in plane as is conventional. This is caused by the H-bonds between the uncoordinated O-atoms of the nitrate and the protonated N-atoms of the two ppo ligands bound to the same metal as the NO_3^-. The two MeCN ligands per asymmetric unit are attached to the Mn centres to which the nitrate ions are also attached. Repeated microanalysis determinations show that these ligands are substituted completely by H_2O molecules upon air exposure to form the corresponding tetrahydrate $[Mn_{14}O_2(OH)_4(ppo)_{18}(Hppo)_4(NO_3)_4(H_2O)_4]$ **1a**.§

The presence of two $\{Mn_{14}\}$ cages within the unit cell may be due to the efficient packing of the cages. The phenyl-rings of the ppo ligands provide a hydrophobic periphery for each cage. However it is noticeable that in some cases Ph groups from one ring inter-digitate with Ph groups from the second cage. The shortest contacts between phenyl ring centroids are *ca.* 4.0 Å.

Bulk, variable temperature magnetic susceptibility data were collected from a polycrystalline sample of **1a** under a constant magnetic field of 100 G.¶ The value of $\chi_m T$ (cm^3 K mol^{-1}) per $[Mn_{14}]$ decreases from 52.2 at 300 K to 4.6 at 1.8 K. The value at room temperature is slightly smaller than the expected for an uncoupled $[Mn^{III}{}_2Mn^{II}{}_{12}]$ system with $g = 2$ (58.5) and the drop with decreasing temperature reflects the presence of strong antiferromagnetic interactions within the cluster, presumably leading to a spin ground state of $S_T = 0$.

No previous coordination chemistry has been reported for ppo, and little for related ligands. For 3-methyl-3-pyrazolin-5-one we have reported a $\{Ni_{24}\}$ cage.[11] Tetradecanuclear cages are rare — not only for Mn but for any 3d-metal. Several polyoxovanadate cages are known,[12] and copper sulfide[13] and phosphide clusters.[14] **1** is therefore only the second $\{M_{14}\}$ cage containing N- or O-donor ligands, after the beautiful $\{Fe_{14}\}$ cage reported by Klüfers.[15] This family of ligands therefore look immensely promising candidates for the generation of new cages.

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Notes and references

† Anal. Calcd (Found) for $C_9H_8N_2O$: C, 67.47 (67.17); H, 5.04 (5.01); N, 17.50 (17.57)%. ^1H NMR (CD_3OD): δ (ppm) = 7.32 (t, 1H, $C_{arom}H$), 7.40 (t, 2H, $C_{arom}H$), 7.61 (d, 2H, $C_{arom}H$). CI, m/z = 161 $[M + H]^+$.

‡ Crystal data for $C_{206}H_{174}N_{52}Mn_{14}O_{40}\cdot Et_2O\cdot 3.5MeCN$, **1**$\cdot Et_2O\cdot 3.5MeCN$: triclinic, $P1$, a = 20.9499(18), b = 22.6189(19), c = 27.567(2) Å, α = 74.856(2), β = 77.870(2), γ = 69.345(2)°, V = 11697.7(17) Å^3, M = 5004.9, Z = 2, T = 123(2) K, $R1$ = 0.0625. Data collection, structure solution and refinement used programs SMART,[7] SAINT[7] and SHELXL.[8] Figures were produced using SCHAKAL.[9] Full details have been deposited and will be published later. CCDC reference number 186867. See http://www.rsc.org/suppdata/cc/b2/b205157p/ for crystallographic data in CIF or other electronic format.

§ Anal. Calcd (Found) for **1a**$\cdot H_2O$: C, 50.46 (50.43); H, 3.68 (3.53); N, 14.27 (14.27)%.

¶ Variable temperature magnetic measurements on **1** in the region 1.8–325 K were made using a SQUID magnetometer (Quantum Design) with samples sealed in gelatine capsules in a 100 G field. The data have been adjusted for the diamagnetism of the sample using Pascal's constants.

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