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Deltahedra as underlying structural motifs in polynuclear metal chemistry: structure of an undecanuclear manganese–potassium cage

Mark Murrie, Simon Parsons and Richard E. P. Winpenny*

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ

The synthesis and crystal structure of a heterometallic undecanuclear complex $[Mn_9K_2(O)_7(O_2CCMe_3)_{15}(HO_2CCMe_3)_2]$ has been determined; the cluster has a metal core related to an icosahedron.

Early crystal structures of gold clusters were rationalised[1] by recognising that the metal sites lay on the vertices of a centred icosahedron before the centred Au_{13} cluster itself was made and characterised.[2] By contrast it is difficult to demonstrate any underlying principle to rationalise the diversity of structures found for polynuclear metal cages. Some such compounds resemble fragments of minerals, others can be related to polyhedra. The diversity of ligands and metals used probably explains this lack of a single unifying structural feature, however recognition of trends in structures is still important to predict future directions for research.

Recently we reported two structural types which appeared to be related.[3,4] A series of nickel and cobalt cages were made with carboxylate and pyridonate ligands which contain polyhedra based on centred tricapped trigonal prisms.[3] When we increased the steric demands of the carboxylate ligand a new structure was observed for a nickel cage, where the ten metal sites occupied vertices of an incomplete fourteen-vertex tetraicosahedron.[4] Both these polyhedra involve fully-triangulated metal faces. Here we report a structure of a manganese complex, which can also be related to a fully-triangulated polyhedron but now with twelve vertices, rather than nine or fourteen.

This manganese cage can be made *via* the synthesis of a hexanuclear mixed-valent compound, $[Mn_6(O)_2(O_2CCMe_3)_{10}(C_4H_8O)_4]$ **1**. Cluster **1** was prepared by reaction of $MnCl_2\cdot 4H_2O$ (7.75 mmol) with excess $Na(O_2CCMe_3)$ (16.3 mmol) in MeOH (70 cm^3) for 24 h. The solution was evaporated to dryness, the product dried *in vacuo* and crystallised from THF giving $\mathbf{1}\cdot C_4H_8O$ as brown blocks in 57% yield (48 h).† X-Ray structural studies ‡ show an edge-sharing bitetrahedral cage bridged by two μ_4-oxides and a mixture of six 1,3- and four 1,1,3-bridging pivalate ligands (Fig. 1). Four THF ligands bind to the wing-tip sites of the metal polyhedron. The structure is closely related to two other Mn_6 cages.[5]

Cluster **1** was dried *in vacuo* prior to further reaction. Cluster **1** (0.28 mmol) was dissolved in CH_2Cl_2 (40 cm^3) and treated with $KMnO_4$ (0.28 mmol) in MeCN (25 cm^3). After stirring for 1 h the solution was filtered and stored at 273 K for 24 h. The heterometallic undecanuclear complex $[Mn_9K_2(O)_7(O_2CCMe_3)_{15}(HO_2CCMe_3)_2]$ **2** forms in 20% yield (24 h),† and X-ray analysis ‡ reveals a $[Mn_9K_2O_7]$ core ligated by fifteen trimethylacetate groups and two molecules of trimethylacetic acid (Fig. 2).

The Mn_9 core is very similar to that observed in $[Mn_9(O)_7(O_2CPh)_{13}(py)_2]$[6] **3** and $[Na_2Mn_9(O)_7(O_2CPh)_{15}(MeCN)_2]$ **4**.[7] The complex crystallises with a two-fold axis passing through Mn(5) and O(1), revealing five distinct co-ordination environments for Mn. Two 'butterfly' $[Mn_4O_2]$ units sharing the central five-co-ordinate manganese atom, Mn(5), comprise the base of the Mn_9 core which is in turn capped by Mn(1) and Mn(1A) through three μ_3-oxides. Examination of each Mn environment leads to the conclusion that all Mn atoms are in the +III oxidation state, as in each case the geometry is distorted in a manner typical for a d^4 metal. For four of the crystallographically unique sites there are four 'short' Mn–O bonds and two 'long', while for Mn(3) there are four short bonds and one long. Nine of the O_2CCMe_3 ligands are bonded in the 1,3-bridging mode whilst the remaining six are bonded in the rarer 1,1,3-bridging mode with one O atom bridging two metals. The two K^+ ions appear six-co-ordinate and are linked to the Mn_9 core *via* both oxide and O_2CCMe_3 bridges. The two monodentate molecules of HO_2CCMe_3, hydrogen bonded to μ_3-O_2CCMe_3 ligands, complete the co-ordination sphere at each K^+ ion.

The metal array does not describe a complete polyhedron. A Mn atom [Mn(5)] lies at the centre of the polyhedron, with six further Mn atoms [Mn(2), Mn(3), Mn(4) and symmetry equivalents] in a boat configuration about this central atom. The two potassiums sit below the plane of the boat, creating exclusively triangular faces, while the final two Mn atoms [Mn(1) and

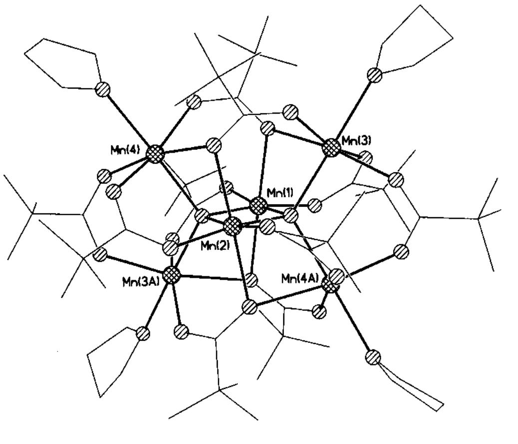

Fig. 1 Structure of cluster **1** in the crystal. Selected bond lengths: Mn(1)–O(1) 1.896, Mn(1)–O(1D) 1.957, Mn(1)–O(1A) 2.247, Mn(2)–O(1) 1.893, Mn(2)–O(1E) 1.953, Mn(2)–O(1B) 2.243, Mn(3)–O(1) 2.166, Mn(3)–O(1C) 2.127, Mn(3)–O(2B) 2.132, Mn(3)–O(2D) 2.145, Mn(3)–O(11) 2.290, Mn(3)–O(1A) 2.348, Mn(4)–O(1′) 2.177, Mn(4)–O(2A) 2.117, Mn(4)–O(2C) 2.117, Mn(4)–O(2E) 2.144, Mn(4)–O(12) 2.305, Mn(4)–O(1B) 2.340 Å [average estimated standard deviation (e.s.d.) 0.003 Å]

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† Complex **1**. Found: C, 47.2; H, 7.7. Calc. for $C_{66}H_{122}Mn_6O_{26}$: C, 47.7; H, 7.4%. Complex **2**. Found: C, 39.4; H, 6.1. Calc. for $C_{85}H_{155}K_2Mn_9O_{41}\cdot 3CH_2Cl_2$: C, 39.7; H, 6.1%.

‡ Crystal data for $C_{66}H_{122}Mn_6O_{26}\cdot C_4H_8O$ **1**: orthorhombic, *Pbcn*, $a = 14.092(2)$, $b = 22.920(3)$, $c = 27.383(4)$ Å, $U = 8844(2)$ Å^3, $M = 1733.4$, $Z = 4$ (the molecule lies on a two-fold axis), μ(Mo-Kα) = 0.899 mm^{-1}, $T = 220.0(2)$ K; refinement used 517 parameters and gave $R1 = 0.0595$ for 5020 data with $F_o > 4\sigma(F)$, $wR2 = 0.1364$ for 7725 unique data ($2\theta \leq 45°$) and 90 restraints. Crystal data for $C_{85}H_{155}K_2Mn_9O_{41}$ **2**: trigonal, $P3_221$, $a = 25.392(5)$, $c = 16.080(3)$ Å, $U = 8978(3)$ Å^3, $M = 2405.8$, $Z = 3$ (the molecule lies on a two-fold axis), μ(Cu-Kα) = 8.701 mm^{-1}, $T = 150.0(2)$ K; refinement used 321 parameters and gave $R1 = 0.0988$ for 3073 data with $F_o > 4\sigma(F)$, $wR2 = 0.2558$ for 6020 unique data ($2\theta \leq 100°$) and 954 restraints. CCDC reference number 186/935. See http://www.rsc.org/suppdata/dt/1998/1423/ for crystallographic files in .cif format.

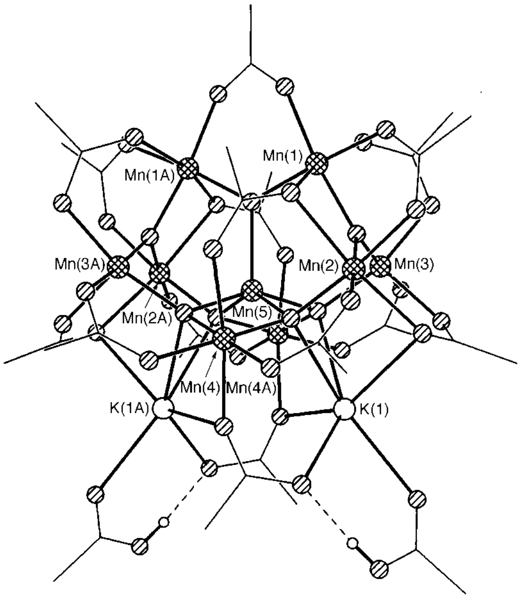

Fig. 2 Structure of cluster **2** in the crystal, with the methyl groups of the trimethylacetate omitted for clarity. Selected bond length ranges: Mn–O ('short') 1.840 to 2.015, Mn–O ('long') 2.075 to 2.295, K–O 2.666 to 3.135 Å (average e.s.d. 0.012 Å)

Mn(1A)] sit above the plane creating two triangular and two pentagonal faces. Addition of further vertices above the centres of these pentagonal faces reveals a centred twelve-vertex icosahedron [Fig. 3(b)]. The Mn···Mn distance between vertices varies from 3.26 to 3.36 Å, while the Mn···K distances are between 3.72 and 3.89 Å and the K···K contact is 4.36 Å. The distortions from a regular icosahedron are therefore due to the larger size of the potassium centres.

This metal polyhedron represents an intermediate between the tricapped trigonal prism [Fig. 3(a)], which we have found for both nickel and cobalt,[3] and the incomplete tetraicosahedron found for a decanuclear nickel cage [Fig. 3(c)].[4] It is worth noting that all these polyhedra are fully-triangulated in a manner reminiscent of boron clusters, however the triangular faces here are caused by the proclivity of oxygen donors to be μ_3-bridging rather than any vertex···vertex bonding. This family of cages where the metal sites occupy some or all of the vertices of deltahedra may prove extensive and is a contrast to cages where the metal sites can be related to mineral archetypes. We could therefore imagine cages falling into genera, one genus containing species where the cages are related to minerals, another where they are related to polyhedra. The structures of both **3** and **4** can also be related to a centred icosahedron, missing four and two vertices respectively.

Preliminary magnetic studies of **2** (field = 1 kG = 10^{-1} T) indicate an antiferromagnetic interaction between the $\mathrm{Mn^{III}}$ centres. At 300 K the value for $\chi_M T$ of 26.7 $\mathrm{cm^3\ K\ mol^{-1}}$ is consistent with nine non-interacting $S = 2$ centres (27 $\mathrm{cm^3\ K\ mol^{-1}}$ assuming $g = 2$). The value of $\chi_M T$ decreases gradually to 12.6 $\mathrm{cm^3\ K\ mol^{-1}}$ at 50 K. Below *ca.* 50 K $\chi_M T$ decreases more rapidly with decreasing temperature to a value of 3.27 $\mathrm{cm^3\ K\ mol^{-1}}$ at 1.8 K consistent with a low-spin ground state of no more than $S = 2$. This contrasts with magnetisation studies on $[\mathrm{Na_2Mn_9(O)_7(O_2CPh)_{15}(MeCN)_2}]$[7] which suggest an $S = 4$ ground state, however these previous studies indicated the presence of low-lying excited states and it is conceivable that minor changes in structure have led to the lowest energy spin state also changing.

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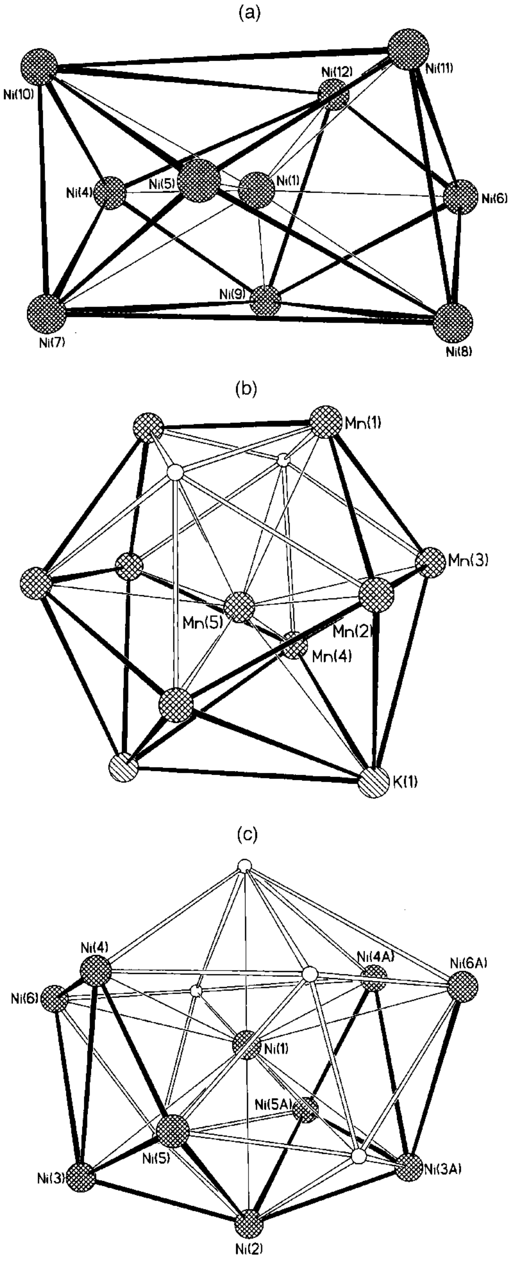

Fig. 3 Metal polyhedra in: (a) a nickel tricapped trigonal prism,[3] (b) complex **2** and (c) a decanuclear nickel complex related to a fourteen-vertex tetraicosahedron.[4] In both (b) and (c) the vacant vertices are shown as open circles

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