DALTON COMMUNICATION

Overcrowding leads to prism reform: new polyhedra for polymetallic cages

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The synthesis and crystal structure of new deca- and octanuclear cages featuring the ligands 6-methyl-2-pyridonate and trimethylacetate (O_2CCMe_3) have been determined; the structures involve polyhedra based on a tetraicosahedron and a cube respectively.

The lability of metal–ligand bonds makes the synthesis of high nuclearity metal cages by stepwise procedures difficult, therefore different strategies are required. Recently we have been successful in making a large number of cobalt(II) and nickel(II) compounds containing seven or more metals,[1] however controlling the aggregation of such species remains difficult. Several of these complexes feature metal polyhedra based on tricapped-trigonal prisms stabilised by carboxylate and pyridonate ligands.[2] Examination of these structures suggested that increasing the steric requirements of the bridging ligands may cause new polyhedra to form. Here we report initial investigations of this concept.

A decanuclear nickel complex† can be synthesised by reaction of hydrated nickel chloride (4.2 mmol) with 2 equivalents of both Na(mhp) (mhp = 6-methyl-2-pyridonate) and Na(O_2-$CCMe_3$) in MeOH (30 cm^3) for 24 h, followed by evaporation to dryness and crystallization of the resulting green paste from MeCN. X-Ray structural analysis‡ of the green crystals, which form in 45% yield in 3 d, reveals a compound of stoichiometry $[Ni_{10}(OH)_4(mhp)_{10}(O_2CCMe_3)_6(MeOH)_2]$ **1** (Fig. 1). The complex crystallises with a two-fold axis passing through Ni(1) and Ni(2) and is held together by four μ_3-OH ligands, six 1,3-bridging carboxylates and ten pyridonate ligands which adopt four different co-ordination modes: chelating; chelating plus μ-bridging through the O atom; chelating plus μ_3-bridging through the O atom; binding to one metal through the ring nitrogen and bridging two further Ni sites through the oxygen donor.

The metal array does not describe a complete polyhedron, however addition of further vertices using molecular graphics reveals a centred fourteen-vertex tetraicosahedron (Fig. 2). The five missing vertices form an equatorial fissure, as if the deltahedron had been cut through the centre with the two sides falling apart slightly. Given the absence of so many vertices the overall geometry is surprisingly regular with Ni(1) at the centre, Ni(3), Ni(3A), Ni(5) and Ni(5A) occupying four of the vertices of one hexagon and Ni(4), Ni(4A), Ni(6) and Ni(6A) four of

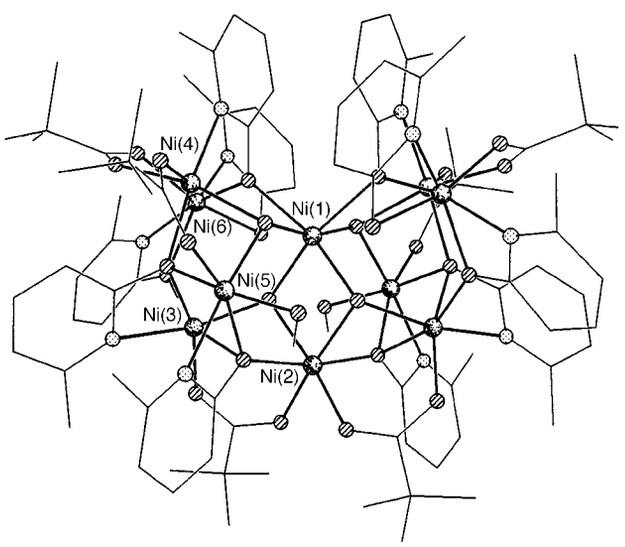

Fig. 1 The structure of complex **1** in the crystal. Selected bond length ranges: Ni–O (OH) 1.997 to 2.062, Ni–O (mhp) 2.005 to 2.268, Ni–O (O_2CCMe_3) 1.998 to 2.019, Ni–O (MeOH) 2.055, Ni–N (mhp) 2.044 to 2.139 Å [average estimated standard deviation (e.s.d.) 0.005 Å]

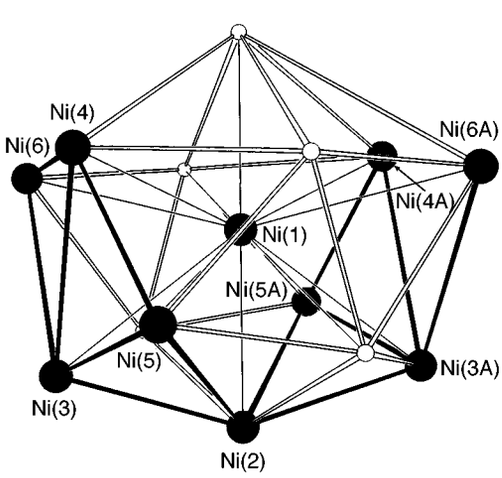

Fig. 2 The metal polyhedron in complexes **1** and **2**, related to a fourteen-vertex tetraicosahedron. The vacant vertices are shown as open circles

† Satisfactory elemental analysis were found for all compounds.

‡ Crystal data for $C_{92}H_{126}N_{10}Ni_{10}O_{28}\cdot 0.58CH_4O$ **1**: rhombohedral, $R\bar{3}c$, $a = 52.372(10)$, $c = 21.805(6)$ Å, $U = 51\,795(20)$ $Å^3$, $M = 2425.8$, $Z = 18$ (the molecule lies on a two-fold axis), $T = 220.0(2)$ K, μ(Cu-Kα) = 2.309 mm^{-1}, $R1 = 0.0684$ for 4818 observed reflections. Crystal data for $C_{90}H_{122}N_{11}Ni_{10}O_{28}\cdot 1.85C_2H_3N\cdot 0.65H_2O$ **2**: monoclinic, $P2_1/n$, $a = 17.005(3)$, $b = 27.670(6)$, $c = 26.474(6)$ Å, $\beta = 96.75(2)°$, $U = 12\,370(5)$ $Å^3$, $M = 2466.7$, $Z = 4$, $T = 220.0(2)$ K, μ(Cu-Kα) = 2.162 mm^{-1}, $R = 0.0814$ for 9895 observed reflections. Crystal data for $C_{66}H_{102}Cl_2N_6Na_2Ni_6O_{24}\cdot 4C_4H_8O$ **3**: orthorhombic, *Cmca*, $a = 26.549(5)$, $b = 21.046(2)$, $c = 18.314(2)$ Å, $U = 10\,233(2)$ $Å^3$, $M = 2121.1$, $Z = 4$, $T = 220.0(2)$ K, μ(Cu-Kα) = 2.358 mm^{-1}, $R1 = 0.0898$ for 2616 observed reflections. Data collection, structure solution and refinement were performed as detailed in ref. 1 using programs SHELXS 86,[3] DIRDIF 96[4] and SHELXL 93.[5] Full details have been deposited and will be published later. CCDC reference number 186/694.

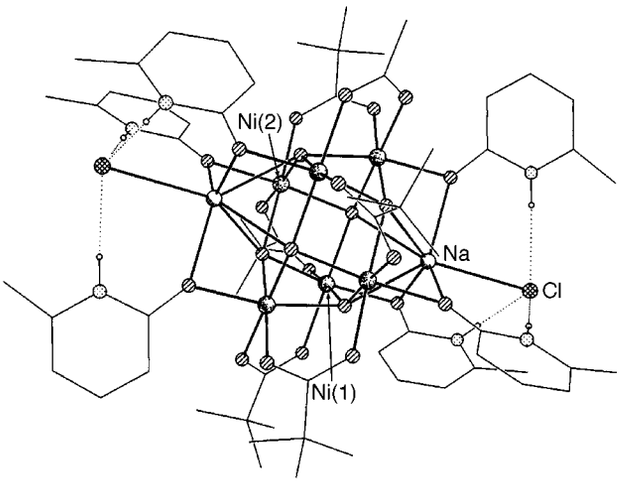

Fig. 3 The structure of complex **3** in the crystal. Selected bond length ranges: Ni–O (OH) 2.054 to 2.099, Ni–O (Hmhp) 2.102 to 2.104, Ni–O (O_2CCMe_3) 2.027 to 2.033, Na–O (OH) 2.576 to 2.632, Na–O (Hmhp) 2.341 to 2.371, Na–Cl 2.988 Å (average e.s.d. 0.005 Å)

the vertices of the second hexagon. Atom Ni(2) caps the former hexagon. Of the six crystallographically independent metal sites, two [Ni(1) and Ni(2)] lie on the two-fold axis and are bound to six O donors with moderately regular octahedral geometries. Two further [Ni(3) and Ni(5)] are found to one N- and five O-donors, with a large distortion from octahedral geometry caused by the narrow bite angle of a chelating mhp ligand. Atom Ni(6) is attached to two chelating mhp ligands, and the two N- and four O-atoms bind in a still more distorted array. Atom Ni(4) is only five-co-ordinate, with a square-based pyramidal geometry. A complex with an identical metal polyhedron and similar co-ordination sites, $[Ni_{10}(OH)_4(mhp)_{10}(O_2CCMe_3)_6(H_2O)_2]$ **2**, can be crystallised‡ from MeCN–EtO_2CMe in lower yield.

It is intriguing that similar reactions using smaller carboxylates, *e.g.* acetate or benzoate, lead to cages based on tricapped-trigonal prisms[2] whilst here the structures are based on a tetraicosahedron. Although the polyhedra have changed due to the steric requirements of the ligands, both cages are part of the family of structures with fully triangulated faces. Further examples will be required to examine whether this observation has wider applicability.

The story is complicated by the solvent dependent nature of this chemistry. If the initial paste is extracted with tetrahydrofuran an octanuclear heterometallic complex $[Ni_6Na_2(\mu_4\text{-}OH)_6(O_2CCMe_3)_6Cl_2(Hmhp)_6]$ **3** forms as green blocks‡ in 8% yield after 2 months (during which time it was necessary to filter the solution repeatedly to remove precipitated Hmhp), and contains a metal cube (Fig. 3), with the two Na sites at opposite ends of a body-diagonal. The six Ni···Ni edges of the cube are spanned by 1,3-bridging O_2CCMe_3 units, and the Ni···Na edges by μ-O-donors from Hmhp ligands. The Ni sites are each bound to six O donors with an octahedral geometry, while the unique Na site is seven-co-ordinate, bound to one Cl- and six O-atoms. The geometry about Na is best described as an elongated tetrahedron consisting of three hydroxide oxygens and the chloride, capped on the O_2Cl faces by three further O donors derived from Hmhp units.

The most unexpected feature of the structure is the six μ_4-hydroxides found at the centre of each face of the cube. The hydroxide is in each case displaced by *ca.* 0.56 Å from the plane described by the four metals bound to it, and is closer to the three Ni atoms than the one Na atom of the face. The bond angles about the O centre (*cis*-M–O–M 80.30–92.03°; *trans*-M–O–M 145.3–153.3°) are consistent with this description, and all H atoms in the structure were located from difference maps. Several examples of μ_4-hydroxide bridges have been reported for barium,[6] molybdenum[7] and alkali metals.[8] For 3d metals the two previous cases involved tetranuclear nickel or copper complexes encapsulated in macrocycles.[9,10] The pyridonate ligands are found in their protonated form, with the N-atoms of the Hmhp ligands forming a cavity in which a Cl counter ion is encapsulated through three H bonds (average Cl···N 3.18 Å).

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