ChemComm

Changing cage structures through inter-ligand repulsions

Alasdair Graham, Stephanie Meier, Simon Parsons and Richard E. P. Winpenny*

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ.
E-mail: repw01@holyrood.ed.ac.uk

Received (in Cambridge, UK) 18th January 2000, Accepted 29th March 2000
Published on the Web 25th April 2000

The synthesis and crystal structure of decanuclear Co and nonanuclear Ni cages are reported: the cages feature carboxylate and pyridonate ligands and demonstrate that inter-ligand repulsions can lead to novel structures.

Considerable progress has been made in the rational design of supramolecular systems.[1] However, there is little element of design in the synthesis of large polynuclear cages. At present the best we can do is take note of similarities between structures, with the hope that the recognition of trends will lead to targeted synthesis in the future. A family of cages exists which are based on tricapped-trigonal prisms (ttps); such cages are known for the 3d metals chromium,[2] iron,[3] cobalt[4,5] and nickel.[5] As this polyhedron seems so favoured, it appeared the ideal candidate for examining whether the core could be disrupted by using ligands which are sterically demanding thus creating unusual cages. We have reported reactions with pivalate (trimethylacetate) which lead to nickel cages based on tetraicosahedral cores,[5] and here we report further studies which indicate that ligands which are either bigger, such as triphenylacetate, or where there are Coulombic inter-ligand repulsions, such as betaine ($O_2CCH_2NMe_3$), can cause further disruption. We feel this is a general method for synthesising novel cage structures.

Reaction of hydrated cobalt chloride (2.1 mmol) with $Na(O_2CCPh_3)$ (2.1 mmol) and Na(mhp) (4.2 mmol) (mhp = 6-methyl-2-pyridonate) in MeOH (50 ml) at room temperature for one day, followed by evaporation to dryness generates a purple paste. This was then extracted with ethyl acetate (10 ml), and the resulting purple solution allowed to stand at room temperature. Over four months the solution required repeated filtration before small red blocks of $[Co_{10}(OH)_6(mhp)_6(O_2CCPh_3)_6(Hmhp)_3(HCO_3)_3]$ **1** formed in *ca.* 4% yield.† X-Ray analysis‡ reveals a centred ttp which lies on a crystallographic C_3 axis (Fig. 1), however, the capping metal atoms are found on the edges of the prism rather than the faces, as in all previous ttp based structures.

At the centre of the cage is a Co(III) site [Co(2)], with all remaining cobalt atoms present in the +2 oxidation state. Both charge balance, and bond length considerations support this view. This site lies on crystallographic three- and two-fold axes, and the metal is surrounded by six μ_3-hydroxides which each bridge to one cobalt at a vertex of the prism, and one capping the edge. The cobalt sites capping the edges of the prism [Co(3) and symmetry equivalents (s.e.)] also lie on the crystallographic two-fold axes, while the cobalt sites [Co(1) and s.e.] at the vertices of the prism are in general positions. Triphenylacetate ligands bridge in a 1,3-fashion between vertex- and edge-capping cobalts, and the mhp ligands chelate to vertex-cobalt sites with the O atom forming a μ_2-bridge to a neighbouring vertex cobalt. Thus the upper- and lower-trigonal faces of the prism are covered by pyridonate ligands, while the sides of the prism have triphenylacetate groups attached.

This latter feature creates another oddity in the structure. The triphenylacetate groups do not pack sufficiently well to cover the surface of the cage, and two coordination sites on each face of the prism are left vacant. These are occupied by disordered Hmhp and HCO_3^- groups. While the assignment of a coordinated Hmhp fragment is uncontroversial, the assignment as coordinated hydrogencarbonate was only arrived at after careful consideration of the diffraction data. This indicates the presence of a trigonal fragment, and charge balance requires a monoanion in half these sites. Nitrate was not present in the reaction at any stage therefore it appears that atmospheric CO_2 has been incorporated into the structure. The requirement for formation of hydrogencarbonate may explain the long crystallisation times and low yield of this reaction. Preliminary results indicate formation of an equivalent cage with 6-chloro-2-pyridonate (chp). While refinement of this structure is incomplete owing to severe disorder problems involving lattice solvent, it is clear that the metal atoms form a tricapped trigonal prism with the same topology as **1**.

Reaction of CO_2 is also involved in the chemistry which leads to the cage $[Ni_9(CO_3)(OH)_6(chp)_3(Hchp)_3(O_2CCH_2NMe_3)_9Cl]^{6+}$ **2**. This is formed from the reaction of hydrated nickel chloride (1 mmol), Na(chp) (1 mmol) and $O_2CCH_2NMe_3$ (1 mmol) in MeOH (20 ml) followed by evaporation to dryness, and extraction of the green powder with EtOAc. Crystallisation takes a period of three months, whereupon green plates are found in 6% yield.† X-Ray analysis‡ shows the formation of the nonanuclear cage **2**, with a complicated set of anions including four $[Ni(chp)_3]^-$, a half-weight chloride and an anion consisting of chp hydrogen-bonded to Hchp.

The structure of **2** (Fig. 2), which lies on a crystallographic threefold axis, is dominated by two features. Firstly, the central carbonate ion which is μ_6-bridging, leading to a planar hexagon of Ni centres [Ni(1), Ni(2) and s.e.]. Secondly, the preference of the tertiary ammonium groups of the nine betaine ligands to lie as far apart as possible also supports a very open structure. Three of the betaines bridge alternate Ni···Ni vectors of the

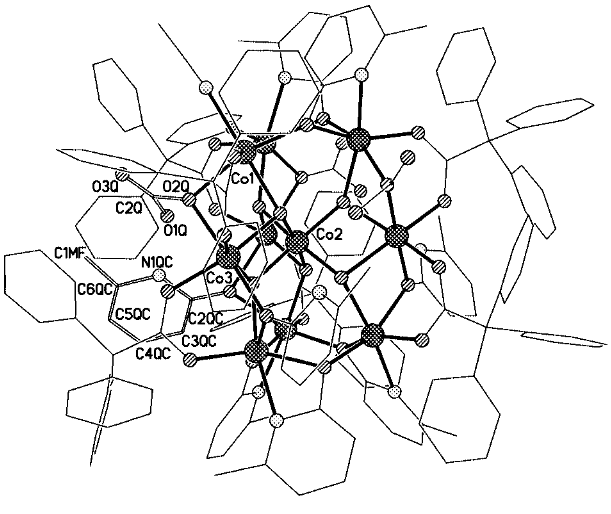

Fig. 1 The structure of **1** in the crystal, viewed perpendicular to the three-fold axis which passes through Co(2). One disordered hydrogencarbonate/Hmhp fragment is shown with open bonds. Selected bond lengths (Å): Co(1)–O(2P) 2.025, Co(1)–O(1A) 2.036, Co(1)–O(2P)′ 2.103, Co(1)–O(1V) 2.128, Co(1)–O(2Q) 2.183, Co(1)–N(1P)′ 2.220, Co(2)–O(1V) 1.898, Co(3)–O(2A) 2.050, Co(3)–O(1V) 2.102, Co(3)–O(2Q) 2.176 Å. Av. esd. 0.008 Å. (Co, cross-hatched; O, diagonal-shaded; N, speckled; C, black lines; H, not shown for clarity).

DOI: 10.1039/b000385i

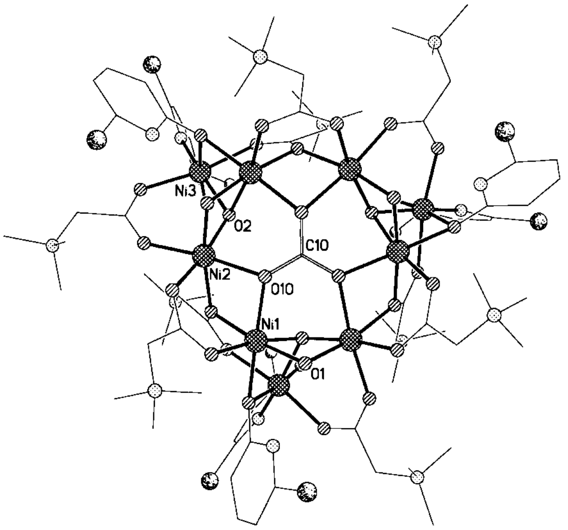

Fig. 2 The structure of hexacation **2** in the crystal, viewed down the threefold axis. The carbonate ion is shown with open bonds. Selected bond lengths: Ni(1)–O(1A) 2.010, Ni(1)–O(2)′ 2.017, Ni(1)–O(1) 2.053, Ni(1)–O(10) 2.057, Ni(1)–O(2B)′ 2.073, Ni(1)–O(21)′ 2.073, Ni(2)–O(2) 1.987, Ni(2)–O(1C) 2.005, Ni(2)–O(2A) 2.022, Ni(2)–O(10) 2.076, Ni(2)–O(1)″ 2.077, Ni(2)–O(2B)′ 2.104, Ni(3)–O(22) 2.000, Ni(3)–O(2) 2.026, Ni(3)–O(2C) 2.030, Ni(3)–O(21) 2.085, Ni(3)–O(1B) 2.097, Ni(3)–N(12) 2.232, Ni(4)–N(13) 2.072, Ni(4)–O(23) 2.118 Å. Av. esd. 0.006 Å. (Ni, cross-hatched; O, diagonal shaded; N, speckled; Cl, heavy random dots; C black lines; H, not shown for clarity).

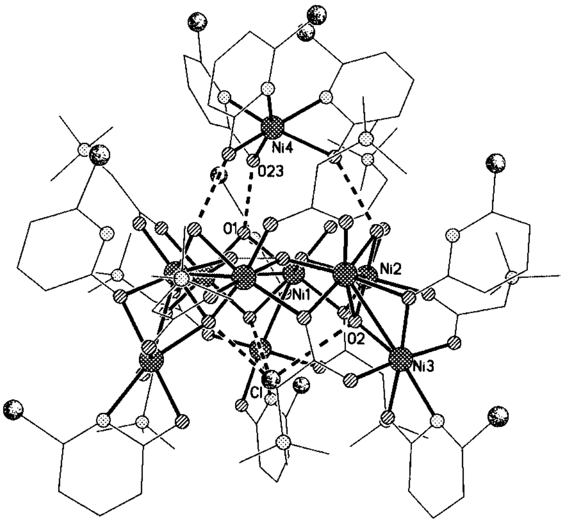

Fig. 3 The H-bonding between **2**, an $[Ni(chp)_3]^-$ unit and a chloride (shading as Fig. 2).

hexagon in a 1,3-fashion. Three further betaines attach three additional Ni atoms below the hexagon (Figs. 2 and 3), while the final three betaines bridge in a 1,1,3-manner, using one O-donor as a μ_2-bridge between Ni atoms within the hexagon, and the second O-donor to bind to one of the Ni atoms below the hexagon.

There are also six hydroxide anions in the cage. Three are μ_3-bridging [O(2) and s.e.], and are also involved in attachment of the three Ni atoms below the hexagonal plane. These three μ_3-OH groups are arranged so that the H atoms point towards the trigonal axis of the cage, and a chloride anion (Cl in Fig. 3) is attached at this point through three H-bonds (O···Cl 3.17 Å). The remaining three OH groups [O(1) and s.e.] are μ_2-bridging and lie above the hexagon, with the H atoms now involved in an interaction with a $[Ni(chp)_3]^-$ anion (Fig. 3). The three chp ligands chelate to the Ni atoms above the hexagon, while the three Hchp ligands act as μ_2-bridges through the O-donors, while forming H-bonds through the protonated N atom (O···N 2.63 Å). We have seen $[Ni(chp)_3]^-$ act as a 'tridentate' H bond acceptor in previous structures.[5]

As in **1**, one fragment, in this case carbonate, must have arisen from reaction of atmospheric CO_2 with the complicated metal–ligand 'soup' present during crystallisation. This, along with the low yields and long crystallisation times suggests that as syntheses these reactions are extremely poor. Conceptually something interesting is happening. By preventing formation of a strongly preferred structure—the ttp cage—we are inevitably going to lower yields and slow reaction times, but this process has also led to activation of small molecules, and, in the case of **2**, incorporation of a templating carbonate ligand which imposes structure on the metal array coordinated to it. This metal array in turn imposes a specific orientation on the zwitterionic betaine ligands, and probably brings them into a proximity they would rather avoid.

We thank the EPSRC for funding for a diffractometer and for a studentship (for A. G.), and the EU for an Erasmus Scholarship (for S. M.).

Notes and references

† Satisfactory elemental analysis obtained.

‡ *Crystal data*: for $C_{177}H_{156}Co_{10}N_9O_{36}\cdot 2H_2O\cdot CH_4O$, $\mathbf{1}\cdot 2H_2O\cdot CH_4O$: rhombohedral, space group $R\bar{3}c$, a = 19.054(3), c = 81.85(2) Å, V = 25737(7) Å^3, M = 3642.5, Z = 6 (the molecule lies on a threefold axis), T = 220.0(2) K, $R1$ = 0.0715.

For $C_{193.5}H_{240.5}Cl_{22.5}N_{30}Ni_{13}O_{65}$ $\mathbf{2}\cdot 4[Ni(C_5H_3ClNO)_3]\cdot 0.5Cl$. $1.5(C_5H_3ClNO\cdots C_5H_4ClNO)\cdot 8.5\ C_5H_{10}O_2$: rhombohedral, space group $R\bar{3}$, a = 30.603(2), c = 46.202(5) Å, V = 37473(5) Å^3, M = 5587.5, Z = 6 (the molecule lies on a threefold axis), T = 220.0(2) K, $R1$ = 0.0794.

Data collection, structure solution and refinement for both structures were performed as detailed in ref. 4 using programs SHELXS-97,[6] DIRDIF,[7] SHELXTL-PC[8] and PLATON.[9] Full details have been deposited and will be published later. CCDC 182/1588. See http://www.rsc.org/suppdata/cc/b0/b000385i/ for crystallographic files in .cif format.

1 R. W. Saalfrank and B. Demleitner, in *Transition Metals in Supramolecular Chemistry*, (ed. J. P. Sauvage), *Perspectives in Supramolecular Chemistry Vol. 5*, Wiley, Weinheim, 1999, p. 1; D. L. Caulder and K. N. Raymond, *J. Chem. Soc., Dalton Trans.*, 1999, 1185; P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502; M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; C. J. Jones, *Chem. Soc. Rev.*, 1998, **27**, 289.
2 A. S. Batsanov, G. A. Timko, Y. T. Struchkov, N. V. Gérbéléu and K. M. Indrichan, *Koord. Khim.*, 1991, **17**, 662.
3 S. M. Gorun, G. C. Papaefthymiou, R. B. Frankel and S. J. Lippard, *J. Am. Chem. Soc.*, 1987, **109**, 3337.
4 W. Clegg, C. D. Garner and M. H. Al-Samman, *Inorg. Chem.*, 1983, **22**, 1534.
5 C. Benelli, A. J. Blake, E. K. Brechin, S. J. Coles, A. Graham, S. G. Harris, S. Meier, A. Parkin, S. Parsons, A. M. Seddon and R. E. P. Winpenny, *Chem. Eur. J.*, 2000, **6**, 883.
6 G. M. Sheldrick, University of Göttingen, 1997.
7 P. T. Beurskens, G. Beurskens, W. P. Bosman, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel and J. M. M. Smits, DIRDIF-96 program system, University Crystallography Laboratory, University of Nijmegen, The Netherlands 1996.
8 SHELXTL-PC, Bruker AXS, Madison, WI, 1995.
9 A. L. Spek, PLATON, Utrecht University, The Netherlands, 1997.