DALTON
FULL PAPER

Structural studies of heptanuclear cobalt complexes and larger oligomers based on heptanuclear fragments

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Received 22nd June 2000, Accepted 8th August 2000
First published as an Advance Article on the web 18th September 2000

The structures of three heptanuclear cobalt cages supported by carboxylates and 6-chloro-2-pyridonate (chp) have been determined. The metal cores can be derived from a square-based pyramid, capped on one edge of the square base and on the neighbouring triangular face of the pyramid. Use of phthalate in a similar reaction results in a tridecanuclear cage which resembles a dimer of the heptanuclear cages, linked through the dicarboxylate ligands. In addition a heterometallic polymer is reported, where heptanuclear cobalt fragments are linked through sodium containing complexes to form a one-dimensional compound. Comparisons are made between these cages and previously reported structures which also involve pyridonate and carboxylate ligands. These indicate that all the cages can be derived from the structure of $Co(OH)_2$.

While the number of polynuclear transition metal complexes reported continues to grow rapidly, some nuclearities remain rare. Heptanuclear complexes are particularly uncommon, for example for cobalt there are a number of heptanuclear carbonyl[1] and sulfide-bridged[2] clusters but no examples of heptanuclear cages containing N- or O-donors. Cobalt is the most extreme example, but there are few heptanuclear cages for the other first row metals. The structures displayed by these heptanuclear cages are mostly irregular. There are a number of "metallocrowns", where six metals and their ligands encapsulate a seventh metal in a similar manner to the way a crown ether co-ordinates. The earliest example of this motif is found for titanium,[3] with more recent examples reported for copper,[4] titanium,[5] manganese,[6,7] nickel,[8] and zinc.[9] There are also a number of examples of vertex-sharing double cubanes for copper[10] and zinc,[11] and two examples from zinc chemistry where oxo-centred vertex-sharing bitetrahedra are found,[12] but the majority[13] of compounds have no easily describable core.

Here we report three heptanuclear cobalt cages and two examples where these heptanuclear fragments are linked into larger oligomers. A preliminary account of two of the structures has been published previously.[14] A further challenge in this field is to discover an underlying structural principle that will allow rationalisation of the structures observed. Here we show that a wide range of structures can be derived from the mineral $Co(OH)_2$, allowing for some distortions in the lattice.

Experimental

Preparation of compounds

All reagents, metal salts and ligands were used as obtained from Aldrich. Sodium salts of benzoic acid, phenylacetic acid, trimethylacetic acid and phthalic acid (H_2phth) and 6-chloro-2-pyridone (Hchp) were obtained by deprotonation of the ligand in MeOH using Na(OMe) followed by evaporation to dryness. Analytical data were obtained on a Perkin-Elmer 2400 Elemental Analyser by the University of Edinburgh Microanalytical Service. Mass spectra were obtained by fast atom bombardment (FAB-MS) of samples in a 3-nitrobenzyl alcohol matrix on a Kratos MS50 spectrometer.

[$Co_7(OH)_2(O_2CPh)_4(chp)_8(MeCN)$] 1. $CoCl_2$ (0.5 g, 3.9 mmol), Na(chp) (1.182 g, 7.8 mmol) and $Na(O_2CPh)$ (1.123 g, 7.8 mmol) were stirred together in MeOH (50 ml) for 24 hours. The solution was then filtered and evaporated to dryness. The resulting purple paste was dried *in vacuo* and extracted with MeCN (25 ml). The purple solution was filtered and allowed to stand, producing purple crystals of complex **1** in 52% yield after 2 days. The same result could be obtained using hydrated cobalt chloride. Found: C, 41.7; H, 2.30; N, 6.25. Calc. for $C_{71}H_{53}Cl_8Co_7N_9O_{19}$: C, 42.0; H, 2.45; N, 6.30%.

[$Co_7(OH)_2(O_2CCMe_3)_4(chp)_8(Hchp)_{0.69}(MeCN)_{0.31}$] 2. This was prepared in an analogous manner to complex **1**, using $Na(O_2CCMe_3)$ in place of $Na(O_2CPh)$. Yield: 15% after 2 days. Found: C, 38.7; H, 3.24; N, 6.49. Calc. for $C_{69.6}H_{74.0}Cl_{8.7}Co_7N_{11.8}O_{18.7}$: C, 38.8; H, 3.39; N, 6.56%.

[$Co_7(OH)_2(O_2CCMe_3)_4(chp)_8(H_2O)_{0.25}(Hchp)_{0.75}$] 3. This was prepared in an analogous manner to complex **1**, using $Na(O_2CCMe_3)$ in place of $Na(O_2CPh)$ and dry CO_2 was bubbled through the reaction for 15 minutes prior to crystallisation. Yield: 11% after 8 weeks. Found: C, 38.4; H, 3.0; N, 5.7. Calc. for $C_{65.8}H_{70.3}Cl_{8.8}Co_7N_{9.8}O_{20}$: C, 38.7; H, 3.4; N, 6.7%.

[$Co_{13}(OH)_2(phth)_2(chp)_{20}$] 4. This was prepared in an analogous manner to complex **1**, replacing $Na(O_2CPh)$ with Na_2(phth) (1.28 g, 7.9 mmol). The compound was crystallised from CH_2Cl_2. Yield of purple crystals: 15%. Found: C, 37.6; H, 1.80; N, 7.49. Calc. for $C_{119}H_{76}Cl_{26}Co_{13}N_{20}O_{30}$: C, 37.6; H, 1.89; N, 7.57%.

[{$Co_7(OH)_2(O_2CCH_2Ph)_4(mhp)_8$}{$CoNa_2(O_2CCH_2Ph)_3(mhp)(Hmhp)$}]$_n$ 5. Hydrated cobalt(II) chloride (1.00 g, 4.21 mmol), Na(mhp) (1.104 g, 8.42 mmol) and $Na(O_2CCH_2Ph)$ (1.330 g, 8.42 mmol) were added to MeOH (30 ml) and the solution stirred for 24 h before being filtered and evaporated to dryness under reduced pressure. The solid produced was dried under vacuum overnight, then extracted with MeCN (20 ml) to give a purple solution which was filtered. Purple crystals of complex **5** grew in very low yield after 14 months. Insufficient material was found for an elemental analysis to be performed.

DOI: 10.1039/b005019i

Crystallography

Crystal data and data collection and refinement parameters for compounds **1**–**5** are given in Table 1, selected bond lengths and angles in Tables 2–7.

Data collection and processing. Data were collected on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device,[15] using graphite-monochromated Cu-Kα radiation for complex **3**, and Mo-Kα radiation for all other structures; ω scans for **1** and **2**, ω–θ scans for **3** and **5**, and ω scans with on-line profile fitting[16] for **4**. Data were corrected for Lorentz and polarisation factors. Semi-empirical absorption corrections based on azimuthal measurements[17] were applied to data for **1**, **2**, **3** and **5**, and a Gaussian absorption correction to data for **4**. All crystals diffracted weakly, and so data were collected to a resolution of 1.04 (for **1** and **5**) and 0.93 Å (for **2** and **4**). Data for **3** were collected with Cu-Kα radiation for its greater intensity and scattering efficiency, although Mo-Kα would normally be preferred for cobalt compounds because of the high value of μ_m(Co).

Structure analysis and refinement. All structures were solved by direct methods using SIR 92,[18] and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement. In complex **1** only Co and Cl atoms, and in **5** only Na and Co atoms, were refined anisotropically. In **2** all non-H atoms were refined anisotropically. In **3** anisotropic refinement was restricted to all full-weight non-H atoms and the O atom of the part weight H_2O/Hchp. In **4** anisotropic refinement was restricted to all full-weight non-H atoms and the part-weight Hchp ligands. Difference Fourier syntheses were employed in positioning idealised methyl-hydrogen atoms which were assigned isotropic thermal parameters [$U(H) = 1.5\ U_{eq}(C)$]. Ring H atoms were included in idealised positions, allowed to ride on their parent C atoms [C–H 0.93 Å], and assigned isotropic thermal parameters [$U(H) = 1.2\ U_{eq}(C)$]. Chemically equivalent bonds and angles in ligands were restrained to be equal in **1**, **2**, **4** and **5**. Similarity restraints were applied to U_{ij} of **4**. In **1** a molecule of MeOH lies disordered about a crystallographic m site. In **3** three O_2CCMe_3 groups exhibit rotational disorder; in each case the components were restrained to be geometrically similar to each other and to have local 3-fold symmetry. In two cases "opposite" C atoms were constrained to have equal anisotropic displacement parameters. One co-ordination site on Co(5) is occupied by Hchp and H_2O in the ratio 75:25; the O-atom position is common to both. There are also two part-weight MeCN molecules in the lattice. In **4** a half-occupancy CH_2Cl_2 of solvation is rotationally disordered about a C–Cl vector, while in **5** there is one part-weight MeCN in the lattice, and one mhp ligand attached to Na(1) exhibits positional disorder in a 66:34 ratio. All refinements were against F^2 and used SHELXL 93[19] or SHELXL 97.[20]

CCDC reference number 186/2135.

See http://www.rsc.org/suppdata/dt/b0/b005019i/ for crystallographic files in .cif format.

Results

Heptanuclear cages

We have been exploring the reactions of cobalt and nickel salts with a range of carboxylate and pyridonate ligands.[21,22] We have found that a large family of cages exists where the core is based on centred pentacapped-trigonal prisms missing between zero and two vertices.[22] These cages can form with cobalt or nickel, normally with 6-methyl-2-pyridonate as one of the ligands present. The discrete heptanuclear cobalt complexes reported here form only from reactions of cobalt salts with 6-chloro-2-pyridonate as one of the two ligands, and we have thus far been unable to make the nickel analogues of these cobalt cages.

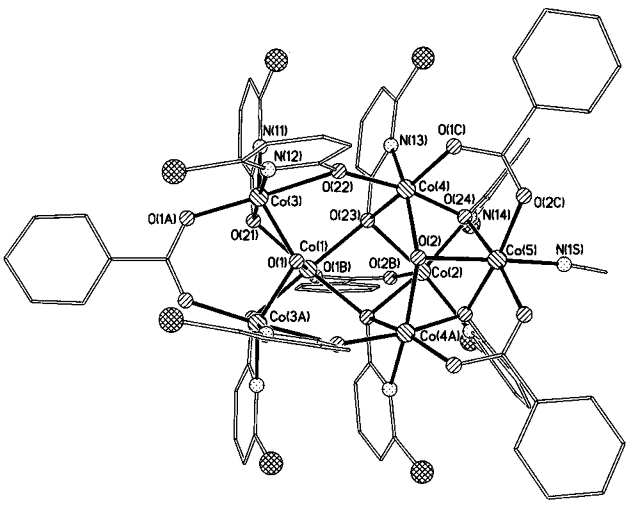


Fig. 1 The structure of complex **1** in the crystal, showing the atom-numbering scheme. The molecule lies on a mirror plane which passes through Co(1), Co(2) and Co(5).

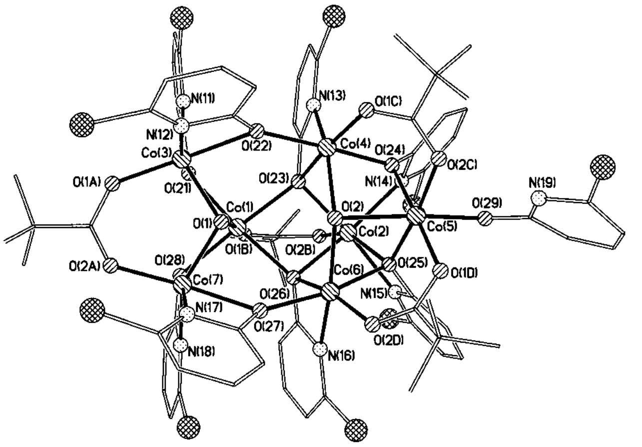


Fig. 2 The structure of complex **2** in the crystal, showing the atom-numbering scheme.

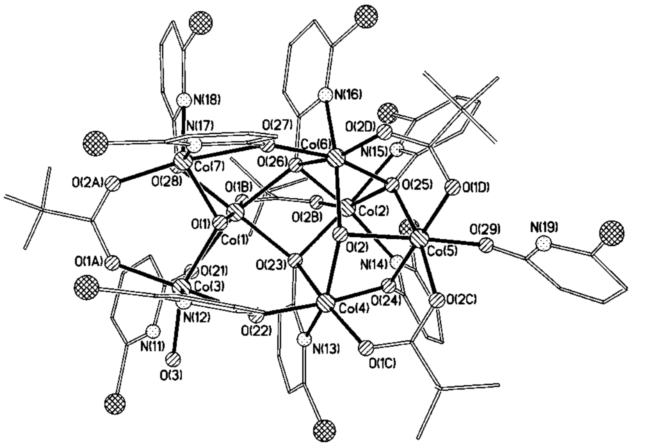


Fig. 3 The structure of complex **3** in the crystal, showing the atom-numbering scheme.

The structures of complexes **1**, **2** and **3** are closely related (Figs. 1, 2 and 3). The metal core is irregular (Fig. 4), and perhaps best described as a square-based pyramid capped on one triangular face and on an adjacent edge by two further cobalt centres. In **1** the molecule crystallises with a mirror plane passing through the cobalt centre at the vertex of the pyramid [Co(1)], the cobalt capping the triangular face [Co(2)] and the edge [Co(5)]. The square base of the pyramid consists of Co(3), Co(4), Co(3a) and Co(4a). Neither **2** nor **3** contains a mirror

Table 1 Experimental data for the X-ray diffraction studies of compounds **1**–**5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{70}H_{49}Cl_8Co_7N_9O_{18}\cdot CH_4O$	$C_{69.57}H_{73.94}Cl_{8.69}Co_7N_{11.75}O_{18.69}$	$C_{65.75}H_{70.25}Cl_{8.75}Co_7N_{9.75}O_{20}$	$C_{116}H_{70}Cl_{20}Co_{13}N_{20}O_{30}\cdot 3CH_2Cl_2$	$C_{116}H_{112}Co_8N_{10}Na_2O_{26}\cdot 2.5C_2H_3N$
M	2032.3	2094.3	2039.76	3953.79	2628.21
Crystal system	Orthorhombic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	*Pnma*	$P\bar{1}$	$P\bar{1}$	*P*2/*c*	$P\bar{1}$
a/Å	24.034(8)	14.407(4)	13.976(7)	17.165(5)	14.325(5)
b/Å	20.018(5)	14.512(4)	15.049(8)	18.243(7)	17.769(5)
c/Å	16.304(4)	23.321(6)	22.158(12)	26.613(8)	25.176(10)
α/°		90.537(14)	86.48(4)		81.11(2)
β/°		93.80(2)	89.39(3)	96.63(4)	76.85(2)
γ/°		113.40(2)	66.66(4)		82.24(3)
U/Å^3	7844(4)	4462(2)	4270(4)	8278(5)	6132(4)
T/K	150.0(2)	220.0(2)	153.0(2)	150.0(2)	220.0(2)
Z	4[a]	2	2	2[b]	2
Crystal shape and colour	Pink lath	Purple rod	Purple block	Purple lath	Purple plate developed in (010)
μ/mm^{-1}	1.792	1.598	13.494	1.753	1.137
Unique data	3788	9627	15140	10866	11476
Unique data with $F_o > 4\sigma(F_o)$	1725	5174	7427	5657	5527
*R*1, *wR*2[c]	0.0897, 0.2317	0.0764, 0.1966	0.0994, 0.2825	0.0926, 0.2744	0.0919, 0.2173

[a] The molecule lies on a mirror plane. [b] The molecule lies on an inversion centre. [c] *R*1 based on observed data, *wR*2 on all unique data.

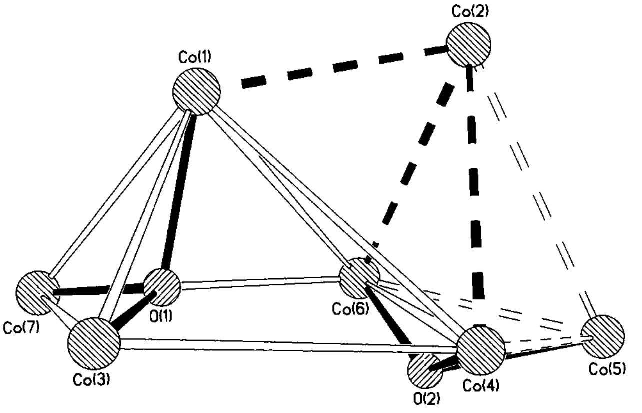


Fig. 4 The heptanuclear metal core of complex **2**.

Table 2 Bond lengths (Å) for compounds **1**, **2** and **3**

	1	**2**	**3**
Co(1)–O(1B)	1.990(17)	2.018(9)	2.007(8)
Co(1)–O(21)	2.076(12)	2.078(8)	2.071(8)
Co(1)–O(28)	[a]	2.112(9)	2.075(8)
Co(1)–O(1)	2.086(17)	2.096(8)	2.060(7)
Co(1)–O(23)	2.155(12)	2.157(8)	2.156(7)
Co(1)–O(26)	[a]	2.156(8)	2.183(7)
Co(2)–O(2B)	2.012(18)	2.002(9)	2.010(8)
Co(2)–O(23)	2.207(12)	2.153(8)	2.182(8)
Co(2)–O(26)	[a]	2.205(8)	2.140(7)
Co(2)–N(14)	2.207(14)	2.156(11)	2.172(9)
Co(2)–N(15)	[a]	2.196(11)	2.184(10)
Co(2)–O(24)	2.427(12)	—	—
Co(2)–O(25)	[a]	2.262(10)	2.251(8)
Co(3)–O(1A)	2.006(13)	1.998(10)	2.006(8)
Co(3)–O(1)	2.009(10)	1.992(8)	2.018(7)
Co(3)–N(11)	2.053(13)	2.101(12)	—
Co(3)–N(12)	2.077(13)	2.091(11)	2.115(10)
Co(3)–O(22)	2.329(11)	2.310(10)	2.313(8)
Co(3)–O(21)	2.444(11)	2.362(9)	2.191(8)
Co(3)–O(1H)	—	—	2.052(8)
Co(4)–O(22)	2.008(11)	2.027(9)	2.016(8)
Co(4)–O(1C)	2.046(14)	2.015(11)	2.039(8)
Co(4)–O(2)	2.082(7)	2.047(8)	2.089(7)
Co(4)–N(13)	2.086(14)	2.060(11)	2.108(9)
Co(4)–O(24)	2.104(13)	2.089(9)	2.040(8)
Co(4)–O(23)	2.377(12)	2.481(10)	2.464(10)
Co(5)–O(2C)	2.022(15)	2.043(11)	2.037(9)
Co(5)–O(1D)	[a]	2.008(11)	2.044(8)
Co(5)–O(24)	2.084(13)	2.028(9)	2.063(7)
Co(5)–O(25)	[a]	2.103(9)	2.088(8)
Co(5)–O(2)	2.165(17)	2.188(9)	2.162(8)
Co(5)–N(1S)	2.17(3)	2.107(13)	—
Co(5)–O(29)	—	2.107(13)	2.114(10)
Co(6)–O(2D)	—	2.022(1)	2.024(8)
Co(6)–O(27)	—	2.038(9)	2.023(8)
Co(6)–O(2)	—	2.061(9)	2.072(8)
Co(6)–N(16)	—	2.117(10)	2.104(9)
Co(6)–O(25)	—	2.158(8)	2.125(8)
Co(6)–O(26)	—	2.339(8)	2.336(7)
Co(7)–O(2A)	—	1.992(10)	1.948(9)
Co(7)–O(1)	—	2.000(8)	1.986(7)
Co(7)–N(17)	—	2.061(12)	2.075(10)
Co(7)–N(18)	—	2.081(11)	2.050(10)
Co(7)–O(27)	—	2.299(10)	2.404(8)
Co(7)–O(28)	—	2.427(12)	2.546(10)

[a] Symmetry equivalent to previous bond.

plane, with the square base defined by Co(3), Co(4), Co(6) and Co(7) and the other three positions numbered as for **1**.

In all three cages the hydroxide and carboxylate ligands behave in an identical fashion. In all cases two μ_3-hydroxides lie at the centre of the cage. The first, O(1), bridges between the cobalt at the vertex of the pyramid [Co(1)] and two Co atoms within the square base [Co(3) and Co(3A) in **1**; Co(3) and Co(7) in **2** and **3**]. The second, O(2), bridges between the remaining Co centres in the square base [Co(4) and Co(4A) in **1**; Co(4) and Co(6) in **2** and **3**] and the edge-capping cobalt [Co(5)]. In all three structures the angles around these two hydroxides are quite different, with O(1) having three Co–O–Co angles near those expected for a pyramidal OH (102.7–117.3°) while O(2) has an extremely distorted geometry with the angle between the two cobalts within the square base close to 140° while the other two angles are between 91.4 and 94.3° (see Table 3).

Four carboxylates also support this core, all displaying the same 1,3-bridging mode. The first bridges between two Co atoms within the square base [Co(3) and Co(3A) in **1**; Co(3) and Co(7) in **2** and **3**]. The second bridges between Co(1) at the vertex of the pyramid and Co(2) which caps a triangular face. The final two each bridge between the edge-capping cobalt [Co(5)] and one of the two remaining cobalt sites within the square base [Co(4) and Co(4A) in **1**; Co(4) and Co(6) in **2** and **3**].

The eight pyridonate ligands show a much wider range of bonding modes. In complex **1** there are four symmetry-equivalent pairs of pyridonates; in **2** and **3** the bonding modes

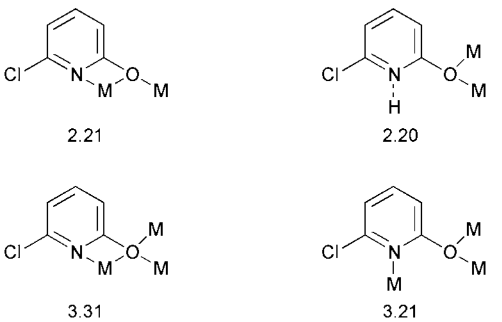
Table 3 Selected bond angles (°) for complexes **1**–**3**

	1	**2**	**3**
O(1B)–Co(1)–O(21)	93.4(5)	93.3(4)	96.7(3)
O(1B)–Co(1)–O(28)	[a]	91.2(3)	89.1(3)
O(1B)–Co(1)–O(1)	177.7(7)	173.5(4)	174.2(3)
O(21)–Co(1)–O(1)	84.8(5)	83.8(3)	81.0(3)
O(1)–Co(1)–O(28)	[a]	83.0(3)	85.7(3)
O(21)–Co(1)–O(28)	82.6(7) [b]	87.7(4)	91.7(3)
O(1B)–Co(1)–O(23)	93.1(5)	94.5(3)	96.0(3)
O(1B)–Co(1)–O(26)	[a]	93.1(3)	93.6(3)
O(21)–Co(1)–O(23)	99.5(5)	95.8(3)	88.4(3)
O(28)–Co(1)–O(26)	[a]	98.2(3)	103.1(3)
O(1)–Co(1)–O(23)	88.7(5)	91.6(3)	89.3(3)
O(1)–Co(1)–O(26)	[a]	90.5(3)	90.1(3)
O(28)–Co(1)–O(23)	173.0(5) [b]	173.2(3)	174.9(3)
O(21)–Co(1)–O(26)	[a]	171.2(3)	162.1(3)
O(23)–Co(1)–O(26)	77.7(6) [c]	77.6(3)	75.9(3)
O(2B)–Co(2)–O(23)	91.6(5)	93.1(4)	93.5(3)
O(2B)–Co(2)–O(26)	[a]	93.3(3)	95.7(3)
O(2B)–Co(2)–N(14)	94.2(5)	103.3(4)	100.1(4)
O(2B)–Co(2)–N(15)	[a]	96.8(4)	99.1(4)
O(23)–Co(2)–N(14)	93.7(5)	93.0(4)	91.8(3)
N(15)–Co(2)–O(26)	[a]	92.4(3)	92.9(3)
O(23)–Co(2)–N(15)	167.9(5) [d]	165.6(4)	164.3(3)
N(14)–Co(2)–O(26)	[a]	161.0(4)	160.8(4)
N(14)–Co(2)–N(15)	96.5(8) [d]	94.8(4)	95.3(4)
O(23)–Co(2)–O(26)	75.6(6) [c]	76.7(3)	76.3(3)
O(2B)–Co(2)–O(25)	145.7(6) [e]	153.6(4)	157.9(3)
O(23)–Co(2)–O(25)	113.9(5) [e]	108.7(3)	106.1(3)
N(14)–Co(2)–O(25)	105.9(5) [e]	90.6(4)	89.7(3)
N(15)–Co(2)–O(25)	56.8(5) [e]	59.2(4)	60.0(3)
O(26)–Co(2)–O(25)	74.4(5) [c,e]	78.1(3)	79.5(3)
O(24)–Co(2)–O(25)	66.9(5) [e]		
O(1A)–Co(3)–O(1)	103.9(6)	102.3(4)	101.0(3)
O(1A)–Co(3)–N(12)	100.0(5)	103.9(5)	103.1(4)
O(1)–Co(3)–N(12)	104.2(7)	110.1(4)	94.4(3)
O(1A)–Co(3)–O(22)	159.2(5)	163.0(4)	163.1(3)
O(1)–Co(3)–O(22)	78.5(5)	79.6(3)	79.4(3)
N(12)–Co(3)–O(22)	59.8(4)	60.1(4)	60.2(3)
O(1A)–Co(3)–O(21)	84.0(4)	84.4(4)	84.1(3)
O(1)–Co(3)–O(21)	77.5(5)	79.1(3)	79.1(3)
N(12)–Co(3)–O(21)	175.0(6)	165.4(4)	171.2(4)
O(22)–Co(3)–O(21)	116.4(5)	112.5(3)	112.3(3)
O(1A)–Co(3)–N(11)	103.2(6)	100.8(4)	—
O(1)–Co(3)–N(11)	124.7(6)	129.3(4)	—
N(12)–Co(3)–N(11)	117.2(6)	107.1(5)	—
N(11)–Co(3)–O(22)	91.6(5)	90.5(4)	—
N(11)–Co(3)–O(21)		59.1(4)	—
O(1A)–Co(3)–O(1H)	—	—	99.1(4)
O(1)–Co(3)–O(1H)	—	—	152.(3)
O(1H)–Co(3)–N(12)	—	—	99.4(4)
O(1H)–Co(3)–O(21)	—	—	84.2(3)
O(1H)–Co(3)–O(22)	—	—	86.8(3)
O(1C)–Co(4)–O(22)	100.0(5)	97.2(4)	97.2(3)
O(1C)–Co(4)–O(2)	95.4(6)	95.3(4)	95.7(3)
O(22)–Co(4)–O(2)	99.1(6)	99.5(3)	96.6(3)
O(1C)–Co(4)–N(13)	105.6(6)	113.3(5)	113.3(4)
O(22)–Co(4)–N(13)	89.2(5)	88.6(4)	89.6(3)
O(2)–Co(4)–N(13)	155.8(6)	149.1(4)	149.4(3)
O(1C)–Co(4)–O(24)	92.7(5)	90.4(4)	89.7(3)
O(22)–Co(4)–O(24)	167.3(5)	171.8(4)	173.1(3)
O(2)–Co(4)–O(24)	79.7(6)	82.7(3)	83.2(3)
N(13)–Co(4)–O(24)	87.3(5)	85.6(4)	87.2(3)
O(1C)–Co(4)–O(23)	161.4(5)	165.6(4)	165.2(3)
O(22)–Co(4)–O(23)	90.5(4)	94.2(4)	94.5(4)
O(2)–Co(4)–O(23)	98.1(5)	91.5(4)	91.8(4)
N(13)–Co(4)–O(23)	58.9(4)	58.0(4)	57.7(3)
O(24)–Co(4)–O(23)	77.3(5)	77.9(4)	78.6(4)
O(1D)–Co(5)–O(24)	170.7(6) [f]	178.0(4)	178.8(4)
O(2C)–Co(5)–O(25)	[a]	173.3(4)	170.8(3)
O(1D)–Co(5)–O(2C)	98.2(9) [f]	90.7(5)	91.1(4)
O(24)–Co(5)–O(2C)	90.9(6)	91.2(4)	89.9(3)
O(1D)–Co(5)–O(25)	[a]	95.6(4)	96.3(3)
O(24)–Co(5)–O(25)	79.9(7) [e]	82.5(3)	82.8(3)
O(2C)–Co(5)–O(2)	98.8(5)	99.0(4)	95.5(3)
O(1D)–Co(5)–O(2)	[a]	98.4(4)	99.7(3)
O(24)–Co(5)–O(2)	78.3(5)	80.7(3)	80.9(3)
O(25)–Co(5)–O(2)	[a]	77.7(3)	77.9(3)
O(29)–Co(5)–O(2)	—	165.4(4)	166.3(4)
O(1D)–Co(5)–O(29)	—	88.9(5)	91.8(4)
O(24)–Co(5)–O(29)	—	91.6(4)	87.6(4)
O(2C)–Co(5)–O(29)	—	93.5(5)	91.7(4)
O(29)–Co(5)–O(25)	—	89.0(4)	93.5(4)
O(2C)–Co(5)–N(1S)	91.7(7)	—	—
O(24)–Co(5)–N(1S)	89.5(7)	—	—
O(2)–Co(5)–N(1S)	164.0(9)	—	—
O(2D)–Co(6)–O(27)	—	98.2(4)	99.9(3)
O(2D)–Co(6)–O(2)	—	96.6(4)	93.6(3)
O(27)–Co(6)–O(2)	—	99.8(4)	94.9(3)
O(2D)–Co(6)–N(16)	—	103.5(4)	103.6(4)
O(27)–Co(6)–N(16)	—	85.6(4)	88.9(3)
O(2)–Co(6)–N(16)	—	158.3(4)	161.5(3)
O(2D)–Co(6)–O(25)	—	98.4(4)	96.1(3)
O(27)–Co(6)–O(25)	—	163.4(4)	163.2(3)
O(2)–Co(6)–O(25)	—	79.3(3)	79.1(3)
N(16)–Co(6)–O(25)	—	89.5(4)	92.1(3)
O(2D)–Co(6)–O(26)	—	162.5(4)	161.8(3)
O(27)–Co(6)–O(26)	—	86.5(3)	88.2(3)
O(2)–Co(6)–O(26)	—	99.3(3)	101.9(3)
N(16)–Co(6)–O(26)	—	59.8(4)	60.0(3)
O(25)–Co(6)–O(26)	—	77.4(3)	77.8(3)
O(2A)–Co(7)–O(1)	—	105.3(4)	101.5(3)
O(2A)–Co(7)–N(17)	—	101.0(5)	104.0(4)
O(1)–Co(7)–N(17)	—	114.1(4)	108.7(3)
O(2A)–Co(7)–N(18)	—	99.4(4)	103.0(4)
O(1)–Co(7)–N(18)	—	126.8(4)	121.5(3)
N(17)–Co(7)–N(18)	—	106.1(5)	115.3(4)
O(2A)–Co(7)–O(27)	—	161.7(4)	159.9(3)
O(1)–Co(7)–O(27)	—	81.2(3)	77.5(3)
N(17)–Co(7)–O(27)	—	61.0(4)	58.5(3)
N(18)–Co(7)–O(27)	—	89.6(4)	94.3(3)
O(2A)–Co(7)–O(28)	—	84.4(4)	82.0(3)
O(1)–Co(7)–O(28)	—	77.4(4)	75.3(3)
N(17)–Co(7)–O(28)	—	164.8(4)	171.5(3)
N(18)–Co(7)–O(28)	—	58.9(4)	56.9(4)
O(27)–Co(7)–O(28)	—	113.8(4)	116.5(3)
Co(7)–O(1)–Co(3)	115.4(8) [g]	115.8(4)	117.3(3)
Co(3)–O(1)–Co(1)	103.1(6)	103.2(3)	102.7(3)
Co(7)–O(1)–Co(1)	[a]	103.5(4)	104.8(3)
Co(6)–O(2)–Co(4)	135.7(9) [h]	140.7(5)	136.8(4)
Co(6)–O(2)–Co(5)	93.5(5)	92.4(3)	92.8(3)
Co(4)–O(2)–Co(5)	[a]	91.4(3)	91.4(3)

[a] Symmetry equivalent to above angle. [b] For this structure O(28) is a symmetry equivalent of O(21). [c] O(26) is a symmetry equivalent of O(23). [d] N(15) is a symmetry equivalent of N(14). [e] O(25) is a symmetry equivalent of O(24). [f] O(1D) is a symmetry equivalent of O(2C). [g] Co(7) is a symmetry equivalent of Co(3). [h] Co(6) is a symmetry equivalent of Co(4).

displayed are less symmetric, but are clearly related to those in **1**. The bonding modes are illustrated in Fig. 5. We have previously[23] introduced "Harris notation"[24] as a method of describing bonding modes of flexible ligands, feeling it is preferable to the currently accepted nomenclature involving η and μ, which we feel to be cumbersome. The binding mode is referred to as $[X.Y_1Y_2Y_3 \ldots Y_n]$, where X is the overall number of metals bound by the whole ligand, and each value of Y refers to the number of metal atoms attached to the different donor atoms. Therefore for chp there will be two values for Y. The ordering of Y is listed by the Cahn–Ingold–Prelog priority rules, hence here O before N.

The first pair of pyridonates [involving N(11) and O(21) and symmetry equivalents in complex **1**; N(11), O(21) and N(18), O(28) in **2**] chelate to one metal either Co(3) or Co(3A) (in **1**) or Co(3) or Co(7) (in **2**) and further bind to Co(1) through the O-donor. Using Harris notation, this is the 2.21 bonding mode, *i.e.* two metals bound to the ligand, two attached to oxygen and one to nitrogen (see Fig. 5). In **3** this pair of pyridonates is not equivalent; the pyridonate involving N(18) and O(28) behaves



2.21 2.20

3.31 3.21

Fig. 5 The bonding modes of chp ligands in complexes **1**–**5**, with the Harris notation (see text).[24]

in this fashion but for the other pyridonate [involving N(11), O(21)] a water molecule [O(3)] has been inserted into the N–Co bond. This ligand therefore adopts the 2.20 mode (Fig. 5).

The second pair of pyridonates [involving N(12), O(22) and symmetry equivalents in complex **1**; N(12), O(22) and N(17), O(27) in **2** and **3**] behaves in an identical manner in all three structures. Each pyridonate adopts the 2.21 mode, chelating to one Co [Co(3) or Co(3A) in **1**; Co(3) or Co(7) in **2** and **3**] and bridging to a further cobalt centre [Co(4) or Co(4A) in **1**; Co(4) or Co(6) in **2** and **3**] through the oxygen atom. The third pair of pyridonates [involving N(13), O(23) and symmetry equivalents in **1**; N(13), O(23) and N(16), O(26) in **2** and **3**] adopt the 3.31 chelating mode, chelating to a cobalt centre [Co(4) or Co(4A) in **1**; Co(4) or Co(6) in **2** and **3**] but bridging to two further cobalt centres [Co(1) and Co(2) in all cases] through the exocyclic oxygen. The final pair of pyridonates in **1** also adopt this mode, chelating to Co(2) and bridging two further cobalt centres through the oxygen [Co(4) and Co(5) or Co(4A) and Co(5) in **1**]. In **2** and **3** these two pyridonates are not equivalent. One [involving N(14), O(24)] displays a further mode, the 3.21 mode, binding to Co(2) through the N-donor and bridging Co(4) and Co(5) through the oxygen. The second pyridonate [involving N(15), O(25)] displays the 3.31 mode, chelating to Co(2) and bridging between Co(5) and Co(7) through O(25). An important feature of the pyridonate ligands is this immense co-ordinative flexibility. In all cases where the pyridonate chelates to a metal, the Co–O bond involving the chelating chp is significantly longer than the other Co–X bonds (Table 2).

The final difference between the co-ordination spheres of the metals in these structures is in the final site attached to Co(5). In complex **1** a molecule of MeCN occupies this site, while in **2** and **3** the site is disordered. In **2** the site is occupied 31% of the time by MeCN and 69% of the time by Hchp, while in **3** the site is occupied 25% of the time by water and 75% of the time by Hchp. Both the variation in co-ordination of terminal sites, and also disorder in such sites, were also found in decanuclear tricapped-trigonal-prismatic cages.[22]

The co-ordination geometries of the cobalt sites are all distorted. That of Co(1) is the most regular, involving six oxygen donors derived from one hydroxide, one carboxylate and four chp ligands. In all three structures two of the bond lengths [Co(1)–O(23) and Co(1)–O(23A) in **1**; Co(1)–O(23) and Co(1)–O(26) in **2** and **3**] are longer, falling between 2.155 and 2.184 Å, than the other four bonds, which lie in the range 1.990 and 2.112 Å (Table 2). The geometry is close to octahedral in all cases.

The Co(2) site in complex **1**, is the most irregular, and is best described as seven-co-ordinate, involving one carboxylate oxygen, two 3.31-pyridonates and the oxygen atoms from two further chp ligands. Six of the seven bonds are longer than any bonds to Co(1), with the bonds to the O atoms of the 3.31-pyridonates the longest [2.427(12) Å] and the bond to O(2) the shortest [2.012(18) Å]. The remaining bonds are identical within error [2.207(14) Å]. In **2** and **3** the Co(2) site is six-co-ordinate, lacking one of the bonds to a pyridonate. The average bond length is significantly shorter [2.17 Å for the five shortest bonds in **1**, 2.14 Å for the equivalent bonds in **2** and **3**]. The bond to the carboxylate is the shortest, and the bond to the O atom of the 3.31-chp is the longest.

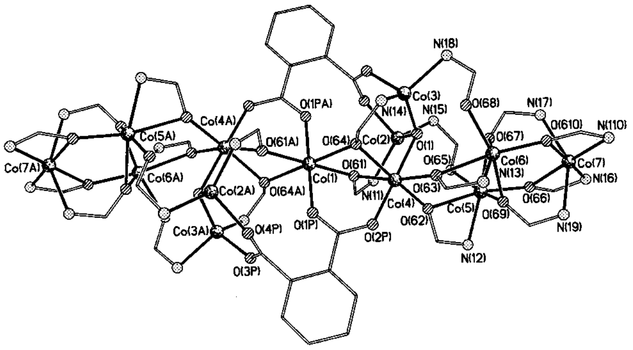


Fig. 6 The structure of complex **4** in the crystal, showing the atom, numbering scheme. Only the C atoms linking the N and O atoms of the chp ligands are shown for clarity.

The Co(3) site in complex **1** is very similar to the Co(3) and Co(7) sites in **2** and the Co(7) site in **3**. In each case the six-co-ordinate metal is bound to two chelating pyridonates, one hydroxide [O(1)] and one carboxylate oxygen. In all cases the Co–X bond involving the O atom of the pyridonate is the longest, and the distortion observed in the geometry is due largely to the narrow bite angle of the chelating chp groups. In **3** the Co(3) site is different, due to the presence of a water molecule which has displaced the N-donor of one chelating pyridonate. The result is a more regular co-ordination geometry, as there is only one chelating group present, and again the longest bond involves the chelating chp ligand.

The Co(4) site in complex **1** is identical to the Co(4) and Co(6) sites in **2** and **3**. The six-co-ordinate cobalt atom is bound to one chelating pyridonate, one hydroxide [O(2)], one carboxylate O atom, and two oxygens from further chp ligands. As before, the distortion in the geometry from a regular octahedron is mainly caused by the chelating ligand, and the longest bond is to the O atom of this group.

The final site is Co(5), and it is very similar in all three structures. This site is bound to five O atoms and one N atom from MeCN in **1**, the same five O-donors and an O-donor from Hchp in **3**, and has a mixture of these two cases in the disordered structure **2**. The five common O atoms come from one hydroxide, two carboxylate oxygens and two pyridonate oxygens. In each case the longest bond is to the hydroxide [2.162–2.188 Å], with no clear-cut trend for the bond lengths involving the other groups.

Oligomers of heptanuclear cages

One of the general aims of groups making polymetallic complexes is to discover routes to higher nuclearity cages. One strategy is to link together smaller cages into larger arrays, and possible linkers include dicarboxylates such as phthalates.[25,26] We recently reported that sodium centres can act to link together dimers of cobalt and nickel into polymeric arrays.[27] We have found that oligomers of heptanuclear cages can be prepared by both strategies, albeit in the latter case in very low yield and with a very long crystallisation time.

The reaction which produces the tridecanuclear cage $[Co_{13}(OH)_2(phth)_2(chp)_{20}]$ **4** is identical to that which produces **1** and **2**, except that the sodium salt of a dicarboxylic acid is used rather than that of a monocarboxylic acid. The result is a large, extremely irregular centrosymmetric cage (Fig. 6). The asymmetric unit contains a square-based pyramid, consisting of Co(2), Co(3), Co(5) and Co(6) within the square base and Co(4) at the vertex of the pyramid (Fig. 7). The Co(5) $\cdots$ Co(6) edge of this pyramid is capped by Co(7), and the triangular face

Table 4 Selected bond lengths (Å) for complex **4**

Co(1)–O(1P)	2.020(9)	Co(1)–O(64)	2.178(7)
Co(1)–O(61)	2.136(7)		
Co(2)–O(4P)#1	1.972(9)	Co(5)–O(66)	1.992(8)
Co(2)–O(1)	2.023(9)	Co(5)–O(65)	2.018(8)
Co(2)–N(15)	2.078(7)	Co(5)–O(69)	2.088(8)
Co(2)–N(11)	2.088(8)	Co(5)–N(12)	2.101(8)
Co(2)–O(61)	2.601(9)	Co(5)–O(67)	2.205(9)
Co(2)–O(65)	2.515(9)	Co(5)–O(62)	2.247(8)
Co(3)–O(1)	1.986(9)	Co(6)–O(610)	1.996(7)
Co(3)–O(3P)#1	1.987(10)	Co(6)–O(68)	2.024(8)
Co(3)–N(14)	2.067(8)	Co(6)–O(69)	2.091(9)
Co(3)–N(18)	2.082(7)	Co(6)–N(13)	2.145(7)
Co(3)–O(64)	2.616(9)	Co(6)–O(63)	2.191(7)
Co(3)–O(68)	2.535(10)	Co(6)–O(67)	2.220(7)
Co(4)–O(2P)	2.023(10)	Co(7)–N(17)	2.172(7)
Co(4)–O(62)	2.035(7)	Co(7)–N(16)	2.184(7)
Co(4)–O(63)	2.058(7)	Co(7)–N(19)	2.188(7)
Co(4)–O(64)	2.122(8)	Co(7)–N(110)	2.214(7)
Co(4)–O(1)	2.136(9)	Co(7)–O(610)	2.221(7)
Co(4)–O(61)	2.142(8)	Co(7)–O(66)	2.225(7)

Symmetry transformation used to generate equivalent atoms: #1 $-x, -y, -z$.

Table 5 Selected bond angles (°) for complex **4**

O(1P)–Co(1)–O(61)	89.6(4)	O(66)–Co(5)–O(65)	106.7(4)
O(1P)–Co(1)–O(64)	90.5(4)	O(66)–Co(5)–O(69)	87.1(3)
O(61)–Co(1)–O(64)	74.1(4)	O(65)–Co(5)–O(69)	157.9(3)
O(4P)#1–Co(2)–O(1)	100.4(4)	O(66)–Co(5)–N(12)	107.5(3)
O(4P)#1–Co(2)–N(15)	102.6(3)	O(65)–Co(5)–N(12)	104.5(4)
O(1)–Co(2)–N(15)	108.0(4)	O(69)–Co(5)–N(12)	87.0(4)
O(4P)#1–Co(2)–N(11)	107.9(4)	O(66)–Co(5)–O(67)	85.2(3)
O(1)–Co(2)–N(11)	123.9(4)	O(65)–Co(5)–O(67)	87.8(3)
N(15)–Co(2)–N(11)	111.4(3)	O(69)–Co(5)–O(67)	76.1(4)
O(4P)#1–Co(2)–O(61)	89.2(4)	N(12)–Co(5)–O(67)	158.5(3)
O(1)–Co(2)–O(61)	77.8(4)	O(66)–Co(5)–O(62)	168.2(3)
N(15)–Co(2)–O(61)	165.2(4)	O(65)–Co(5)–O(62)	81.3(4)
N(11)–Co(2)–O(61)	55.7(4)	O(69)–Co(5)–O(62)	88.1(3)
O(4P)#1–Co(2)–O(65)	159.6(4)	N(12)–Co(5)–O(62)	61.5(2)
O(1)–Co(2)–O(65)	85.5(4)	O(67)–Co(5)–O(62)	104.1(2)
N(15)–Co(2)–O(65)	57.2(4)	O(610)–Co(6)–O(68)	106.7(4)
N(11)–Co(2)–O(65)	84.3(4)	O(610)–Co(6)–O(69)	86.9(3)
O(61)–Co(2)–O(65)	111.2(4)	O(68)–Co(6)–O(69)	156.3(3)
O(1)–Co(3)–O(3P)#1	100.5(4)	O(611)–Co(6)–N(13)	111.8(3)
O(1)–Co(3)–N(14)	122.8(4)	O(68)–Co(6)–N(13)	98.0(4)
O(3P)#1–Co(3)–N(14)	106.5(5)	O(69)–Co(6)–N(13)	94.6(4)
O(1)–Co(3)–N(18)	110.2(4)	O(610)–Co(6)–O(63)	171.5(4)
O(3P)#1–Co(3)–N(18)	105.0(3)	O(68)–Co(6)–O(63)	80.4(4)
N(14)–Co(3)–N(18)	109.8(4)	O(69)–Co(6)–O(63)	88.1(3)
O(1)–Co(3)–O(64)	76.6(3)	N(13)–Co(6)–O(63)	61.8(3)
O(3P)#1–Co(3)–O(64)	87.7(4)	O(610)–Co(6)–O(67)	82.1(3)
N(14)–Co(3)–O(64)	55.5(4)	O(68)–Co(6)–O(67)	86.8(3)
N(18)–Co(3)–O(64)	163.7(4)	O(69)–Co(6)–O(67)	75.7(3)
O(1)–Co(3)–O(68)	85.5(4)	N(13)–Co(6)–O(67)	163.0(3)
O(3P)#1–Co(3)–O(68)	161.6(3)	O(63)–Co(6)–O(67)	103.3(3)
N(14)–Co(3)–O(68)	84.2(4)	N(17)–Co(7)–N(16)	97.0(5)
N(18)–Co(3)–O(68)	56.8(4)	N(17)–Co(7)–N(19)	145.4(3)
O(64)–Co(3)–O(68)	110.6(4)	N(16)–Co(7)–N(19)	99.1(5)
O(2P)–Co(4)–O(62)	94.3(4)	N(17)–Co(7)–N(110)	101.7(4)
O(2P)–Co(4)–O(63)	92.6(4)	N(16)–Co(7)–N(110)	122.5(4)
O(62)–Co(4)–O(63)	89.6(4)	N(19)–Co(7)–N(110)	95.1(4)
O(2P)–Co(4)–O(64)	92.7(4)	N(17)–Co(7)–O(610)	79.8(4)
O(62)–Co(4)–O(64)	168.6(3)	N(16)–Co(7)–O(610)	176.2(4)
O(63)–Co(4)–O(64)	98.9(3)	N(19)–Co(7)–O(610)	82.6(4)
O(2P)–Co(4)–O(1)	178.0(4)	N(110)–Co(7)–O(610)	60.5(4)
O(62)–Co(4)–O(1)	87.3(3)	N(17)–Co(7)–O(66)	81.3(4)
O(63)–Co(4)–O(1)	86.3(3)	N(16)–Co(7)–O(66)	60.8(2)
O(64)–Co(4)–O(1)	85.9(3)	N(19)–Co(7)–O(66)	80.3(3)
O(2P)–Co(4)–O(61)	94.2(2)	N(110)–Co(7)–O(66)	174.9(4)
O(62)–Co(4)–O(61)	95.5(3)	O(610)–Co(7)–O(66)	116.5(4)
O(63)–Co(4)–O(61)	171.2(4)	Co(3)–O(1)–Co(4)	103.1(4)
O(64)–Co(4)–O(61)	75.1(4)	Co(3)–O(1)–Co(2)	122.3(4)
O(1)–Co(4)–O(61)	86.8(3)	Co(2)–O(1)–Co(4)	101.9(4)

Symmetry transformation used to generate equivalent atoms: #1 $-x, -y, -z$.

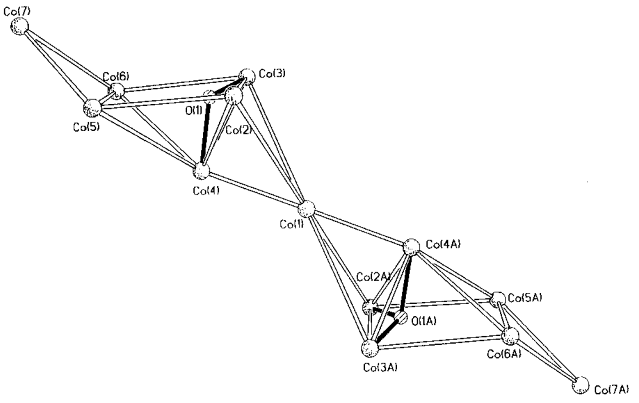


Fig. 7 The tridecanuclear metal core of complex **4**.

Co(2), Co(3), Co(4) is capped by Co(1). Co(1) lies on an inversion centre, and therefore caps the triangular faces of two symmetry-equivalent pyramids. The presence of the square-based pyramid suggests a structural relationship to cages **1**–**3**, and we will return to this question in the discussion.

One unique μ_3-hydroxide site [O(1)] is found in the structure, bridging Co(2), Co(3) and Co(4), thus occupying a similar position to O(1) in complexes **1**–**3**. Bond angles at this hydroxide range from 101.9(4) to 122.3(4)° (Table 5). The two symmetry-equivalent phthalate ligands are tetradentate, bound to Co(1) and to Co(4) within one square-based pyramid, and to Co(2A) and Co(3A) in the symmetry related pyramid.

The structure is dominated by the co-ordination of the pyridonate ligands. Of the ten crystallographically distinct pyridonates, two [those containing N(17), O(67); N(19), O(69)] adopt the 3.21 co-ordination mode (Fig. 5), binding to one metal through the N-donor, and bridging two further metals through the oxygen. A further six [those containing N(12), O(62); N(13), O(63); N(15), O(65); N(16), O(66); N(18), O(68); N(110), O(610)] adopt the 2.21 mode, chelating to one metal and bridging to a second through the oxygen, while the final two pyridonates [those containing N(11), O(61); N(14), O(64)] adopt the 3.31 mode, chelating to one cobalt and bridging two further metal centres through the oxygen.

The cobalt co-ordination sites are more diverse than in complexes **1**–**3**. Co(1) is bound to six oxygen donors, from four chp and two phthalate ligands, in an octahedral array which is only slightly distorted from a regular geometry. Co(2) and Co(3) have four bonds between 1.972 and 2.088 Å to a hydroxide, two N atoms from chp ligands and one phthalate oxygen (Table 4). The geometry of both sites is distorted from a regular tetrahedron, with angles varying from 100.3(4) to 123.8(4)°. For both Co(2) and Co(3) there are also two further long contacts [2.515–2.616 Å] to the O atom of one of the chp ligands bound to the site through the nitrogen. Co(4) is six-co-ordinate, being bound to the hydroxide, four oxygens from chp ligands and one phthalate. As for Co(1), the geometry is close to octahedral. Co(5) and Co(6) are also six-co-ordinate, and are bound to the N- and O-donors of a chelating chp ligand and to four O atoms from four further chp. The geometry is in both cases distorted from octahedral by the small bite angle of the chelating chp (N–Co–O *ca.* 61.6°). Co(7) is bound to two chelating chp ligands, and two further N-donors from chp resulting in a very distorted six-co-ordination.

The structural relationship between complex **4** and **1**–**3** is not immediately apparent, but can be shown by modelling (see below). The relationship between the one-dimensional polymer $[\{Co_7(OH)_2(O_2CCH_2Ph)_4(mhp)_8\}\{CoNa_2(O_2CCH_2Ph)_3(mhp)(Hmhp)\}]_n$ **5** and **1**–**3** is much more obvious. **5** formed unexpectedly from reaction of cobalt(II) chloride with Na(mhp) and Na(O_2CCH_2Ph); this reaction, with other carboxylates in place of phenylacetate, normally produces decanuclear cobalt cages with structures based on tricapped-trigonal prisms.[21] On

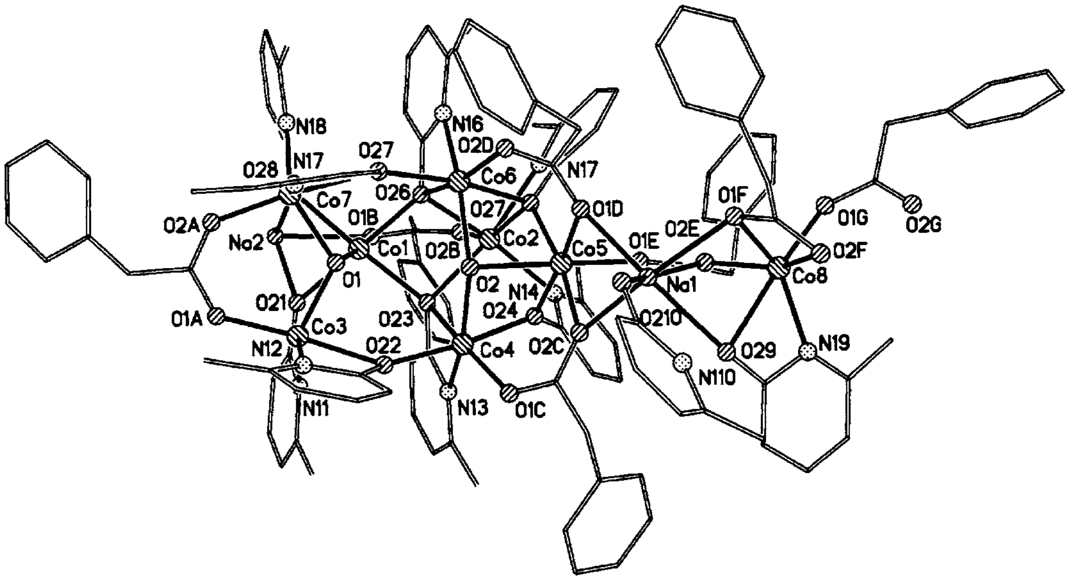


Fig. 8 The asymmetric unit of complex **5**, showing the atom-numbering scheme.

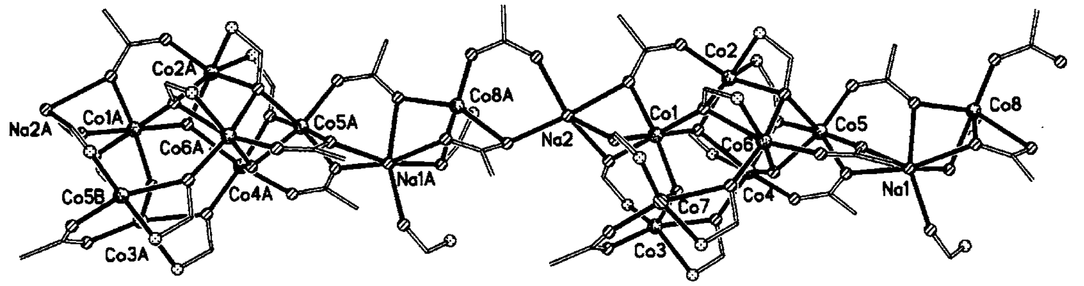


Fig. 9 A fragment of the one-dimensional polymer **5**. Only the C atoms linking the N and O atoms of the mhp ligands are shown for clarity.

Table 6 Selected bond lengths (Å) for complex **5**

Co(1)–O(1B)	2.074(10)	Co(2)–O(2B)	2.032(9)
Co(1)–O(1)	2.101(9)	Co(2)–O(26)	2.160(9)
Co(1)–O(26)	2.102(9)	Co(2)–N(14)	2.173(10)
Co(1)–O(21)	2.103(9)	Co(2)–N(15)	2.218(10)
Co(1)–O(28)	2.126(9)	Co(2)–O(23)	2.234(9)
Co(1)–O(23)	2.149(9)	Co(2)–O(25)	2.246(9)
Co(3)–O(1)	1.959(9)	Co(7)–O(2A)	1.995(10)
Co(3)–O(1A)	1.988(10)	Co(7)–O(1)	2.004(9)
Co(3)–N(11)	2.047(11)	Co(7)–N(18)	2.044(11)
Co(3)–N(12)	2.102(10)	Co(7)–N(17)	2.051(11)
Co(3)–O(22)	2.303(9)	Co(7)–O(27)	2.370(9)
Co(4)–O(24)	2.024(10)	Co(6)–O(27)	2.031(9)
Co(4)–O(22)	2.029(9)	Co(6)–O(2D)	2.050(9)
Co(4)–N(13)	2.078(10)	Co(6)–O(2)	2.080(8)
Co(4)–O(1C)	2.086(9)	Co(6)–N(16)	2.085(10)
Co(4)–O(2)	2.105(9)	Co(6)–O(25)	2.142(10)
Co(4)–O(23)	2.352(9)	Co(6)–O(26)	2.387(9)
Co(5)–O(24)	2.060(9)	Co(8)–O(1G)	1.977(10)
Co(5)–O(1D)	2.065(9)	Co(8)–N(19)	2.050(12)
Co(5)–O(1E)	2.067(10)	Co(8)–O(2E)	2.055(10)
Co(5)–O(2C)	2.078(9)	Co(8)–O(1F)	2.096(10)
Co(5)–O(25)	2.079(9)	Co(8)–O(2F)	2.362(10)
Co(5)–O(2)	2.171(9)	Co(8)–O(29)	2.404(11)
Na(1)–O(210)	2.289(19)	Na(1)–O(1F)	2.462(11)
Na(1)–O(2E)	2.326(12)	Na(2)–O(2G)#1	2.265(12)
Na(1)–O(21′)	2.37(3)	Na(2)–O(2F)#1	2.298(12)
Na(1)–O(1D)	2.396(11)	Na(2)–O(28)	2.343(11)
Na(1)–O(29)	2.450(12)	Na(2)–O(21)	2.371(10)
Na(1)–O(2C)	2.389(11)	Na(2)–O(1B)	2.440(11)

Symmetry transformation used to generate equivalent atoms: #1 x, $y + 1$, z.

this occasion crystals of the expected decanuclear cage were not formed, but those of **5** grew after a period of months.

The structure consists of heptanuclear cobalt cages similar to those of complexes **1**–**3**, linked through sodium and cobalt containing fragments (Fig. 8). The heptanuclear cage is identical to those in **1**–**3**, with the seven cobalt centres held together by two μ_3-hydroxides, four 1,3-bridging carboxylates and eight pyridonate ligands which display a variety of bonding modes. The terminal site on Co(5), which is occupied by MeCN or Hchp in **1**–**3**, is occupied by an O-donor [O(1E)] from a carboxylate group, and this carboxylate is part of the linking fragment. The second oxygen of this ligand binds to Na(1) and Co(8), while Na(1) and Co(5) also share the oxygen donors of two further carboxylates [O(1D) and O(2C)]. Na(1) and Co(8) are bridged by two oxygens [O(29) and O(1F)] derived from mhp and O_2CCH_2Ph ligands which chelate to Co(8). The second oxygen of this carboxylate ligand [O(2F)] also bridges to the second sodium site in the structure [Na(2)]. Na(2) and Co(8) are further bridged by a 1,3-carboxylate containing O(1G) and O(2G). The polymeric structure results as Na(2) is also attached to three O-donors from a neighbouring heptanuclear cage, symmetry equivalents of O(21), O(28) and O(1B). The neighbouring cages are related by translational symmetry (Fig. 9).

The co-ordination sites of the seven cobalts within the cages are identical to those in complex **2**. Co(8) has a distorted six-co-ordinate geometry as it is bound to a chelating mhp ligand, a chelating carboxylate, and two O-donors from two further O_2CCH_2Ph groups. Na(1) is six-co-ordinate, being bound to oxygen donors from four carboxylates, one mhp and a terminal Hmhp ligand [O(210)]. Na(2) is five-co-ordinate, being bound to O atoms from three carboxylates and two pyridonates. Both sodium co-ordination geometries are extremely irregular, as is typical for this metal.

Discussion

A noticeable feature of the structures of metal cages with pyridonate and carboxylate ligands is their apparent irregularity. Compared with low oxidation state clusters, which can

Table 7 Selected bond angles (°) for complex **5**

O(1B)–Co(1)–O(1)	173.9(4)	O(2B)–Co(2)–O(26)	92.4(4)
O(1B)–Co(1)–O(26)	94.5(4)	O(2B)–Co(2)–N(14)	96.3(4)
O(1)–Co(1)–O(26)	90.4(4)	O(26)–Co(2)–N(14)	168.2(4)
O(1B)–Co(1)–O(21)	86.1(4)	O(2B)–Co(2)–N(15)	93.8(4)
O(1)–Co(1)–O(21)	89.0(4)	O(26)–Co(2)–N(15)	92.4(4)
O(26)–Co(1)–O(21)	179.4(4)	N(14)–Co(2)–N(15)	94.9(4)
O(1B)–Co(1)–O(28)	86.7(4)	O(2B)–Co(2)–O(23)	90.9(3)
O(1)–Co(1)–O(28)	88.9(4)	O(26)–Co(2)–O(23)	74.5(3)
O(26)–Co(1)–O(28)	99.1(3)	N(14)–Co(2)–O(23)	97.3(4)
O(21)–Co(1)–O(28)	80.9(4)	N(15)–Co(2)–O(23)	166.4(6)
O(1B)–Co(1)–O(23)	94.8(4)	O(2B)–Co(2)–O(25)	151.9(3)
O(1)–Co(1)–O(23)	89.8(4)	O(26)–Co(2)–O(25)	79.6(3)
O(26)–Co(1)–O(23)	77.5(3)	N(14)–Co(2)–O(25)	96.1(4)
O(21)–Co(1)–O(23)	102.4(3)	N(15)–Co(2)–O(25)	60.1(3)
O(28)–Co(1)–O(23)	176.4(3)	O(23)–Co(2)–O(25)	112.3(3)
O(1)–Co(3)–O(1A)	103.4(4)	O(2A)–Co(7)–O(1)	101.2(4)
O(1)–Co(3)–N(11)	121.0(4)	O(2A)–Co(7)–N(18)	98.5(4)
O(1A)–Co(3)–N(12)	95.3(4)	O(1)–Co(7)–N(18)	125.7(4)
O(1)–Co(3)–N(12)	104.6(4)	O(2A)–Co(7)–N(17)	104.5(4)
O(1A)–Co(3)–N(12)	102.5(4)	O(1)–Co(7)–N(17)	105.6(4)
N(11)–Co(3)–N(12)	125.1(4)	N(18)–Co(7)–N(17)	117.5(4)
O(1)–Co(3)–O(22)	81.7(3)	O(2A)–Co(7)–O(27)	162.3(4)
O(1A)–Co(3)–O(22)	162.8(4)	O(1)–Co(7)–O(27)	78.6(3)
N(11)–Co(3)–O(22)	96.0(4)	N(18)–Co(7)–O(27)	95.8(4)
N(12)–Co(3)–O(22)	60.4(3)	N(17)–Co(7)–O(27)	59.2(3)
O(24)–Co(4)–O(22)	173.3(4)	O(27)–Co(6)–O(2D)	98.6(4)
O(24)–Co(4)–N(13)	90.5(4)	O(27)–Co(6)–O(2)	97.7(4)
O(22)–Co(4)–N(13)	89.8(4)	O(2D)–Co(6)–O(2)	95.9(4)
O(24)–Co(4)–O(1C)	89.5(4)	O(27)–Co(6)–N(16)	87.7(4)
O(22)–Co(4)–O(1C)	96.8(4)	O(2D)–Co(6)–N(16)	105.3(4)
N(13)–Co(4)–O(1C)	108.4(4)	O(2)–Co(6)–N(16)	157.0(4)
O(24)–Co(4)–O(2)	81.6(4)	O(27)–Co(6)–O(25)	165.5(4)
O(22)–Co(4)–O(2)	95.4(4)	O(2D)–Co(6)–O(25)	95.8(4)
N(13)–Co(4)–O(2)	155.6(4)	O(2)–Co(6)–O(25)	78.9(4)
O(1C)–Co(4)–O(2)	94.6(4)	N(16)–Co(6)–O(25)	90.2(4)
O(24)–Co(4)–O(23)	81.3(3)	O(27)–Co(6)–O(26)	89.8(3)
O(22)–Co(4)–O(23)	93.0(3)	O(2D)–Co(6)–O(26)	162.3(4)
N(13)–Co(4)–O(23)	60.2(3)	O(2)–Co(6)–O(26)	98.5(3)
O(1C)–Co(4)–O(23)	165.1(4)	N(16)–Co(6)–O(26)	59.2(3)
O(2)–Co(4)–O(23)	95.6(3)	O(25)–Co(6)–O(26)	76.8(3)
O(24)–Co(5)–O(1D)	174.5(4)	O(1G)–Co(8)–N(19)	115.0(5)
O(24)–Co(5)–O(1E)	89.3(4)	O(1G)–Co(8)–O(2E)	99.1(4)
O(1D)–Co(5)–O(1E)	96.1(4)	N(19)–Co(8)–O(2E)	103.5(5)
O(24)–Co(5)–O(2C)	92.8(4)	O(19)–Co(8)–O(1F)	99.5(4)
O(1D)–Co(5)–O(2C)	86.6(4)	N(19)–Co(8)–O(1F)	141.3(5)
O(1E)–Co(5)–O(2C)	94.7(4)	O(2E)–Co(8)–O(1F)	87.1(4)
O(24)–Co(5)–O(25)	82.0(3)	O(19)–Co(8)–O(2F)	95.9(4)
O(1D)–Co(5)–O(25)	97.8(4)	N(19)–Co(8)–O(2F)	99.0(4)
O(1E)–Co(5)–O(25)	92.8(4)	O(2E)–Co(8)–O(2F)	144.4(4)
O(2C)–Co(5)–O(25)	170.9(4)	O(1F)–Co(8)–O(2F)	58.5(3)
O(24)–Co(5)–O(2)	79.2(4)	O(19)–Co(8)–O(29)	174.7(4)
O(1D)–Co(5)–O(2)	95.4(4)	N(19)–Co(8)–O(29)	59.8(4)
O(1E)–Co(5)–O(2)	166.3(4)	O(2E)–Co(8)–O(29)	81.9(4)
O(2C)–Co(5)–O(2)	93.3(4)	O(1F)–Co(8)–O(29)	85.7(4)
O(25)–Co(5)–O(2)	78.3(3)	O(2F)–Co(8)–O(29)	86.1(4)
O(210)–Na(1)–O(2E)	158.2(6)	O(2E)–Na(1)–O(1F)	73.3(4)
O(2E)–Na(1)–O(21′)	163.9(8)	O(21′)–Na(1)–O(1F)	105.6(11)
O(210)–Na(1)–O(2C)	109.8(7)	O(2C)–Na(1)–O(1F)	164.3(5)
O(2E)–Na(1)–O(2C)	90.9(4)	O(1D)–Na(1)–O(1F)	105.5(4)
O(21′)–Na(1)–O(2C)	89.5(11)	O(29)–Na(1)–O(1F)	77.3(4)
O(210)–Na(1)–O(1D)	105.2(5)	O(2G)#1–Na(2)–O(2F)#1	84.4(4)
O(2E)–Na(1)–O(1D)	86.9(4)	O(2G)#1–Na(2)–O(28)	120.6(4)
O(21′)–Na(1)–O(1D)	108.6(7)	O(2F)#1–Na(2)–O(28)	109.7(4)
O(2C)–Na(1)–O(1D)	72.9(3)	O(2G)#1–Na(2)–O(21)	157.3(4)
O(210)–Na(1)–O(29)	93.8(5)	O(2F)#1–Na(2)–O(21)	110.8(4)
O(2E)–Na(1)–O(29)	75.7(4)	O(28)–Na(2)–O(21)	71.2(3)
O(21′)–Na(1)–O(29)	88.3(7)	O(2G)#1–Na(2)–O(1B)	91.4(4)
O(2C)–Na(1)–O(29)	99.1(4)	O(2F)#1–Na(2)–O(1B)	175.3(5)
O(1D)–Na(1)–O(29)	160.9(4)	O(28)–Na(2)–O(1B)	74.1(4)
O(210)–Na(1)–O(1F)	85.8(7)	O(21)–Na(2)–O(1B)	72.7(4)

Symmetry transformation used to generate equivalent atoms: #1 x, $y + 1$, z.

frequently be rationalised using Wade's rule (polyskeletal electron pair theory), there appear to be no governing principles which decide structure. At present all we are able to do is to note similarities between cages.

The five cages reported belong to one family. This is obvious in the cases of **1**–**3** and **5**, but less clear for **4**. We can quantify the degree of similarity between cages by calculating root mean square deviations of metal sites between structures. This can be done conveniently using the OFIT sub-routine within the SHELXTL PC package.[20] The results are shown in Table 8. The

Table 8 Comparison of metal polyhedra found in structures **1**–**6**

Structure	1	2	3	4	5	6
1	0	0.0927	0.1150	0.1833	0.0633	0.3202
2	0.0927	0	0.1781	0.1881	0.1292	
3	0.1150	0.1781	0	0.2074	0.1028	0.3185
4	0.1833	0.1881	0.2074	0	0.1933	0.2980
5	0.0633	0.1292	0.1028	0.1933	0	
6	0.3202		0.3185	0.2980		0

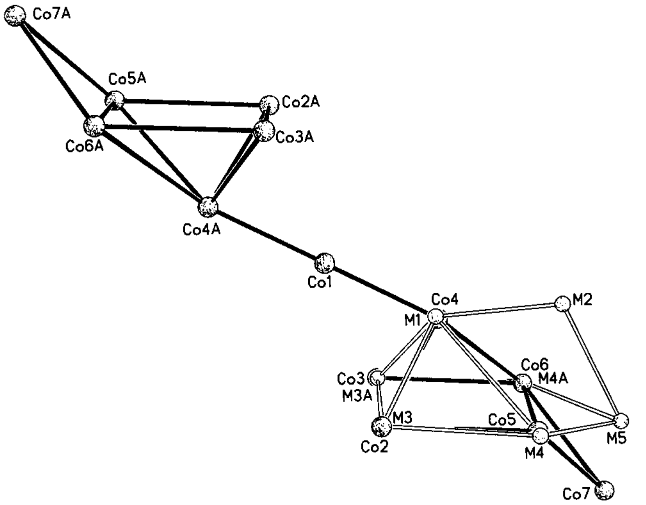


Fig. 10 The superposition of the metal cores of complex **4** (shown as full lines, labelled CoX) and **1** (shown as open lines, labelled MX).

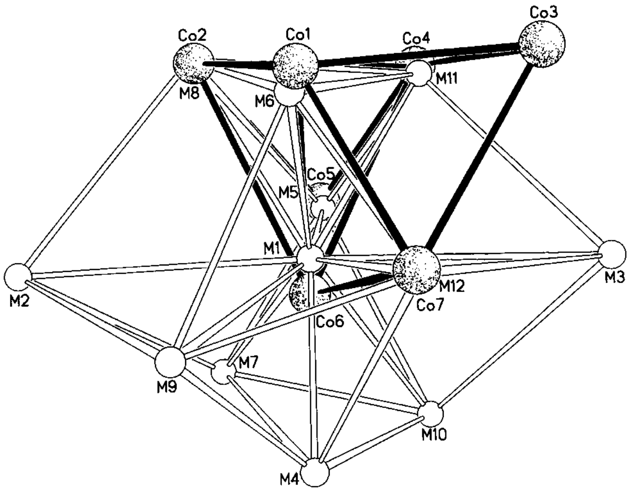


Fig. 11 The superposition of the metal cores of complex **3** (shown as full lines, labelled CoX) and **6** (shown as open lines, labelled MX).

close resemblance between **1**–**3** and **5** is shown by the small value for the rms deviation in each case. Comparison of the metal cores of these four structures with that of **4** also gives a small value for the rms deviation, however in this case only five of the seven unique metal sites in **4** could be matched with sites in **1**–**3** or **5**. Fig. 10 illustrates this comparison with a superposition of the metal sites of **1** and **4**. The five cobalt sites which outline the square based pyramid within **4** [Co(2), Co(3), Co(5) and Co(6) within the base, Co(4) at the vertex] match well with the five structurally equivalent vertices in **1**–**3** and **5**. Co(7), the cap on the edge of the square base in **4**, is in a similar position to Co(5) (M5 in Fig. 10) in **1**–**3** and **5**, but has a much greater rms deviation and was excluded from the fit. **4** does not possess any equivalent metal site to Co(2) (M2 in Fig. 10) in **1**–**3** or **5**, and Co(1) in **4** does not find an equivalent in **1**–**3** or **5**.

While it is curious that these cages are related we also wished to see if they could be compared with the tricapped-trigonal prisms which result, in general, when a mixture of carboxylates and 6-methyl-2-pyridonate (mhp) is used in similar reactions[22] to those described here. Intriguingly the fit is extremely good between a representative example of these tricapped-trigonal prisms and **1**–**3** and **5**. Fig. 11 shows a superposition of the metal vertices of **3** and $[Ni_{12}(OH)_6(mhp)_{12}(O_2CCH_2Cl)_6]$ **6**.[22] Of the seven metal vertices of **3**, six match well with those of the centred-pentacapped-trigonal prism in **6**. The centred-pentacapped-trigonal prism has four chemically distinct nickel sites, at the centre of the polyhedron [labelled M1 in Fig. 11], at the vertices of the trigonal prism [M7, M8, M9, M10, M11 and M12]; capping the trigonal faces of the prism [M2 and M3] and capping the rectangular faces of the prism [M4, M5 and M6]. The fit to **3** shows that Co(6) is close to the central metal from **6**; Co(2), Co(4) and Co(7) lie near vertices to the trigonal prism of **6**; Co(1) and Co(5) lie close to caps on the square faces in **6**. No metal site in **6** has an equivalent position to Co(3). It is also possible to match four of the sites of **4** with sites within **6**, but the remaining three unique positions do not match well (Fig. 12). The rms deviation between **4** and **6** given in Table 8 uses only the four positions where reasonable matches occur.

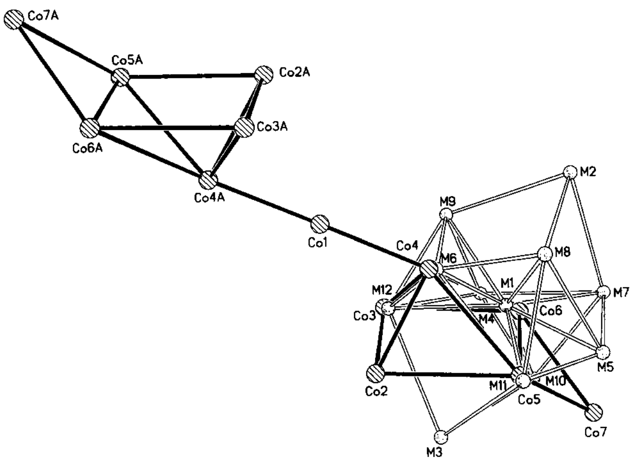


Fig. 12 The superposition of the metal cores of complex **4** (shown as full lines, labelled CoX) and **6** (shown as open lines, labelled MX).

Therefore, work using "blends" of pyridonate and carboxylate with cobalt and nickel has thus far produced sixteen structures, **1**–**3** and **5**, and twelve further structures discussed elsewhere,[22] which can be derived from a centred-pentacapped trigonal prism. The structures vary in the number and type of vertices missing. Two dodecanuclear cages exist (one with cobalt,[28] one with nickel[22]) which have the complete polyhedron. Three undecanuclear nickel cages are known which each miss one vertex which caps a trigonal face.[22] Four decanuclear cages exist (two for Co, two for Ni) where both trigonal caps are removed, and three decanuclear cages (one Co, two Ni) have been formed where two metal centres at one edge of the trigonal prism are missing.[22] The four heptanuclear fragments reported here are also related, but are missing the two caps on trigonal faces, three vertices of the trigonal prism, and one cap on a rectangular face (Fig. 11). It is also worth noting that cages based on pentacapped-trigonal prisms are also found for chromium(III)[29] and iron(III).[30]

This observation begs the question: why a centred-pentacapped-trigonal prism? Our initial thoughts were that we had "trapped" a fragment of a common mineral. Some resemblance to corundum can be found (*i.e.* the structure adopted by M_2O_3 oxides such as Al_2O_3, Cr_2O_3 or Fe_2O_3), however the similarity is not striking, and there is little obvious reason for cages of M^{2+} centres adopting a core based on an M^{3+} mineral.

We therefore looked at the problem from the reverse direction, and created a "parent" lattice based on a capped trigonal-prismatic core. The result is shown in Fig. 13. The parent lattice is derived from the capped trigonal-prismatic core by making each cap on a rectangular face the centre of a further trigonal prism. This creates a lattice of alternating hexagonal and trigonal planes, with the capping/centring metal sites of the cages belonging to hexagonal planes, and the sites describing the prism belonging to the trigonal planes. It is also necessary for a good fit to the cage structures to impose a ratio of 3:1 between the repeat distance within the planes compared with the interplanar spacing. For the fit of this lattice to the metal polyhedra described above it is necessary to include three hexagonal and two trigonal layers of the lattice.

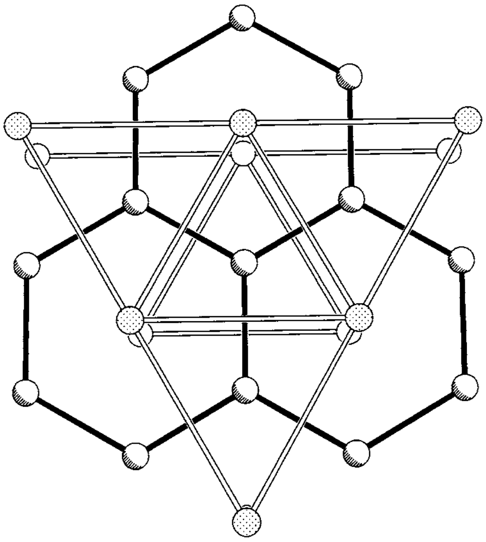


Fig. 13 Three layers of the "parent" lattice which results if the pentacapped-trigonal-prismatic core is expanded into an extended 3-D structure. One hexagonal layer is shown as lightly shaded atoms, joined by full lines. The two trigonal layers are shown as dotted or open atoms, joined by open lines.

What is immediately striking is that all the metal sites in complexes **1**–**4**, even those which do not fit well with the pentacapped-trigonal prism, fit extremely well with metal sites from within this lattice. This is illustrated in Fig. 14. Therefore all the metal sites in the sixteen structures which we have reported resulting from these reactions can be derived from this one lattice. Even more surprisingly the metal core of the cyclic, planar Ni_{12} cage[31] we have reported can also be derived from this lattice (Fig. 14).

The lattice can also be derived from $Co(OH)_2$ (which adopts the cadmium iodide structure, as does $Ni(OH)_2$). $Co(OH)_2$ is a layered structure, consisting of CoO_6 octahedra sharing edges. If every third metal centre of the $Co(OH)_2$ structure drops into an octahedral hole between the layers it creates a triangular net between the layers, and leaves a honeycomb lattice within the layer. This is illustrated in Fig. 15. This lattice is an extension of that shown in Fig. 13, the only difference being the inclusion of the oxygen atoms of the mineral.

We have previously made[32] a Co_{24} cage where the metal array is identical to the layered structure of $Co(OH)_2$. The observation here that several other structures are related to the same mineral, albeit in a less obvious way, suggests that some principle to explain the structures observed for polynuclear metal cages may be found in the future. Such a principle will require a rational method for choosing a specific mineral, an explanation of any deviations observed from the ideal mineral, and finally

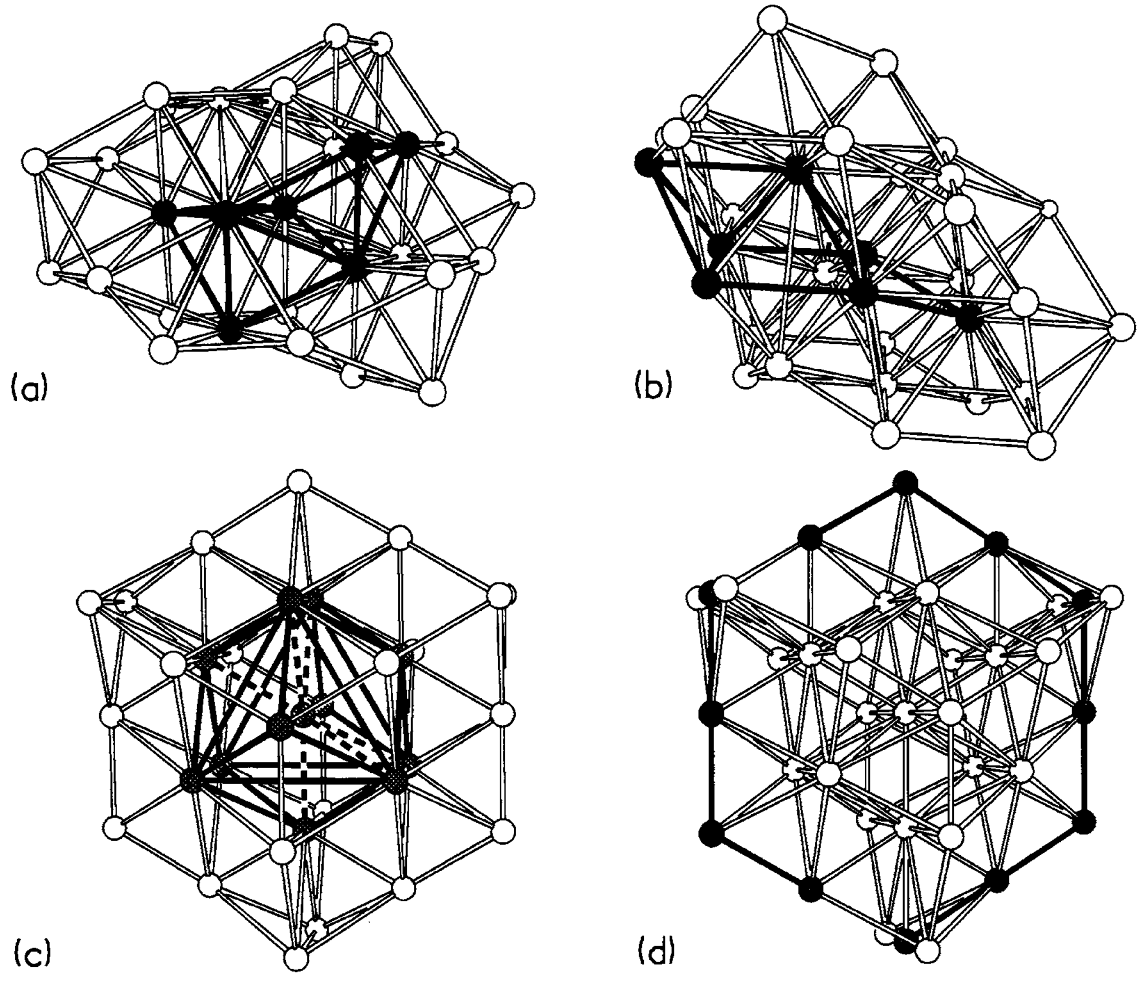


Fig. 14 The cores of metal cages (shown as shaded atoms joined by full lines) picked out of five layers of the parent lattice. The cores are for: (a) complexes **1**–**3**, **5**; (b) the asymmetric unit of **4**; (c) the pentacapped-trigonal prism $[Ni_{12}(OH)_6(mhp)_{12}(O_2CCH_2Cl)_6]$;[22] (d) the cyclic structure $[Ni_{12}(chp)_{12}(O_2CMe)_{12}(H_2O)_6(THF)_6]$.[31]

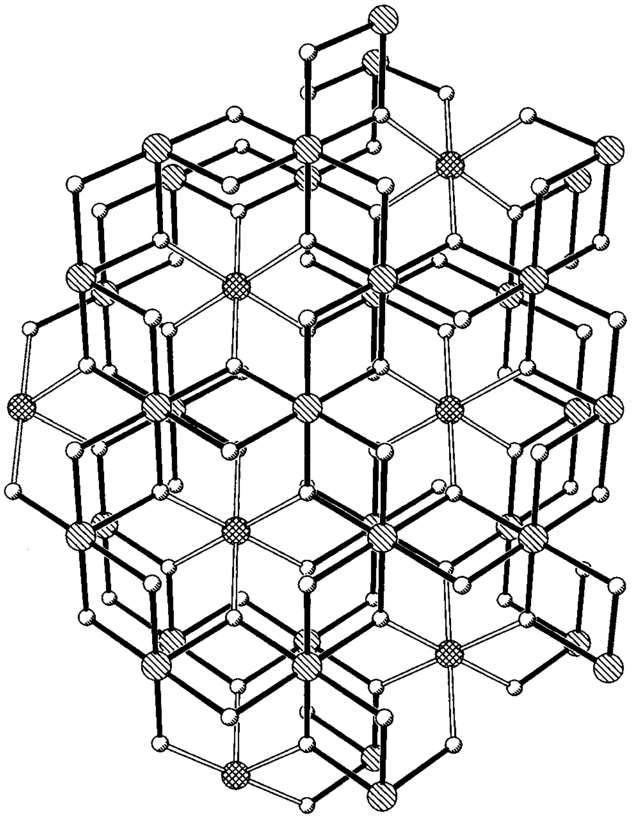


Fig. 15 Three layers of the parent lattice derived from $Co(OH)_2$. The layers of $Co(OH)_2$ are shown with the metal centres diagonally shaded (top right, bottom left) and oxygen atoms (lightly shaded) joined by full lines. The metal centres lying between the layers are shown as cross-hatched circles, joined to the layers by open lines.

an understanding of which of the metal sites of the lattice occur in the specific polymetallic core.

Acknowledgements

We are grateful to the EPSRC for funding for a diffractometer and for studentships (to E. K. B. and A. G.) and to Drs Robert Gould and Steven Harris for helpful discussions.

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