Desolvating cubes and linking prisms: routes to high-nuclearity cobalt complexes

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Four new Co complexes are reported which illustrate routes to high nuclearity species; these include a dodecanuclear 'chain of cubes' and a tridecanuclear species which features a tetranucleating phthalate ligand.

The major challenge facing chemists interested in polymetallic compounds remains design of reliable synthetic strategies.[1–5] Here we report studies where we have attempted to link small polynuclear compounds into larger units.

Reaction of $Co(O_2CMe)_2$ (2 mmol) with molten Hchp (4.2 mmol; Hchp = 6-chloro-2-pyridone) at 130 °C under N_2, followed by extraction with MeOH (30 ml) which contained NaOMe (2 mmol) gives a purple solution from which crystals of a tetranuclear Co complex can be grown in 60% yield.† X-Ray analysis‡ reveals a stoichiometry $[Co_4(\mu_3\text{-}OMe)_4(\eta^2\text{-}chp)(chp)_3(MeOH)_7]$ **1**, which has a cubane structure analogous to a Ni cubane we reported previously (see Fig. 2 in ref. 6). The complex is held together by μ_3-MeO groups, with the coordination of the Co atoms completed by chp ligands, or by MeOH. The presence of terminal solvate molecules suggests that desolvation might cause oligomerisation of such cubanes by forcing the chp ligands to bridge, thus filling coordination sites vacated by displaced MeOH.

Reaction of $CoCl_2$ (3.9 mmol) with Na(chp) (8 mmol) in MeOH (40 ml) for 3 h at 290 K, followed by evaporation to dryness leads to a material which contains **1** and other Co species.§ Heating of this material, which presumably drives off MeOH, followed by recrystallisation of the solid from CH_2Cl_2–Et_2O gives purple crystals of $[Co_{12}(chp)_{18}(OH)_4(\mu_2\text{-}Cl)_2(Hchp)_2(MeOH)_2]$ **2** suitable for X-ray analysis‡ in 15% yield.

2 is a centrosymmetric dodecanuclear species [Fig. 1(*a*)] which contains two $[Co_4O_3Cl]$ cubes linked by a central eight-membered ring involving four Co atoms and four μ-O atoms derived from chp ligands. Co(5) and Co(5a) are each part of a cube and of the eight-membered ring, with Co(6) and Co(6a) the other Co atoms within the eight-membered metallocycle. The other three Co atoms in the cube are Co(2), Co(3) and Co(4), and both Co(2) and Co(4) share μ-O atoms with Co(6) or Co(6a). The non-metal vertices of the cubes are a μ_3-O atom from chp, two μ_3-OH and a Cl. The cubes are not ideal as the Cl group only bridges Co(3) and Co(5), with a long (3.22 Å)

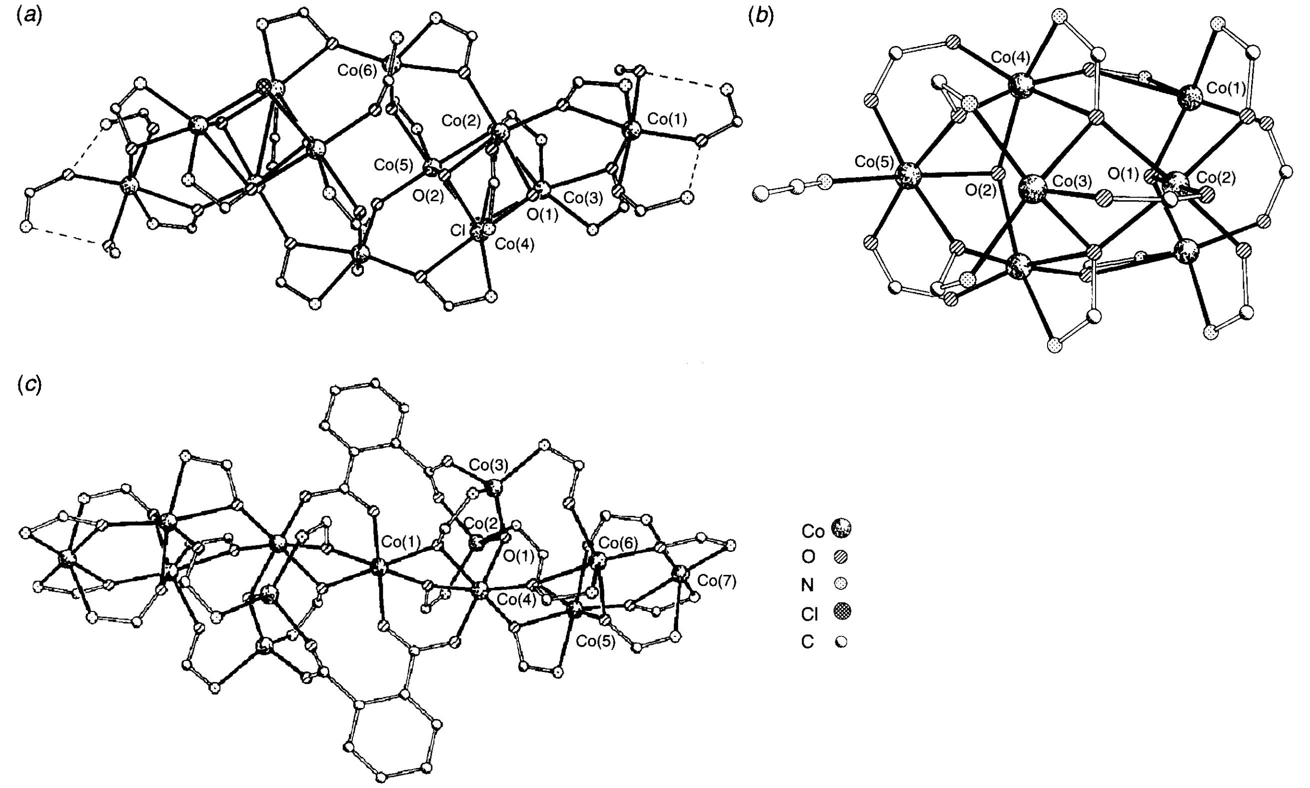

Fig. 1 The structure of (*a*) **2**, (*b*) **3**, (*c*) **4** in the crystal, only atoms involved in bridging between metals shown for clarity. (*a*) Bond length ranges (Å): Co–O (OH) 1.993–2.121, Co–O (chp) 1.979–2.393, Co–O (MeOH) 2.150, Co–N (chp) 2.048–2.187, Co–Cl 2.374–2.400 (av. esd. 0.003 Å). (*b*): Co–O (OH) 2.01–2.16 Co–O (chp) 2.01–2.38, Co–O (O_2CPh) 2.00–2.03, Co–N (chp) 2.05–2.21, Co–N (MeCN) 2.18 (av. esd. 0.02 Å). (*c*): Co–O (OH) 1.986–2.136, Co–O (chp) 1.991–2.247, Co–O (phth) 1.987–2.023, Co–N (chp) 2.067–2.214 (av. esd. 0.003 Å).

contact to Co(4). Co(4) is the only metal in **2** which is not six-coordinate; the vacant site is blocked by the distant chloride group. The shortest Co···Co contact of 2.970 Å is between Co(2) and Co(5).

The final unique site [Co(1)] is at the periphery of the molecule, attached to the cube by two μ-O atoms shared with Co(2) and Co(3). This bridging is identical to that between Co(6) and the cube. The coordination sphere of Co(1) is completed by the only residual MeOH, which suggests that synthesis of a larger oligomer involving cubes should be possible if total desolvation could be achieved.

Christou and co-workers[1] have shown that larger assemblies can be made by replacing a binucleating ligand, which holds together a small cage, with a tetranucleating ligand, which can fulfil the first function and link the cages. Therefore we performed reactions where, in addition to chp, we have benzoate or phthalate (phth) ligands present.

$CoCl_2$ (3.9 mmol) was reacted with 2 equiv. of both Na(chp) and $Na(O_2CPh)$ in MeOH (50 ml) before evaporation to dryness. The resulting purple residue was dried in air, then extracted with MeCN (25 ml). Crystals of a heptametallic complex $[Co_7(\mu_3\text{-}OH)_2(O_2CPh)_4(chp)_8(MeCN)]$ **3** [Fig. 1(*b*)]‡ grew in 2 d from this solution with a 52% yield. The polyhedron of Co atoms is irregular but is loosely based on a trigonal prism capped by Co(5) on the 'upper' triangular face. The Co atoms [Co(1), Co(1a), Co(2)] in the lower triangular face are bound to a μ_3-OH [O(1)]. The three edges of the triangle are spanned by one 1,3-bridging benzoate and two μ-O atoms derived from chp.

The upper triangular face of the prism [Co(3), Co(4), Co(4a)] is bound to the first by two μ_3-O atoms from chp, two μ-O atoms from chp and one 1,3-bridging benzoate. The Co(3)–Co(4) and Co(3)–Co(4a) edges within this face are bridged by the μ_3-O from chp and by two further chp which bind to Co(3) through the ring N and to Co(4) or Co(4a) *via* the O atom. These O atoms are themselves μ-bridging, binding to the 'capping' Co atom, Co(5). This is also attached to Co(4) and Co(4a) by 1,3-bridging benzoates and by the second μ_3-OH group [O(2)]. Five of the seven Co atoms are six-coordinate, bound to bridging and chelating benzoates, pyridonates and hydroxides. Co(5) is also six-coordinate, but the final site is occupied by MeCN. Co(3) is five-coordinate, with the vacant site pointing towards the centre of the metal polyhedron. All coordination geometries are distorted. The shortest Co···Co contact in **3** is 3.621 Å between Co(3) and Co(5).

The analogous reaction using Na_2(phth) in place of $Na(O_2CPh)$ resulted in a tridecanuclear complex, $[Co_{13}(chp)_{20}(phth)_2(OH)_2]$ **4** [Fig. 1(*c*)] which was crystallised from CH_2Cl_2–Et_2O in 10% yield. Co(1) is on an inversion centre and has an octahedral coordination geometry. It can be regarded as part of two linked Co_7 units, and is bound to four μ-O atoms from chp, all shared with Co(4) or its symmetry equivalent, and two oxygens from phth groups. The carboxylate group of which these oxygen atoms are a part bridges in a 1,3-fashion to Co(4). The second carboxylate of phth links to two further Co atoms [Co(2), Co(3)] which both have tetrahedral coordination geometries, bound to two O- and two N-donors. The Co(2)···Co(3) vector is further bridged by a μ_3-OH [O(1)], which also bonds to Co(4). The chp groups which connect Co(1) and Co(4) through the O atoms, bind to Co(2) and Co(3) through their N-donors.

This central phth-bridged region containing seven Co atoms is attached to the remaining Co atoms through bridging chp groups. Co(5), Co(6) and Co(7) are all six-coordinate, bound exclusively to N- and O-donors derived from chp groups. Co(5) and Co(6) are bound to five O and one N atoms, while Co(7) is bound to four N- and two O-donors. For each metal site at least one chp ligand is chelating, therefore geometries are distorted from octahedral due to the small bite angle. In **4** the chp ligands demonstrate three coordination modes: trinucleating, *e.g.* bound to Co(1), Co(3) and Co(4); binucleating, *e.g.* connecting Co(3) and Co(6); chelating and binucleating, *e.g.* chelating to Co(5) and additionally attached to Co(4). The dicarboxylate is tetranucleating, bonding to Co(1), Co(2), Co(3) and Co(4a).

Polynuclear cobalt complexes have been little investigated with O- and N-donors, with the only fully characterised complexes of similar size to the species reported here being Co_{12}[7] and Co_8[8] complexes; larger clusters are known with CO ligands.[9] Here we have demonstrated routes to several such species. More importantly the ideas of oligomerisation *via* desolvation and *via* introduction of rigid linking groups should prove applicable to many other systems.

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Footnotes

† Satisfactory elemental analysis were obtained for all compounds.

‡ *Crystal data*: $C_{32}H_{56}Cl_4Co_4N_4O_{16}$ (**1**·MeOH): triclinic, space group $P\bar{1}$, $a = 12.892(4)$, $b = 14.235(5)$, $c = 14.244(5)$ Å, $\alpha = 91.35(2)$, $\beta = 112.00(2)$, $\gamma = 101.43(2)°$, $U = 2362(2)$ Å^3, $Z = 2$, $R1 = 0.0424$.

$C_{107}H_{92}Cl_{32}Co_{12}N_{20}O_{30}$ (**2**·$4H_2O$·$5CH_2Cl_2$): monoclinic, space group $P2_1/n$, $a = 18.286(4)$, $b = 16.294(4)$, $c = 26.609(6)$ Å, $\beta = 108.41(2)°$, $U = 7522(3)$ Å^3, $Z = 2$, $R1 = 0.0956$.

$C_{71}H_{47}Cl_8Co_7N_9O_{19}$ (**3**·MeOH): orthorhombic, space group *Pnma*, $a = 24.034(8)$, $b = 20.018(5)$, $c = 16.304(4)$ Å, $U = 7844(4)$ Å^3, $Z = 4$, $R1 = 0.0912$.

$C_{119}H_{76}Cl_{26}Co_{13}N_{20}O_{30}$ (**4**·$2CHCl_3$): monoclinic, space group $P2/c$, $a = 17.165(5)$, $b = 18.243(7)$, $c = 26.613(8)$ Å, $\beta = 96.63(4)°$, $U = 8278(5)$ Å^3, $Z = 2$, $R1 = 0.0926$. Mo-Kα. Data collection at 150 K, structure solution and refinement were performed as in ref. 6, using SHELXS-86, G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 1990, **46**, 467; SIR92, A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343; SHELXL-93, G. M. Sheldrick, University of Göttingen, 1993. Full details will be published later. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/99.

§ Recrystallisation of this material from MeOH leads to **1** in moderate yield. Analysis indicates a mixture of products are present at the crude stage.

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