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Phosphonate ligands encourage a Platonic relationship between cobalt(II) and alkali metal ions

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Two new cobalt(II) cages are reported where the metal core has a high symmetry related to a Platonic solid; the choice of alkali metal used in the base used for deprotonation appears to influence the resulting structures.

The number of new polymetallic paramagnetic cages structurally characterised continues to grow, seemingly exponentially.[1] One feature is the comparatively irregular structures often found – which contrasts with the orderly behaviour of the metal carbonyl clusters, where the structures appear to obey rules and often the metal vertices form a fragment of a metallic lattice.[2] The seeming chaos of the paramagnetic cages is both intriguing and challenging. Still more extraordinary are the very large polyoxometallate cages reported by Müller[3] and Pope:[4] here it can be possible to identify fragments that repeat between structures, and form the "blocks" from which the cage is constructed, but where the overall structure remains incommensurate. There are major exceptions, perhaps the most exciting being "Keplerate" reported by Müller and co-workers,[5] where the thirty Fe(III) centres lie on the vertices of an Archimedean solid, the icosidodecahedron. Here we report two smaller clusters where the metal vertices lie on the vertices of Platonic solids including the tetrahedron, octahedron and icosahedron.

Phosphonates are rarely used in making polymetallic cage complexes, largely due to the extreme insolubility of the metal phosphonates. Zubieta has solved this problem for vanadates by use of solvathermal conditions,[6] while Chandrasekhar has reported an interesting dodecanuclear copper(II) cage by using a co-ligand (3,5-dimethylpyrazole) to increase solubility.[7] Recently we have shown phosphonates can be used to link trinuclear iron(III) cages into larger arrays.[8] Here we report cobalt(II) chemistry, related to the Chandrasekhar approach, but using deprotonated 6-chloro-2-pyridone (Hchp) as the co-ligand.

Hydrated cobalt chloride (2 mmol) was dissolved in MeOH (25 ml), and Hchp (3.2 mmol), $PhPO_3H_2$ (0.85 mmol) and a 0.5M NaOMe solution in methanol (10 ml) was added, giving a deep purple solution. The solution was stirred for 6 h, filtered and the solvent removed *in vacuo* to give a purple solid. Recrystallization from MeCN/Et_2O gave deep purple crystals of $[Co_6Na_8(chp)_{12}(O_3PPh)_4(MeCN)_4]$ **1** in a yield of 50%.†

Structural characterisation‡ shows formation of a regular structure (Fig. 1). The four P atoms from phenylphosphonates are found at the alternate corners of a cube, with Na atoms at the other corners – the Na atoms therefore describe a tetrahedron. The six Co(II) ions are found above each face of this central cube – hence forming an octahedron of cobalt centres. The final four Na atoms lie above four of the edges of the cube, lowering the symmetry of the assembly of P, Na and Co to D_{2d} – which is non-crystallographic.

The four phosphonates in **1** show the 7.322 bridging mode (Harris notation[10]) – which is unusual. The μ_3-O atom bridges two Na and one Co, while the two μ_2-oxygens bridge between one Na and one Co site. The chp ligands show the 3.21 or 3.31 bridging modes, chelating to a cobalt site and additionally binding to either one or two Na atoms. The cobalt sites are either six- or five-coordinate, with irregular geometries, while the coordination of Na ions is still more irregular. The four Na sites within the cube are six-coordinate, while the four "capping" Na sites are four-coordinate.

The involvement of sodium in **1** suggested that variation of the alkali metal cation might generate further new structures. Therefore in a similar reaction, hydrated cobalt chloride (2 mmol) was dissolved in MeOH (25 ml) and Hchp (4 mmol), $PhPO_3H_2$ (0.33 mmol) and 1M LiOMe solution in MeOH (4.7 ml) was added. The solution was stirred for 6 h, filtered and the solvent removed *in vacuo* to give a purple solid. Recrystallization from EtOAc/hexane gave deep purple crystals of $[Co_6Li_9(chp)_{14}(PO_4)Cl_4(Hchp)_4)$ **2** in low, but reproducible yield, *ca.* 5%. A fine purple powder is precipitated shortly after the crystals.†

The structure‡, which has crystallographic three-fold symmetry, is entirely unexpected (Fig. 2). At the centre is a bridging phosphate, which adopts the 12.3333 bridging mode: one O-atoms binds to three Co atoms, while the others each bind to three lithium centres. The twelve metal centres bound to the PO_4^{3-} lie on the vertices of an icosahedron (Fig. 3). The metal–metal contacts within this polyhedron vary with Li···Li contacts lying in the range 3.03 to 3.28 Å, the Co···Co contact 3.22 Å and the Co···Li contacts ranging from 3.33 and 3.77 Å. The presence of the phosphate must be due to decomposition of the phenylphosphonic acid used in the reaction – and this is reproducible. Phosphate is rarely found bound to metals in molecular complexes of the 3d-metals due to the insolubility of metal phosphate phases. *In situ* formation of phosphate by decomposition of a ligand is allowing its incorporation in **2**, but unfortunately this also contributes to the low yield. Formation of phosphate may account for the purple powder that is deposited almost immediately after the crystals are formed.

The final three Co(II) centres are found outside the icosahedron, lying on the points of an equilateral triangle. Four μ_3-chloride ions

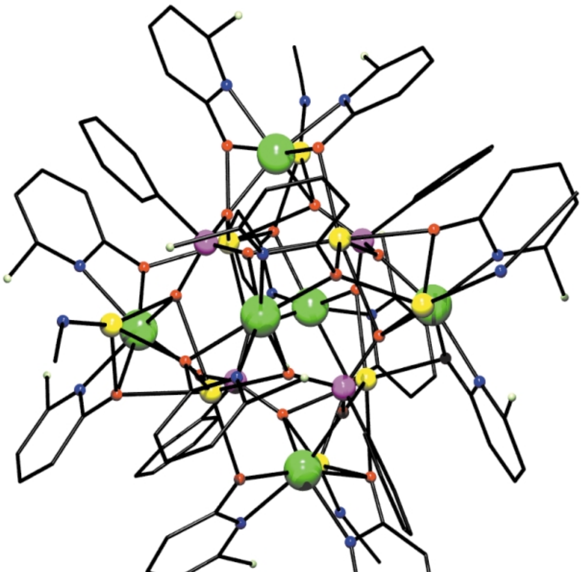

Fig. 1 The structure of **1** in the crystal. Colour scheme: Co, green; P, purple; Na, yellow; N, blue; O, red; C, black lines; Cl, light green. Bond length ranges: Co–O(O_3PPh) 2.007 – 2.045 Å.

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are also found; these lie on the points of a tetrahedron, with three bridging between one Co and two Li atoms, and the fourth (which lies on the three-fold axis) bridging three Li centres. The Li centres are all four-coordinate with tetrahedral geometries while the Co centres are all six-coordinate with distorted octahedral geometries. This distortion is chiefly due to the presence of chelating chp ligands, with a narrow "bite" angle; the pyridonates all show the 2.21 binding mode, while the four Hchp ligands present are 2.20 bridging.

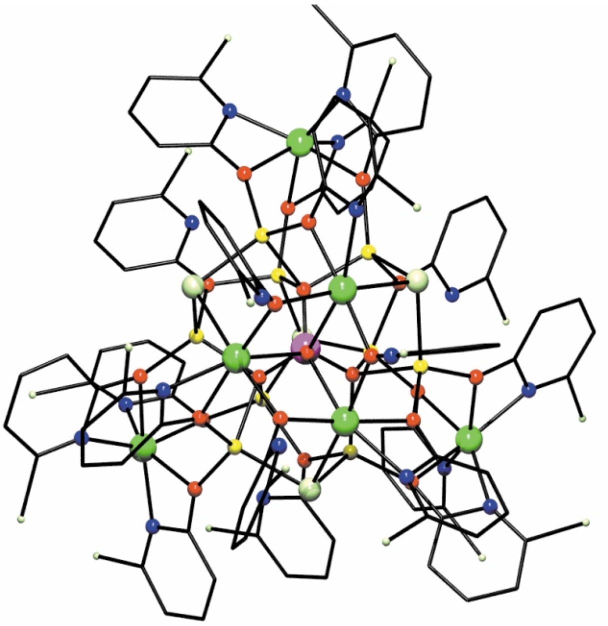

Fig. 2 The structure of **2** in the crystal. Colour scheme: as Fig. 1, with Li, light yellow.

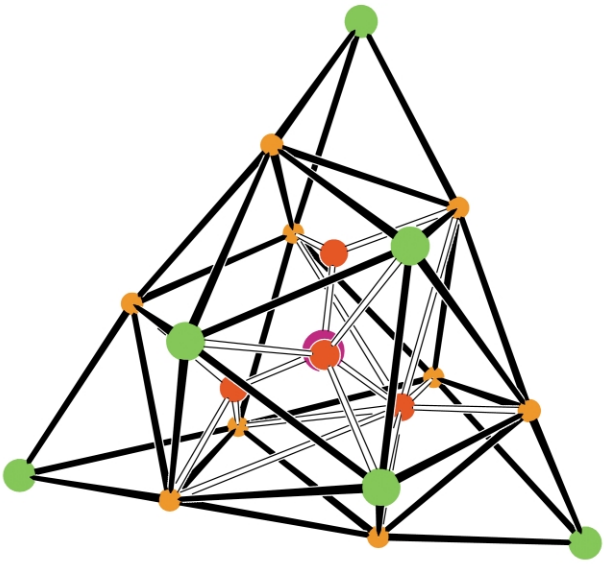

Fig. 3 The phosphate ion encapsulated in a tricapped icosahedron of metal centres in **2**. Colour scheme: as Fig. 2, except Li, orange. Heavy lines indicate the tricapped icosahedral array of metal ions, and do not imply bonding.

These results suggest two new paths to explore. The extreme flexibility of the phosphonate ligands clearly supports formation of new clusters with surprisingly high symmetry: such high symmetry has led to new physics[11] for the Keplerate phases and therefore this path is worth exploring further. The *in situ* formation of phosphate suggests a method of inclusion of phosphate as a "templating" agent for formation of new cages. Clearly our synthetic approach for the latter chemistry needs to be improved, probably by using less stable phosphonate ligands in the reactions and by examining more forcing conditions.

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Notes and references

† Anal. Calcd (Found): for **1** for $C_{92}H_{80}Co_6N_{16}O_{24}P_4Cl_{12}Na_8$: C 38.4 (37.7), H 2.8 (2.3), N 7.8 (7.4); for **2** for $C_{90}H_{58}Cl_{22}Co_6Li_9N_{18}O_{22}P$: C 36.4 (37.0). H 2.0 (2.7), N 8.5 (9.1).

‡ Crystal data for $C_{102}H_{83}Cl_{12}Co_6N_{21}Na_8O_{24}P_4$ **1**: orthorhombic, $P\,na2_1$, $a = 32.668(2)$, $b = 24.2542(17)$, $c = 16.2044(11)$ Å, $V = 12839(2)$ Å^3, $M = 3073.7$, $Z = 4$, $T = 100(2)$ K, $\mu(\text{Mo–K}_\alpha) = 1.2$ mm^{-1}, 73251 reflections measured, 25786 unique ($R_{\text{int}} = 0.0316$) which were used in all calculations, final $wR(F^2) = 0.081$ (all data). Crystal data for $C_{109.5}H_{100}Cl_{22}Co_6Li_9N_{18}O_{23}P$ **2**: trigonal, $P\bar{3}$, $a = 23.5886(12)$, $c = 15.9501(14)$ Å, $V = 7686.0(9)$ Å^3, $M = 3263.0$, $Z = 2$ (the molecule lies on a three-fold axis), $T = 100(2)$ K, $\mu(\text{Mo–K}_\alpha) = 1.4$ mm^{-1}, 45119 reflections measured, 10519 unique ($R_{\text{int}} = 0.0465$) which were used in all calculations, final $wR(F^2) = 0.174$ (all data). In **2**, atoms within the disordered solvent molecule (hexane) were not refined anisotropically, and H-atoms were not included for solvent molecules. Data collection, structure solution and refinement used the SHELX-PC programme package.[9] Full details have been deposited as CCDC 210157 and 222026 and will be published later. See http://www.rsc.org/suppdata/cc/b3/b312769a/ for crystallographic data in .cif or other electronic format.

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