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Self-assembly by ligand disassembly?—formation of an unusual dodecanuclear [Co(II)$_6$Co(III)$_6$] cluster

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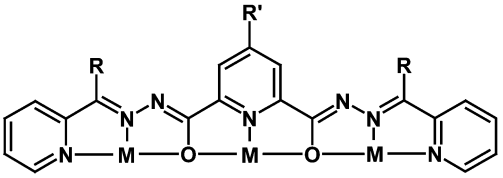
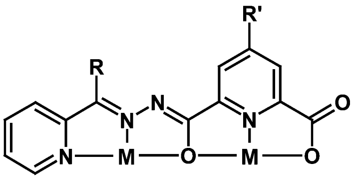
A sterically encumbered 'tritopic' picolinic-dihydrazone ligand reacts with cobalt(II) nitrate in air to give a dodecanuclear [Co(II)$_6$Co(III)$_6$] cluster, in which six ligands are hydrolyzed to mono-carboxylate analogues.

'Tritopic' ligands based on a 2,6-dipicolinic-hydrazone core, *e.g.* 2poap, represent a unique ligand class, which preferentially forms [3 × 3] nonanuclear grid complexes. Examples with Mn(II)$_9$ and Cu(II)$_9$ are well documented, and provide novel multi-spin platforms for magnetic, electronic and surface studies.[1–8] A Mn(II)$_9$ system has been shown to exhibit quantum-magneto oscillations in the field dependence of magnetic torque at low temperature.[9] 2poap and related ligands form grids with essentially square core structures, but 2popp, which has bulky phenyl end groups, exerts a major distortion in the complex [Mn$_9$(2popp)$_6$](NO$_3$)$_6$·12H$_2$O, which has a diamond shaped core.[8] However, despite the pronounced distortion, the magnetic properties are normal for grids in this class.



R'=H,R=NH$_2$(2poap);R'=Cl,R=NH$_2$(Cl2poap),R'=Cl, R=phenyl(Cl2popp) (L1),R'=H,R= phenyl(2popp)



L2

2popp and Cl2popp are produced by condensation of the appropriate precursor dihydrazide with phenyl pyridyl ketone, and are classic Schiff base ligands. Hydrolytic instability of the C=N linkages in such ligands can be promoted in the presence of metal (Lewis acid) centres. We have discovered numerous examples of such metal ion directed hydrolyses of vulnerable hydrazone ligand sites, which have only been revealed from structural studies on the reaction products.[10] The present study reports a rather unusual hydrolysis reaction of Cl2popp, in the presence of Co(II) and Co(III), leading to a novel, mixed ligand, dodecanuclear cobalt cluster.

Cl2popp (L1) was added to a solution of Co(NO$_3$)$_2$·6H$_2$O in CH$_3$CN–MeOH, and the mixture stirred in air.†A red solution formed, which deposited dark red crystals suitable for structural analysis on standing for several days.‡

The crystal structure reveals a complex with thirteen cobalt centres, with the formula $[(\text{L1–2H})_3(\text{L2–2H})_6\text{Co(III)}_6\text{Co(II)}_6(\text{H}_2\text{O})_6(\text{NO}_3)_6][\text{Co(H}_2\text{O)}_6](\text{NO}_3)_8(\text{CH}_3\text{CN})_3(\text{H}_2\text{O})_6$ (**1**), where L2 is a partially hydrolyzed ligand with a carboxylate group at a pyridine 2-position. Twelve cobalt ions form a dodecanuclear cluster (Fig. 1, viewed down the trigonal axis; phenyl rings bound to C(6) (L2) and C(31) (L1) removed for clarity; the phenyl ring bound to C(6) is disordered over two positions‡), with the [Co(H$_2$O)$_6$]$^{2+}$ cation appearing in the lattice, presumably required for overall charge balance. Several 'oxygen' atom sites have been located inside the cluster, and are assigned as water molecules (*e.g.* O(17), O(18)). The dodecanuclear cluster shows three-fold symmetry, with two almost planar hexanuclear halves, comprising three L2 ligands each binding two six-coordinate cobalt centres, which are bridged by a deprotonated hydrazone oxygen atom (O(1)). Each dinuclear subunit is bridged internally by a carboxylate in a *syn-anti* conformation (O(2)–O(3)), linking the three dinuclear subunits together *via* Co(2) to form the hexanuclear layer. The abbreviated asymmetric dinuclear core subunit is shown in Fig. 2 (Co(2) is bridged through O(3)).

The inner group of cobalt centres (Co(2); CoNO$_5$) have Co–L distances in the range 2.022–2.321 Å indicating them to be Co(II) ions. The outer group of three cobalt centres (Co(1); *cis*-CoN$_4$O$_2$) has Co–L distances in the range 1.846–1.938 Å indicating that they are Co(III) ions. Apical ligands to each Co(II) centre are monodentate nitrate (O(5)) on the outer surface, and an inner water molecule (O(14)). The hexanuclear subunits are cross-linked by three full ligands (L1), which provide an N$_2$O donor grouping from

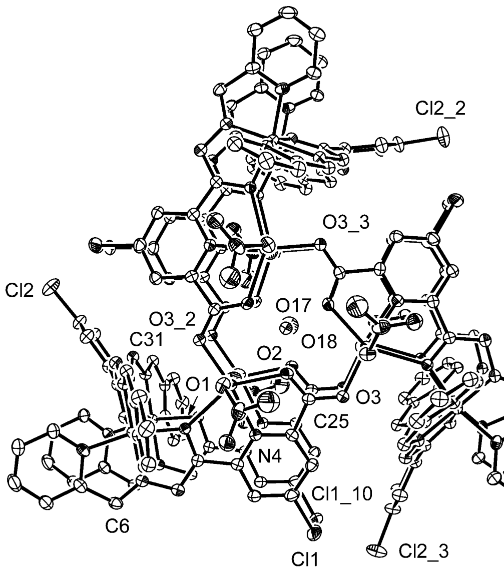


Fig. 1 Structural representation for **1**. Phenyl groups are removed for clarity.

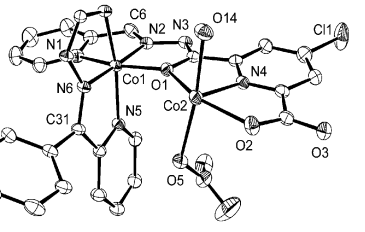


Fig. 2 Structural representation of the asymmetric dinuclear subunit in **1**.

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the ends of each ligand (the central pyridine remains uncoordinated). This can be seen more clearly in Fig. 3 (phenyl rings removed and axially bonded nitrates abbreviated to bound oxygen), which is viewed across the hexacobalt subunits, and reveals the overall structure of the triangular based prism (dimensions 20 Å across and 17.6 Å deep).

Cl2popp is synthesized in a two step process from the diethyl ester of 4-chloro-2,6-dipicolinic acid, by reaction with hydrazine, followed by reaction with phenyl 2-pyridyl ketone. Two different hydrolytically susceptible C=N linkages exist, with the hydrazone being the most vulnerable in the present case. Since ligands of this type typically produce trinuclear and nonanuclear complexes, with three ligand compartments occupied by metal ions, it is reasonable to assume that this occurs initially in the present case. The unusual grid distortion in the case of complex $[Mn_9(2popp)_6](NO_3)_6\cdot 12H_2O$,[8] would suggest a similar distortion in the present case in a putative grid, and in combination with the cobalt aerial oxidation to produce Co(III) may provide the right circumstances for metal ion promoted hydrazone hydrolysis to the carboxylic acid. A similar hydrolysis of Cl2popp occurs in the presence of copper acetate, with the formation of L2, 4-chloro-pyridine-2,6-dicarboxylate, and 3-phenyl-triazolo[1,5-*a*]pyridine, all in the same dinuclear copper complex structure.[10] It is also of interest to note that the reaction of Cl2popp with $NiCO_3$ in CH_3CN–CH_3OH gives a red square planar, neutral mononuclear complex [Ni(Cl2popp)], in high yield, with no ligand decomposition.[10]

The Co(II) centres are separated by 5.180 Å, and arranged within each hexanuclear layer in a triangular array, bridged by three *syn–anti* carboxylate groups. Such an arrangement would not be expected to lead to significant magnetic exchange between the metal centres, partly because of the long distance of separation, but also because a symmetry mis-match of magnetic orbitals would result.[11,12] This is reflected in the variable temperature magnetic properties, which show an essentially constant magnetic moment (per mole) between 300 and 100 K (10.2–11.0 μ_B), which then drops slightly to 8.5 μ_B at 2 K. The room temperature moment is consistent with the presence of seven essentially isolated Co(II) centres. The drop in moment below 100 K might signal the presence of intramolecular antiferromagnetic exchange, but if present it would be very weak.

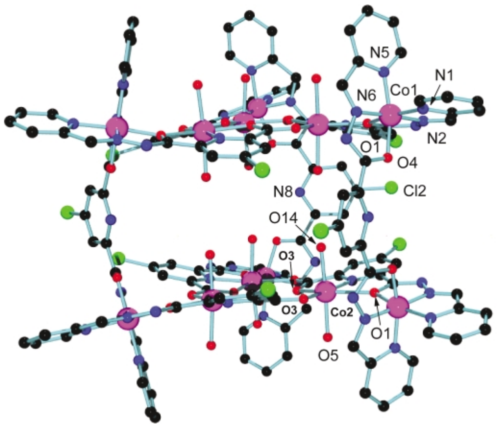

Fig. 3 Core structural representation for **1** (Povray ©); magenta = Co, blue = nitrogen, red = oxygen, black = carbon, green = chlorine).

The conclusion from this and related studies is that novel and unexpected results can occur through hydrolytic chemical reactions at vulnerable ligand sites in the presence of metal ions, and the products are frequently not fully revealed without a structural analysis. The fortuitous combination of the heptadentate ligand L1, and the pentadentate ligand L2 in the present case, has produced a novel dodecanuclear mixed oxidation state cobalt [6 + 6] cluster. A full report on this and other ligand hydrolysis reactions will be presented elsewhere.[10]

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Notes and references

† Cl2popp was prepared by reacting 4-chloro-pyridine-2,6-dihydrazide with phenyl pyridyl ketone as reported for 2popp.[8] It was characterized by MS, NMR and elemental analysis. Reaction of Cl2popp (0.10 g, 0.018 mmol) with $Co(NO_3)_2\cdot 6H_2O$ (0.17 g, 0.06 mmol) in warm CH_3CN–MeOH (1 : 1) (25 mL), without exclusion of air, produced a clear dark red solution. Dark red crystals (30 mg) formed on prolonged standing.

‡ *Crystal data*: $[(L1)_3(L2)_6Co(III)_6Co(II)_6(H_2O)_6(NO_3)_6][Co(H_2O)_6](NO_3)_8(CH_3CN)_3(H_2O)_6$. 193 K, hexagonal, $P6_3/m$, a = 24.2682(6), c = 29.470(2) Å, V = 15030.9(8) Å^3, Z = 2, D_c = 1.332 g cm^{-3}, $2\theta_{max}$ = 52.8°, μ(0.71073 Å) = 8.61 cm^{-1}. 96973 collected reflections, 10478 unique were used for refinement (570 variables). The disordered phenyl group was modeled using a rigid group for the 25% occupancy component. The 75% component was refined isotropically. The final R values were R_1 = 0.093, wR_2 = 0.326. The highest electron density on the final difference map was 1.63 e Å^{-3}. CCDC 236722. See http://www.rsc.org/suppdata/cc/b4/b405131a/ for crystallographic data in .cif format.

1 L. Zhao, C. J. Matthews, L. K. Thompson and S. L. Heath, *Chem. Commun.*, 2000, 265.
2 L. Zhao, Z. Xu, L. K. Thompson, S. L. Heath, D. O. Miller and M. Ohba, *Angew. Chem., Int. Ed.*, 2000, **39**, 3114.
3 O. Waldmann, R. Koch, S. Schromm, P. Müller, L. Zhao and L. K. Thompson, *Chem. Phys. Lett.*, 2000, **332**, 73.
4 O. Waldmann, L. Zhao and L. K. Thompson, *Phys. Rev. Lett.*, 2002, **88**, 66401.
5 L. Zhao, Z. Xu, L. K. Thompson and D. O. Miller, *Polyhedron*, 2001, **20**, 1359.
6 L. K. Thompson, L. Zhao, Z. Xu, D. O. Miller and W. M. Reiff, *Inorg. Chem.*, 2003, **42**, 128.
7 Z. Xu, L. K. Thompson and D. O. Miller, *Polyhedron*, 2002, **21**, 1715.
8 L. Zhao, Z. Xu, H. Grove, V. A. Milway, L. N. Dawe, T. S. M. Abedin, L. K. Thompson, T. L. Kelly, D. O. Miller, L. Weeks, J. G. Shapter and K. J. Pope, *Inorg. Chem.*, 2004, **43**, 3812.
9 O. Waldmann, S. Carretta, P. Santini, R. Koch, A. G. M. Jansen, T. Guidi, R. Caciuffo, G. Amoretti, L. Zhao and L. K. Thompson, *Phys. Rev. Lett.*, 2004, **92**, 96403.
10 T. L. Kelly, E. Krupicka, V. A. Milway, H. Grove, V. Niel, T. S. M. Abedin, L. K. Thompson, L. Zhao, R. G. Harvey and D. O. Miller, work in progress.
11 E. Colacio, J. M. Domínguez-Vera, M. Ghazi, R. Kivekäs, M. Klinga and J. M. Moreno, *Eur. J. Inorg. Chem.*, 1999, 441.
12 E. Colacio, M. Ghazi, R. Kivekäs and J. M. Moreno, *Inorg. Chem.*, 2000, **39**, 2882.