

# Synthesis, structural characterisation and preliminary magnetic studies of a tetraicosanuclear cobalt coordination complex

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**The highest nuclearity complex containing cobalt consists of cubic-close packed planes of hydroxide, methoxide or chloride anions, bridging cobalt(II) centres; preliminary magnetic studies indicate a high-spin ground state and the possibility of superparamagnetic behaviour.**

Polymetallic compounds of metals in high oxidation states have been reported which contain as many as 154 metal centres.<sup>1</sup> High-nuclearity clusters of low oxidation states rival these species in size, with chalcogenide bridged complexes involving 146 metals structurally characterised.<sup>2</sup> Complexes where the metals are in moderate oxidation states do not approach these behemoths in nuclearity, with the largest reported being an Fe<sub>40</sub> compound.<sup>3</sup>

The route to one of the largest of these complexes, Powell's Fe<sub>19</sub> 'crust' **2**,<sup>4</sup> involves arresting the formation of iron hydroxide in an aqueous solution by addition of a polydentate ligand; the rate of nucleation can be controlled by pH and by the iron:ligand ratio. We reasoned that an alternative procedure would be to perform reactions in solvents with a known propensity for absorbing atmospheric moisture which might thus serve as a source of bridging hydroxides. The solvent we chose for these experiments was ethyl acetate, from which an Fe<sub>17</sub> complex has previously been synthesised using this approach.<sup>5</sup> Ethyl acetate can contain up to 3% by mass of dissolved water; in these experiments the water content is around 0.1%.

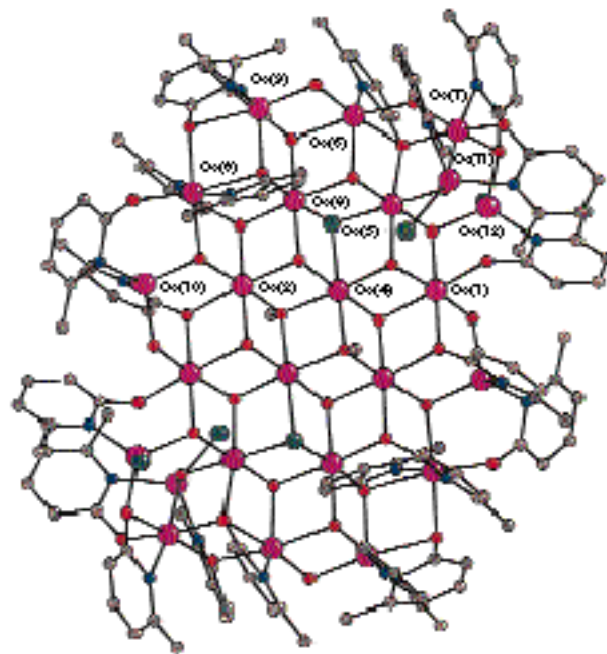
Reaction of CoCl<sub>2</sub> (3.9 mmol) with Na(mhp) (Hmhp = 2-methyl-6-hydroxypyridine) (8 mmol) in MeOH (40 ml) for 24 h at 290 K, followed by evaporation to dryness gives an uncharacterised purple paste. Dissolution of this paste in ethyl acetate, followed by filtration, gave purple crystals† in 3 days. The synthesis is reproducible, however the yield varies between 5 and 20%, possibly depending on the exact water content of the EtOAc used. Structural analysis‡ reveals a complex of formula [Co<sub>24</sub>(μ<sub>3</sub>-OH)<sub>14</sub>(μ-OH)<sub>4</sub>(μ<sub>3</sub>-OMe)<sub>2</sub>(μ<sub>3</sub>-Cl)<sub>2</sub>Cl<sub>4</sub>(mhp)<sub>22</sub>] (Fig. 1) which has a centrosymmetric structure related to many minerals, and indeed to **2**.<sup>4</sup> The cages pack parallel to the crystallographic *ab*-plane.

The structure is based on [Co<sub>3</sub>(OH)<sub>4</sub>]<sup>2+</sup> cubes with one corner missing, and in some cases with one of the hydroxide vertices occupied by methoxide or chloride groups. The array is therefore held together by OH bridges. Of the twelve crystallographically independent Co sites, five [Co(1), Co(2), Co(3), Co(4), Co(5)] have a coordination geometry close to a regular octahedron. There are no chelating ligands attached to these metal sites. Three further sites [Co(6), Co(7), Co(8)] have one chelating ligand and four monodentate ligands attached, and have more distorted octahedral geometries. Co(12) also has one chelating ligand and three further contacts, and is probably best described as based on a distorted tetrahedral geometry [four bonds between 1.971(5) and 2.265(3) Å] with one much longer contact [2.884(5) Å]. The final three distinct sites [Co(9), Co(10), Co(11)] each have two chelating mhp ligands attached, with in each case the bond to the O-donor much longer than the bond to the N-donor of the group. Two further monodentate

ligands lead to a coordination geometry best described as involving four short contacts in a distorted tetrahedral array [1.971(5)–2.282(3) Å] and two longer contacts [2.310(5)–3.022(5) Å]. The shortest Co...Co contact observed in **1** is 3.014(3) Å between Co(7) and Co(11).

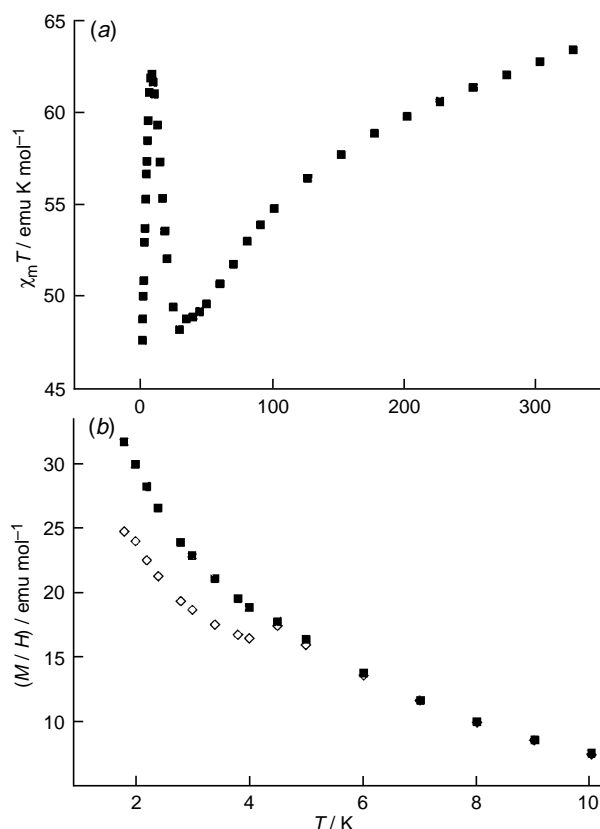
The exterior of the molecule is covered by twenty-two pyridonate ligands. These adopt three distinct bonding modes: binucleating, binding to differing Co atoms through the N- and O-donors; chelating to one Co atom and then bridging to a second Co through the exocyclic O atom; trinucleating, binding to one Co through the ring nitrogen only, and bridging two further Co centres through the oxygen. Such behaviour is typical for these ligands, and perhaps explains why such a simple bridging ligand can stabilise such a large metal-hydroxide structure where previously it has been suggested a polydentate ligand is required.

Preliminary magnetic studies§ of **1** have been performed [Fig. 2(a)]. At room temperature the value of the product  $\chi_m T$  is ca. 63 emu K mol<sup>-1</sup> ( $\chi_m$  is the molar magnetic susceptibility). We assume that this value corresponds to that for 24 non-interacting *S* = 3/2 centres, which would lead to a calculated value of 64.8 emu K mol<sup>-1</sup> [assuming *g* = 2.4, which is reasonable for high-spin Co<sup>II</sup>].  $\chi_m T$  declines steadily until 30 K where it increases sharply to a value of 62 emu K mol<sup>-1</sup> at 8 K.



**Fig. 1** The structure of **1** in the crystal. Selected bond length ranges (Å): Co–O(hydroxide) 1.971–2.194, Co–O(methoxide), 2.054–2.120, Co–O(mhp), 2.019–2.376, Co–N(mhp), 2.024–2.246, Co–Cl, 2.265–2.608 Å (av. esd 0.005 Å). These ranges treat Co(9)–Co(12) as four-coordinate and exclude the longer contacts. (Co, magenta; O, red; N, blue; Cl, green; C, grey. Figure drawn using CAMERON.<sup>9</sup>)

Below this temperature it falls again, possibly due to intermolecular interactions or zero-field splitting within the spin ground state. If the 8 K value is due to a non-degenerate spin state we can estimate that this is approximately an  $S = 9$  state, however further experiments are required to confirm this estimation. Given the structural resemblance between **1** and **2**,<sup>4</sup> a high-spin state would be unsurprising as the latter has a ground state of at least  $S = 33/2$ . More exciting are differences observed between the field-cooled and zero-field cooled  $M/H$  curves of **1** [Fig. 2(b)] ( $M$  = magnetisation,  $H$  = applied field). This provides evidence for freezing of the spins and may be an indication of superparamagnetic behaviour. Such behaviour has been observed for nanoscale cobalt particles prepared in inverse micelles<sup>10</sup> and for a dodecanuclear manganese complex.<sup>11</sup>



**Fig. 2** (a) Plot of  $\chi_m T$  vs.  $T$  for **1** measured in a 1000 G field. (b) Plot of  $M/H$  vs.  $T$  for **1** measured in a 100 G field; zero-field cooled  $M/H$  shown as open diamonds, field-cooled as filled squares. ( $M/H = \chi_m$  if  $M$  is linear with  $H$ ).

Further studies are being undertaken to confirm this behaviour.

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#### Footnotes

† Elemental analysis for **1**: Found: C, 37.3; H, 3.7; N, 7.0. Calc., C, 36.8; H, 3.6; N, 7.0%.

‡ *Crystal data* for  $C_{134}H_{156}Cl_6Co_{24}N_{22}O_{42} \cdot C_4H_8O_2$  **1**: triclinic, space group  $P\bar{1}$ ,  $a = 15.459(6)$ ,  $b = 18.619(8)$ ,  $c = 21.402(9)$  Å,  $\alpha = 76.43(3)$ ,  $\beta = 70.04(2)$ ,  $\gamma = 72.70(2)^\circ$ ,  $U = 5467(4)$  Å<sup>3</sup>,  $M = 4461.9$ ,  $Z = 1$  (the molecule lies on an inversion centre),  $T = 220.0(2)$  K,  $R_1 = 0.0572$ . Data collection, structure solution and refinement were performed as detailed in ref. 5 using programs SHELXS-86,<sup>6</sup> SHELXL-93<sup>7</sup> and PLATON.<sup>8</sup> 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 182/412.

§ Variable-temperature magnetic measurements on **1** in the region 1.8–325 K were made using a SQUID magnetometer (Quantum Design) with samples sealed in gelatine capsules. Field-cooled/zero-field cooled measurements were made in a 100 G field, all other measurements in a 1000 G field. The data have not been adjusted for the diamagnetism of the sample. Compound **1** was also studied embedded in silicon grease to confirm that crystallite orientation was not playing a significant part in the observed behaviour. The magnetic data are available as supplementary material from the authors on request.

#### References

- 1 A. Müller, K. Krickemeyer, J. Meyer, H. Bögge, F. Peters, W. Plass, E. Diemann, S. Dillinger, F. Nonenbruch, M. Randerath and C. Menke, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2122.
- 2 H. Krautscheid, D. Fenske, G. Baum and M. Semmelmann, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1303.
- 3 J.-F. You, G. C. Papafethymiou and R. C. Holm, *J. Am. Chem. Soc.*, 1992, **114**, 2697.
- 4 A. K. Powell, S. L. Heath, D. Gatteschi, L. Pardi, R. Sessoli, G. Spina, F. Del Giallo and F. Pieralli, *J. Am. Chem. Soc.*, 1995, **117**, 2491.
- 5 S. Parsons, G. A. Solan and R. E. P. Winpenny, *J. Chem. Soc., Chem. Commun.*, 1995, 1987.
- 6 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- 7 G. M. Sheldrick, SHELXL-93, University of Göttingen, 1993.
- 8 P. van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, 194.
- 9 L. J. Pearce, C. K. Prout and D. J. Watkin, CAMERON: a program for graphical representation of structural data, Chemical Crystallography Laboratory, University of Oxford, 1994.
- 10 J. P. Chen, C. M. Sorensen, K. J. Klabunder and G. C. Hadjipanayis, *J. Appl. Phys.*, 1994, **78**, 6318.
- 11 R. L. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1993, **115**, 1804.

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