High nuclearity cobalt–copper and nickel–copper co-ordination complexes

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The synthesis, structures and some properties of new M–Cu complexes of pyridonate ligands have been reported (where M = Co or Ni): these are a nonanuclear complex $[Co_7Cu_2(OH)_2(chp)_{10}(O_2CMe)_6]$ and two octanuclear complexes $[M_6Cu_2(\mu_3\text{-}OH)_4(mhp)_2(O_2CPh)_{10}(Hmhp)_4(H_2O)_2]$ (Hchp and Hmhp = 6-chloro- and 6-methyl-2-pyridone respectively).

We have been using pyridonate ligands to stabilise polynuclear complexes of 3d metals[1–3] and heterometallic Cu–Ln complexes (where Ln = any lanthanoid).[4–6] We were curious whether we could expand this work further to synthesise heterometallic complexes of 3d metals, in this case cobalt or nickel and copper, using routes designed for homometallic species. Although a number of di- and tri-nuclear Co–Cu and Ni–Cu species are known,[7–9] higher nuclearity species are limited and thus far have only been found with copper(I).[10–12] A polymer containing both Co and Cu in the +2 oxidation state has also been reported.[13] Here we report molecular octa- and nona-nuclear species containing Cu^{II} and either Co^{II} or Ni^{II} centres.

Cobalt acetate (4 mmol) and copper acetate (4 mmol) were intimately mixed with 6-chloro-2-pyridone (Hchp) (16 mmol) and fused at 130 °C. After 1 h the acetic acid formed was removed by heating under reduced pressure for 20 min and the resultant paste was extracted with CH_2Cl_2 (25 cm^3) and filtered. Purple crystals were formed in 60% yield (based on Co) by diffusion of diethyl ether vapour into this solution and structural analysis† showed formation of a nonametallic species $[Co_7Cu_2(OH)_2(chp)_{10}(O_2CMe)_6]$ **1** (Fig. 1).

The metal co-ordination sites were assigned to the differing metals based on structure refinement and on elemental analysis‡ by atomic absorption spectroscopy. The elemental analysis indicates a Co_7Cu_2 core and X-ray crystallographic refinement leads to consistent displacement parameters for the metal sites only if they are assigned as shown in Fig. 1. These results lead to the cobalt sites being a mixture of five six-co-ordinate, each with a geometry based on a distorted octahedron, and two five-co-ordinate sites [Co(5) and Co(9)]. The remaining two sites are also five-co-ordinate with extremely distorted geometries, typical of copper(II). Refining all five-co-ordinate sites as copper atoms leads to a marked increase in the displacement parameters for M(5) and M(9) only. All five-co-ordinate sites are bound to two N- and three O-donors, Co(2) and Co(6) are bound to one N and five O atoms and the remaining three Co sites are bound exclusively to O donors.

The polyhedron defined by the metal sites is extremely irregular (Fig. 1). The Co sites can be described as belonging to four oxygen-centred Co triangles, with Co(1) a vertex of all four triangles. Thus Co(1), Co(2), Co(4) and Co(1), Co(6), Co(8) form triangles about μ_3-oxygen atoms from chp ligands. The atoms Co(1), Co(4), Co(5) and Co(1), Co(8), Co(9) describe triangles about μ_3-hydroxides. This Co_7 array is far from planar, with Co(2), Co(4), Co(6) and Co(8) within one plane, and Co(1), Co(5) and Co(9) considerably above this plane. The two Cu atoms are also part of O-centred triangles; Cu(3), Co(2),

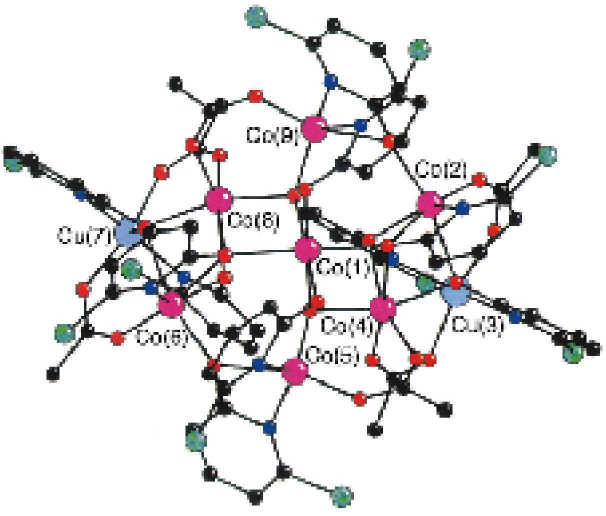

Fig. 1 The structure of the nonanuclear complex **1**. Bond length ranges: Co–O (from OH) 2.007 to 2.107, Co–O (O_2CMe) 1.974 to 2.032, Co–O (chp) 1.977 to 2.368, Co–N (chp) 2.055 to 2.100, Cu–O (O_2CMe) 1.922 to 1.940, Cu–O (chp) 2.412 and 2.426, Cu–N (chp) 1.981 to 2.016 Å [ave. estimated standard deviation (e.s.d.) 0.007 Å] (C, black; Cl, green; N, blue; Co, pink; Cu, light blue; O, red. Figure produced with CAMERON[15])

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† Crystal data for $C_{64}H_{54.5}Cl_{14}Co_7Cu_2N_{10}O_{25.25}$ **1**: $M = 2403.6$, monoclinic, space group $P2_1/n$, $a = 14.523(4)$, $b = 38.611(14)$, $c = 16.826(5)$ Å, $\beta = 112.20(3)^\circ$, $U = 8736$ Å^3, $Z = 4$, $T = 150.0(2)$ K, purple lath, 0.66 × 0.37 × 0.14 mm, $\mu = 2.28$ mm^{-1}; $R1 = 0.0625$ for 8083 data with $F > 4\sigma(F)$, $wR2 = 0.1699$ for 11 382 independent reflections ($2\theta \leqslant 45^\circ$) and 106 restraints.[14]

Crystal data for $C_{106}H_{98}Co_6Cu_2N_6O_{32}\cdot 2C_6H_7NO\cdot 5.6C_4H_8O_2$ **2**·2Hmhp·5.6EtO_2CCH_3: $M = 3160.2$, triclinic, space group $P1$, $a = 14.633(6)$, $b = 17.143(7)$, $c = 18.038(8)$ Å, $\alpha = 94.95(2)$, $\beta = 111.54(2)$, $\gamma = 114.59(2)^\circ$, $U = 3671$ Å^3, $Z = 1$ (the molecule lies on an inversion centre), $T = 150.0(2)$ K, yellow-brown block, 0.56 × 0.47 × 0.27 mm, $\mu = 1.03$ mm^{-1}; $R1 = 0.0638$ for 9138 data with $F > 4\sigma(F)$, $wR2 = 0.1747$ for 12 890 independent reflections ($2\theta \leqslant 50^\circ$) and 94 restraints.[14]

Crystal data for $C_{106}H_{98}Cu_2N_6Ni_6O_{32}\cdot 2C_6H_7NO\cdot 4.8C_4H_8O_2$ **3**·2Hmhp·4.8EtO_2CCH_3: $M = 3087.8$, triclinic, space group $P1$, $a = 14.569(9)$, $b = 17.036(10)$, $c = 17.394(10)$ Å, $\alpha = 94.93(3)$, $\beta = 111.27(3)$, $\gamma = 114.53(3)^\circ$, $U = 3515$ Å^3, $Z = 1$ (the molecule lies on an inversion centre), $T = 150.0(2)$ K, green lath, 0.47 × 0.12 × 0.08 mm, $\mu = 1.89$ mm^{-1}; $R1 = 0.0814$ for 6087 data with $F > 4\sigma(F)$, $wR2 = 0.2472$ for all 10 178 independent reflections ($2\theta \leqslant 120^\circ$) and 336 restraints.[14] CCDC reference number 186/680.

‡ Complex **1**. Found: C, 33.7; H, 2.4; Co, 18.6; Cu, 5.4; N, 6.1. Calc. for **1**: C, 33.6; H, 2.5; Co, 18.6; Cu, 5.7; N, 6.3%. Complex **2**. Found: C, 53.1; H, 4.0; Co, 15.3; Cu, 4.5; N, 4.3. Calc. for **2**·2Hmhp: C, 53.3; H, 4.0; Co, 13.3; Cu, 4.8; N, 4.2%. Complex **3**: Found: C, 52.6; H, 4.0; Cu, 5.1; N, 4.1; Ni, 14.2. Calc. for **3**·Hmhp: C, 52.6; H, 3.9; Cu, 5.0; N, 3.8; Ni, 13.8%.

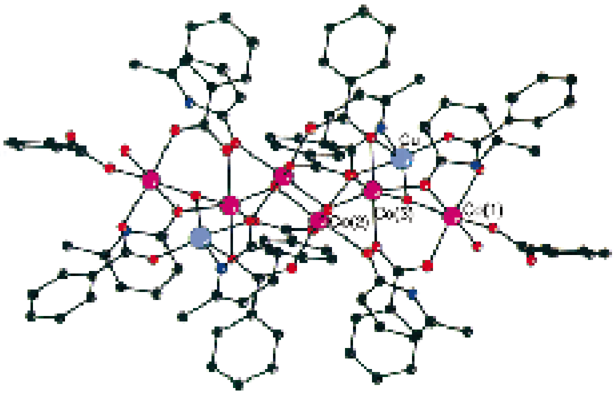

Fig. 2 The structure of the octanuclear complex **2**. Bond length ranges: Co–O (from OH) 2.019 to 2.119, Co–O (O_2CPh) 2.045 to 2.145, Co–O (mhp) 2.114 to 2.193, Cu–O (OH) 1.917, Cu–O (O_2CPh) 1.924 and 2.395, Cu–O (mhp) 2.027, Cu–N (mhp) 2.030 Å (ave. e.s.d. 0.004 Å). Complex **3** is isostructural. Bond length ranges: Ni–O (from OH) 1.952 to 2.080, Ni–O (O_2CPh) 1.965 to 2.081, Ni–O (mhp) 2.055 to 2.143, Cu–O (OH) 1.875, Cu–O (O_2CPh) 1.883 and 2.436, Cu–O (mhp) 1.972, Cu–N (mhp) 1.975 Å (ave. e.s.d. 0.006 Å) (details as in Fig. 1)

Co(4) and Cu(7), Co(6), Co(8) each define triangles about μ_3-O atoms from chp units. The Cu atoms lie below the plane of Co(2), Co(4), Co(6) and Co(8).

The co-ordination modes adopted by the chp ligands are complicated. Some chp ligands use both possible donor sites, binding to one metal through both N- and O-donors [*e.g.* Co(2), Co(6), Cu(3), Cu(7)] while providing the central μ_3-O atom in four of the six metal triangles. Other chp ligands chelate to one metal [*e.g.* Co(5), Co(9)] while bridging in a μ_2 manner using the exocyclic oxygen [*e.g.* between Co(5) and Co(6), or Co(2) and Co(9)]. Finally two chp ligands act as 1,3-bridges, binding to one metal through the N-donor and to a second through the oxygen [*e.g.* Co(1) and Co(9) or Co(1) and Co(5)]. The six acetate ligands bridge edges of the metal triangles in a 1,3-fashion.

We have thus far been unable to obtain the nickel analogue of **1**, however a similar reaction in which metal benzoate salts were fused with 6-methyl-2-pyridone (Hmhp) at 130 °C works for both cobalt and nickel benzoate (2.7 mmol of each metal benzoate was used and 10.7 mmol of Hmhp). Crystals were grown by extracting the paste with EtO_2CCH_3 (25 cm^3), and allowing the solution to stand at room temperature. Structural analysis† shows isostructural complexes with stoichiometries of $[M_6Cu_2(\mu_3\text{-}OH)_4(mhp)_2(O_2CPh)_{10}(Hmhp)_4(H_2O)_2]$ (M = Co **2** or Ni **3**) (Fig. 2). Again the structures are dominated by oxygen-centred metal triangles. Thus for complex **2**, at the midpoint of the complex is a bitriangular unit sharing an edge, with Co(2) and Co(2a) in the common edge and Co(3) or its symmetry equivalent completing the triangles. The atoms Co(3) and Co(3a) are present in the other crystallographically unique triangle, made up of Co(3), Co(1) and Cu. At the centre of each triangle is a μ_3-hydroxide. The three unique Co sites are all bound to an octahedral array of O donors, while the one Cu site is bound to four O donors and one N atom. Again assignment of metal sites was made on the basis of both X-ray crystallographic refinement and elemental analysis.‡ For complex **2** analysis gave a cobalt content a little higher than that calculated.

The bridging in complexes **2** and **3** is dominated by the carboxylate ligand, whereas in **1** the chp groups played the chief role. Three of the benzoates within the asymmetric unit bridge in a 1,3-fashion; one is trinucleating bridging Co(2a), Co(3) and Cu; the final unique benzoate is monodentately bound to Co(1), but forms a strong H-bond to a terminally co-ordinated water molecule. Two of the unique pyridone ligands are protonated, and bound only through the O atom, although even here variety is found as one Hmhp bridges between Co(1) and Co(3), while the second Hmhp is terminally bound to Co(2). The only mhp group in the asymmetric unit chelates to the copper site and also binds to Co(2) through the O atom.

These results again illustrate the extraordinary structural flexibility of mixed carboxylate–pyridonate systems. The ratio of metals in the reaction mixture does not appear to influence the reaction product. In both cases a side-product of the reaction appears to be homometallic copper pyridonate complexes; for **1** it is the known complex $[Cu_2(chp)_4]$.[16] The side-products observed explain the lower Cu : Co ratio in the structurally characterised complexes than in the substrates.

Initial magnetic studies§ of complexes **1** and **3** indicate antiferromagnetic exchange between the metals causing a decrease in the product $\chi_m T$ as the temperature is lowered (χ_m is the molar magnetic susceptibility). For **1** the measured value for $\chi_m T$ of 19.2 cm^3 K mol^{-1} at room temperature is close to that expected for a Co_7Cu_2 compound with non-interacting centres (calculated value for $\chi_m T = 18.9$ cm^3 K mol^{-1} for $g_{Co} = 2.35$ and $g_{Cu} = 2.10$). For complex **3** the room temperature value of $\chi_m T$ is 9.1 cm^3 K mol^{-1}, again similar to that expected for a non-interacting array of Ni_6Cu_2 (calculated value for $\chi_m T = 8.4$ cm^3 K mol^{-1} for $g_{Ni} = 2.25$ and $g_{Cu} = 2.10$). In both cases the value of $\chi_m T$ measured at 2 K is below 2 cm^3 K mol^{-1}, indicating a ground state with $S = 1.5$ at most.

Acknowledgements

We thank the EPSRC for studentships (to E. K. B. and S. G. H.) and for funding for a diffractometer and a SQUID susceptometer.

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§ Variable-temperature magnetic measurements in the region 2–300 K were made on a SQUID magnetometer (Quantum Design) in a field of 1000 G (G = 10^{-4} T) on samples sealed in gelatin capsules. In all cases diamagnetic corrections for the sample holders and samples were applied to the data.

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Received 18*th June* 1997; *Communication* 7/04273F