Reactions of a Dimeric Copper Compound: Synthesis and Structures of New Dinuclear, Tetranuclear, Octanuclear and Polymeric Copper Complexes

Alexander J. Blake, Craig M. Grant, Paul E. Y. Milne, Jeremy M. Rawson and Richard E. P. Winpenny*

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, Scotland EH9 3JJ

Four reactions of $Cu_2(chp)_4$ (where chp = the anion of 6-chloro-2-pyridone) are reported which lead to new dinuclear, tetranuclear, octanuclear and polymeric copper complexes all of which have been structurally characterised.

We have been investigating the use of the anion of 2-pyridone and related ligands as bridges between unlike metal atoms, in particular copper and lanthanoids.[1–4] While carrying out this work we became aware that a dimeric copper complex $Cu_2(chp)_4$ 1 (chp = C_5H_3ClNO, the anion of 6-chloro-2-pyridone) displayed unusual reactivity with a number of common reagents and this has led us to further examine these reactions. We report here the preliminary results of our studies into this chemistry. A tetranuclear copper(I) complex of 6-methyl-2-pyridone[5] and a dinuclear copper(II) complex of 3-ethyl-2-pyridone[6] have been reported previously.

1, synthesised as described previously,[3] dissolves in dichloromethane to give a dark-red solution which is EPR silent, indicating strong interaction of the two copper centres. Addition of a variety of donor solvents such as methanol, pyridine, and even diethyl ether causes the solution to become green and EPR studies suggest the presence of isolated Cu^{II} centres. This is consistent with dissociation of the dimeric copper complex into $Cu(chp)_2(S)_2$ (where S = solvent molecules) and other similar fragments, but we were unable to crystallise any of these dissociated species as slow evaporation of the solution led to isolation of 1. However, from a dilute solution of 1 (0.02 mmol) in a mixture of 1:1 methanol:dichloromethane (10 ml) lilac crystals grew which structural analysis[†] reveals contain $Cu_4(chp)_4(OMe)_4$ 2. The yield for this reaction is *ca.* 40%.

The structure of 2 is shown in Fig. 1 and consists of a parallelogram of copper atoms with alternate sides bridged either by two chp ligands or by two methoxides. Each copper is four coordinate, bound to three oxygens and one nitrogen donor. The inter-metal distances are Cu(1)–Cu(2) 2.966(1) and Cu(1)–Cu(2a) 2.811(1) Å. The copper–oxygen distances vary between 1.896 and 1.927 Å while the Cu–N distances are longer, averaging 1.993 Å. The largest divergence from square
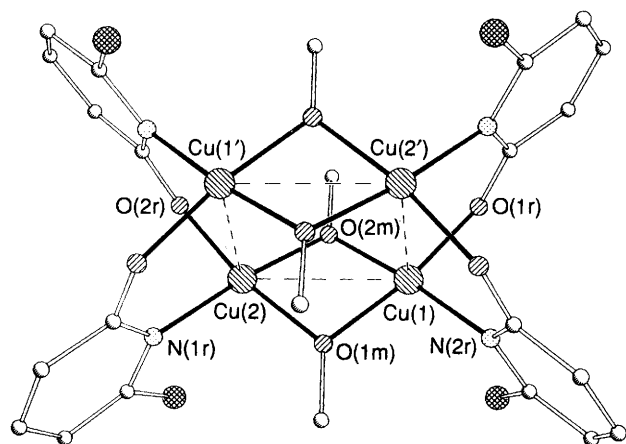
planar geometry occurs for the acute angle between the two bridging methoxide oxygens which averages 76.1(1)°.

In an attempt to isolate a dissociated, mononuclear product, potentially bidentate ligands were used. Reaction of 1 with bipyridine in CH_2Cl_2 gave a green solution which displayed an EPR spectrum consistent with a square planar CuN_4 centre (CH_2Cl_2, 293 K: g = 2.143, a_{Cu} = 59.6 G; CH_2Cl_2, 77 K: g_z = 2.279, a_z = 177 G, g_{xy} = 2.089). Crystallisation by diffusion of ether vapour into this solution gave dark green plates of 3 in 92% yield. Structural analysis[†] reveals a centrosymmetric dimer of formula $[Cu(chp)_2(bipy)]_2$ as shown in Fig. 2. As a powder the compound is EPR silent, presumably because of strong anti-ferromagnetic coupling of the Cu ions bridged by two μ_2-oxygens from chp units. The copper atoms have square pyramidal coordination to an N_2O_3 donor set, which is inconsistent with the EPR spectra in solution and as a frozen glass. Despite the fact that chp remains deprotonated[‡] the ring nitrogens are not involved in bonding to copper, nor are they involved in any hydrogen bonding. This is an unprecedented coordination mode for deprotonated pyridone ligands, although neutral pyridone ligands have been shown to bridge through the exocyclic oxygen alone.[7] The Cu–Cu distance of 3.33 Å is much longer than the metal–metal distances in 2.

Reaction of 1 (0.024 mmol) with ethane-1,2-diol (2 ml) in a mixture of CH_2Cl_2 (15 ml) and MeCN (10 ml) gave a small quantity of dark green crystals, yield *ca.* 14%, which structural analysis[†] revealed to be a one-dimensional polymer of stoichiometry $[Cu_3(chp)_4(OCH_2CH_2OH)_2]_n$ 4 (Fig. 3). Unlike in 2 and 3 there are two chemically distinct copper sites in the asymmetric unit. Cu(1) is bound to two oxygens from the deprotonated diol, one chp oxygen and one chp nitrogen in a similar arrangement to the copper sites in 2. Cu(1) shares the two diol oxygens with its symmetry equivalent, forming a Cu_2O_2 ring. Cu(1) is also bridged to Cu(2) by two chp ligands. Cu(2) is on a crystallographic inversion centre and is bound to two N and two O donors from chp units. The four chp ligands
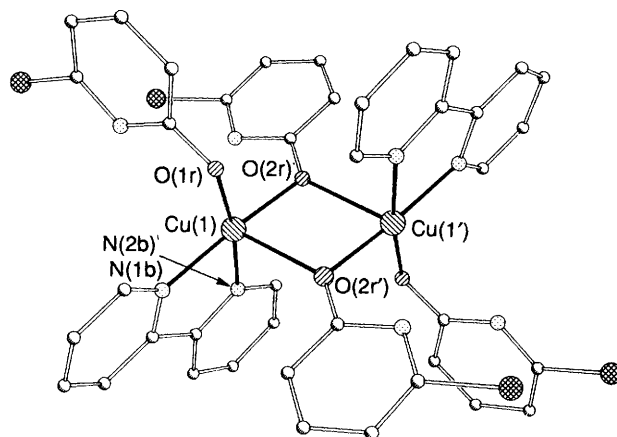

Fig. 1 The structure of 2 in the crystal. Selected bond lengths and angles: Cu(1)–O(1M) 1.918, Cu(1)–O(2M) 1.896, Cu(1)–O(1R) 1.917, Cu(1)–N(2R) 1.989, Cu(2)–O(1M) 1.924, Cu(2)–O(2M) 1.901, Cu(2)–O(2R) 1.927, Cu(2)–N(1R) 1.997 Å (av. esd 0.003 Å); O(1M)–Cu(1)–O(2M) 76.24, O(1M)–Cu(1)–O(1R) 170.34, O(1M)–Cu(1)–N(2R) 97.75, O(2M)–Cu(1)–O(1R) 94.26, O(2M)–Cu(1)–N(2R) 173.91, O(1R)–Cu(1)–N(2R) 91.70, O(1M)–Cu(2)–O(2M) 76.00, O(1M)–Cu(2)–O(2R) 169.16, O(1M)–Cu(2)–N(1R) 97.68, O(2M)–Cu(2)–O(2R) 93.27, O(2M)–Cu(2)–N(1R) 173.67, O(2R)–Cu(2)–N(1R) 93.04° (av. esd 0.12°).

Fig. 2 The structure of 3 in the crystal. Selected bond lengths and angles: Cu(1)–O(1R) 1.9283, Cu(1)–O(2R) 1.9420, Cu(1)–N(1B) 2.0100, Cu(1)–N(2B) 2.0224, Cu(1)–O(2R′) 2.3391 Å (av. esd 0.0017); N(1B)–Cu(1)–N(2B) 80.10, N(1B)–Cu(1)–O(1R) 93.04, N(1B)–Cu(1)–O(2R) 174.49, N(1B)–Cu(1)–O(2R′) 100.38, N(2B)–Cu(1)–O(1R) 171.88, N(2B)–Cu(1)–O(2R) 94.62, N(2B)–Cu(1)–O(2R′) 93.80, O(1R)–Cu(1)–O(2R) 92.34, O(1R)–Cu(1)–O(2R′) 91.72, O(2R)–Cu(1)–O(2R′) 78.30° (av. esd 0.07°).
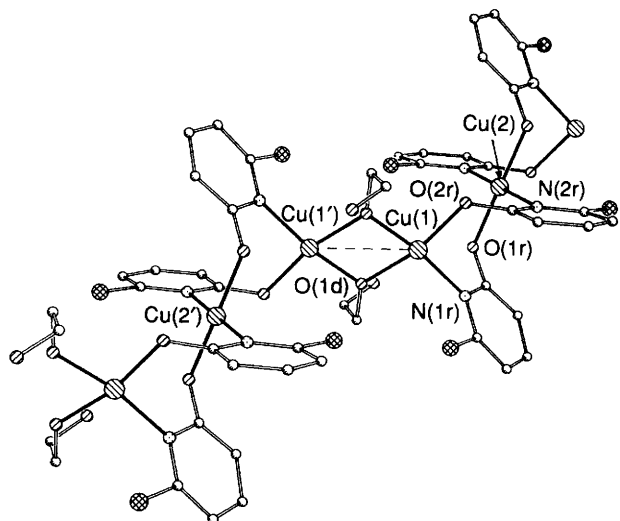
Fig. 3 A portion of the polymeric structure of 4. Selected bond lengths and angles: Cu(1)–O(1D) 1.927, Cu(1)–O(1D') 1.924, Cu(1)–N(1R) 1.986, Cu(1)–O(2R) 1.913, Cu(2)–O(1R) 1.944, Cu(2)–N(2R) 1.992 Å (Av. esd 0.005 Å); O(1D)–Cu(1)–O(1D') 77.7, O(1D)–Cu(1)–N(1R) 97.56, O(1D)–Cu(1)–O(2R) 166.61, O(1D')–Cu(1)–N(1R) 170.02, O(1D')–Cu(1)–O(2R) 92.19, N(1R)–Cu(1)–O(2R) 94.49, O(1R)–Cu(2)–N(2R) 92.81° (av. esd 0.21°).

bound to Cu(2) bridge to two Cu(1) atoms leading to a polymeric structure. The protonated oxygen atoms of the diol are involved in neither long distance bonding to copper atoms nor in hydrogen bonding.

Reaction of 1 with 2 equiv. of copper acetate in CH_2Cl_2 leads to a further unusual compound 5. 5 crystallises from CH_2Cl_2 on diffusion of ether vapour, yield ca. 75%, and structural analysis† reveals an octanuclear copper complex of formula $Cu_8(O)_2(O_2CCH_3)_4(chp)_8$ (Fig. 4). At the centre of the structure is an edge-sharing oxygen-centred bitetrahedron of copper atoms. Although oxo-centred tetrahedra of copper atoms are known[8,9] we believe this to be the first example of such a bitetrahedron. There are two chemically distinct coppers in this bitetrahedron, the two in the shared edge and the four at the other vertices. The two coppers at the shared edge are bridged by the two μ_4-O atoms§ and each such Cu is further bridged to the four coppers at the external vertices by, alternately, μ_2-oxygens from chp ligands and by acetates. The shared edge is therefore coincident with a non-crystallographic S_4 axis. The two coppers in this edge are each bound to six oxygens made up of the two μ_4-oxygens, two μ_2-O from chp and two acetate oxygens. Their geometries are related to a tetragonally elongated octahedron. The four remaining coppers of the bitetrahedron are each four coordinate, bound to one μ_4-oxygen, one μ_2-oxygen from a chp, one acetate oxygen and a nitrogen from a chp ligand. The geometries are considerably distorted from square planar.

The edges of the bitetrahedron are inequivalent in length. The shortest Cu–Cu contact is along the shared edge (2.955 Å) followed by the edges bridged by acetates which vary between 2.968 and 3.035 Å. The edges bridged by μ_2-oxygens from chp vary between 3.065 and 3.1057 Å, while the longest contacts are the two unbridged edges between the external vertices Cu(2)–Cu(5) and Cu(3)–Cu(4) which are 3.489 and 3.525 Å long respectively (av. e.s.d. 0.002 Å).

Around this central $[Cu_6(O)_2(O_2CCH_3)_4]^{4+}$ core are arranged two $[Cu(chp)_4]^{2-}$ units. These provide the edge-bridging oxygens discussed above and are also bound to the external vertices of the central unit by nitrogen donors. The coppers in these units [Cu(6) and Cu(8)] are four coordinate with a square planar trans-array of two oxygen and two nitrogen donors from the chp ligands. These sites therefore resemble the Cu(2) site in 4, or indeed the copper sites in 1.
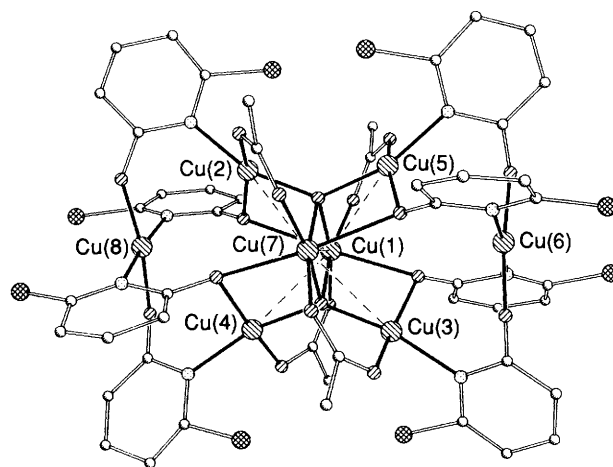

Fig. 4 The structure of 5 in the crystal. Bond length ranges: Cu–μ_4O 1.861 to 1.976, Cu(1) or Cu(7)–μ_2O (from chp) 2.354 to 2.436, Cu(2), Cu(3), Cu(4) or Cu(5) to μ_2O (from chp) 1.964 to 1.981, Cu–O (from OAc) 1.933 to 2.005, Cu–μ_1O (from chp) 1.926 to 1.945, Cu–N (from chp) 1.960 to 2.022 Å (av. esd 0.011 Å).

Octanuclear complexes of this type can also be synthesised by two further routes. First, 5 can be made by reaction of copper acetate with molten Hchp. Garner and coworkers have previously reported[10] a cobalt complex of formula $Co_{12}(OH)_6(O_2CMe)_6(mhp)_{12}$ (where mhp = the anion of 6-methyl-2-pyridone), again synthesised from the acetate salt of the metal reacted in the molten ligand. The bridging motifs in this dodecanuclear cobalt complex are similar to those in 5, consisting of a mixture of μ_3-hydroxy groups, μ_2-oxygens from mhp units and bridging binucleating acetates. Secondly, a modification of 5, $Cu_8(O)_2(O_2CMe)_3(O_2CH)(chp)_8$ 5b is unexpectedly formed in low yield, ≤10%, when 1 is dissolved in acetone and the solution allowed to stand for a period of three weeks. 5b has been characterised by X-ray crystallography,† which shows the compound is almost identical to 5 except that one of the methyl groups of an acetate is absent so that in 5b there is a bridging formate group in addition to three bridging acetates. The Cu–Cu contacts within the bitetrahedron are very similar to those in 5. We do not understand this reaction, although we have shown it to be reproducible. We suspect that the carboxylate ligands are present as impurities in the acetone.

Footnotes

† Crystal Data for $C_{24}H_{24}Cl_4Cu_4N_4O_8$ 2, M = 892.4, triclinic, space group P$\bar{1}$, a = 7.782(3), b = 9.149(4), c = 11.549(4) Å, α = 86.874(22), β = 76.526(22), γ = 74.809(23)°, V = 771.7 Å³ [from 2θ values of 30 reflections measured at ±ω (30 ≤ 2θ ≤ 32°), λ̄ = 0.71073 Å)], Z = 1 (the molecule lies about an inversion centre), D_c = 1.92 g cm⁻³, T = 150 K, deep-lilac tablet, μ = 3.13 mm⁻¹.

For $C_{40}H_{28}Cl_4Cu_2N_8O_4$ 3, M = 953.6, triclinic, space group P$\bar{1}$, a = 9.681(5), b = 9.786(5), c = 10.156(7) Å, α = 91.40(5), β = 91.61(5), γ = 97.35(4)°, V = 954 Å³ [from 2θ values of 13 reflections measured at ±ω (28 ≤ 2θ ≤ 32°), λ̄ = 0.71073 A], Z = 1(the molecule lies about an inversion centre), D_c = 1.66 g cm⁻³, T = 150 K, green plate, μ = 1.45 mm⁻¹.

For $C_{24}H_{22}Cl_4Cu_3N_4O_8$ 4, M = 826.9, monoclinic, space group P2_1/c, a = 9.7366(13), b = 10.0527(9), c = 15.6947(15) Å, β = 102.367(8)°, V = 1500.5 Å³ [from 2θ values of 44 reflections measured

at $\pm\omega$ ($24 \leqslant 2\theta \leqslant 26°$), $\bar{\lambda} = 0.71073$ Å)], $Z = 2$ (the molecule is polymeric, the value given is for the stoichiometric unit), $D_c = 1.83$ g cm^{-3}, $T = 298$ K, dark-green needles, $\mu = 2.53$ mm^{-1}.

For $C_{48}H_{36}Cl_8Cu_8N_8O_{18}\cdot4$ CH$_2$Cl$_2$ **5**, $M = 2144.5$, triclinic, space group $P\bar{1}$, $a = 13.402(7)$, $b = 15.089(9)$, $c = 18.993(13)$ Å, $\alpha = 83.91(4)$, $\beta = 80.35(5)$, $\gamma = 85.74(4)°$, $V = 3759$ Å^3 [from 2θ values of 22 reflections measured at $\pm\omega$ ($28 \leqslant 2\theta \leqslant 32°$), $\bar{\lambda} = 0.71073$ Å], $Z = 2$, $D_c = 1.89$ g cm^{-3}, $T = 150$ K, dark-green tablet, $\mu = 2.87$ mm^{-1}.

For $C_{47}H_{34}Cl_8Cu_8N_8O_{18}\cdot4$ MeCOMe **5b**, $M = 2023.0$, monoclinic, space group $P2_1/n$, $a = 19.463(4)$, $b = 18.949(4)$, $c = 20.530(8)$ Å, $\beta = 97.537(23)$, $V = 7506$ Å^3 [from 2θ values of 31 reflections measured at $\pm\omega$ ($20 \leqslant 2\theta \leqslant 21°$), $\bar{\lambda} = 0.71073$ Å], $Z = 4$, $D_c = 1.79$ g cm^{-3}, $T = 150$ K, dark-green plate, $\mu = 2.59$ mm^{-1}.

Data collection and processing: Stoë STADI-4 four-circle diffractometer with Oxford cryosystems low-temperature device (J. Cosier and A. M. Glayer, *J. Appl. Cryst.*, 1986, **19**, 105), graphite-monochromated Mo-Kα X-radiation, ω-2θ scans. The structures were solved by the heavy atom method using SHELXS-86 (G. M. Sheldrick, *Acta. Crystallogr. Sect. A*, 1990, **46**, 467). The data were corrected for absorption. **2**, **3**, **4** and **5b** were refined with all non-hydrogen atoms anisotropic [except for solvent molecules in **5b**] to give: for **2** $R = 0.0270$ ($wR = 0.0358$) for 1695 independent observed reflections [$2\theta \leqslant 45°$, $F > 4\sigma(F)$]; for **3** $R = 0.0233$ ($wR = 0.0348$) for 2238 independent observed reflections [$2\theta \leqslant 45°$, $F > 4\sigma(F)$]; for **4** $R = 0.0421$ ($wR = 0.0531$) for 1415 independent observed reflections [$2\theta \leqslant 45°$, $F > 4\sigma(F)$]; for **5b** $R = 0.0638$ ($wR = 0.0708$) for 5650 independent observed reflections [$2\theta \leqslant 45°$, $F > 4\sigma(F)$]. **5** was refined with the copper, chlorine and oxygen atoms anisotropic to give $R = 0.0993$ ($wR = 0.1389$) for 7407 independent observed reflections [$2\theta \leqslant 45°$, $F > 4\sigma(F)$]. All refinements used SHELX76 (G. M. Sheldrick, University of Cambridge, England 1976).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ For this structure all hydrogens were located in a difference map and were refined isotropically without constraints.

§ The μ_4-O is probably derived from water molecules of the hydrated copper acetate.

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