New Routes to Copper–Lanthanoid Complexes—*via* a Metal Dimer

Alexander J. Blake, Robert O. Gould, Paul E. Y. Milne and Richard E. P. Winpenny*

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

The synthesis and structure of a dimeric copper complex of 6-chloro-2-hydroxypyridine [ClLH] is reported; treatment with lanthanum nitrate gives a novel $LaCu_3$ complex, and with ytterbium nitrate gives a new Yb_2Cu_2 complex, both of which are also structurally characterised.

In order to study magnetic and electronic interactions between d- and f-block elements on a molecular scale, we have undertaken synthesis of a series of novel copper–lanthanoid complexes using derivatives of 2-hydroxypyridine as ligands.[1] The best synthetic strategy appears to be isolation of polynuclear copper complexes of the ligands, before further reaction of these complexes with lanthanoid salts.[2] Here, we report results using the 6-chloro derivative of 2-hydroxypyridine [ClLCl], which contrast markedly with results using the 6-methyl derivative.[2]

Hydrated copper nitrate and the potassium salt of 6-chloro-2-hydroxypyridine were mixed intimately, as solids, in a 1 : 2 mole ratio,[†] and the resulting dark-green paste extracted with dichloromethane to give a dark-red solution. From this solution dark-red crystals suitable for X-ray diffraction analysis[‡] were grown by ether diffusion.

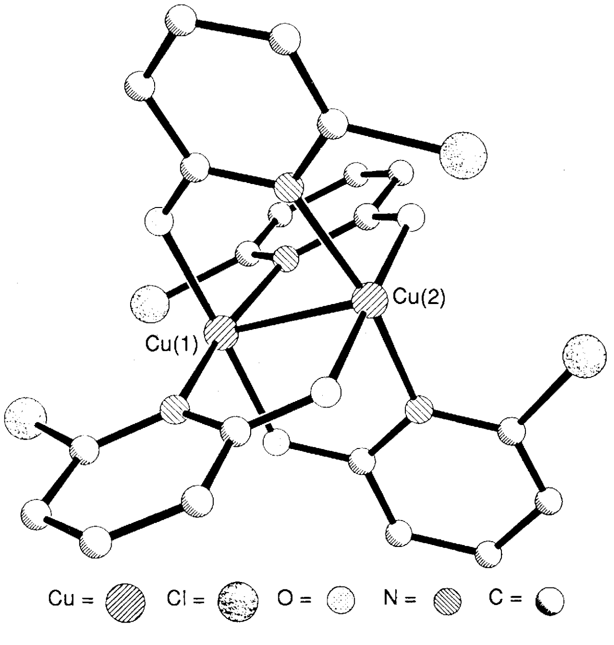

Fig. 1 The dimeric copper complex **1**. Average bond lengths are Cu–N 2.014 ± 0.014, Cu–O 1.928 ± 0.004 Å. The *cis*-angles at Cu vary from 88.25(22) to 91.80(21)°. The N–Cu–N angles average 167.3 ± 0.2°; the O–Cu–O angles average 178.3 ± 0.9°.

[†] *CAUTION*: copper nitrate can react violently with some substances in the solid form.

[‡] *Crystal data* for $C_{20}H_{12}Cl_4Cu_2N_4O_4$ **1**: $M = 641$, orthorhombic, space group $P2_12_12_1$, $a = 15.3943(20)$, $b = 15.8925(13)$, $c = 18.4974(20)$ Å, $V = 4525.5$ Å^3 [from 2θ values of 69 reflections measured at ±ω ($22 \leqslant 2\theta \leqslant 24°$), $\bar{\lambda} = 0.71073$ Å)], $Z = 8$, $D_c = 1.88$ g cm^{-3}, $T = 150$ K, deep-red plate, $\mu = 2.40$ mm^{-1}.

Crystal data for $C_{28}H_{24}Cl_5Cu_3LaN_8O_{17}\cdot 1.5\ CH_4O\cdot 0.5\ C_4H_{10}O$ **2**, $M = 1336$, triclinic, space group $P\bar{1}$, $a = 11.2055(19)$, $b = 12.9050(28)$, $c = 17.059(4)$ Å, $\alpha = 81.345(13)$, $\beta = 85.310(11)$, $\gamma = 76.025(13)°$, $V = 2364$ Å^3 [from 2θ values of 19 reflections measured at ±ω ($30 \leqslant 2\theta \leqslant 32°$), $\bar{\lambda} = 0.71073$ Å)], $Z = 2$, $D_c = 1.88$ g cm^{-3}, $T = 150$ K, green plate, $\mu = 2.59$ mm^{-1}.

Crystal data for $C_{26}H_{30}Cl_4Cu_2N_8O_{22}Yb_2\cdot CH_4O\cdot 2\ C_4H_{10}O$ **3**, $M = 1605$, triclinic, space group $P\bar{1}$, $a = 8.601(8)$, $b = 13.436(10)$, $c = 25.584(10)$ Å, $\alpha = 92.840(6)$, $\beta = 91.000(8)$, $\gamma = 104.100(6)°$, $V = 2862$ Å^3 [from 2θ values of 23 reflections measured at ±ω ($27 \leqslant 2\theta \leqslant 28°$), $\bar{\lambda} = 0.71073$ Å)], $Z = 2$, $D_c = 1.86$ g cm^{-3}, $T = 150$ K, green column, $\mu = 4.23$ mm^{-1}.

Data collection and processing: Stoe STADI-4 four-circle diffractometer, graphite-monochromated Mo-Kα X-radiation, ω-2θ scans with learnt-profile method (W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22). All structures were solved by heavy-atom methods. In each case the data were corrected for absorption and the structure refined anisotropically to give: for **1** $R = 0.0440$ ($wR = 0.0494$) for 2036 independent observed reflections [$2\theta \leqslant 45°$, $F > 4\sigma(F)$]; for **2** $R = 0.0291$ ($wR = 0.0364$) for 5628 independent observed reflections [$2\theta \leqslant 45°$, $F > 4\sigma(F)$]; for **3** $R = 0.0546$ ($wR = 0.0636$) for 6489 independent observed reflections [$2\theta \leqslant 45°$, $F > 4\sigma(F)$]. All calculations used SHELX76 (G. M. Sheldrick, University of Cambridge, England 1976). In **2** and **3** solvent molecules were located in the lattice. They were disordered and refined isotropically in **2**, but ordered and refined anisotropically in **3**.

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

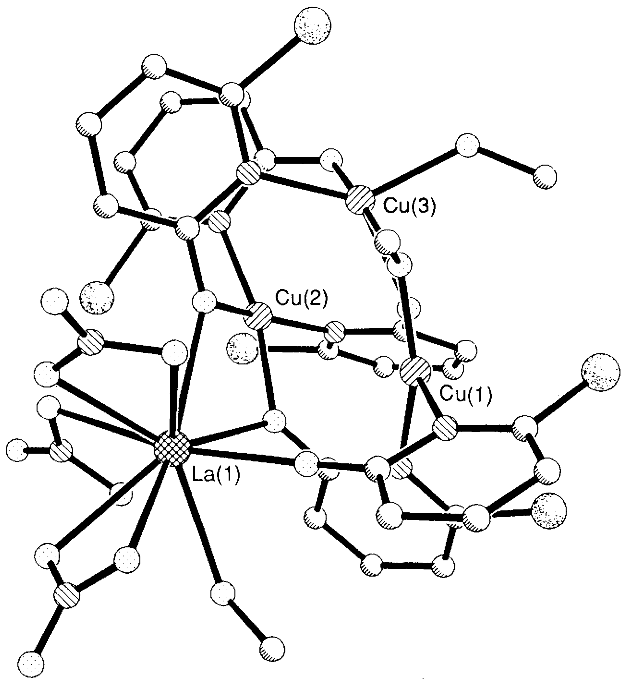

Fig. 2 The structure of **2** in the crystal. Bond length ranges: Cu–N 1.960 to 2.053; Cu–O 1.899 to 2.245; La–O (from ClL) 2.366 to 2.630; La–O (from NO_3 or MeOH) 2.599 to 2.744 Å (av. esd 0.003 Å).

Structural analysis reveals a dimeric copper compound **1** (Fig. 1), similar to those found[3] for the 3-methyl and 3-ethyl derivatives of 2-hydroxypyridine. The presence of the Cl atom in the 6-position prevents any axial ligation taking place, and this perhaps accounts for the Cu–Cu bond being shorter than those previously reported, *e.g.* 2.4989(11) Å in **1** *cf.* 2.56 Å in the dimer with 3-methyl-2-hydroxypyridine.[3] Also interesting is a distinct compression of the Cu–O bonds and slight lengthening of the Cu–N bonds. This appears to result from Cl–Cl repulsions which causes the ligands to tilt, forcing the O donors nearer whilst the N donors move apart. Preliminary electrochemical experiments show two irreversible reductions at −0.21 and −0.88 V, indicating that the Cu atoms are interacting. The EPR spectrum (frozen solution in CH_2Cl_2) is essentially featureless at 77 K, indicating strong anti-ferromagnetic coupling. The magnetic moment at room temperature is 1.58 BM per formula unit.

The analogous reaction of a dichloromethane solution of **1** with a methanol solution of hydrated lanthanum nitrate, in a 1 : 1 mole ratio, leads to a colour change to green. From this solution dark-green crystals were grown by ether diffusion. Structural analysis‡ reveals that the copper dimer has reacted with the lanthanum salt to give a new $LaCu_3$ complex **2** (Fig. 2). The complex is highly asymmetric, with each of the three copper atom sites chemically distinct. The La atom is ten coordinate, with six of the sites occupied by three bidentate nitrates, and a seventh by a methanol. The remaining three sites are occupied by oxygens from deprotonated pyridone ligands. One ligand is binucleating, linking La to Cu(1), the other two are trinucleating, with μ_2-oxygen atoms [O(2) and O(5)] linking La to Cu(2) and the nitrogens then bridging to Cu(1) and Cu(3). The coppers are further linked by a trinucleating ClL unit, Cu(1) and Cu(3) sharing a μ_2-oxygen [O(4)] with the nitrogen bound to Cu(2). Cu(1) and Cu(3) share a further μ_2-oxygen, this one from a deprotonated methoxide, and Cu(2) and Cu(3) are further bridged by binucleating ClL unit. All the copper coordination geometries are distorted; for Cu(1) and Cu(2) the distortion is slight, and clearly based on a square-planar arrangement. For Cu(3), which is five-coordinate, the distortion is considerable, and the coordination geometry is perhaps best described as distorted trigonal bipyramidal, with the axial sites occupied by an oxygen from a binucleating ClL unit [O(3)] and by the μ_2-methoxide [O(0M1]. The short metal–metal contacts are Cu(2)–La 3.719, Cu(1)–Cu(3) 3.108 and Cu(2)–Cu(3) 2.970 Å.

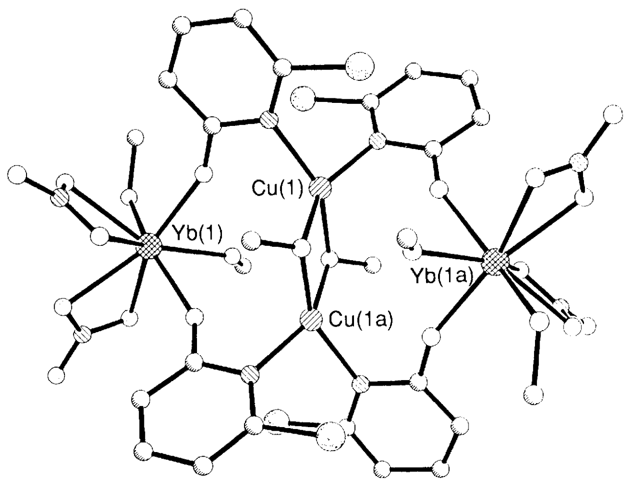

Fig. 3 The structure of one of the molecules of **3** in the crystal. Bond length ranges: Cu–N 1.965 to 1.991; Cu–O 1.943 to 1.959; Yb–O (from ClL) 2.179 to 2.192; Yb–O (from NO_3) 2.364 to 2.434; Yb–O (from MeOH) 2.291 to 2.322 Å (av. esd 0.008 Å).

The analogous reaction of **1** with ytterbium nitrate leads to a quite different, crystallographically characterised product **3**. Here a centrosymmetric Yb_2Cu_2 complex is formed (Fig. 3), with two, nearly identical molecules in the asymmetric unit. At the centre of each molecule is a Cu_2O_2 ring, with the oxygens coming from deprotonated methanol. The copper atoms are each four coordinate, with the remaining two sites occupied by nitrogens from ClL ligands. These ligands then bridge to two Yb atoms, each of which is eight coordinate, with bonds to two bidentate nitrates and two methanols in addition to these bonds to two oxygens from ClL. If the nitrates are considered to occupy one site only the Yb coordination geometries are close to octahedral. The copper geometry is again distorted, this time with the N–Cu–N plane twisted by 40.3° from the O–Cu–O plane in molecule one, and by 41.3° in molecule two. The Cu–Cu bonds are 2.9438(19) and 2.9352(17) Å in the two molecules. The shortest Yb–Cu contact is 4.265(1) Å.

The change in structure from **2** to **3** is difficult to explain. The major change in moving from La to Yb is merely a reduction in the ionic radius, which is reflected in the lower coordination number of the lanthanoid in **3**. It is not clear why such a change should so drastically alter the molecular structure. Similar effects have been reported previously.[4] From elemental analysis it appears that the cerium and gadolinium analogues have structure **2**, whilst elemental analysis and a unit cell determination suggest that the dysprosium analogue has structure **3**.

The use of the 6-methyl derivative of 2-hydroxypyridine gave quite different results,[2] a hexanuclear copper complex rather than a dimer, and an extraordinary La_8Cu_{12} complex rather than **2** or **3**. For the homometallic copper complexes steric factors seem strongly influential as reaction conditions in both cases were identical, the steric requirements of the methyl group being sufficient to prevent formation of a dimer; for the mixed metal complexes it seems highly probable that reaction conditions are the decisive factor, the La_8Cu_{12} complex resulting from a mixed phase reaction similar to those used in zeolite synthesis, while the reactions reported here are exclusively solution phase. These results, taken together, show that by using simple ambidentate ligands it is possible to synthesise a large number of mixed-metal complexes. Physical studies of all the complexes reported are progressing. Preliminary magnetic measurements on **2** and **3** give room temperature magnetic moments of 2.63 and 5.81 BM per formula unit, respectively.

We thank the SERC for a research studentship (to P. E. Y. M.).

Received, 6th December 1991; Com. 1/06165H

References

1 A. J. Blake, P. E. Y. Milne, P. Thornton and R. E. P. Winpenny, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1139.
2 A. J. Blake, R. O. Gould, P. E. Y. Milne and R. E. P. Winpenny, *J. Chem. Soc., Chem. Commun.*, 1991, 1453.
3 Y. Nishida and S. Kida, *Bull. Chem. Soc. Jpn*, 1985, **58**, 383.
4 D. M. L. Goodgame, D. J. Williams and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1989, 1439.

Typeset and printed by Black Bear Press Limited, Cambridge, England