New Routes to Copper–Lanthanoid Complexes I: *via* a Metallomacrocycle

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, UK

We report the synthesis and structure of a novel hexanuclear copper complex of the anion of 6-methyl-2-hydroxypyridine (MeL), which undergoes reaction with lanthanum nitrate to give $[La_8Cu_{12}(OH)_{24}(NO_3)_{22}(MeLH)_{13}(H_2O)_6][NO_3]_2[MeLH]_2{\cdot}CH_2Cl_2$, a copper–lanthanoid complex with several unique structural features.

There is a perceived need for model compounds to investigate interactions between lanthanoids and d-block elements on a molecular level,[1] and also for precursor molecules for synthesis of mixed-metal oxides. Our approach[1b] is based on the ambidentate ligand 2-hydroxypyridine and its derivatives, and recently[2] we reported the structures and unusual magnetic properties of hexanuclear Ln_2Cu_4 and octanuclear Ln_4Cu_4 complexes. Here we report first results of a new stepwise synthetic approach, involving isolation and characterisation of a novel copper metallocycle, and its further reaction with lanthanum nitrate to give a unique mixed-metal species.

Hydrated cupric nitrate and the potassium salt of 6-methyl-2-hydroxypyridine (MeLH) were mixed intimately together,† as solids, in a 1:2 mole ratio, and the resulting light-green solid extracted with dichloromethane giving a dark-green solution and a colourless residue. Diffusion of diethyl ether into this solution gave dark-green cubes, suitable for X-ray diffraction analysis.‡

The crystallographic study revealed a novel 'metallomacrocycle', $[Cu_6(MeL)_{12}Na][NO_3]$ **1**, the cation of which is illustrated in Fig. 1. The presence of the central sodium ion is serendipitous. Each copper atom is in a distorted square-planar environment, with three symmetry equivalent coppers having a *trans*-arrangement of 2N and 2O donors, and three a *cis*-arrangement. The central Na^+ ion, which lies on a crystallographic threefold rotation axis, has a trigonally compressed octahedral array of oxygen atoms. All metal to donor atom bond lengths are unexceptional, with the Na–O distances of *ca.* 2.26 Å ruling out any possibility that the central atom should be refined as a potassium with partial occupancy, despite the much greater concentration of potassium in the starting material.

This hexanuclear structure contrasts markedly with the dimeric structure found for copper complexes of 3- and 4-substituted pyridones.[3] The structural change is probably caused by unfavourable steric interactions between the methyl groups of the ligand if a dimer were to form, though the balance must be a fine one; the copper complex of 6-chloro-2-hydroxypyridone is dimeric,[4] and chromium, tungsten and molybdenum dimers of MeL are known.[5]

The oxygen-lined cavity suggested that **1** might function as a chelator for further metal ions in addition to sodium. Initial reactions with a wide range of metal salts appear to confirm this suspicion. When a dichloromethane solution of **1** was reacted with an excess of hydrated lanthanum nitrate the green solution lost all colour and small blue plates of diffraction quality were formed. Structural analysis‡ revealed

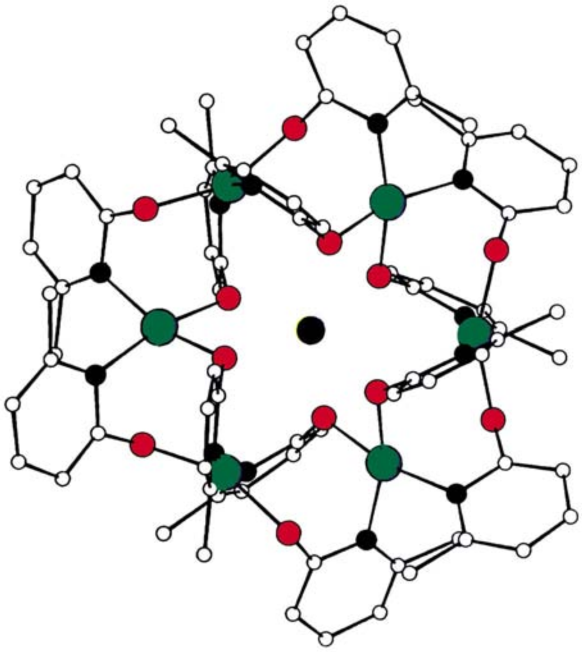

Fig. 1 The hexanuclear copper metallocycle in **1** showing the encapsulated sodium ion. Average bond lengths are Cu–N 2.015 ±0.016, Cu–O 1.962 ±0.010 and Na–O 2.265 ±0.004 Å. The angles at the Cu atoms vary from 81.9(5) to 95.6(6)°. (Colours: Cu, green; O, red; N, black; Na, dark blue; C white).

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

‡ *Crystal data* for $C_{72}H_{72}Cu_6N_{13}NaO_{15}$ **1**, $M = 1763.6$, cubic, space group $Pa\bar{3}$, $a = 26.7414(2)$ Å, $V = 19122.8$ Å^3 [from 2θ values of 10 setting reflections ($24 \leqslant 2\theta \leqslant 26°$), $\lambda = 0.71073$ Å)], $Z = 8$ (the molecule lies about a threefold rotation axis), $D_c = 1.23$ g cm^{-3}, $T = 298$ K, dark-green cube mounted in a glass capillary containing mother liquor, $\mu = 1.375$ mm^{-1}. *Crystal data* for $C_{91}H_{143}Cl_2$-$Cu_{12}La_8N_{39}O_{117}$ **2**, $M = 5599.4$, monoclinic, space group $P2_1/n$, $a = 15.4628(21)$, $b = 32.535(5)$, $c = 18.469(3)$ Å, $\beta = 98.725(18)°$, $V = 9184$ Å^3 [from 2θ values of 40 reflections measured at ±ω ($21 \leqslant 2\theta \leqslant 22°$), $\lambda = 0.71073$ Å)], $Z = 2$ (the molecule lies about an inversion centre), $D_c = 2.03$ g cm^{-3}, $T = 278$ K, blue plate, $\mu = 3.326$ mm^{-1}.

Data collection and processing:—Stoë STADI-4 four-circle diffractometer, graphite-monochromated Mo-Kα X-radiation, ω-2θ scans. Both structures were solved by heavy-atom methods and iterative difference Fourier synthesis. For **1** the data were corrected for absorption and the structure refined anisotropically (including H-atoms in calculated positions) to give $R = 0.1019$ ($R_w = 0.1274$) for 1877 independent observed reflections [$2\theta \leqslant 45°$, $F_o > 3\sigma(F)$] using SHELX76 (G. M. Sheldrick, University of Cambridge, England 1976). For **1** D_c appears low. Measured values are 1.21 g cm^{-3} for freshly prepared crystals, and 1.48 g cm^{-3} for day old material. The largest feature in the final difference map is a peak of 0.95 eÅ^{-3}. For **2** the data were corrected for absorption, and the structure refined with the metal atoms and oxygen atoms of hydroxide ions anisotropic and the remaining atoms isotropic (no hydrogens included) to give $R = 0.0838$ ($R_w = 0.1004$) for 6416 independent observed reflections [$2\theta \leqslant 45°$, $F_o > 3\sigma(F)$]. In **2** there is considerable disorder amongst peripheral ligands. One MeLH unit attached to La(2) does not refine as full weight except for the oxygen, and was modelled as 50:50 water:MeLH. A second, unattached MeLH shows two orientations, one of which overlaps with the half weight MeLH, the other does not. The three nitrates attached to La(4) appear disordered. One was modelled in two orientations, the remaining two as 75:25 nitrate:water. The largest feature in the final difference map is a trough of 1.2 eÅ^{-3}. The nitrate at the centre of the cavity is on an inversion centre, and therefore disordered. A partial weight solvent molecule was also located.

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

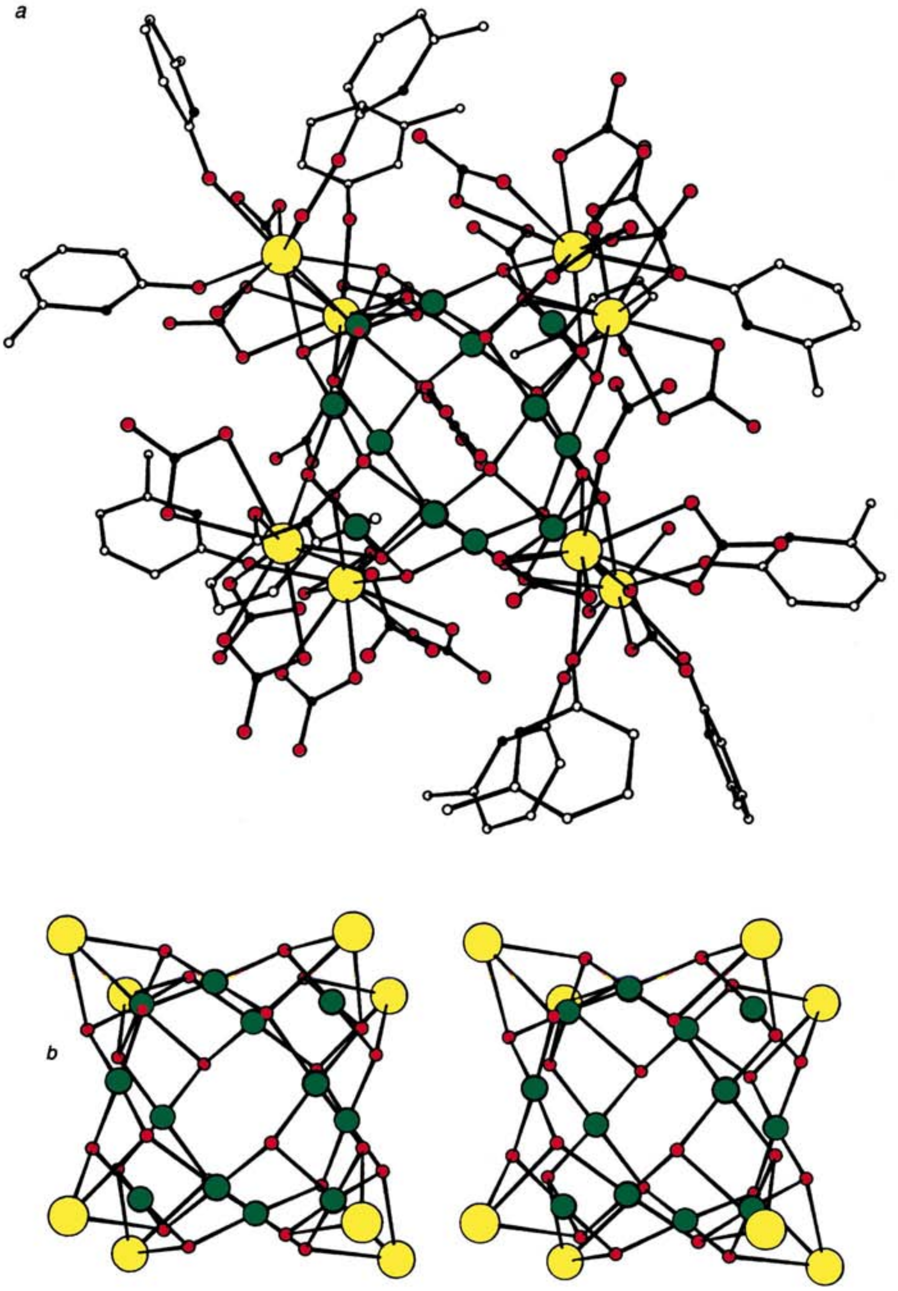

Fig. 2 (*a*) The complete cation of **2**, showing the mixed-metal hydroxide core, surrounded by nitrates and MeLH ligands. (*b*) A stereoview of the central $La_8Cu_{12}(OH)_{24}$ core in **2** viewed from the same vantage point. Bond lengths vary from 1.922(15) to 1.997(14) Å for Cu–O. The La–O bonds divide into three groups. The shortest, to MeLH oxygens, vary from 2.354(21) to 2.469(21) Å. The next, to OH^- or H_2O, vary from 2.561(14) to 2.710(14) Å. Finally contacts to nitrate oxygens vary between 2.55(3) and 2.818(21) Å. (Colours: La, orange; Cu, green; O, red; N, black; C, white).

an extraordinary compound of formula $[La_8Cu_{12}(OH)_{24}(NO_3)_{22}(MeLH)_{13}(H_2O)_6][NO_3]_2[MeLH]_2{\cdot}CH_2Cl_2$ **2**, the cation of which is illustrated in Fig. 2.

The central feature of this cation consists of eight La and twelve Cu atoms bridged by 24 μ_3-hydroxide ions. The structure can be understood by describing each lanthanum and the three nearest neighbour copper atoms as constituting a tetrahedron. Each $LaCu_2$ face is bridged by one μ_3-OH, and each Cu atom is part of two such tetrahedra. The shared copper atoms link eight such tetrahedra to form a cube, with the eight La atoms at the corners. The Cu atoms are at the centres of the edges, though displaced towards the centre of the unit, and thus are at the vertices of a cuboctahedron. The OH ions lie on the diagonals of the cube. The $La_8Cu_{12}(OH)_{24}$ unit thus has non-crystallographic O_h symmetry, making allowance for distortions. The edge distances between the vertices of the La_8 cube average 6.57 Å, varying between 6.30 and 6.71 Å. The average intervertex distance for the Cu_{12} cuboctahedron is 3.37 Å, with the distances varying between 3.21 and 3.46 Å.

The metal ions have usual coordination numbers and geometries. The coppers are each bound to four hydroxide ions in a distorted square-planar arrangement, with further long contacts (>2.37 Å) to nitrate oxygens; the lanthanum atoms have high coordination numbers, varying between nine and ten, again exclusively to oxygen donors. The lanthanum coordination spheres are completed by monodentate and bidentate nitrate ions, water molecules and MeLH units, in addition to bonds to three bridging hydroxides as mentioned above. There is considerable disorder amongst several of these peripheral ligands, though this does not affect the central core.

The formation of **2** raises many questions. The presence of hydroxide bridges suggests formation *via* a mechanism involving protonation of pyridone ligands in **1** by highly polarized $[La(H_2O)_n]^{3+}$ ions. One imagines that this process must be strongly pH dependent, and larger or smaller La_xCu_y species might result in the presence of acid or base. Use of well characterised metallochelates might therefore be an alternative synthetic route to mixed-metal oxides, allowing more control than the sol-gel approach. It is even possible, if unproven, that species like **2** are intermediates in sol-gel processes.

The structure of **2** is unprecedented; perhaps most closely resembling polyoxovanadate structures[6] in having an oxygen bridged array of metals creating a large central cavity. Even here **2** is very different, in that the atoms nearest the centre of the cavity are twelve coppers in a cuboctahedral array. It is therefore unsurprising that an anion (a disordered nitrate) is found at the centre of the cavity, in contrast with the cations conventionally found within polyoxoanions or zeolites. The chemical and physical properties of **2** remain to be explored. Compound **1** also reacts with other lanthanoids, with other trications such as iron and aluminium, and also with some dications; characterisation of the products of these reactions is progressing.

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