Copper Complexes of 1,1-Di-2-pyridylethanol: *X*-Ray Structures and Reaction with Oxygen

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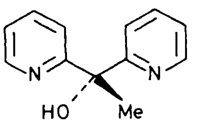
The mixed-valence Cu^I/Cu^{II} complex $[Cu_2I_4][Cu(LH)_2]$ (**1**) (LH = 1,1-di-2-pyridylethanol) reacts with dioxygen to give the Cu^{II} complex $[Cu_2I_2L_2]$ (**2**); both (**1**) and (**2**) have been characterized by *X*-ray structure determination.

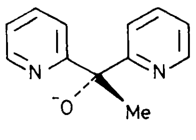
A number of copper proteins are known to contain binuclear copper centres as active sites.[1] In recent years a few binuclear copper complexes with ligands co-ordinated through two or more nitrogen atoms and an endogenous oxygen bridge have been proposed as models of the active site of haemocyanin.[2–4] From the *X*-ray structures of (**1**) and (**2**) we find that 1,1-di-2-pyridylethanol (LH), a ligand easily synthesized, acts as a tridentate ligand for both mono- and di-nuclear copper centres. Furthermore, in the oxidation of (**1**) to (**2**) by dioxygen, the required protons are supplied by the co-ordinated ligand. This reaction is similar to oxidase activities of some of the copper proteins.

The ligand LH is made by the reduction of di-2-pyridyl ketone with MeMgI. Whereas di-2-pyridyl ketone is a bidentate ligand capable of two different modes of co-ordination,[5] reduction of the keto group produces a potential tridentate ligand. Reaction of copper(I) iodide with LH in acetonitrile gives (**1**) and another Cu^I complex that has yet to be characterized. Oxidation of (**1**) in acetonitrile with dioxygen forms (**2**). Oxygen uptake measurements indicate the stoicheiometry shown in equation (1). A copper to dioxygen molar ratio of 4:1 is also found when oxygen uptake measurements are carried out on a 1:1 molar mixture of $[Cu(MeCN)_4]ClO_4$ (**3**) and LH. Pale violet micro-crystals of a species formulated as $[Cu_2L_2(MeCN)_2](ClO_4)_2$ (**4**) are obtained,† suggesting the reaction shown in equation (2).

LH =



L =



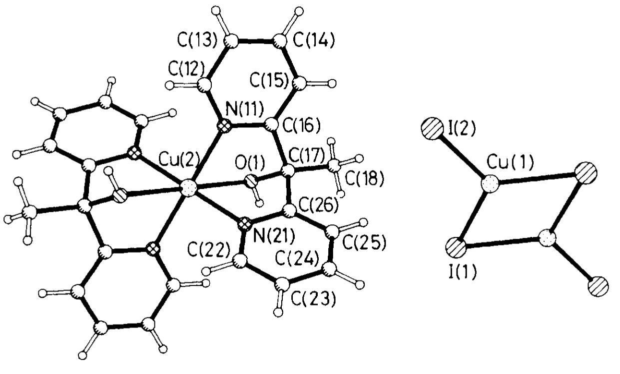


Figure 1. Complex (**1**) showing the atom numbering scheme of the asymmetric unit. Radii are arbitrary. Bond lengths (see also text and deposited material): Cu(2)–N(11) 2.011(4), Cu(2)–N(21) 1.998(4) Å.

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† Satisfactory analytical data (C,H,N,Cu) were obtained for (**1**), (**2**), and (**4**). I.r.: LH (neat) 3380(br.,m), 1595(vs), 1575(s), 1150(br,s) cm^{-1}; (**1**) and (**2**) (KBr and Nujol) 1600(vs) 1680(m), 1145(m); (**3**) (KBr) 2260(vw), 1600(s), 1575(m), 1100(br.,vs) cm^{-1}. (**1**), (**2**) and (**4**) give e.s.r. signals with hyperfine structures. Cyclic voltammetry on (**1**) in CH_2Cl_2 with Ag/AgCl as the reference electrode shows three irreversible oxidations at 0.44, 1.0, and 1.33 V.

$$4\,(\mathbf{1}) + O_2 \rightarrow 4\,(\mathbf{2}) + 4CuI + 4HI + 2H_2O \qquad (1)$$

$$4\,(\mathbf{3}) + 4LH + O_2 \rightarrow 2\,(\mathbf{4}) + 2H_2O + 12MeCN \qquad (2)$$

Single crystal *X*-ray structure determinations of (**1**) and (**2**) have been carried out,‡ since analytical, electrochemical, and spectroscopic (i.r., e.s.r.) data did not indicate unambiguously the precise co-ordination of the copper atoms.† The anion of (**1**), $[Cu_2I_4]^{2-}$, contains trigonal planar copper(I) and is well documented in the literature.[6] The cation of (**1**) contains copper(II) in a tetragonally distorted octahedral environment. Both ions display crystallographically imposed centrosymmetry (Figure 1). The mononuclearity of $[Cu(LH)_2]^{2+}$ is unusual since only bridged, dinuclear copper cores have so far been observed in structurally characterized copper(II) complexes with bi- or tri-dentate ligands of the LH type.

In (**2**), two slightly distorted trigonal bipyramidal co-ordination spheres around the copper(II) share a common edge (Figure 2). Similar co-ordination at dinuclear copper centres has recently been reported.[3a] The Cu · · · Cu distance in (**2**) is 2.830(2) Å. The Cu–O distances in (**1**) and (**2**) are 2.410(3) (twice); 1.939, 2.004(3) Å, respectively. The substantial shortening of the Cu–O bond, resulting mainly from the loss of the proton from LH, is also associated with a less marked change in the C–O distance, from 1.448(6) to 1.411(5) Å. Crystallographic two-fold symmetry is imposed on (**2**).

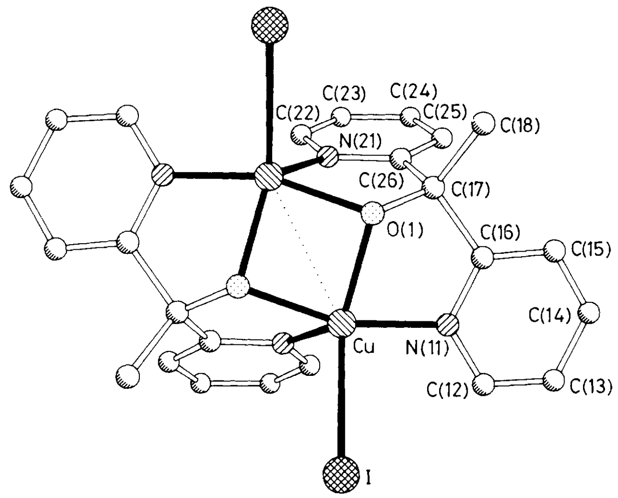

Figure 2. Complex (**2**) showing the atom numbering scheme of the asymmetric unit. Radii arbitrary, H atoms omitted. Bond lengths (see also text and deposited material): Cu-N(11) 1.982(4), Cu-N(21′) 2.119(4), Cu-I 2.729(2) Å.

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‡ *Crystal data* for (**1**): $C_{24}H_{24}$-$CuN_4O_2{}^{2+}Cu_2I_4{}^{2-}$, M_r = 549.4, space group $P2_1/n$, a = 10.129(2), b = 12.311(2), c = 12.881(2) Å, β = 105.35(2)°, U = 1549 Å^3, Z = 2, D_c = 2.36 g cm^{-3}, $F(000)$ = 1022, μ(Mo-K_α) = 6.0 mm^{-1}. The structure was solved by the heavy atom method and refined to R 0.038 for 2705 unique observed reflections.

Crystal data for (**2**): $C_{24}H_{22}Cu_2I_2N_4O_2$, M = 779.4, space group *Pbcn*, a = 14.113(2), b = 10.113(2), c = 17.900(3) Å, U = 2555 Å^3, Z = 4, D_c = 2.03 g cm^{-3}, $F(000)$ = 1496, μ(Mo-K_α) = 4.1 mm^{-1}. The structure was solved by the heavy atom method and refined to R 0.042 for 2202 unique observed reflections. Full details of both structure determinations (atom co-ordinates, temperature factors, structure factors, bond lengths and angles) have been deposited at the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote the reference number CSD 52677 and the full literature citation. Atomic co-ordinates, bond lengths and angles, and thermal parameters have also been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.