

Hydroxo at the Heart of a Hydrophobic Cavity: a Square Planar Cu₄O Assembly

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The product of the action of O₂ on a dinuclear macrocyclic complex is shown, by X-ray crystallographic structure determination, to consist of a planar Cu₄O assembly incorporated in a near-spherical complex ion.

Many dicopper complexes have useful catalytic properties in the mild oxidation¹ of organic substrates by O₂.

In our recent investigations of the autoxidation of dicopper complexes of small Schiff's-base macrocycles which function as redox catalysts,² the observed O₂-uptake of 0.5 mol per mol Cu₂ complex suggests that an aggregation step in the mechanism blocks reversible uptake and release of oxygen, thus preventing the complex from operating as an oxygenation, as opposed to a dehydrogenation, catalyst. The macrocycle L¹ was synthesised in an attempt to introduce hydrophobicity and some degree of steric inhibition of the aggregation process. However, with the introduction of aromatic substituents into the macrocycle, only copper(II) complexes [Cu₂L¹(RCN)₂](ClO₄)₂ (**1**; R = Me) were isolated. These do show interesting fluxional behaviour on the n.m.r. time-scale; study of the temperature dependence of the ¹H n.m.r. spectrum of (**1**) in (CD₃)₂SO reveals an activation energy for

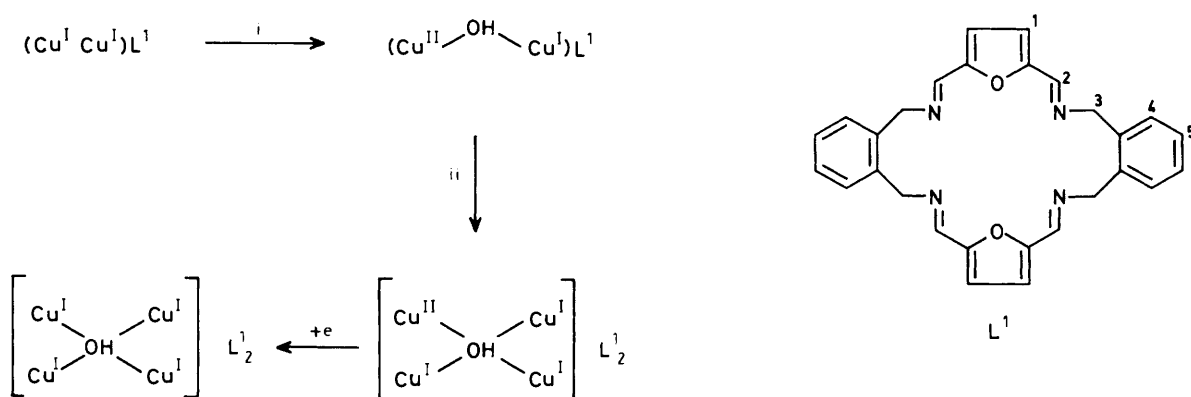
flipping of the xylyl groups about the axis through the *ortho*-methylene carbons of *ca.* 55.6 kJ mol⁻¹.

Acetonitrile solutions of (**1**) show no tendency to interact with oxygen, retaining indefinitely the yellow colour typical of Cu^I imine complexes and an unchanged ¹H n.m.r. spectrum (Table 1). In *N,N*-dimethylacetamide (DMA), however, a red-brown colour developed on standing in air, which was absent from solutions kept strictly under argon. Manometric measurements on DMA solutions of (**1**) registered a slow uptake of O₂ amounting, after 24 h, to *ca.* 0.30 mol per mol (**1**). The ¹H n.m.r. spectrum of an O₂ saturated solution in (CD₃)₂SO does not show broadening, which might be expected to result if the product of the reaction were paramagnetic. Instead a new sharp ¹H n.m.r. spectrum (Table 1), different from that of (**1**), progressively develops with time. This new spectrum is shifted upfield with respect to (**1**) and exhibits splitting of furan- and imino-proton signals into

Table 1. ^1H n.m.r. spectra of (1) and (2)

Complex	Solvent ^a	H(1)	Macrocyclic ligand protons ^b		
			H(2)	H(3)	H(4) + H(5)
$[\text{Cu}_2\text{L}^1(\text{MeCN})_2](\text{ClO}_4)_2$ (1)	CD_3CN	7.08(s)	8.27(s)	4.94(s)	7.35(s)
$[\text{Cu}_2\text{L}^1(\text{MeCN})_2](\text{ClO}_4)_2$	$(\text{CD}_3)_2\text{SO}$	7.53(s)	8.72(s)	5.57(br) 4.67(br)	7.45(t) 7.41(t)
$[\text{Cu}_4\text{L}_2^1\text{OH}](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (2)	CD_3CN	6.90(d)	8.10(d)	4.79(m)	7.24(m) 6.74(m)
	$(\text{CD}_3)_2\text{SO}$	7.04(d)	8.02(d)	4.89(m)	7.34(br) 6.69(m)

^a SiMe₄ reference. ^b Integral ratios H(1) : H(2) : H(3) : [H(4) + H(5)] = 4 : 4 : 8 : 8.



Scheme 1. Reagents: i, 0.25 O_2 , 0.5 H_2O ; ii, $(\text{Cu}^I \text{ Cu}^I)\text{L}$.

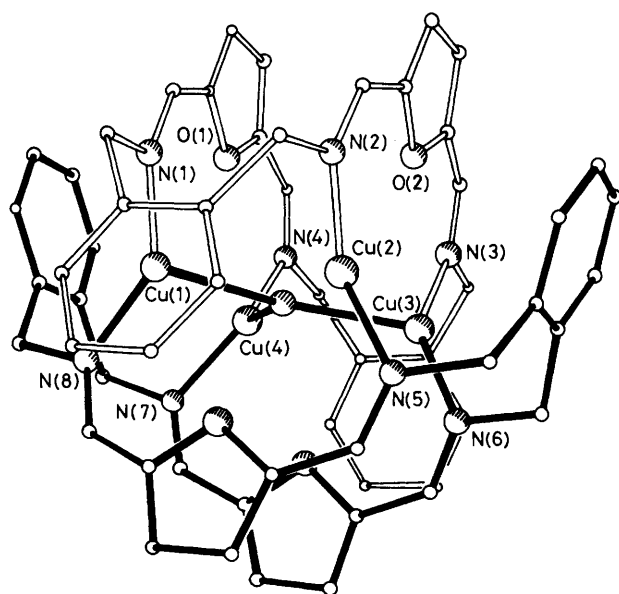


Figure 1. Perspective view of the $[\text{Cu}_4\text{L}_2\text{OH}]^{3+}$ cation showing the disordered hydroxo group in one of the two possible sites. Selected bond lengths and angles: N(1)–Cu(1) 1.948(7), N(8)–Cu(1) 1.923(7), N(2)–Cu(2) 1.961(7), N(5)–Cu(2) 1.956(7), N(1)–Cu(1)–N(8) 142.5(3) Å; N(1)–Cu(1)–O(x) 114.4(3), N(8)–Cu(1)–O(x) 102.8(3), N(4)–Cu(4)–N(7) 130.6(3), N(7)–Cu(4)–O(x) 115.0(3), N(4)–Cu(4)–O(x) 114.4(3), N(2)–Cu(2)–N(5) 125.9(3)°.

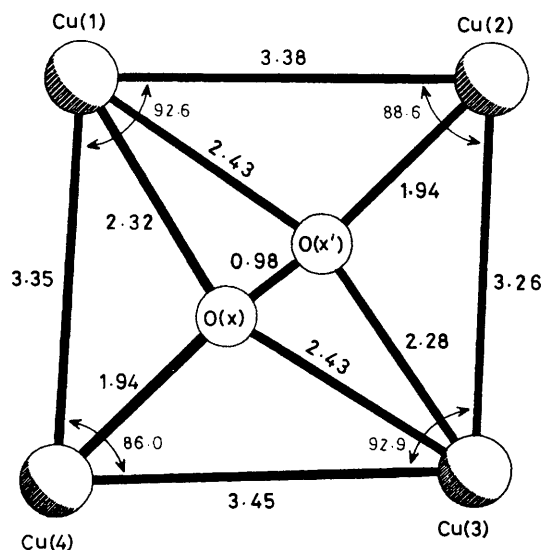


Figure 2. Structure of the Cu_4OH cluster with bond distances (Å) and angles (°).

doublets, the inequivalence suggesting the presence of two macrocyclic units in the product.

Red crystals analysing as $[\text{Cu}_4\text{L}_2^1\text{OH}](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (2) were isolated from the reaction mixture upon addition of ether. This compound has the conductivity expected for a 1:3 electrolyte and shows a sharp ν_{OH} i.r. absorption at 3560 cm^{-1} attributable to non-hydrogen-bonded OH, suggesting that the

hydroxo lies remote from any H-bond acceptor. The red colour of (2) derives from a pair of shoulders (at 25 600 and 20 000 cm^{-1}) on the u.v. $\pi\text{-}\pi^*$ ligand transition. These shoulders have moderately high intensity suggesting a charge transfer origin.

An X-ray crystallographic structure determination [on the acetonitrile solvate of (2) obtained by vapour diffusion of ether into an MeCN solution] was undertaken in order to establish the nature of the aggregate.

Each asymmetric unit contains one $[\text{Cu}_4\text{L}_2^1\text{OH}]^{3+}$ cation, three perchlorate anions, and two molecules of acetonitrile solvate. The structure of the cation is shown in Figure 1;† it contains four coplanar copper centres each co-ordinated to two imino nitrogens, one from each of two L^1 macrocycles. Within the square plane of the four copper atoms is an hydroxide ion, disordered between the two positions O(x) and O(x'). In both sites the hydroxide is co-ordinated to one copper [O(x)–Cu(4) 1.945(9), O(x')–Cu(2) 1.938(8) Å] with weaker interactions to two other copper atoms [O(x) 2.32(1) and 2.43(1), O(x') 2.43(1) and 2.28(1) Å, to Cu(1) and Cu(3), respectively].

The N–Cu–N bonds are non-linear, with angles in the range 123–143°, reflecting these interactions. There is a non crystallographic C_2 axis passing through the centre of the Cu_4 plane and perpendicular to it.

Each macrocycle is folded in a boat conformation so that the two furan rings are approximately parallel and close enough to suggest some π -interaction. The mean planes of furan rings containing O(1) and O(2) are inclined at 11(1)° to each other with a mean separation of 3.9 Å. For the rings containing O(3) and O(4) the corresponding figures are 6(1)° and 3.7 Å. The interlocking macrocycles both cap the four copper atoms, one from each side of the Cu_4 plane ('tennis-ball' configuration) so that the metal centres are enclosed within an almost spherical complex ion. The copper atoms form an almost square quadrilateral with the dimensions shown in Figure 2.

The Cu–Cu distances are too large to allow the hydroxide ion to interact with all four copper ions and this is probably the reason for the observed disorder. Related work³ has shown that a square array of Cu^{2+} ions of side 3.0 Å can accommodate a four-co-ordinate, square-planar oxygen atom.

There are no unusual bond lengths or angles within the macrocyclic ligands and no evidence of any significant interaction between the cations and anions or solvate molecules.

† Crystal data: $\text{C}_{60}\text{H}_{55}\text{Cl}_3\text{Cu}_4\text{N}_{10}\text{O}_{17}$, monoclinic, space group $P2_1/a$, red, crystal dimensions $0.22 \times 0.16 \times 0.14$ mm, $a = 20.788(5)$, $b = 14.107(2)$, $c = 21.730$ Å, $\beta = 103.46(1)^\circ$, $U = 6197(2)$ Å³, $Z = 4$, $F(000) = 3151$. 8098 Unique reflections were collected in the range $4 < 2\theta < 45^\circ$ using 1.6° ω -scans at $3.91^\circ \text{min}^{-1}$; 4261 reflections for which $I > 3\sigma(I)$ were used in the structural analysis. Data were collected at -120°C on a Nicolet R3m four-circle diffractometer using graphite monochromated Mo- K_α radiation; they were corrected for Lorentz–polarisation and absorption effects. The structure was solved by Patterson methods and the refinement converged with $R = 0.0518$ and $R_w = 0.0577$. All programs used for data collection and structure solution are contained in the SHELXTL (version 4.1) package.⁴

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

The role of O_2 in the formation of this aggregate deserves comment. Despite the steric hindrance introduced by fluxionality of the xyllyl substituents, it seems that an aggregation step in the course of the interaction positions the imino nitrogens in the second macrocycle appropriately to allow interchange of one of the imino donors between the first and second macrocycles with loss of chelation (chelation, with a 4-C link between imino nitrogens, is in this case expected to involve a certain degree of steric strain). Examination of the electronic spectrum of the reacting mixture (1) in O_2 -saturated DMA, reveals the presence of a new band close to 800 nm, in a region characteristic of the intervalence transfer $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ transition when mediated by OR^- . The intensity of the band, assuming an extinction coefficient around $400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, as found for related $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ mixed-valence compounds,^{5,6} suggests that up to 20% of the macrocyclic complex is present as the mixed valent form in the early stages of the reaction. Aggregation would be assisted by the presence of an OH bridge, which, being co-ordinatively unsaturated, could serve to anchor the Cu^{I} site in the second macrocycle while the imino donor interchange takes place. A possible sequence of events is given in Scheme 1.

Reduction of the complex in the final step must be accompanied by oxidation of some proportion of the ligand as no Cu^{II} containing product was isolated from the reaction mixture.

It is interesting that this aggregation and scrambling process leaves a co-ordinated hydroxo group at the heart of the spherical hydrophobic cavity. It has been suggested⁷ that the hydrophobic nature of the binding site in haemocyanin argues against the hypothesis that hydroxide is the exogenous bridge. The implication of the structure described above is that hydroxide can coexist with and even assist in the formation of a hydrophobic cavity.

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