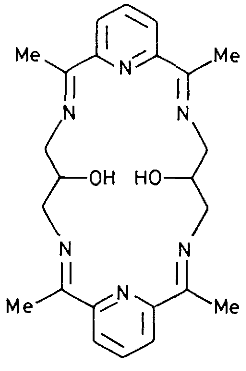
Synthesis and *X*-Ray Structure of a Bicopper(II) Schiff Base Macrocyclic Complex having a Single Endogenous Alkoxy Bridge

Vickie McKee* and Jackie Smith

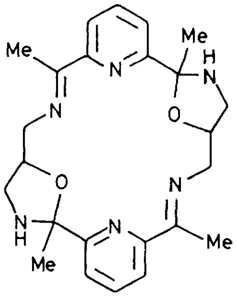
Department of Chemistry, University of Canterbury, Christchurch 1, New Zealand

A bicopper(II) Schiff base macrocycle having an internal alkoxy bridge and strong antiferromagnetic coupling has been synthesised and its structure determined; the complex has similar co-ordination geometry and properties to those reported for oxy- and met-haemocyanin.

The presence of bridged and strongly antiferromagnetically coupled bimetallic active sites in the type III copper proteins,[1] haemerythrin,[2] and photosystem II[3] is now well established. To study further the intrinsic properties of such endogenously bridged systems we have synthesised the Schiff base macrocycle (L) containing secondary alcohol groups as potential internal bridging species. The macrocycle (L) was prepared by a template reaction from 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane in methanol solution containing barium perchlorate. $Ba(L)(ClO_4)_2{\cdot}2H_2O$ was obtained in good yield and identified by i.r. and ^{13}C n.m.r. spectroscopy and microanalysis. Use of Pb^{2+} as template resulted in formation of the ring-contracted product $Pb(L')(ClO_4)_2{\cdot}MeOH$; a similar complex has been characterised by Fenton and his co-workers.[4]



(L)



(L′)

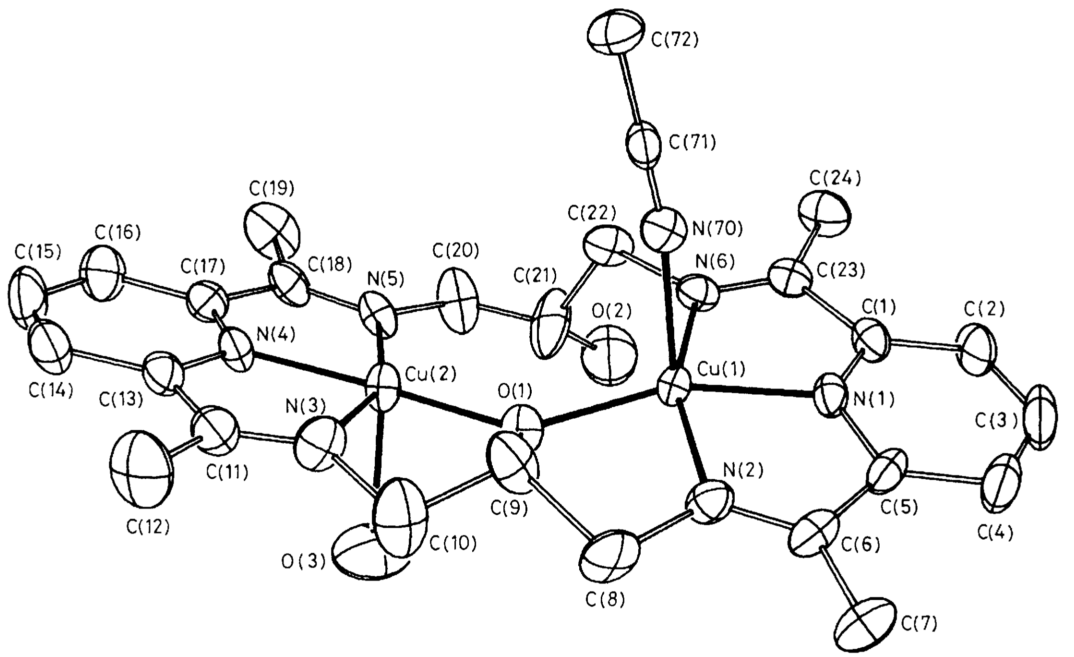


Figure 1. SHELXTL plot of the $[Cu_2(L)(MeCN)(H_2O)]^{3+}$ cation (20% thermal ellipsoids). Selected bond lengths (Å) and angles (°): Cu(1)–Cu(2) 3.642(2); Cu(1)–O(1) 1.977(8); Cu(1)–N(1) 1.927(9); Cu(1)–N(2) 1.980(8); Cu(1)–N(6) 2.010(9); Cu(1)–N(70) 2.271(13); Cu(2)–O(1) 1.958(7); Cu(2)–N(4) 1.900(8); Cu(2)–N(3) 1.999(12); Cu(2)–N(5) 2.100(10); Cu(2)–O(3) 2.388(18); ∠Cu(1)–O(1)–Cu(2) 135.5(4); N(6)–Cu(1)–N(1) 79.4(4); N(6)–Cu(1)–O(1) 118.4(3); N(6)–Cu(1)–N(2) 157.4(3); N(6)–Cu(1)–N(70) 89.9(4); N(1)–Cu(1)–N(2) 78.4(4); N(1)–Cu(1)–O(1) 159.3(3); N(1)–Cu(1)–N(70) 98.3(4); N(2)–Cu(1)–O(1) 82.7(3); N(2)–Cu(1)–N(70) 97.5(4); O(1)–Cu(1)–N(70) 92.6(4); N(3)–Cu(2)–N(4) 77.3(4); N(3)–Cu(2)–N(5) 155.8(4); N(3)–Cu(2)–O(1) 82.0(4); N(3)–Cu(2)–O(3) 95.8(5); N(4)–Cu(2)–N(5) 78.5(4); N(4)–Cu(2)–O(1) 158.2(5); N(4)–Cu(2)–O(3) 97.6(5); N(5)–Cu(2)–O(1) 121.8(4); N(5)–Cu(2)–O(3) 88.7(5); O(1)–Cu(2)–O(3) 91.2(4).

A bimetallic copper(II) complex was prepared by transmetallation with copper perchlorate in methanol.[5] The resulting blue microcrystalline compound analysed as $Cu_2(L)(ClO_4)_3{\cdot}2H_2O$; it shows no detectable e.s.r. signal at room temperature as either a solid or acetonitrile solution. Taken together, the analysis and e.s.r. data suggest a bridged structure involving a mono-deprotonated ligand and exhibiting strong antiferromagnetic coupling. The complex was recrystallised from acetonitrile and the crystal structure of the solvate $Cu_2(L)(ClO_4)_3{\cdot}MeCN{\cdot}H_2O$ was determined.

Crystal data: $C_{26}H_{34}Cl_3Cu_2N_7O_{15}$, $M = 790.9$, crystal dimensions 0.45 × 0.37 × 0.30 mm, triclinic, $a = 12.881(5)$, $b = 13.173(4)$, $c = 12.374(5)$ Å, $\alpha = 118.11(3)$, $\beta = 90.03(3)$, $\gamma = 94.44(3)°$, $U = 1843(1)$ Å^3, $D_m = 1.67$, $D_c = 1.65$ g cm^{-3}, $Z = 2$, space group $P\bar{1}$, Mo-K_α radiation ($\lambda = 0.71069$ Å), μ(Mo-K_α) = 14.49 cm^{-1}, $F(000) = 936$.

Intensity data were collected on a Nicolet R3m four-circle diffractometer using graphite monochromated Mo-K_α radiation and the θ–2θ scan method in the range $3 < 2\theta < 50°$. 6126 reflections were collected and corrected for Lorentz-polarisation effects and for absorption. 3159 unique reflections for which $I > 3\sigma(I)$ were used for the structure determination. The two copper atoms were located by standard Patterson techniques; the remaining non-hydrogen atoms were located from difference Fourier maps and refined by blocked cascade least-squares methods. Hydrogen atoms were included at calculated positions (C–H = 0.96 Å). The refinement converged at $R = 0.083$, $R_w = 0.091$, with all the non-hydrogen atoms anisotropic; the function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + 0.0014\,F_o^2]^{-1}$. There is severe disorder about one of the perchlorate groups; attempts to model this did not improve the fit and since the interest in this structure lies in the geometry of the cation it was not pursued further. All computer programmes used are part of the SHELXTL (version 3.0) package.†

The structure of the cation is shown in Figure 1. Each copper atom has approximately square pyramidal geometry and is co-ordinated to three ligand nitrogen atoms, the bridging alkoxide, and an axial solvate molecule [acetonitrile for Cu(1) and water for Cu(2)]. As expected, the axial bonds are considerably longer than those in the square plane. The equatorial alkoxy bridge has optimal geometry for antiferromagnetic coupling between the two $(d_{x^2-y^2})^1$ copper atoms and this is presumably responsible for the lack of e.s.r. signal.

Binuclear copper(II) complexes involving single bridges are quite rare and mono-μ-alkoxy species have not been structurally characterised. Crystal structures of four mono-μ-hydroxy complexes[6–9] have been reported, however, and in three cases[7–9] the OH^- bridge lies in the equatorial plane of the tetragonal copper centres. The extent of the antiferromagnetic coupling in these compounds ($-J$ = 120—500 cm^{-1}) is a function of the Cu–O–Cu angle (132.2—143.7°). The present complex, with a bridge angle of 135.5°, lies at the lower end of this range, and its strong coupling may be due to an increase in electron density on the oxygen atom compared with the hydroxide ion.[5,10,11]

In spite of the non-biological nature of the macrocyclic ligand, the complex is a useful structural model for the oxidised (e.s.r. silent) haemocyanin active site. The latter is

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

thought to involve two tetragonal copper(II) centres[1] bridged by a light atom (probably oxygen) and with a Cu–Cu distance of *ca.* 3.6 Å,[12] compared with 3.642 in the present compound. This work also supports the suggestion[13] that the main superexchange pathway in the protein is *via* the endogenous bridge which is likely to be alkoxide from serine or threonine of the protein.

Note added in proof: the second alcohol group is not coordinated to either copper atom [Cu(1)–O(2) 4.22, Cu(2)–O(2) 4.77(2) Å] but is hydrogen bonded to the equivalent atom in a neighbouring macrocycle [O(2)–O(2′) 2.48(2) Å, ORTEP code for O(2′) = 45502]. The almost planar macrocycles are stacked parallel to one another in the unit cell.

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