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The Coexistence of Two hydroxo-bridged and One Bis-hydroxo Dicopper(II) Complexes of 2,6-Bis-((salicylideneamino)methyl)-4-nitrophenol: a Comment on the Need for Flexibility in Dinuclear Models for Haemocyanins

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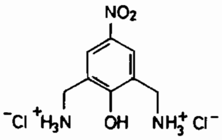
Although the nature of the dinuclear copper(I) site in deoxyhaemocyanin (ex-*panulirus interruptus*) has been revealed through X-ray crystal structure determination [1], the corresponding dinuclear copper(II) site in oxyhaemocyanin remains the subject of conjecture. Cumulative spectroscopic studies [2] indicate that there is present an endogenous bridge, variously proposed as deriving from a hydroxide [3], tyrosinyl [4], threonyl or seryl ligand [5] and an exogenous bridge shown to be peroxide. EXAFS studies on oxyhaemocyanins from different sources indicate a Cu–Cu separation of 3.58–3.66 Å [6].

The prospect of a tyrosinyl bridge has led to the study of a number of model compounds in which there is present a phenoxide bridge [7]. Many of these models are based on binucleating Schiff base ligands derived from 2-hydroxy-5-methylisopthalaldehyde [8, 9], in which the two copper atoms are further bridged by an appropriate exogenous ligand. The systems are, however, relatively rigid and constrain the Cu–Cu separation to *ca.* 3.0 Å [10], considerably shorter than that in the cuproprotein.

In an attempt to increase the flexibility of the binucleating ligand, and the viability of the model, we have synthesised 2,6-bis(aminomethyl)-4-nitrophenol as its dihydrochloride salt **1** and used it to prepare the potassium salt of the pentadentate Schiff base 2,6-bis((salicylideneamino)methyl)-4-nitrophenol (**2**) [11] by liberating the free diamine with KOH and subsequent reaction with salicylaldehyde. In **2** the imino groups are no longer adjacent to the 4-nitrophenol aromatic rings and the presence of the now adjacent methylene groups should give a flexibility to the ligand.



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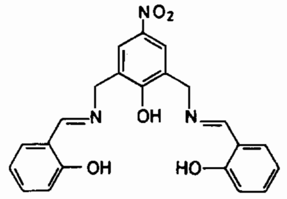

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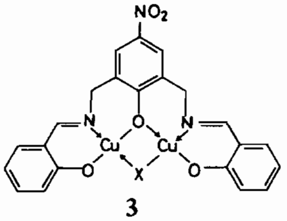

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The reaction of the potassium salt of **2** with copper(II) ethanoate in 1:2 stoicheiometric ratio in 2-methoxymethanol gave a complex with analysis close to **3** (X = OH). The crystal structure of this compound was determined.

Three-dimensional X-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3m diffractometer by the omega-scan method. The 6846 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by image-seeking Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Refinement converged at $R = 0.0471$ (anisotropic thermal motion of all non-hydrogen atoms, anomalous scattering of copper and chlorine).

Crystal Data

$(\mu\text{-Cl})(\mu\text{-L})[Cu_3(L)(OH)(dmf)]_2 \cdot 2(dmf)$, $C_{78}H_{78}ClCu_6N_{13}O_{21}$, $M = 1950.23$, crystallised from dmf as irregular, green blocks; mean crystal dimensions $0.48 \times 0.28 \times 0.25$ mm. Triclinic, $a = 13.288(10)$, $b = 14.678(7)$, $c = 22.591(23)$ Å, $\alpha = 102.96(6)$, $\beta = 89.07(7)$, $\gamma = 113.15(5)°$, $U = 3935(5)$ Å^3, $D_m = 1.61$, $D_c = 1.646$ g cm^{-3}, $Z = 2$; space group $P\bar{1}$ (C_i, No. 2), graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å), μ(Mo Kα) = 17.12 cm^{-1}, $F(000) = 1992$. The atomic coordinates for this work are available, see 'Supplementary Material'.

The molecule (Fig. 1) comprises six copper atoms in two approximately equilateral triangular clusters (mean Cu–Cu 3.01 Å), each of which is triply bridged by a hydroxyl ligand. One pair of coppers within each triangular cluster (Cu(2) and Cu(3); Cu(5) and Cu(6)) is coordinated by the three phenolic oxygen and two imino hetero-atoms of a Schiff base ligand L**, with the phenolic oxygen of the central 4-nitrophenolic group as the endogenous bridging atom

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L is the triply deprotonated tri-anion of **2.

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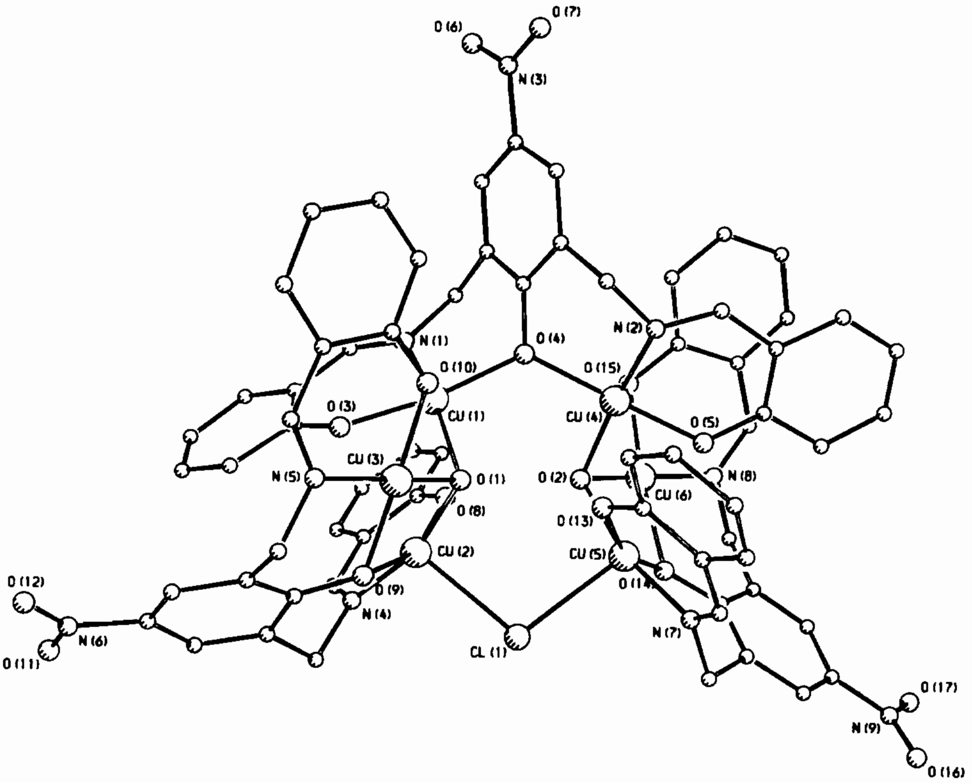

Fig. 1. The molecular structure of the copper(II) complex.

and one of the μ^3-hydroxides as the exogenous bridging atom. The remaining pair of coppers (Cu(1) and Cu(4)), one in each cluster, are also endogenously bridged in a similar manner, but at a greater Cu–Cu separation of 3.50 Å, by a third Schiff base ligand L and with no exogenous bridge. The hydroxide ligands (O(1); O(2)) may be regarded as being monoligated, one to each of the copper atoms in this pair, Cu(1) and Cu(4) respectively. A further bridge between the clusters is through a chlorine atom which forms long interactions to a different pair of copper atoms; the chlorine arising as a consequence of the synthetic procedure. Two other long contacts are made to dmf solvent molecules by the two copper atoms, one in each cluster, which are not involved in inter cluster bridging. Eight further long Cu–O contacts are made to the six salicylidine oxygen atoms so that each such atom can be viewed as either doubly or triply bridging. The whole hexanuclear molecule has approximate C_2 symmetry and the asymmetric unit is completed by two uncoordinated dmf molecules; it may be viewed as arising from the coexistence of two hydroxo-bridged and one bis-hydroxo copper(II) moieties.

Each copper atom has a tetragonally elongated octahedral coordination geometry. Two of the equatorial planes are significantly tetrahedrally twisted [those of Cu(1) and Cu(4)] and for the others the copper atoms are displaced markedly from the mean equatorial planes away from weakly bonded salicylidine oxygen atoms. The presence of saturated carbon atoms as immediate substituents on the 4-nitrophenolic central ring of each ligand 2, instead of the sp^2 hybridised carbon in the related Schiff base complexes, introduces a degree of flexibility in that one of the three ligands in the molecule has the two terminal salicylidine-imino fragments positioned on either side of the central 4-nitrophenolic plane, with approximate C_2 symmetry, thereby allowing the ligand to bridge two more widely separated copper atoms. The remaining two ligands have the two terminal chelate fragments on the same side of the central 4-nitrophenolic plane and present curved faces to the metal core, leading to the much lesser copper–copper separations which are characteristic of the spacings in the equilateral triangular clusters. The two μ^3-hydroxyl groups are each hydrogen bonded to a salicylidine oxygen atom in the other cluster.

From the structural information we draw the following conclusions. First the value of introducing flexibility to the ligand is demonstrated in the opening up of the Cu–Cu separation in the bis-hydroxo dinuclear unit to 3.50 Å as opposed to 3.01 Å in the exogenously bridged units. This may be compared favourably with the Cu–Cu separations determined, by EXAFS, for met-aquo-, (3.39–3.45 Å) and met-fluorohaemocyanin (3.50 Å), in which each copper(II) is monoligated and the integrity of the endogenous bridge is retained [6]. Second, a recent study of peroxide coordination to a dicopper-(II) centre indicated that it was not possible, using vibrational spectroscopy, to distinguish between the different possible bonding modes, μ-1,1 or μ-1,2, of the peroxide [12]. The presence of a 1,1-bridging ligand in the flexible system (**3**, X = OH) requires a short Cu–Cu separation, and such a bridge is destroyed as the separation increases. This observation reinforces the view that any binding of dioxygen to the exogenous site in oxyhaemocyanin would be as a 1,2-peroxo bridge. Furthermore for the directly related azido complex (**3**, $X = N_3^-$) magnetic studies reveal an antiferromagnetically coupled copper(II) pair with a $2J$ value of -238 cm^{-1}. This indicates that the azide is bridging in a 1,3-bridging mode; if the azide had been binding in a 1,1-mode a ferromagnetic interaction would have been expected [13]. The capability of the flexible ligands to accept multi-atom bridges is also evidenced in the recent presentation of a μ-1,2-pyrazolato dinuclear copper-(II) complex of a similar ligand, in which the *para*-substituent is a methyl group [14]. A detailed account of the electrochemical behaviour of the complex was presented but no structural information was given.

Supplementary Material

The atomic coordinates for this work are available from the authors on request.

Acknowledgements

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