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Dinuclear Copper(II) Complexes of Macrocycles Providing endogenous Bridges: an Unusual Environment for the Perchlorate Anion

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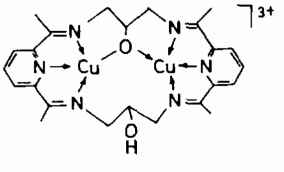
The synthesis of dinuclear copper(II) complexes of tetraimine Schiff base macrocycles may be accomplished by application of the metal template effect, using barium or lead salts, in the condensation of heterocyclic dicarbonyls and 1,n-alkanediamines, followed by transmetallation of the product complex with copper(II) salts [1]. We have used this approach to prepare the dinuclear copper(II) complex of the macrocycle derived from 2,6-diacetylpyridine and 1,3-diamino-2-propanol (1) [2]. In this complex the antiferromagnetically coupled copper(II) atoms are separated by 3.64 Å; one lateral diamine-derived side-chain provides an endogenous hydroxo-bridge [3]. The molecule may be regarded as providing a simplistic model for the proposed bimetallobiosite in oxyhaemocyanin (2) [4].



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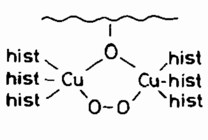
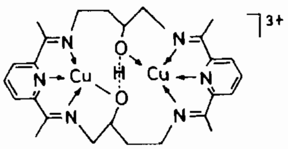


2

The molecule 1 is relatively rigid, and the presence of the lateral chain inhibits any equatorial approach of substrate to the dicopper(II) unit. In an attempt to introduce greater flexibility to the system the diamines 1,4-diamino-2-butanol and 1,5-diamino-3-pentanol have been used to provide the lateral units in the binucleating '2 + 2' macrocycles derived from 2,6-diacetylpyridine by use of template and transmetallation procedures [5, 6]. The consequence of this has been a loss of the endogenous bridge in the products, $[Cu_2(m/c\text{-}H)](ClO_4)_3 \cdot nH_2O$, (3, 4).



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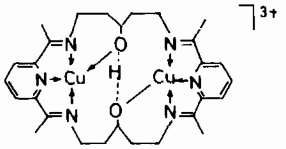

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The coordination of the copper(II) ions by the ligands is as depicted in the molecular formulae 3 and 4; this was established by X-ray structural studies. The structure of 3 comprises two dinuclear copper(II) macrocyclic units related by C_2 symmetry, one perchlorate and two water ligands, and five ionic perchlorates. Each copper atom is coordinated by the three N atoms of a diiminopyridyl head unit and by one of the O atoms from a singly deprotonated pair of endogenous alcohol groups. The alkoxide does not bridge the copper(II) atoms, which are 4.71 Å apart, although the mean Cu···O contact of 3.32 Å is less than that found in 4 below. The fifth coordination sites on each copper are occupied by water or by monodentate perchlorate ligands respectively. The perchlorate is situated on a C_2 axis and bridges the two symmetry related copper atoms from different binuclear units. The atoms of the endogenous alcohol groups are very closely spaced (2.36 Å); this is indicative of a very short, strong hydrogen bond [7].

The structure of 4 likewise comprises two binuclear copper(II) macrocyclic units (cation **I** and cation **II**), each of which possesses crystallographically imposed C_2 symmetry. Also present are two perchlorate and two water ligands, four ionic perchlorates and two waters of crystallisation. Each of the macrocyclic units contains two copper(II) atoms which are coordinated by the three N atoms of the diiminopyridyl head unit and one O atom provided by deprotonation of one lateral alcohol. The alkoxide does not act as a bridge, the copper(II) atoms being 4.82 Å (cation **I**) and 4.90 Å (cation **II**) apart and the mean Cu···O distances being 3.54 Å. The fifth coordination sites in cation **I** are occupied by two monodentate perchlorate ions, both on the outer face of the folded ligand, and in cation **II** by the two water molecules also on the outer surface of the macrocycle. Cation **I** is thus formally monopositively charged and cation **II** is tripositively charged.

In each molecule the oxygen atoms of the endogenous alcohol groups are closely spaced (2.46 Å, cation **I** and 2.47 Å, cation **II**). Location of the hydrogen atoms reveals a disordered, asymmetric hydrogen bond in cation **I**, and a symmetric hydrogen bond in cation **II**.

The two macrocycles are orientated so that the copper–copper vectors are mutually perpendicular and the macrocycles are folded around an intervening perchlorate anion (Fig. 1). The Cu–O separations are 2.98 Å and 3.08 Å and so are rather too long to call bonds. The encapsulated perchlorate may be regarded

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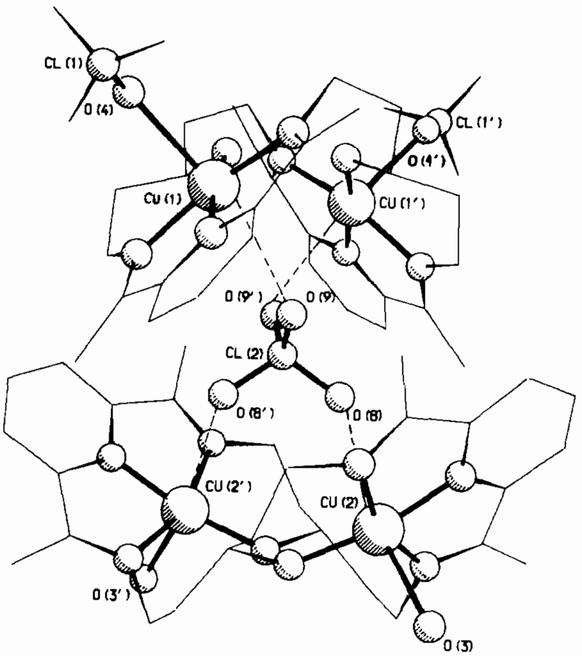

Fig. 1. Molecular structure of $[Cu_4(m/c\text{-}H)_2(ClO_4)_3(H_2O)_2]^{3+}$.

as weakly tetradentate and using its oxygen atoms to help orientate the structure.

The complexes **3** and **4** are paramagnetic with no evidence for antiferromagnetic coupling between the pairs of copper atoms. Electrochemical studies on **4** show that in DMSO solution, using $n\text{-}BuN_4BF_4$ as the supporting electrolyte, two monoelectronic transfers occur. The first couple ($E^1_{pc} = -0.51$ V; $E^1_{pa} = -0.43$ V) is reversible but the second reduction process is complicated by a follow-up reaction ($E^2_{pc} = -0.67$ V; $E^2_{pa} = -0.58$ V; $E^3_{pc} = +0.16$ V). Since the complex is recovered unchanged after a two electron reduction followed by a two electron oxidation the process responsible for the electrochemical irreversibility is believed to be a stereochemical change involving significant ligand reorganisation.

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