Structural, Magnetic, and Redox Properties of Dicopper Complexes of a New Binucleating Ligand involving Sulphides and Benzimidazoles in Addition to a Phenoxide Bridge

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The structure of the chloro-derivative (**1**) of the new ligand (H–L1) is reported together with the electrochemical and magnetic studies of this and three related complexes; it shows that (H–L1) is able to mediate a strong antiferromagnetic interaction between the two copper(II) ions in the complex, whilst enforcing their high reduction potential.

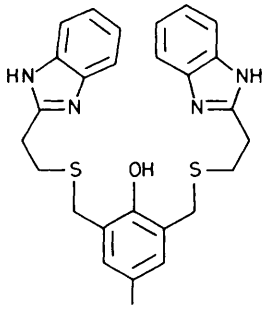
In their oxidized form, the binuclear active sites of multicopper enzymes (tyrosinase, laccase) are strongly antiferromagnetically coupled and behave as high potential two-electron acceptors.[1] Although both of these properties have been reproduced, separately, in a few compounds, complexes of naphthyridine,[2] phthalazine, and pyridazine[3] ligands are the only systems which have so far been reported to reproduce both properties simultaneously. In order to confer both properties on dicopper complexes, we have synthesized ligand (H–L1) which provides both the phenoxide endogenous bridge known as an efficient mediator of antiferromagnetic coupling,[4] and the sulphur and benzimidazole groups which stabilize the Cu^{I} oxidation state.[5] Here we describe the synthesis, the electrochemical and magnetic properties of four dicopper complexes of (H–L1), and the structure determination of the chloro-derivative (**1**).

Reaction of (H–L1) with various copper salts in acetone in the presence of triethylamine affords compounds with the general formula $Cu_2(L1)X_3$ [(**1**), X = Cl; (**2**), X = Br; (**3**), X = NO_3]. In the case of copper perchlorate, $Cu_2(L1)(OH)(ClO_4)_2$ (**4**) is obtained. All compounds have been satisfactorily characterized by elemental analyses and spectroscopic techniques. Sulphur co-ordination to the copper atoms is suggested by the presence in every complex of a moderately strong (ε 800—1400 cm^{-1} dm^3 mol^{-1}) charge transfer transition in the 550—580 nm region. From the known chemistry of these kinds of compounds, it is most likely that the two coppers are bridged by the endogenous phenoxide group and also an exogenous anion X or hydroxide.[4] This assumption has been verified by *X*-ray diffraction in the case of (**1**·MeOH).†

The structure of complex (**1**) is depicted in Figure 1. The two copper atoms are bridged by a chloride ion and the phenoxide oxygen. The copper–copper distance is 3.255 Å, and the Cu–O–Cu angle is rather obtuse (113.3°). Each copper atom is in a square-pyramidal environment with a terminal chloride ion occupying the apical position. The basal planes are constituted by a nitrogen atom, a sulphur atom and the two bridging atoms.

The temperature dependence of the magnetic susceptibility of the four complexes has been studied over the range 6—300 K. They all exhibit strong antiferromagnetic coupling of the two copper(II) centres. The magnitudes of the singlet–triplet energy splitting, E_{ST}, within the series [(**1**) E_{ST} −442, (**2**) E_{ST} −446, (**3**) E_{ST} −359, (**4**) E_{ST} −808 cm^{-1}] are consistent with literature data. It is noteworthy that all complexes are far more strongly coupled than their analogues in which the sulphur has been replaced by nitrogen. For example, in the case of the chloride derivative (**1**), the nitrogen counterpart has a far lower E_{ST} of −84 cm^{-1}.[6] This difference can be attributed to a lower Cu–O–Cu angle [105.8 *cf.* 113.3° for (**1**)]; but, from orbital considerations, the presence of sulphur is also expected to increase the singlet–triplet energy gap.[7]

The electrochemical behaviour of the complexes was investigated in dimethyl sulphoxide solution. Complex (**1**) exhibits one redox couple with E_c 0.17, E_a 0.40 V *vs.* standard calomel electrode (s.c.e.). Coulometric analyses indicate that



'H-L1'

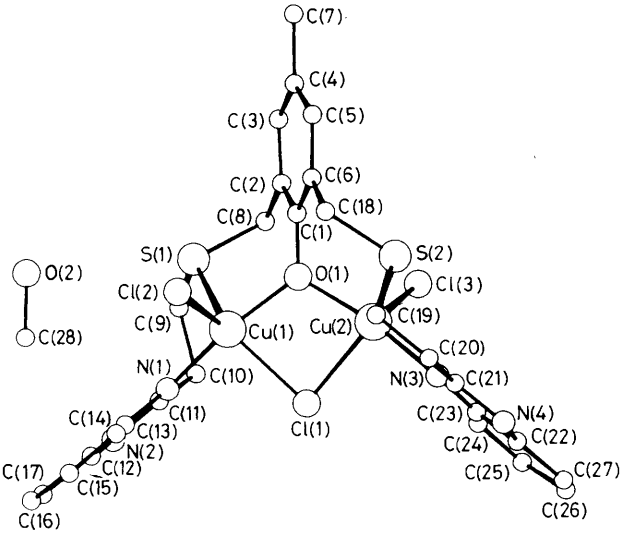


Figure 1. Crystal structure of $Cu_2(L1)Cl_3$·MeOH (**1**·MeOH). Bond lengths: Cu(1)–O(1) 1.952, Cu(2)–O(1) 1.945, Cu(1)–Cl(1) 2.385, Cu(1)–Cl(2) 2.375, Cu(2)–Cl(1) 2.385, Cu(2)–Cl(3) 2.325, Cu(1)–S(1) 2.388, Cu(2)–S(2) 2.459, Cu(1)–N(1) 1.984, Cu(2)–N(3) 1.972 Å. Bond angles: Cu(1)–O(1)–Cu(2) 113.3, Cu(1)–Cl(1)–Cu(2) 86.1, Cl(1)–Cu(1)–O(1) 79.9, Cl(1)–Cu(2)–O(1) 80.1°.

† *Crystal data for* (**1**): $C_{28}H_{29}Cl_3Cu_2N_4O_2S_2$, M = 738.1, orthorhombic, space group $Pna2_1$, a = 15.801(5), b = 23.15(1), c = 8.190(3) Å, (Mo-K_α), λ = 0.7107 Å, T = 20 °C, U = 2995.8 Å^3, Z = 4, D_c = 1.64 g cm^{-3}. Data were collected with an Enraf-Nonius four-circle diffractometer with graphite monochromated Mo-K_α radiation. 4942 unique reflections were measured, of which 2461 with $I > 4\sigma(I)$ were used in the structural analysis. The structure was solved using direct methods and gave final R = 0.035 and R_w = 0.039. 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 corresponding process is bielectronic, and no evidence has been found for a one-electron mixed-valence intermediate. Complexes (**2**), (**3**) and (**4**) also exchange two electrons at positive potentials [(**2**) E_c 0.08, E_a 0.38; (**3**) E_c 0.03, E_a 0.30; (**4**) E_c 0.02, E_a 0.54 V *vs*, s.c.e.]. These transfers are not electrochemically reversible. The resulting bis-copper(I) species are stable toward disproportionation, and react rapidly with dioxygen.

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