Dicopper Complexes of a New Binucleating Ligand involving Sulphides and Benzimidazoles

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The new binucleating ligand (**1**) is able to achieve high stabilization of the copper(I) ion and to mediate interaction between the two copper sites; this leads to the isolation of dicopper(II), mixed-valence, and dicopper(I) derivatives depending on reaction conditions.

Copper proteins have attracted much interest recently owing to their striking spectroscopic properties as well as their reactivity toward dioxygen.[1] Accordingly, mimics for the proteins' active site using low molecular weight complexes have been sought.[2] In this respect, numerous studies have appeared which tried to duplicate the environment of 'type I' copper with chelating ligands involving nitrogen and sulphur donor atoms.[3] Conversely, much less attention has been paid to dicopper complexes of binucleating ligands with the same donor atoms.[4] In this communication we report preliminary results on the synthesis and properties of such a ligand (**1**) and several of its dicopper complexes.

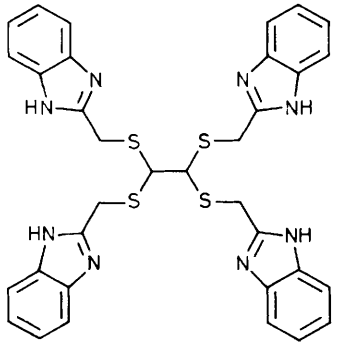
The ligand (**1**) is obtained through Phillips condensation[5] of the corresponding, commercially available, tetra-acid with phenylenediamine. Reaction of (**1**) with two equivalents of tetra-acetonitrile copper(I) tetrafluoroborate in acetonitrile

affords $Cu_2(1)(BF_4)_2$, (2), as a white powder. The reaction of (1) with copper(II) salts is dependent on the nature of the metal counter-anion and on the solvent. When $Cu(ClO_4)_2 \cdot 6H_2O$ is treated with (1) in ethanol at 0 °C the mixed-valence compound $Cu_2(1)(ClO_4)_3$, (3), is formed after 12 hours. On the other hand, after the addition of $CuCl_2 \cdot H_2O$ to a methanolic solution of (1) and rapid precipitation with diethyl ether, the dicopper(II) complex $Cu_2(1)Cl_4$, (4), is obtained. All compounds have been characterized through elemental analyses and spectroscopic techniques. The syntheses are depicted in Scheme 1.

Figure 1 illustrates the cyclic voltammograms of (2) and (4) in Me_2SO solution with tetrabutylammonium tetrafluoroborate as the supporting electrolyte. Complex (2) exhibits two oxidation peaks at Ep_a^1 0.52 and Ep_a^2 0.84 V and two reduction peaks at Ep_c^1 0.07 and Ep_c^2 0.22 V. Coulometric analyses indicate that both oxidation processes are monoelectronic; the redox changes can be summarized as in equation (1). Compound (6) is not stable and slowly reverts to (5). Spectroscopic and electrochemical techniques show that the latter is identical to (3). On the other hand, complex (4) presents only one redox couple with Ep_a 0.44 and Ep_c 0.16 V. Coulometric analyses point to a two-electron exchange between the di-Cu^{II} and the di-Cu^{I} species without any evidence for the mixed-valence $Cu^{I}Cu^{II}$ intermediate. However, these experiments are disturbed by the slow spontaneous reduction of (4).

$$\underset{(2)}{Cu_2(1)^{2+}} \overset{-e^-}{\rightleftharpoons} \underset{(5)}{Cu^{I}Cu^{II}(1)^{3+}} \overset{-e^-}{\rightleftharpoons} \underset{(6)}{Cu^{II}Cu^{II}(1)^{4+}} \qquad (1)$$

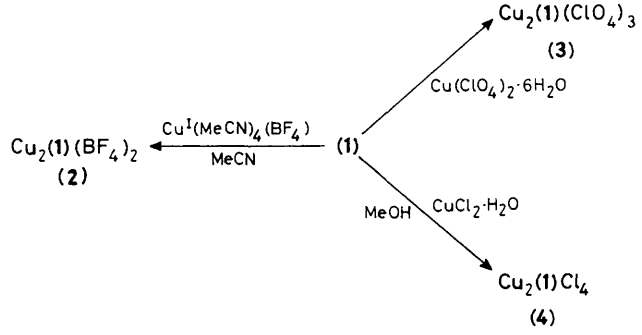
Magnetic susceptibility measurements over the range 6—300 K show that (4) closely follows the Curie–Weiss law, thus indicating that the two copper atoms are not interacting magnetically. Taken together, this property and the bielectronic nature of the redox process strongly suggest that in complex (4) the two copper sites are identical and independent of each other. The latter feature is in sharp contrast to the behaviour of complexes (2) and (3). The existence of the mixed-valence species (3) and (5) and their 'class I' nature,[6] deduced from e.s.r. studies, indicate that an interaction between the two copper atoms is operative. This raises the question of the exchange pathway. Through-bond transmission *via* the carbon framework seems to be ruled out by the aliphatic nature of the ligand. On the other hand, sulphur atoms have been shown[7] to be excellent mediators of magnetic couplings. Thus, an attractive proposal would be that the interaction between the copper sites occurs *via* the sulphide sulphur atoms. These would be co-ordinated to the Cu^{II} ions in compounds (3), (5), and (6) where weakly co-ordinating anions (BF_4^- or ClO_4^-) are present. The opposite situation would prevail in (4) where chloride is a strong enough ligand to bind Cu^{II}. Nevertheless, sulphur co-ordination probably occurs in the reduced form of (4) since the half-wave potential appears about 0.5 V higher than in another complex involving an N_2Cl_2 donor set.[8]



(1)

Another matter of interest is the spontaneous autoreduction process exhibited by all di-Cu^{II} derivatives of (1). As a matter of fact, the present ligand bears some resemblance to 2,5-dithiahexane which, depending upon reaction conditions with copper(II) perchlorate, gives a Cu^{I}, mixed valence, or Cu^{II} complex.[9] A preliminary mechanistic investigation of this reaction seems to rule out any involvement of the sulphide moiety.[10] Light-induced copper-catalysed oxidation of the solvent could account for the observed behaviour.[11]

In summary, the ligand system described above is able to mediate interactions between the two co-ordination sites and to provide the copper atoms with an environment perfectly suited to Cu^{I} stabilization. The potentials for the Cu^{II}/Cu^{I} couples observed in this study (*ca.* 0.75 V *vs.* normal hydrogen electrode) are higher than those reported for blue copper proteins[3a] and for copper complexes.[12] This peculiarity is



Scheme 1

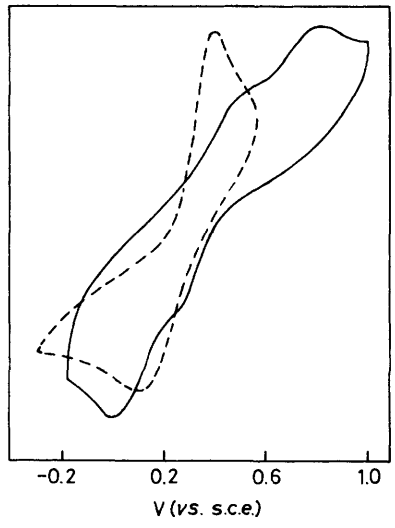


Figure 1. Cyclic voltammograms of (2) (solid line) and (4) (dashed line) in Me_2SO 0.1 mol dm^{-3} in $N(C_4H_9)_4(BF_4)$ at 3 V min^{-1}. Volts are referenced to the saturated calomel electrode (s.c.e.).

probably the main reason for the instability of the di-Cu^{II} derivatives as well as for the poor reactivity of the di-Cu^{I} complexes toward O_2.

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