# Redox and Magnetic Properties of Binuclear Copper Complexes

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Metalloenzymes which interact with dioxygen have long attracted both biochemists and chemists [1]. Early work in this field was devoted mainly to iron enzymes, but recently emphasis has also been put on multicopper enzymes [2]. These complex copper proteins can perform a great variety of functions: O_2 transport (hemocyanin), O_2 activation (tyrosinase) or O_2 reduction (polyphenols oxidases). All of these multicopper proteins have a similar binuclear active site which behaves as a high potential two-electron acceptor and which, in its oxidized state, exhibits a very strong antiferromagnetic coupling between the two cupric ions. Duplicating these two features with simple binuclear copper complexes has become a major goal among inorganic chemists in the past few years [3]. However, only a few complexes have been found to accept two electrons at once [4] and more investigations are needed to correlate redox and magnetic properties of dicopper entities. In this communication we report preliminary results of redox and magnetic studies of dicopper complexes of the new ligand **HL**.

HL
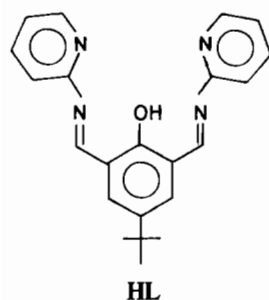
Experimental

HL was obtained through condensation of 2-aminopyridine with 2,6-diformyl-4-tert-butylphenol [5] in absolute ethanol. Addition of the chosen copper salt in ethanol and concentration of the solution under reduced pressure yielded the desired complexes $Cu_2L(OH)Cl_2$ or $Cu_2L(OH)(H_2O)_2(NO_3)_2$ as green powders. Both compounds were characterized by elemental analyses and spectroscopic techniques.

Electrochemical studies were performed in 0.1 M dimethylformamide solutions in tetrabutylammonium tetrafluoroborate, using a conventional three-electrode cell with a saturated calomel reference electrode and a platinum working electrode. The electrochemical apparatus consisted of a PAR 173 potentiostat/galvanostat driven by a PAR 175 Universal Programmer, a PAR 179 coulometer and a Sefram TGM 164 XY recorder.

Magnetic susceptibilities were determined through the use of an SHE Corp. variable temperature superconducting magnetometer at a field of 5.6 kG. Data for each compound were corrected for small amounts of ferromagnetic impurities.

The magnetic data were least-squares fitted while allowing the TIP to vary the minimized quantity R: $[\Sigma[\chi_M^{corr}(obsd) - \chi_M^{corr}(calc)]^2/\Sigma[\chi_M^{corr}(obsd)]^2]^{1/2}$ was 1.19×10^{-4} for the nitrate and 4.87×10^{-5} for the chloride.

Results and Discussion

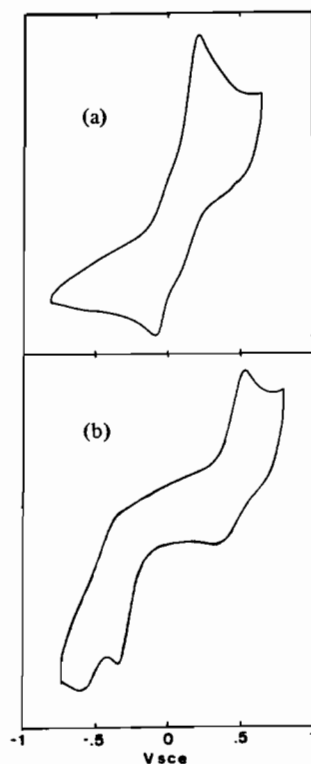Figure 1 depicts the cyclic voltammograms of both compounds in dimethylformamide solution. The

Fig. 1. Cyclic voltammograms of (a) $Cu_2L(H_2O)_2(NO_3)_2$ and (b) Cu_2LCl_2 in dimethylformamide at a sweep rate of 3 V/mn.

nitrate derivative (curve 1a) shows two reductions at $Ep_c^1 = +0.06$ V and $Ep_c^2 = -0.08$ V and two reoxidations at $Ep_a^1 = +0.25$ V and $Ep_a^2 = +0.04$ V at a sweep rate of 3 V/mn. Peak separations and the dependence of peak potentials on the sweep rate point to non-reversible behaviour for the two couples. Coulometric analyses at +0.05 V and −0.5 V successively indicate that both transfers are monoelectronic. On the other hand, the chloride (curve 1b) exhibits two reduction peaks at $Ep_c^1 = -0.38$ V and $Ep_c^2 = -0.62$ V and only one reoxidation at $Ep_a = 0.53$ V. Both reduction transfers are monoelectronic from coulometric analyses. The huge difference between reduction and oxidation peak potentials suggests that an important structural rearrangement is associated with the electron transfers.

The magnetic properties of both complexes are illustrated in Fig. 2 as the molar susceptibility *vs.* temperature curves over the range 6–300 K. The nitrate (curve a) clearly follows the Curie-Weiss law with $g = 2.20$ and $\theta = -0.12$, as deduced from simulation of the data. On the other hand, the chloride exhibits a dimer behaviour. Simulation of the data using the well-known Bleaney-Bowers equation [6], while taking into account a small amount (0.8%) of a monomeric Curie-behaved impurity, leads to the following parameters: $g = 2.28$ and $-2J = 503$ cm^{-1}.

Thus in spite of their close similarity, the two complexes behave in a drastically different manner. In the chloride, the two coppers are strongly interacting, as indicated by the high singlet-triplet separation observed in the oxidized state. Moreover, electro-

chemical experiments show that the electron transfer induces a drastic structural change. This finding is further supported by the class I nature [7] of the mixed valence $Cu^{II}Cu^{I}$ derivative (deduced from ESR analysis). The two coppers of the nitrate complex are magnetically independent and exhibit a markedly less irreversible electrochemical behaviour, indicating far smaller stereochemical changes. A possible explanation for these differences is that in the nitrato complex coordination of the pyridine in a very strained situation would severely distort the binuclear unit from planarity, thus leading to the disappearance of the exchange pathway. In the chloro complex, on the contrary, the planar structure would be maintained with Cl⁻ acting as an equatorial ligand. Further discussions are premature in the absence of structural data.

The above results re-emphasize the difficulty of obtaining dicopper systems capable of exchanging two-electrons at a time. Of course, structural rearrangement associated with the Cu^{II}/Cu^{I} valence change is the main obstacle to overcome if it is desired to maintain equivalence of the two sites throughout the whole two-electron transfer. Accordingly, the present complexes appear to be neither rigid nor flexible enough to impose or accomodate structural equivalence of the sites during the redox process. Further work is in progress to substantiate this explanation with the help of X-ray diffraction data.

Fig. 2. Corrected molar magnetic susceptibility *vs.* temperature curves: (a) $Cu_2L(H_2O)_2(NO_3)_2$; (b) Cu_2LCl_2. The solid lines are the data best fits using the parameters given in the text.

References

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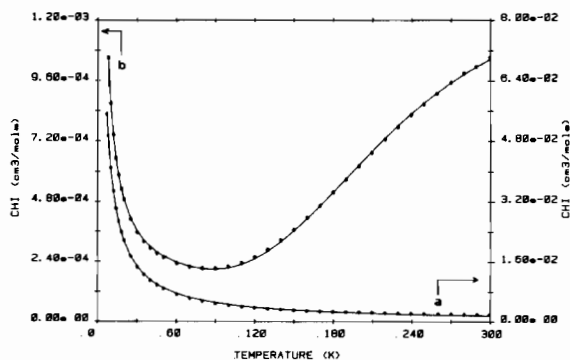7 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, *10*, 247 (1967).