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Electrochemical Properties of Bridged and Non-bridged Dinuclear Copper Complexes Using a Flexible Ligand

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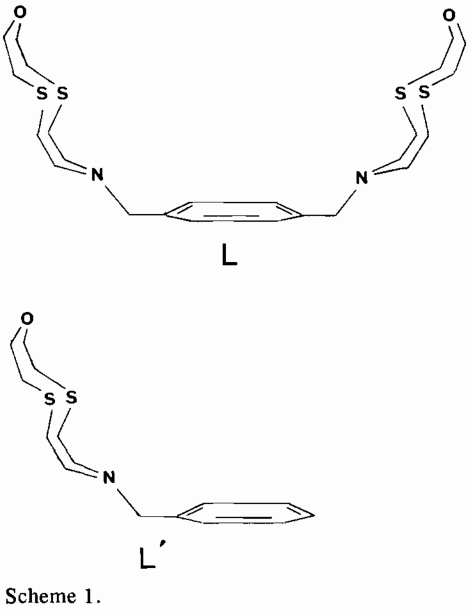
Abstract

We have investigated the redox behavior of a series of dinuclear copper(II) complexes Cu_2L^{4+}, $Cu_2(\mu\text{-}OH)L^{3+}$ and $Cu_2(\mu\text{-}Im)L^{3+}$ where L is 1,4-bis((1-oxa-4,10-dithia-7-azacyclododec-7-yl)methyl)benzene, a ligand which is capable of holding two copper centers in close proximity. Electrochemical studies of the three dinuclear complexes in propylene carbonate reveal that Cu_2L^{4+} exhibits a sequential two-electron reduction at the same positive potential whereas in $Cu_2(\mu\text{-}OH)L^{3+}$ and $Cu_2(\mu\text{-}Im)L^{3+}$ which involve bridging groups, reduction to their dinuclear Cu^I species occurs via two successive monoelectronic transfers at positive potentials. The relevance of these studies to those found for type III copper proteins is briefly discussed.

Introduction

Interest in mimicking properties of type III copper proteins is still widespread although partial structural information on certain of the active sites is now available [1]. The nature of the donor atom ligands in model systems as well as the accompanying electronic and magnetic properties have retained the attention of several workers, more so than their electrochemical properties. However, a scattering of papers concerning dinuclear copper centers has led to a classification of their electrochemical behavior. Reduction of the two copper(II) ions occurs via two monoelectronic steps either at distinct potentials as commonly described [2–5] or at identical potentials. In the second case however, a detailed analysis based on the theoretical study of Polcyn and Schain [6] allows the non-interacting metal sites [7] and magnetically coupled systems [8, 9] to be distinguished. Type III copper proteins are believed to undergo a two-electron reversible reduction to Cu_2^I [10].

We wish to report here a systematic investigation on the redox properties of a series of Cu^{II} complexes. A particular interest in this study stems from the variety of complexes which are herein available: the same NS_2O donor set can provide mononuclear and dinuclear complexes with the ligands L′ and L represented in Scheme 1.



Scheme 1.

The syntheses and characterizations of CuL'^{2+} (**1**), Cu_2L^{4+} (**2**) and $Cu_2(\mu\text{-}OH)L^{3+}$ (**3**) were reported in previous papers [11, 12]; in particular, the binucleating ligand L is capable of holding two copper centers either far apart as in Cu_2L^{4+} or in close proximity using different bridging ligands as in $Cu_2(\mu\text{-}OH)L^{3+}$ and $Cu_2(\mu\text{-}Im)L^{3+}$ (**4**) (where Im =

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imidazole anion), creating consequently different magnetic properties. It was especially of interest to determine the electrochemical behavior of **3** where two coppers separated by a distance of 3.384(9) Å are strongly antiferromagnetically coupled with a singlet–triplet separation $-2J$ of 850 cm^{-1}, similar to that found in the type III copper proteins.

Experimental

Starting materials

The ligands L′ and L as well as the complexes **1**, **2** and **3** were prepared by published procedures [12]. Compound **4** can be obtained by a variety of synthetic methods which will be described in detail elsewhere [13] but the exchange reaction in butanone of OH^- by Im^- by treating **3** with imidazole is the preferred method. The full characterization of **4** will be reported in a forthcoming paper [13].

Electrochemistry Measurements

Reagent grade propylene carbonate was dried over CaO, distilled under reduced pressure at 70 °C and stored under nitrogen. The supporting electrode $LiClO_4$ (Merck) was dried prior to use under vacuum for 48 h at 70 °C.

Polarographic and coulometric measurements were performed with a Tacussel PRG5 polarograph coupled with a Tacussel EPL2 recorder. Cyclic voltammetry was carried out on a Bruker EI310M potentiostat connected to a XY Ifelec 3802 recorder with a three-electrode system: either a platinum or a mercury electrode as working electrode, a Pt-wire coil as auxiliary electrode and a saturated calomel electrode as reference were used. The reference electrode was separated from the bulk of the solution by a glass tube fitted on the bottom with a fine-porosity sintered glass frit and was immersed in a propylene carbonate solution containing $LiClO_4$ (0.1 M). Experiments were carried out at 22 ± 1 °C in solutions previously degassed for 20 min with argon of high purity. Potentials are reported versus the saturated calomel electrode (SCE).

Results

The electrochemical behavior of the mononuclear and dinuclear systems were investigated by polarography and cyclic voltammetry in propylene carbonate and also in water where redox potentials of type III copper proteins have been measured. The nature of the copper species present in solution (water or PC) has been previously determined by detailed potentiometric and spectroscopic studies [12].

Reduction of the Mononuclear Species CuL'^{2+} (1)

Polarograms in water show a reduction into two waves of equal height which are proportional to the concentration of CuL'^{2+}. Although there is some overlap with the mercury oxidation curve, the half-wave potential could be measured as +0.17 V. The second wave proceeds irreversibly with a half-wave potential of −0.38 V. It possesses the features of kinetic waves: height independent of the height of the mercury reservoir and dependent on the temperature (increase of 10% per degree). Addition of an excess of Cu^{2+} to a solution of CuL'^{2+} increases the second wave without modification of the first one. A 'EEC' mechanism can thus be proposed:

$$CuL'^{2+} + e^- \rightleftharpoons CuL'^{+}$$

$$CuL'^{+} + e^- \rightleftharpoons Cu + L'$$

$$L' + Cu^{2+} \rightleftharpoons CuL'^{2+}$$

Two coulometric measurements performed at 0.0 and −0.6 V confirmed this scheme; within the experimental error, each wave corresponds to the transfer of one electron. In addition, cyclic voltammetry was performed using a Pt electrode to avoid the oxidation of mercury. The ratio I_{pc}/I_{pa} is almost equal to 1; the value of $E_{pa} - E_{pc}$ is 60 mV for a scan of 12.5 mV s^{-1}, but increases with the scan rate, both results indicating a quasi-reversible process. The $E_{1/2}$ potential is then 0.24 V. Furthermore, the plot of I_{pc} versus the scan rate shows slight curvature due to some absorption feature.

The polarographic and coulometric measurements in propylene carbonate indicate that the same reduction scheme occurs: the potentials corresponding to two one-electron processes are observed at 0.48 and −0.40 V. The slope of the logarithmic analysis of the first wave is 66 ± 4 mV, the height of which is proportional to the square root of the mercury reservoir height and to the concentration of CuL'^{2+}. These results demonstrate that the reduction current is controlled by a diffusion phenomenon.

The cyclic voltammetry of **1** was also examined using a mercury electrode. The following features are observed:

$I_{pa}/I_{pc} \sim 1$

$E_{pa} - E_{pc} = 59$ mV with $\nu = 400$ mV s^{-1}

$(E_{pa} + E_{pc})/2 = 0.48$ V

I_{pa} and I_{pc} proportional to $\sqrt{\nu}$

Such characteristics are in agreement with a quasi-reversible reduction and a slight absorption of the copper(I) complex.

Reduction of the Dinuclear Complex Cu_2L^{4+} (2)

The study has been carried out only in propylene carbonate because the formation of the hydroxo species $Cu_2(\mu\text{-}OH)L^{3+}$ is observed concomitant to the dissolution of **2** in water. Although the presence of the latter species cannot be avoided even in extensively dried propylene carbonate, its concentration has been demonstrated by spectrophotometric measurements as being less than 4% under the conditions used.

The polarographic waves of equal height are observed at 0.42 and −0.35 V. The limiting diffusion currents follow a linear law in function of the concentration of the complex. Coulometric reductions confirm that two Faradays are respectively exchanged per mole of complex for each wave. The logarithmic analysis of the first wave leads to a slope of 59.6 mV which corresponds to a difference of the standard potentials of each monoelectronic step $E^\circ_1 - E^\circ_2 =$ 36.5 mV. A cyclic voltammogram of **2** at a mercury electrode confirms this redox behavior: the experimental value $E_p - E_{p/2}$ of 55 mV corresponds to $E^\circ_2 - E^\circ_1 = 36$ mV, estimated according to Myers and Shain [14] in the case of a system which is reversible and not complicated by chemical reaction. Both values are in good agreement with the theoretical value of 35.6 mV characteristic of two metal centers having no interaction in a dinuclear unit [15, 16].

Reduction of the Dinuclear Complex $Cu_2(\mu\text{-}OH)L^{3+}$ (3)

In water, the polarogram of **3** reveals two main reduction waves of the same height, each corresponding to the two electron transfer reaction. The first one ($E_{1/2}$ = 0.17 V) is overlapped by the oxidation of mercury; the second ($E_{1/2}$ = −0.5 V) is typical of an irreversible reduction. An additional wave of very low intensity was detected at −0.15 V and is not observed when a rotating Pt electrode is used, we believe that its presence results from the chemical reduction of the hydroxo complex by Hg. A controlled coulometric reduction at $E = -0.25$ V indicates the involvement of two electrons per mole of complex together with the formation of a white precipitate which, by addition of O_2, regenerates a dinuclear Cu^{II} species with electrochemical properties which correspond closely to that of **3**.

In propylene carbonate, the polarographic study shows, as in water, two reduction waves with $E_{1/2}$ = 0.40 V and $E_{1/2}$ = −0.38 V, both corresponding to two one-electron transfers. While the latter is attributed to the reduction of Cu^I to Cu^0, more interestingly the first wave can be resolved using differential pulse polarography into two equal peaks separated by 180 mV. This combined with the cyclic voltammetric study supports the existence of an intermediate $Cu^{II}Cu^I$ species. Figure 1 displays the cyclic voltammogram of **3**. Two reduction peaks as well as the two corresponding oxidation peaks are observed but the latter are of higher intensity indicating that absorption of the reduced products is occurring. The four electrochemical reactions are relatively slow as demonstrated by the dependence of the peak potentials with the sweep rate. Although the observed waves are complicated by an absorption phenomenon which does not allow a quantitative analysis of the voltammetric data, the electrochemical scheme can be summarized by two reversible steps of successive one-electron transfer viz

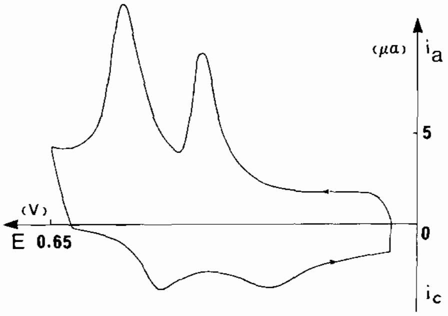

Fig. 1. Cyclic voltammetry of $Cu_2(\mu\text{-}OH)L^{3+}$ in propylene carbonate (Hg electrode, $LiClO_4$ 0.1 M, scan rate 5 V s^{-1}).

$$Cu_2^{II}(\mu\text{-}OH)L^{3+} \overset{+e^-}{\rightleftharpoons} Cu^{II}Cu^{I}(\mu\text{-}OH)L^{2+} \overset{+e^-}{\rightleftharpoons} Cu_2^{I}(\mu\text{-}OH)L^{+}$$

Interestingly, it would seem probable that the hydroxo bridge is retained during these processes and surprisingly [17] this bridge is relatively stable (*vis-à-vis* the CV scan rate) in the $Cu_2^I(\mu\text{-}OH)L^+$ complex. Moreover the intermediate mixed-valence $Cu^{II}Cu^I$ species has a stability which can be expressed by the conproportionation equilibrium constant (K_{con} = 1100) typical of the following reaction

$$Cu_2^{II}(\mu\text{-}OH)L^{3+} + Cu_2^{I}(\mu\text{-}OH)L^{+} \overset{K_{con}}{\rightleftharpoons} 2Cu^{II}Cu^{I}(\mu\text{-}OH)L^{2+}$$

Reduction of the Dinuclear Complex $Cu_2(\mu\text{-}Im)L^{3+}$ (4)

As in the case of **2**, the study has been carried out only in propylene carbonate because of the fast formation of **3** in water.

By polarography, two reduction waves are observed: the first one at about 0.35 V is spread out and due to the reduction of Cu^{II} into Cu^I whereas the second one at −0.4 V corresponds to the reduction of Cu^I to Cu^0. The cyclic voltammetry shows in the 0.2–0.6 V area two redox couples which somewhat overlap. The pulse polarography allows us to detect two peaks of equal intensity at 0.30 and 0.41 V, with a separation value of 110 mV which is much smaller than for **3** and which again indicates a relatively stable $Cu^{II}Cu^I$ species.

TABLE 1. Redox potentials and conproportionation constants for complexes **1**–**4** in PC

Complexes	E_1 (V) (vs. SCE)	E_2 (V) (vs. SCE)	$E_1 - E_2$ mV	K_{con}
1 CuL'^{2+}	0.480			
2 Cu_2L^{4+}	0.456	0.420	36	4
3 $Cu_2(\mu\text{-}OH)L^{3+}$	0.440	0.260	180	1100
4 $Cu_2(\mu\text{-}Im)L^{3+}$	0.410	0.300	110	73

Discussion

Table 1 summarizes the electrochemical data concerning complexes **1**–**4**. The markedly positive values of the reduction potentials of the complexes studied are a consequence of the nature of the donor atoms [18], especially the two sulfur atoms present in the binucleating ligand. The reduction potential of Cu^{II} into Cu^{I} in the mononuclear complex CuL^{2+} is very close to the first reduction potential observed in the dinuclear complexes **2**, **3** and **4**. This observation can be interpreted by the major influence of the coordination of the donor set NS_2O of the ligand L compared to that of the bridging atoms on this electrochemical step. However, the complexes **2**, **3** and **4** show significant differences in overall behavior. In **2**, reduction to Cu^{I} occurs at each copper site independently. In contrast, reduction in **3** and **4** occurs in two successive monoelectronic steps, passing via a stable $Cu^{II}Cu^{I}$ species as an intermediate. Further, the reduction of this intermediate into the $Cu^{I}Cu^{I}$ species depends on the nature of the bridging groups, the OH group appearing to favor the stabilization of the mixed-valence species $Cu^{II}Cu^{I}$ more than the imidazolate anion. This is reflected in the conproportionation constant which is considerably higher for **3** than for **4**. Part of this may result from the relatively lower stability of the $Cu^{I}Cu^{I}$ species with OH^- compared with Im^-, copper(I) in general being better stabilized by nitrogen than by oxygen donor ligands. We may add that the stabilization of the mixed-valence $Cu^{II}Cu^{I}$ by a bridging hydroxo ligand is to our knowledge unusual; for example, there is no evidence for such species being observed in a similar series of dinuclear complexes [19].

Another interesting aspect of this study lies in the electrochemical behavior of **2** as compared with that of other dielectronic receptors possessing two equivalent and non-interacting redox centers. A change of ligand conformation in **2** can easily occur because of the known flexibility of L, but nevertheless, electrochemical behavior is found analogous to that which is observed in more rigid cryptate complexes [7].

These dinuclear complexes thus have similar redox properties and magnetic behavior to type III proteins such as high positive potentials in the range of 0.4–0.7 V (versus NHE) as found for tyrosinase [20], laccase [10] and hemocyanin [21] as well as strongly magnetically coupled Cu^{II} ions. However, although the ligand construction imparts of these dinuclear copper systems certain properties which find analogy in nature, the presence of thioether donors in the ligand (which are seemingly absent in the type III sites in proteins) limits the application of such complexes as realistic models for such sites.

References

1 (a) W. P. J. Gayema, W. G. J. Hol, J. M. Vereijken, N. M. Soeter, H. J. Bak and J. J. Beintema, *Nature (London), 309* (1984) 23; (b) W. G. J. Hol and A. Volbeda, *Rev. Port. Quim., 27* (1985) 42.

2 R. R. Gagné, C. A. Koval, T. J. Smith and M. C. Cimolino, *J. Am. Chem. Soc., 101* (1979) 4571.

3 R. C. Long and D. N. Hendrickson, *J. Am. Chem. Soc., 105* (1983) 1513.

4 A. W. Addison, *Inorg. Nucl. Chem. Lett., 12* (1976) 899.

5 S. K. Mandal, B. Adhikary and K. Nag, *J. Chem. Soc., Dalton Trans.*, (1986) 1175.

6 D. S. Polcyn and I. Shain, *Anal. Chem., 38* (1966) 370.

7 J. P. Gisselbrecht, M. Gross, A. H. Alberts and J. M. Lehn, *Inorg. Chem., 19* (1980) 1386.

8 D. E. Fenton and R. L. Lintvedt, *J. Am. Chem. Soc., 100* (1978) 6367.

9 D. E. Fenton, R. R. Schroeder and R. L. Lintvedt, *J. Am. Chem. Soc., 100* (1978) 1931.

10 J. A. Fee, *Struct. Bonding (Berlin), 23* (1975) 1.

11 P. L. Burk, J. A. Osborn, M.-T. Youinou, Y. Agnus, R. Louis and R. Weiss, *J. Am. Chem. Soc., 103* (1981) 1273.

12 M.-T. Youinou, J. A. Osborn, J.-P. Collin and P. Lagrange, *Inorg. Chem., 25* (1986) 453.

13 M.-T. Youinou and J. A. Osborn, in preparation.

14 R. L. Myers and I. Shain, *Anal. Chem., 41* (1969) 980.

15 F. Ammar and J. M. Saveant, *J. Electroanal. Chem., 47* (1973) 215.

16 J. B. Flanagan, S. Margel, A. J. Bard and F. C. Anson, *J. Am. Chem. Soc., 100* (1978) 4248.

17 N. A. Bailey, D. E. Fenton, J. Lay, P. B. Roberts, J.-M. Latour and D. Limosin, *J. Chem. Soc., Dalton Trans.*, (1986) 2681.

18 G. S. Patterson and R. H. Holm, *Bioinorg. Chem., 4* (1975) 257.

19 S. K. Mandal, L. K. Thompson and A. W. Hanson, *J. Chem. Soc., Chem. Commun.*, (1985) 709.

20 N. Makino, P. McMahill, H. S. Mason and T. H. Moss, *J. Biol. Chem., 249* (1974) 6062.

21 J. B. Conant, B. F. Chow and E. B. Schoenbach, *J. Biol. Chem., 101* (1933) 463.