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Electrochemical Studies on Some Mono- and Dinuclear Copper(II) Complexes of Macrocyclic Schiff-Base Ligands

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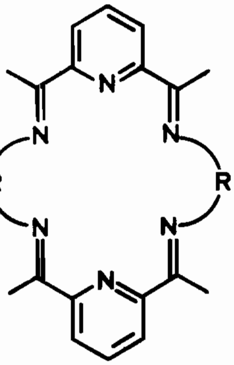
Introduction

An important property of several Type 3 copper proteins, containing dinuclear active sites, is their ability to transfer two electrons in a cooperative manner thereby by-passing the energetically unfavourable (and biologically undesirable) formation of superoxide [1]. Among the synthetic di-Cu(II) systems recently reported two types of electrochemical behaviour [2] have been recognised, *viz.* (i) reduction of the two Cu(II) ions to Cu(I) at the same potential [3, 4] and (ii) stepwise reduction at different potentials [5, 6]. The reasonable expectation that di-electronic transfers of the first type might be associated with closely juxtaposed and strongly interacting metal centres, as, indeed has been observed for some di-Cu(II)-triketonates [3], is not always borne out in practice. In fact, the more commonly observed behaviour, whether for magnetically coupled or non-interacting metal centres, is a two-step reduction at different potentials. It seems that factors other than, or in addition to, magnetic interaction are important and there is a need for studies of a wider range of structurally characterised synthetic systems. We here report some cyclic voltammetric studies on five di-Cu(II) (and one mononuclear Cu(II)) complexes of the macrocyclic tetraimine ligands L^1–L^3 derixed from the cyclic [2 + 2] Schiff base condensation of 2,6-diacetylpyridine with, respectively, 3,6-dioxaocta-1,8-diamine, 3-thiapenta-1,5-diamine and 1,3-diaminopropane.



L^1, R = $(CH_2)_2$–O–$(CH_2)_2$–O–$(CH_2)_2$
L^2, R = $(CH_2)_2$–S–$(CH_2)_2$
L^3, R = $(CH_2)_3$

Experimental

The preparation and structural characterisation of the complexes have been described previously [7–9].

The electrochemical experiments were performed at 25 ± 0.01 °C in dry dimethylacetamide under O_2-free conditions using a PAR model 174 polarographic analyser, a PAR model 175 universal programmer and a Houston Omnigraph 2000 X–Y recorder. In the three-electrode system the working electrode was either a hanging mercury drop electrode (HMD) or a glassy carbon electrode (C). The counter electrode was a platinum spiral and the reference electrode was saturated calomel. The supporting electrolyte was tetrabutyl ammonium perchlorate (0.1 *M*). All solutions were 10^{-3}–10^{-4} *M* in complex.

Preliminary experiments were carried out to determine the best combination of experimental parameters (working electrode, solvent, scan rates). Cyclovoltammetric waves were classified as reversible, quasi-reversible or irreversible on the basis of constancy (or otherwise) of E_{p_c}, E_{p_a} and ΔE_p with scan rate, the magnitude of ΔE_p, and the ability to reproduce the wave on successive scans. Tests based on peak currents were more difficult to apply because the wave profiles prevented the measurement of such currents with reasonable accuracy in most cases. Selected data are summarised in Table I.

Results and Discussion

The macrocyclic ligands L^1–L^3 all contain two planar trimethine 'N_3' donor groups linked by two saturated chains which vary in length and in the

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TABLE I. Electrochemical data for the complexes.

	Complex	Electrode	Scan Rate[a]		E_{p_c} [b]	E_{p_a} [b]	ΔE_p [b]	$E_{1/2}$ [f b]		Comments
(*1*)	$[CuL^1][ClO_4]_2 \cdot H_2O$	HMD	50		−445	−335	110	−390		Quasi-reversible
		HMD	100		−445	−335	110	−390		
(*2*)	$Cu_2L^1(ClO_4)_4 \cdot 2H_2O$	HMD	50	(i)	−90	+25	115	−33	(i)	Quasi-reversible
				(ii)	−470	−400	70	−435	(ii)	Reversible
(*3*)	$Cu_2L^1(OH)(ClO_4)_3 \cdot H_2O$	HMD	50	(i)	−190					No anodic peak for (i)
		HMD	50	(ii)	−440	−340	100	−390	(ii)	Quasi-reversible
		HMD	100	(i)	−200					
		HMD	100	(ii)	−440	−350	90	−395		
(*4*)	$Cu_2L^1(im)(ClO_4)_3$	HMD	50	(i)	−250					No anodic peak for (i)
		HMD	50	(ii)	−430	−360	70	−395	(ii)	Quasi-reversible
(*5*)	$Cu_2L^2(im)(ClO_4)_3 \cdot H_2O$	C	20		−280	−190	90	−235		Additional ill-defined anodic peak at +65 mV
		C	50		−290	−180	110	−235		
(*6*)	$Cu_2L^3(OH)(ClO_4)_3 \cdot H_2O$	C	100	(i)	−300	−235	65	−268	(i)	Reversible
		C	100	(ii)	−600				(ii)	Irreversible

[a] $mV\ s^{-1}$. [b] mV(±5) *vs.* SCE.

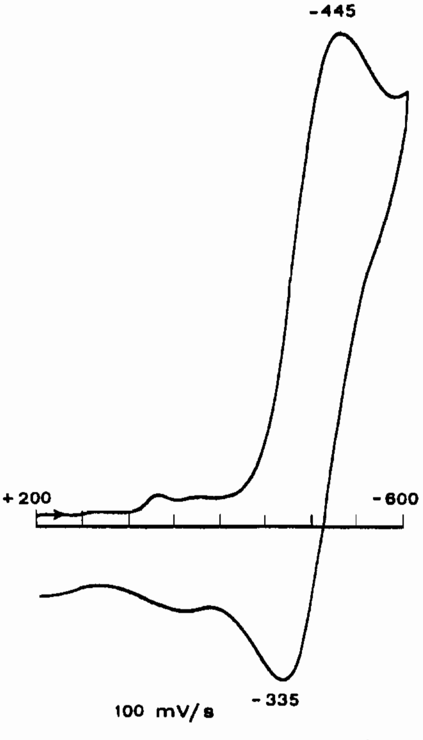


Fig. 1. Cyclic voltammogram of $[CuL^1][ClO_4]_2 \cdot H_2O$ (*1*) in dimethylacetamide, HMD electrode *vs.* SCE.

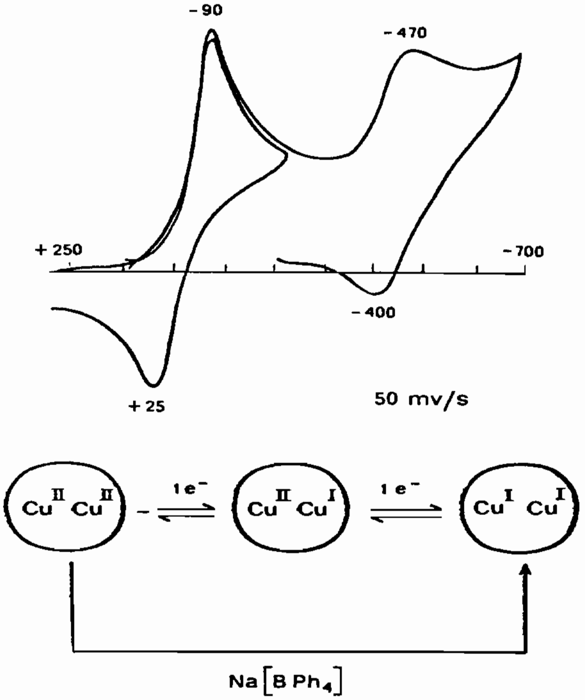


Fig. 2. Cyclic voltammogram of $Cu_2L^1(ClO_4)_4 \cdot 2H_2O$ (*2*) in dimethylacetamide, HMD electrode *vs.* SCE.

presence, or otherwise, of one or more heteroatoms (O, S). As revealed by X-ray structural studies [7–9] of complexes (*3*)–(*6*) each trimethine group occupies three sites of a distorted square plane with the fourth equatorial site being taken by a bridging anionic ligand [OH^- or imidazolate (*im*)]; the heteroatoms of L^1 and L^2 are not coordinated [10]. One or both of the axial sites at each Cu(II) centre are occupied by (weakly bound) ClO_4^- ions or H_2O molecules to give, in all cases, an overall [4 + 1] or [4 + 2] coordination geometry. In the tetra-perchlorate complex (*2*) no anionic bridge exists between the metal centres although the occurrence of a H_2O bridge in the solid state cannot be excluded [7]; however, an aqua bridge, if present, is unlikely to survive in solution. In all the other di-Cu complexes electronic and ESR spectra and electrical conductance measurements indicate that the bridge is retained in

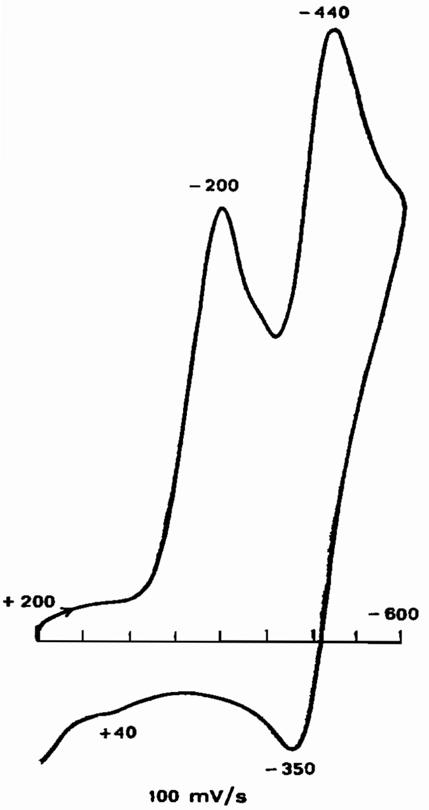
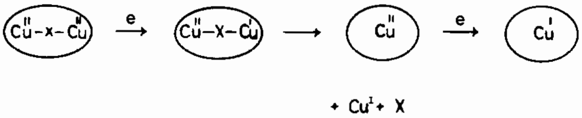


Fig. 3. Cyclic voltammogram of $Cu_2L^1(OH)(ClO_4)_3 \cdot H_2O$ (*3*) in dimethylacetamide, HMD electrode *vs.* SCE.

solution. The mononuclear complex (*1*) is assigned a 6-coordinate structure comprising the two tridentate trimethine moieties disposed mutually at ~90° [11] as found by diffraction studies of the corresponding Fe(II) and Co(II) complexes [12]; as with the other complexes the oxygen atoms of the polyether chains are not coordinated. Variable temperature magnetic susceptibility measurements have established that in all four of the 'bridged' complexes the Cu(II) ions are antiferromagnetically coupled, the singlet–triplet separation (2J) being –240, –42, –42, and –64 cm^{-1} for (*3*), (*4*), (*5*), and (*6*), respectively [7–9].

The mononuclear complex (*1*) showed a quasi-reversible wave at $E_{1/2}^f = -390$ mV which may be assigned to a Cu(II)/Cu(I) redox process (Fig. 1). For the di-Cu(II) complex of the same macrocycle L^1 in which the metal centres are not linked by any intramolecular bridge two reductions are seen in the 0 to –500 mV range (Fig. 2). The first quasi-reversible wave occurred at a considerably more positive potential ($E_{1/2}^f = -33$ mV) than found for the mononuclear complex (*1*), while the second (almost reversible) wave occurred at a slightly more negative potential ($E_{1/2}^f = -435$ mV). Coulometric experiments carried out at –600 mV established that the two processes together correspond to the transfer of two electrons so we may reasonably conclude that each wave represents a one-electron process. The separation ($\Delta E_{1/2}^f \sim 400$ mV) of the two waves (corresponding to a conproportionation constant, K_{con}, of $\sim 10^7$) represents an appreciable stabilisation of the Cu(I)$\cdots$Cu(II) mixed valence species although this has not been prepared chemically. Di-Cu(I) derivatives have been isolated, however, by treatment of complex (*2*) with two equivalents of $Na[BPh_4]$ [7].

Quite different electrochemical behaviour was observed for the di-Cu(II) complexes (*3*) and (*4*) of the same macrocycle in which the metal centres are now linked intramolecularly via an anionic bridge [OH^- in (*3*), *im* in (*4*)]. As before, two distinct reduction processes were seen but this time with a smaller separation between the cathodic peaks (Fig. 3). The first reduction was irreversible (little or no anodic peak) and its position depended on the nature of the anionic bridge (see Table I). The second reduction was quasi-reversible and was independent of the nature of the bridge. In fact, this wave had the same electrochemical characteristics as that found for the mononuclear complex (*1*) (compare Fig. 1 with Fig. 3). We interpret this in terms of an ejection of the Cu(I) ion along with the anionic bridge (X) from the macrocyclic cavity once the first Cu(II) ion has been reduced, as indicated diagrammatically in the Scheme. This observation is consistent with earlier chemical studies which showed, firstly, that the mononuclear complex (*1*) readily 'unwraps' in the presence of excess free Cu(II) to accommodate a second Cu(II) ion, and, secondly, that air oxidation of solutions of the di-Cu(I) complex affords the mononuclear Cu(II) complex (*1*). It seems, in this case, that the effect of the anionic bridge is to destabilise the mixed valence species.



When the cavity size of the macrocycle is reduced from 30 member atoms (as in L^1) to 24 member atoms (as in L^2) no ejection of a Cu(I) ion following reduction to the μ-imidazolato-di-Cu(II) complex (*5*) was observed. In fact, only a single reduction process was seen in the +500 to –800 mV range. Although apparently quasi-reversible ($\Delta E_p \sim 90$ mV) the anodic peak was rather broad and a second ill-defined anodic peak of unknown origin was discernible at +65 mV. The fact that, unlike complexes (*3*) and (*4*), no metal was ejected from the macrocycle cavity can be understood in terms of the length of the saturated chains of L^2 which are too short to allow the formation of a stable mononuclear complex analogous to (*1*).

For the μ-hydroxo-di-Cu(II) complex (*6*) containing the smallest (20-membered) macrocycle L^3 a reversible wave at $E_{1/2}{}^f = -268$ mV was followed by an irreversible process at ~−600 mV with no discernible anodic counterpart. The results indicate that a stable di-Cu(I) complex is not to be expected for this system and, indeed, attempts to prepare such a species were unsuccessful. However, the separation of ~300 mV in the cathodic peaks coupled with the reversibility of the first reduction process hold out some promise for the isolation of a mixed valence complex by chemical means.

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References

1 B. G. Malmstrom, in 'New Trends in Bio-inorganic Chemistry', ed. R. J. P. Williams and J. R. R. F. Da Silva, Academic Press, London (1978).
2 D. S. Polcyn and I. Shain, *Anal. Chem.*, *38*, 370 (1966).
3 D. E. Fenton and R. L. Lindvedt, *J. Am. Chem. Soc.*, *100*, 6367 (1978); see also R. L. Lindvedt, in 'Copper Coordination Chemistry; Biochemical and Inorganic Perspectives', ed. K. D. Karlin and J. Zubieta, Adenine Press, New York (1983).
4 J. P. Gisselbrecht, M. Gross, A. H. Alberts and J. M. Lehn, *Inorg. Chem.*, *19*, 1386 (1980);
R. Louis, Y. Agnus, R. Weiss, J. P. Gisselbrecht and M. Gross, *Nouv. J. Chim.*, *5*, 71 (1981).
5 R. R. Gagne, C. A. Koval and T. J. Smith, *J. Am. Chem. Soc.*, *99*, 8367 (1977);
R. R. Gagne, C. A. Koval, T. J. Smith and M. C. Cimolino, *ibid.*, *101*, 4571 (1979).
6 A. W. Addison, *Inorg. Nucl. Chem. Lett.*, *12*, 899 (1976).
7 M. G. B. Drew, M. McCann and S. M. Nelson, *J. Chem. Soc. Dalton*, 1868 (1981).
8 M. G. B. Drew, C. Cairns, A. Lavery and S. M. Nelson, *J. Chem. Soc. Chem. Comm.*, 1122 (1980).
9 M. G. B. Drew, J. Nelson, F. S. Esho, V. McKee and S. M. Nelson, *J. Chem. Soc. Dalton*, 1837 (1982).
10 Complex (*3*) is an exception, in that an ether oxygen atom is weakly bonded to one of the Cu(II) ions in an apical position.
11 S. M. Nelson, M. McCann, C. Stevenson and M. G. B. Drew, *J. Chem. Soc. Dalton*, 1477 (1979).
12 M. G. B. Drew, M. McCann and S. M. Nelson, *Inorg. Chim. Acta*, *41*, 213 (1980).