

## Dinuclear Metal Complexes. Part 4.† Electrochemical Studies of Macrocyclic Dicopper(II) Complexes. Investigation of the Effect of Solvents, Donor Groups, and Steric Constraints on the Stability of Mixed-valence Copper(II)–Copper(I) Complexes‡

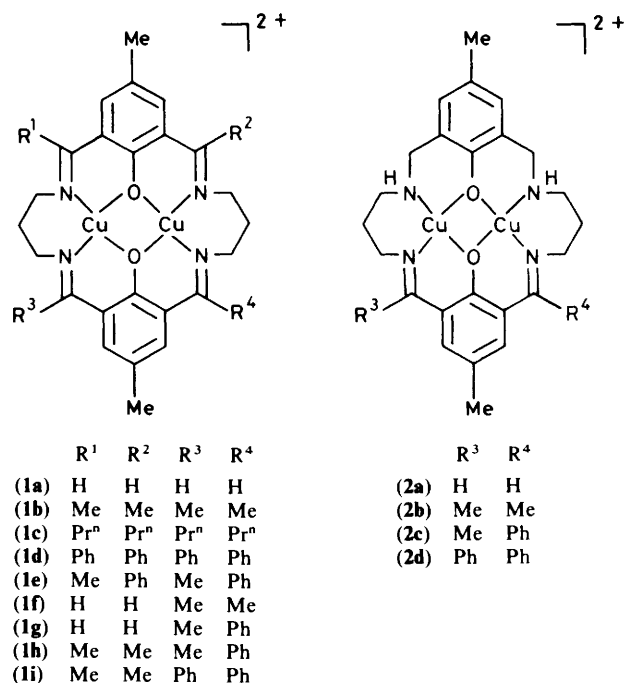
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Two series of macrocyclic dicopper(II) complexes of stoichiometry  $[\text{Cu}_2\text{L}][\text{ClO}_4]_2 \cdot 2\text{H}_2\text{O}$  have been synthesized and characterized. Compounds belonging to series (1) are derived from the 6,12,18,24-substituted (H,H,Me,Me; H,H,Me,Ph; Me,Me,Me,Ph; Me,Me,Ph,Ph) macrocycle 7,11;19,23-dimetheno-9,21-dimethyl-1,5,13,17-tetra-azacyclotetracos-5,7,9,12,17,19,21,24-octaene-25,26-diol ( $\text{H}_2\text{L}$ ). Complexes belonging to series (2) are related to those of series (1) by replacement of two of the  $-\text{CH}=\text{N}-$  linkages by  $-\text{CH}_2-\text{NH}-$  groups and the segment containing two azomethine linkages having the 6,12-substituents H,H; Me,Me; Me,Ph; Ph,Ph. The electrochemistry of these compounds has been investigated in MeCN and  $\text{CH}_2\text{Cl}_2$  solvents using platinum and glassy carbon electrodes. In all cases cyclic voltammograms show sequential one-electron transfers at two different potentials, and from these data the conproportionation constant ( $K_c$ ) and free energy of the mixed-valent species ( $\Delta G_c$ ) have been evaluated. Electrochemical results have been analysed in terms of the effect due to solvent, donor groups, and steric constraints. Values of  $K_c$  for all of the compounds are greater in MeCN than those in  $\text{CH}_2\text{Cl}_2$ , and the  $K_c$  value for any compound belonging to series (1) is greater than its analogue in series (2). Factors affecting stability and intramolecular electron-transfer rates of  $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}\text{L}^+$  species are discussed.

In recent years electrochemical studies of macrocyclic dicopper(II) complexes<sup>1-5</sup> obtained by condensing 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde and its analogues with various diamines have underlined the relevance of determining the conproportionation constant,  $K_c$ , which measures the relative stability of the mixed-valent species over the equilibrium mixture of the iso-valent species. Such studies are becoming increasingly important in the realm of intramolecular electron transfer in mixed-valence compounds.<sup>6-12</sup> In general, the magnitude of  $K_c$  can be related to several factors,<sup>2,11-14</sup> of which the energy of electron delocalisation plays a key role. Concerning the stability of the mixed-valent species,  $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ , in the macrocyclic system, one would expect that larger  $K_c$  values indicate greater electron delocalisation energy. However, analysis of the recently obtained results<sup>5</sup> (see below) indicates that this may not be the case. Until now the determination of  $K_c$  was mostly limited to measurements made in a single solvent. It is not known to what extent the stability of a mixed-valent species will be affected by solvents which preferentially bind to metal ions either in the oxidized or reduced states. Such a solvent effect on  $K_c$  has been reported<sup>15</sup> recently in a study dealing with dinuclear copper(II) complexes of 4-butyl-2,6-bis-(*N*-{[(heptylthio)mercapto]methyleneimino}formimidoyl)-phenol.

In a previous paper we reported<sup>4</sup> the synthesis and cyclic voltammetric studies of the macrocyclic systems (1a)–(1e) in acetonitrile using a hanging mercury drop electrode (h.m.d.e.). The goal of the present study is to investigate the electrochemical behaviour of the compounds (1f)–(1i) and (2a)–(2d) in two different solvents, *viz.* MeCN and  $\text{CH}_2\text{Cl}_2$  which differ greatly in their co-ordinating abilities. The voltammetric studies reported here were made with Pt and glassy carbon electrodes in order to observe the electrode effect. As illustrated above, the



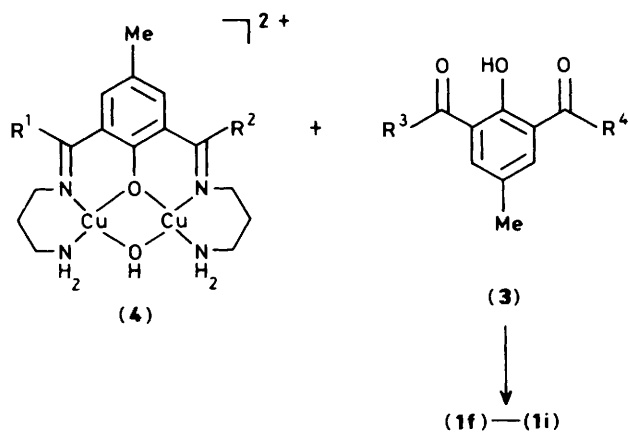
compounds (1) differ from their counterparts (2) by two  $-\text{CH}=\text{N}-$  linkages in the former replaced by two  $-\text{CH}_2\text{NHCH}_2-$  groups in the latter. Thus a comparative study of their electrochemistry will reflect the effect of functional groups as well as steric constraints in the macrocyclic systems.

### Experimental

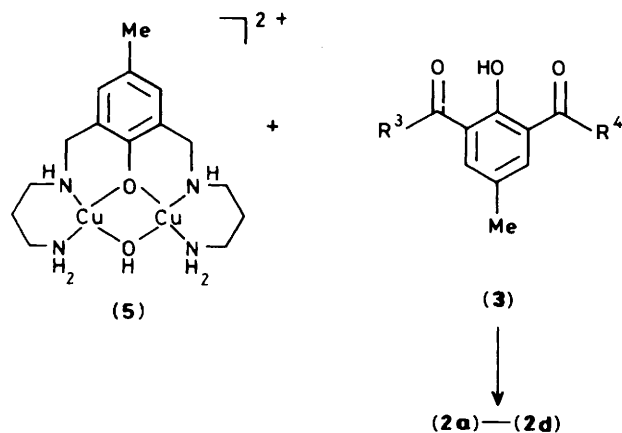
**Materials.**—All chemicals were reagent grade and used as received. 2-Hydroxy-5-methylbenzene-1,3-dicarbaldehyde (3a),

† Part 3 is ref. 16.

‡ *Non-S.I. units employed:* B.M. =  $9.27 \times 10^{-24} \text{ J T}^{-1}$ , cal = 4.184 J.



Scheme 1. (4a)  $R^1 = R^2 = H$ ; (4b)  $R^1 = R^2 = Me$ ; (3b)  $R^3 = R^4 = Me$ ; (3c)  $R^3 = Me, R^4 = Ph$ ; (3d)  $R^3 = R^4 = Ph$



Scheme 2. (3a)  $R^3 = R^4 = H$ ; (3b)–(3d) as in Scheme 1

1,3-diacetyl-2-hydroxy-5-methylbenzene (3b), 3-benzoyl-2-hydroxy-5-methylacetophenone (3c), and 1,3-dibenzoyl-2-hydroxy-5-methylbenzene (3d) were prepared as described earlier.<sup>4</sup> The perchlorate salts of the hydroxo-bridged dicopper(II) complexes (4a)·H<sub>2</sub>O, (4b)·2H<sub>2</sub>O, and (5)·H<sub>2</sub>O were prepared according to the previously described methods.<sup>16</sup> MeCN and CH<sub>2</sub>Cl<sub>2</sub> used for electrochemical measurements were purified by literature methods.<sup>17</sup> Reagent grade tetraethylammonium perchlorate (teap) and tetrabutylammonium perchlorate (tbap) were recrystallized from ethanol and dried exhaustively in vacuum before use.

**Physical Measurements.**—Infrared spectra were recorded on a Perkin-Elmer model 783 i.r. spectrophotometer in KBr pellets. Electronic spectra in solution were obtained with a Pye-Unicam SP8-150 spectrophotometer. A PAR model 155 vibrating sample magnetometer was used to measure the magnetic susceptibility of the compounds at room temperature. Calibration of the magnetometer was made with Hg[Co(SCN)<sub>4</sub>].

**Electrochemistry.**—Cyclic voltammetric measurements were carried out with a Bioanalytical Systems Inc. CV-1B instrument equipped with a three-electrode system. The working electrode used was either a platinum button or a glassy carbon (g.c.) electrode. The reference electrode used was a saturated calomel electrode (s.c.e.) with a porous Vycro bridge. The auxiliary electrode was a Pt-wire coil. The redox potentials reported in this work were referenced to a ferrocene-ferrocenium (fc-fc<sup>+</sup>) couple. The oxidation wave for ferrocene ( $5 \times 10^{-4}$  mol dm<sup>-3</sup>) in the electroactive solution was used as the internal reference for voltage measurements. The concentration of the dicopper(II) complexes was in the range  $9 \times 10^{-4}$ – $1.2 \times 10^{-3}$  mol dm<sup>-3</sup> in MeCN and  $(6-8) \times 10^{-4}$  mol dm<sup>-3</sup> in CH<sub>2</sub>Cl<sub>2</sub>. For MeCN solutions teap was used as the supporting electrolyte, while for CH<sub>2</sub>Cl<sub>2</sub> solutions the supporting electrolyte was tbap. All measurements were carried out at ambient temperature under an atmosphere of argon. Prior to measurements the solution was purged with argon saturated with solvent vapour for ca. 10 min to remove dissolved oxygen.

**Preparation of the Complexes.**—Compounds (1f)–(1i). These compounds were obtained according to the previously described procedure.<sup>16</sup> A mixture (1:1 mol ratio) of (4a) and (3b) [for (1f)], (4a) and (3c) [for (1g)], (4b) and (3c) [for (1h)], and (4b) and (3d) [for (1i)] in methanol (50 cm<sup>3</sup> for 2 mmol of each reactant) was refluxed for 36 h. After partial removal of the solvent, the solution was allowed to crystallize at ambient

temperature. The crystals that deposited on standing overnight were collected by filtration and recrystallized from methanol. All were obtained as dihydrates.

**Compounds (2a)–(2d).** These compounds were prepared essentially in the same way as described above. The following combinations were used: (5) and (3a) [for (2a)], (5) and (3b) [for (2b)], (5) and (3c) [for (2c)], and (5) and (3d) [for (2d)]. Compound (2a) was recrystallized from water and (2b)–(2d) from methanol. All were obtained as dihydrates.

All of the compounds prepared have the composition [Cu<sub>2</sub>L][ClO<sub>4</sub>]<sub>2</sub>·2H<sub>2</sub>O (H<sub>2</sub>L = neutral macrocycle) and gave satisfactory analytical results for C, H, N, and Cu analyses. Analytical data for some of these compounds reported previously<sup>16</sup> agreed satisfactorily with the present set of preparations.

## Results and Discussion

**Synthesis and Characterization.**—The macrocyclic dicopper(II) complexes (1f)–(1i) containing azomethine linkages were obtained according to Scheme 1. It is important to note that unlike the derivatives (1a)–(1e), these compounds cannot be prepared directly by template condensation of bis(1,3-diaminopropane)copper(II) perchlorate with appropriate derivatives of (3). The mechanism of formation of the product according to Scheme 1 was delineated previously.<sup>16</sup> The binuclear macrocyclic complexes (2a)–(2d) which contain two amino and two azomethine groups were synthesized as shown in Scheme 2.

Complexes (1f)–(1i) are characterized by the presence of a broad band due to water molecules at ca. 3 450 cm<sup>-1</sup>, a strong band at ca. 1 620 cm<sup>-1</sup> due to the  $\nu(C=N)$  vibration, and another strong band at ca. 1 540 cm<sup>-1</sup> due to the  $\nu(C=O)$  vibration of the phenol. Compounds (2a)–(2d) also contain these i.r. bands almost at the same positions, but in addition display a  $\nu(N-H)$  vibration at ca. 3 230 cm<sup>-1</sup>. The magnetic moments of the compounds (1f)–(1i) and (2a)–(2d), after diamagnetic corrections,<sup>18</sup> are found to lie in the narrow range 0.65–0.78 B.M. and indicate considerable separation between singlet and triplet energy states ( $-2J \geq 600$  cm<sup>-1</sup>).<sup>19</sup> The electronic spectra of all of the macrocyclic complexes exhibit two absorption bands at ca. 17 000 and 28 000 cm<sup>-1</sup> due to copper-based  $d-d$  transition(s) and C=N originated  $\pi-\pi^*$  transition, respectively. However, as expected, the molar absorptivity ( $\epsilon$ ) of the absorption occurring at 28 000 cm<sup>-1</sup> in the compounds (1f)–(1i) [ $\epsilon$  ca. 13 500 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>] is considerably stronger than that of (2a)–(2d) [ $\epsilon$  ca. 8 400 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>].

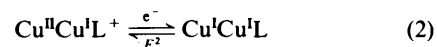
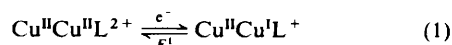
**Table 1.** Electrochemical data<sup>a</sup> for the macrocyclic dicopper(II) complexes

Complex	Solvent	Electrode	$v/\text{mV s}^{-1}$	$E^1/\text{V}^b$	$\Delta E_p/\text{mV}^c$	$E^2/\text{V}^d$	$\Delta E_p^2/\text{mV}^e$
(1f)	MeCN	Pt	50–500	–0.83	120–200	–1.37	100–140
	MeCN	g.c.	50–300	–0.83	120–180	–1.37	120–180
	CH <sub>2</sub> Cl <sub>2</sub>	Pt	25–1 000	–0.905	110–170	–1.36	120–240
(1g)	MeCN	Pt	50–500	–0.825	100–130	–1.36	85–120
	MeCN	g.c.	50–500	–0.82	100–140	–1.36	95–140
	CH <sub>2</sub> Cl <sub>2</sub>	Pt	100–1 000	–0.905	150–230	–1.38	140–280
(1h)	MeCN	Pt	100–600	–0.845	90–120	–1.46	120–160
	MeCN	g.c.	200	–0.84	90	–1.45	120
	CH <sub>2</sub> Cl <sub>2</sub>	Pt	200	–0.91	150	ca. –1.4 <sup>e</sup>	
(1i)	MeCN	Pt	200	–0.85	120	–1.42	140
	MeCN	g.c.	50–500	–0.85	80–110	–1.41	130–170
	CH <sub>2</sub> Cl <sub>2</sub>	Pt	25–500	–0.96	100–200	ca. –1.4 <sup>e</sup>	
(1d)	MeCN	Hg <sup>f</sup>	50	–0.865	65	–1.415	60
	dmf	g.c.	50	–0.87	90	–1.415	100
	CH <sub>2</sub> Cl <sub>2</sub>	Pt	100–1 000	–0.93	120–240	–1.41	160–260
(2a)	MeCN	g.c.	50–500	–0.96	100–150	–1.25	150–250
	CH <sub>2</sub> Cl <sub>2</sub>	Pt	50–700	–1.03	80–160	–1.25	110–200
(2b)	MeCN	g.c.	50–500	–0.93	100–160	–1.31	130–260
	CH <sub>2</sub> Cl <sub>2</sub>	Pt	50–500	–1.01	120–250	–1.34	220–340
(2c)	MeCN	g.c.	50–200	–0.95	80–120	–1.33	120–160
	CH <sub>2</sub> Cl <sub>2</sub>	Pt	25–400	–1.05	120–300	–1.38	200–400
(2d)	MeCN	g.c.	200	–0.95	80	ca. –1.4 <sup>e</sup>	
	CH <sub>2</sub> Cl <sub>2</sub>	Pt	200	–1.05	140	–1.42	240

<sup>a</sup> Potentials are referenced to  $\text{fc}-\text{fc}^+$  couple. <sup>b</sup>  $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}-\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$  couple. <sup>c</sup>  $\Delta E_p = E_{p,c} - E_{p,a}$ . <sup>d</sup>  $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}-\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$  couple. <sup>e</sup> Irreversible reduction. <sup>f</sup> Data taken from ref. 4.

**Electrochemistry.**—As already mentioned, cyclic voltammetric studies were carried out for the unsaturated macrocyclic complexes (1d), (1f)–(1i), and the partially saturated compounds (2a)–(2d) in MeCN and CH<sub>2</sub>Cl<sub>2</sub> using Pt and g.c. electrodes. In order to normalize the redox potentials obtained in two different solvents and also to circumvent any variations in junction potentials with time, or ohmic drop due to uncompensated solution resistance,<sup>2</sup> the reduction potentials listed in Table 1 were referenced to the  $\text{fc}-\text{fc}^+$  couple. The advantage of using  $\text{fc}-\text{fc}^+$  couple, which occurs at +0.40 V vs. aqueous n.h.e. and shows nominal solvent dependence, as an internal standard is well documented.<sup>20–22</sup>

The electrochemical responses observed for compounds (1f)–(1i) were quite similar. Figure 1 shows the cyclic voltammograms for (1g) in MeCN at various scan rates with a Pt electrode, and is typical of the compounds of this category in MeCN solvent. The electrochemical behaviour of the unsaturated macrocyclic systems in CH<sub>2</sub>Cl<sub>2</sub> is illustrated in Figure 2 by the cyclic voltammograms of (1d) obtained with a Pt electrode. The electrochemical data of (1d) and (1f)–(1i) in the two solvents and using both Pt and g.c. electrodes are given in Table 1. We previously investigated<sup>4</sup> the electrochemistry of the compounds (1a)–(1e) in MeCN using a h.m.d.e. and noted adsorption of the one-electron reduced species on the electrode. However, when this adsorption problem was overcome the two sequential electron transfers occurred reversibly. In the present study as is evident from Figures 1 and 2, and Table 1, no such adsorption problem occurred in either of the solvents when Pt and g.c. electrodes were used. The data given in Table 1 clearly indicate that in terms of formal redox potentials [ $E^j = 0.5(E_{p,a} + E_{p,c})$ ], as well as separation of peak potentials ( $\Delta E_p = E_{p,c} - E_{p,a}$ ) the electrochemical responses observed with the two electrodes were identical. In general, irrespective of the solvents and electrodes used, the two stepwise one-electron transfers (1) and (2) occurred quasi-reversibly as is evident from the adherence to the following criteria. (i) The  $E^j$  values ( $j = 1$

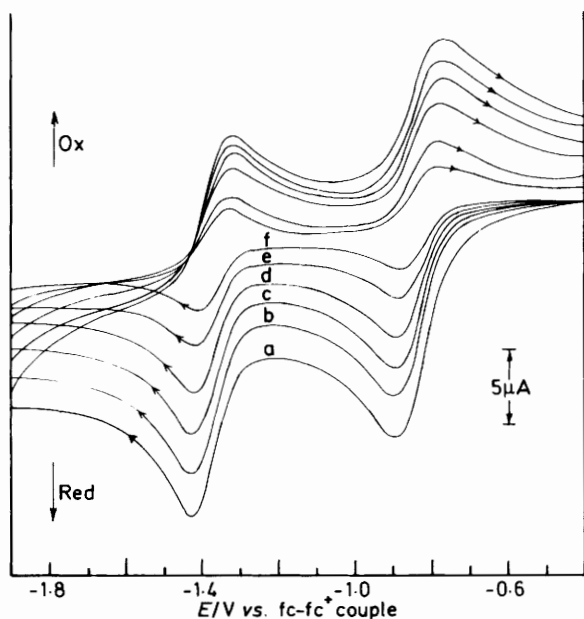


or 2) were independent of scan rates ( $v$ ). (ii) the  $\Delta E_p$  values increased with scan rates and were always greater than 60 mV. (iii) The ratio of the peak currents due to cathodic ( $i_{p,c}$ ) and anodic ( $i_{p,a}$ ) sweeps were close to unity at different scan rates. (iv) The product  $i_{p,c} \cdot v^{-1}$  remained constant. The formal redox potentials thus obtained can be regarded as thermodynamic values.

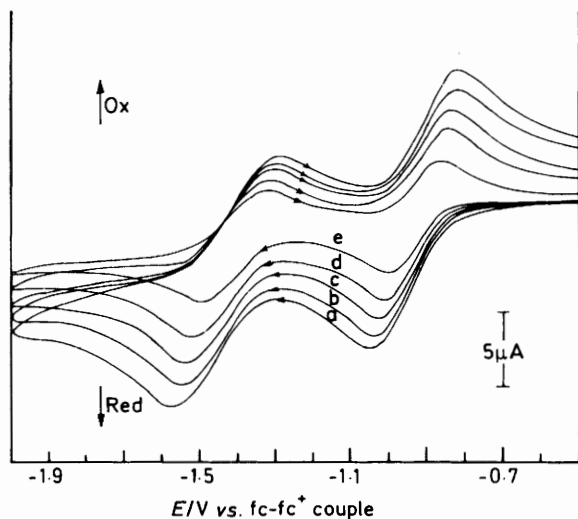
The electrochemical behaviour of the partially saturated macrocyclic complexes (2a)–(2d) is exemplified by the voltammograms of (2a) in CH<sub>2</sub>Cl<sub>2</sub> with a Pt electrode (Figure 3) and (2b) in MeCN with a g.c. electrode (Figure 4). The relevant electrochemical data for these compounds are set out in Table 1. Here also the dicopper(II) complexes are reduced in two steps, and the electron transfers occur quasi-reversibly.

Concerning the redox potentials due to the first electron transfer ( $E^1$ ) in compounds (1f)–(1i), it may be noted that both in MeCN and CH<sub>2</sub>Cl<sub>2</sub>, the  $E^1$  values remain unchanged showing no substitution effect. On the other hand,  $E^2$  values show some dependence on the nature of the peripheral substituents. The constancy of  $E^1$  with substituents can be rationalised in terms of electron transfer occurring at the triplet state.<sup>2,4</sup> The variation of  $E^2$  is a sequel to the difference in electron-releasing power of the substituents. However, unlike compounds (1b)–(1d),<sup>4</sup> no linear relationship between  $E^2$  and Hammett  $\sigma_m$  values could be obtained for (1f)–(1i).

The voltammetric behaviour of the compounds (2a)–(2d) shows similar substitution effects to those observed for (1f)–(1i). A comparison of the  $E^1$  values of the unsaturated systems with those of the partially saturated analogues indicates that in either of the solvents the first electron transfer occurs at more negative potentials in the partially saturated compounds. Clearly, the amino groups which serve as stronger donors for copper(II) have stabilized the dicopper(II) system further and thus shifted the potential to a more negative value. On this basis one would expect that a completely saturated system will be even more difficult to reduce. In fact, we have recently



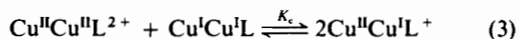
**Figure 1.** Cyclic voltammograms of (1g) in MeCN with a Pt electrode at different scan rates: (a) 500, (b) 400, (c) 300, (d) 200, (e) 100, and (f) 50  $\text{mV s}^{-1}$ . Concentration of (1g),  $1.1 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{NEt}_4][\text{ClO}_4]$ ,  $0.1 \text{ mol dm}^{-3}$



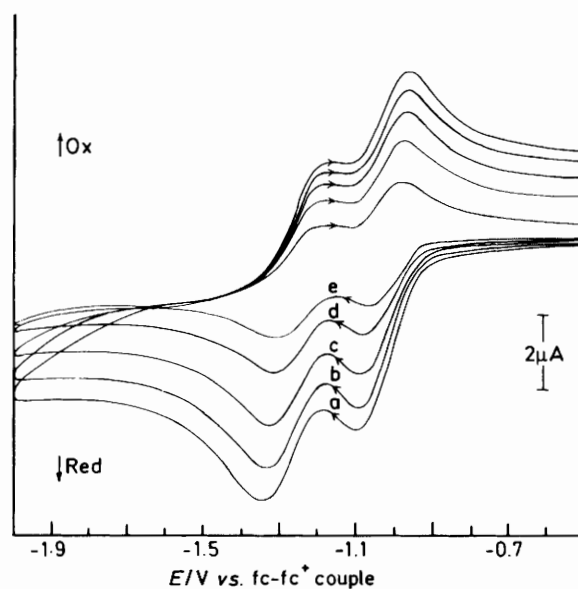
**Figure 2.** Cyclic voltammograms of (1d) in  $\text{CH}_2\text{Cl}_2$  with a Pt electrode at different scan rates: (a) 900, (b) 800, (c) 600, (d) 400, and (e) 200  $\text{mV s}^{-1}$ . Concentration of (1d),  $6.5 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[\text{NBu}_4][\text{ClO}_4]$ ,  $0.1 \text{ mol dm}^{-3}$

synthesized<sup>23</sup> a dicopper(II) complex of the completely saturated analogue of (1a) and have noted that  $E^1 = -1.18$  and  $E^2 = -1.45 \text{ V vs. fc-fc}^+$  couple.

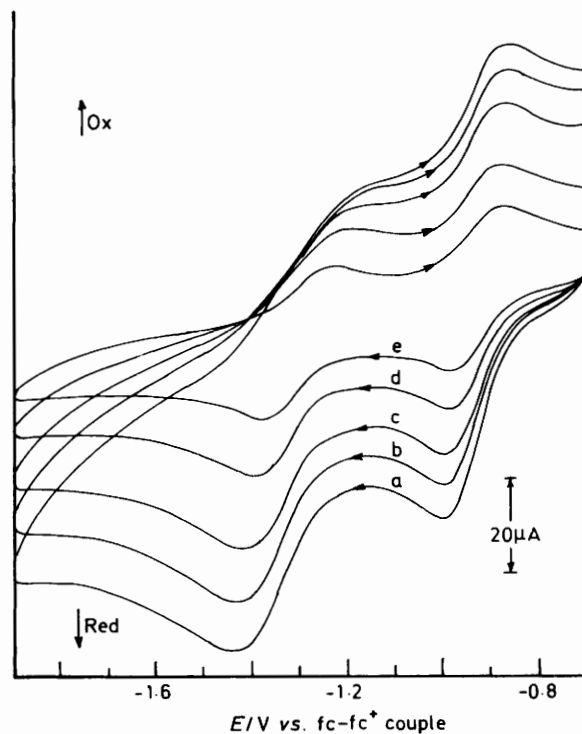
Of greater interest was to determine the relative stability of the mixed-valent species,  $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}\text{L}^+$ , in the equilibrium mixture of  $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{L}^{2+}$  and  $\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{L}$ , as given by the conproportionation constant,  $K_c$  for reaction (3). The value of  $K_c$  can be readily



determined by cyclic voltammetry, when the difference between the formal redox potentials ( $\Delta E = E^1 - E^2$ ) is greater than 36 mV, by using the relation  $K_c = 10^{\Delta E/0.0591}$ . The free energy of



**Figure 3.** Cyclic voltammograms of (2a) in  $\text{CH}_2\text{Cl}_2$  with a Pt electrode at different scan rates: (a) 500, (b) 400, (c) 300, (d) 200, and (e) 100  $\text{mV s}^{-1}$ . Concentration of (2a),  $6 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[\text{NBu}_4][\text{ClO}_4]$ ,  $0.1 \text{ mol dm}^{-3}$



**Figure 4.** Cyclic voltammograms of (2b) in MeCN using a glassy carbon electrode at different scan rates: (a) 500, (b) 400, (c) 300, (d) 200, and (e) 100  $\text{mV s}^{-1}$ . Concentration of (2b),  $1 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{NEt}_4][\text{ClO}_4]$ ,  $0.1 \text{ mol dm}^{-3}$

stabilization per mol of  $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}\text{L}^+$ ,  $\Delta G_c$ , can be obtained from the relation (4)<sup>12</sup> [the factor 4 is a statistical contribution to

$$\Delta G_c = -(RT/2) \ln(K_c/4) \quad (4)$$

**Table 2.** Conproportionation constants and free energies

Complex	Solvent	$K_c^a$	$\Delta G_c^b/\text{kcal mol}^{-1}$	$\Delta\Delta G_s^c/\text{kcal mol}^{-1}$
(1f)	MeCN	$1.4 \times 10^9$	5.9	1.0
	CH <sub>2</sub> Cl <sub>2</sub>	$5 \times 10^7$	4.9	
(1g)	MeCN	$1.1 \times 10^9$	5.8	0.7
	CH <sub>2</sub> Cl <sub>2</sub>	$1.1 \times 10^8$	5.1	
(1h)	MeCN	$2.5 \times 10^{10}$	6.7	
(1i)	MeCN	$3 \times 10^9$	6.1	
(1d)	MeCN	$2 \times 10^9$	6	0.8
	CH <sub>2</sub> Cl <sub>2</sub>	$1.3 \times 10^8$	5.2	
	dmf	$1.7 \times 10^9$	5.9	
(2a)	MeCN	$8.1 \times 10^4$	2.9	0.8
	CH <sub>2</sub> Cl <sub>2</sub>	$5.3 \times 10^3$	2.1	
(2b)	MeCN	$2.7 \times 10^6$	4	0.6
	CH <sub>2</sub> Cl <sub>2</sub>	$3.8 \times 10^5$	3.4	
(2c)	MeCN	$2.7 \times 10^6$	4	0.6
	CH <sub>2</sub> Cl <sub>2</sub>	$3.8 \times 10^5$	3.4	
(2d)	CH <sub>2</sub> Cl <sub>2</sub>	$1.8 \times 10^6$	3.9	

<sup>a</sup>  $K_c = 10^{(E_1 - E_2)/0.0591}$ . <sup>b</sup>  $\Delta G_c = (RT/2)\ln(K_c/4)$ . <sup>c</sup>  $\Delta\Delta G_s = \Delta G_c^{\text{MeCN}} - \Delta G_c^{\text{CH}_2\text{Cl}_2}$ .

$K_c$ ]. The values of  $K_c$  and  $\Delta G_c$  for the systems under consideration are listed in Table 2.

It may be noted that the  $K_c$  values for the compounds lie in the wide range  $8 \times 10^4$  to  $3 \times 10^{10}$ . For any particular system the value of  $K_c$  in MeCN is greater than the corresponding value in CH<sub>2</sub>Cl<sub>2</sub>, showing greater stability of the mixed-valent species in MeCN. The extra stabilization energy of the mixed-valent species in MeCN over CH<sub>2</sub>Cl<sub>2</sub> is given by the  $\Delta\Delta G_s$  values in Table 2. With the available set of data we note that the  $\Delta\Delta G_s$  values lie between 0.6 and 1 kcal mol<sup>-1</sup>.

The magnitude of  $\Delta G_c$  after allowing for the contribution due to statistical factors ( $K_c = 4$ ) can be associated to several effects.<sup>2,11-13,24</sup> (i) The stability of the mixed-valent species will increase with the increase in electron delocalization energy ( $\Delta G_{\text{del}}$ ). (ii) Major structural changes ( $\Delta G_{\text{struct}}$ ) such as bond making or bond breaking, or change in co-ordination number and environment, can shift conproportionation equilibria and hence affect  $\Delta G_c$ . (iii) A purely electrostatic factor ( $\Delta G_{\text{el}}$ ) will favour the stability of the mixed-valent state over the isovalent states. (iv) Variation in magnetic superexchange ( $\Delta G_{\text{mag}}$ ) between two paramagnetic centres may also change  $K_c$ . Hence we may write equation (5).

$$\Delta G_c = \Delta G_{\text{del}} + \Delta G_{\text{struct}} + \Delta G_{\text{el}} + \Delta G_{\text{mag}} \quad (5)$$

In our systems  $\Delta G_{\text{mag}}$  can be neglected because it has been shown<sup>2</sup> that the difference between the observed potential for the first electron transfer in (1a) for which  $J = -293 \text{ cm}^{-1}$  and the calculated value assuming  $J = 0$  is only 6 mV (equivalent to 0.14 kcal mol<sup>-1</sup>) showing that a wide range of variation of magnetic superexchange can affect  $K_c$  values very little. Concerning the electrostatic effect,  $\Delta G_{\text{el}}$  was evaluated<sup>25</sup> in the past in Ru<sup>III</sup>Ru<sup>II</sup> systems on the basis of a point charge model in a dielectric continuum. More recently these  $\Delta G_{\text{el}}$  values were calculated<sup>13</sup> on the basis of a more sophisticated ellipsoidal model.<sup>26,27</sup> The values of  $\Delta G_{\text{el}}$  thus obtained in various bridged [(NH<sub>3</sub>)<sub>5</sub>Ru-L-Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>5+</sup> type complexes (L = neutral ligand) were 0.09–0.15 kcal mol<sup>-1</sup>.<sup>13</sup> Considering such low values of  $\Delta G_{\text{el}}$  in ruthenium complexes we believe that this factor is not going to contribute significantly in our copper complexes. It should also be noted that the magnitude of  $\Delta\Delta G_s$  values cannot be attributed to the differences of  $\Delta G_{\text{el}}$  values in MeCN and CH<sub>2</sub>Cl<sub>2</sub>. Thus the remaining two factors,  $\Delta G_{\text{del}}$  and

$\Delta G_{\text{struct}}$ , appear to play decisive roles in deciding the stability of a mixed-valent complex in a particular solvent. It is important to note that the structural factor is of no consequence in mixed-valent ruthenium complexes, because both ruthenium(II) and ruthenium(III) form robust low-spin octahedral complexes. The situation is quite different with Cu<sup>II</sup>Cu<sup>I</sup> complexes, however. In the case of copper(II), while square planar and square pyramidal configurations are preferred, there is very little tendency to acquire a tetrahedral steric environment. On the other hand, for copper(I) both tetrahedral and square pyramidal environments are preferred, and there is great reluctance to achieve a square planar arrangement.

As regards electron delocalisation energy in Cu<sup>II</sup>Cu<sup>I</sup>L<sup>+</sup> macrocyclic complexes, useful information has been obtained from e.s.r. studies.<sup>1,3,5</sup> It may be argued that when both copper(II) and copper(I) centres are in a nearly square planar arrangement, the Cu<sup>II</sup>-O and Cu<sup>I</sup>-O distances will be shorter than in the other geometries, and the intramolecular electron transfer rate will be faster, which in effect will increase the electron delocalization energy. In the case of Cu<sup>II</sup>Cu<sup>I</sup>L<sup>+</sup> derived from (1a), the  $K_c$  value was found to be  $(4.0 \pm 0.1) \times 10^6$  ( $\Delta G_c = 4.1 \text{ kcal mol}^{-1}$ )<sup>1</sup> in *N,N*-dimethylformamide (dmf), and  $\Delta G_{\text{del}}$  was estimated to be 3.2 kcal mol<sup>-1</sup>.<sup>2</sup> The e.s.r. spectra of this compound in solution, at room temperature, gave a seven-line hyperfine structure<sup>1</sup> characteristic of a delocalized valence electron. From variable-temperature measurements<sup>1</sup> in CH<sub>2</sub>Cl<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>Me (2:3 v/v), the electron transfer rate,  $k_{\text{th}}$ , was found to be  $1.7 \times 10^{10} \text{ s}^{-1}$  at 298 K, and the activation energy for adiabatic electron transfer ( $E_{\text{th}}$ ) was estimated to be 3.5 kcal mol<sup>-1</sup>. More recently<sup>5</sup> intramolecular electron transfer rates were determined in a series of macrocyclic Cu<sup>II</sup>Cu<sup>I</sup> complexes related to (1a). In these dicopper(II) complexes the macrocycles were obtained by condensing 4-*t*-butyl-2,6-diformylphenol with various diamines, and maintaining or varying the co-ordination sites for copper(II). The  $K_c$  values in these compounds lie in the range  $3.7 \times 10^6$  to  $7.1 \times 10^8$  in dmf, and their room-temperature e.s.r. spectra in acetone were characteristic of either e.s.r.-delocalized or -localized states. Out of the seven, the four delocalized systems gave  $k_{\text{th}}$  values in the range  $1.6 \times 10^{10}$ – $2.9 \times 10^9 \text{ s}^{-1}$  at 298 K with corresponding  $E_{\text{th}}$  values 3.6–4.2 kcal mol<sup>-1</sup>. For the e.s.r. localized systems,  $k_{\text{th}}$  and  $E_{\text{th}}$  values were estimated<sup>5</sup> to be  $< 2.2 \times 10^7 \text{ s}^{-1}$  and  $> 7.4 \text{ kcal mol}^{-1}$ , respectively. No correlation could be obtained between  $K_c$  and  $k_{\text{th}}$ . For example, the complex having lowest  $K_c$  ( $3.7 \times 10^6$ ) gave an e.s.r.-localized state ( $k_{\text{th}} = 5.6 \times 10^9 \text{ s}^{-1}$ ), whereas the complex with highest  $K_c$  ( $7.1 \times 10^8$ ) gave a localized spectrum ( $k_{\text{th}} < 2.2 \times 10^7 \text{ s}^{-1}$ ). More importantly, the Cu<sup>II</sup>Cu<sup>I</sup>L<sup>+</sup> cation derived from (1b) gave a high value of  $K_c$  ( $1.2 \times 10^{13}$ )<sup>4</sup> in MeCN, but the e.s.r. spectra of this compound in MeCN at room temperature gave evidence<sup>3</sup> for the single unpaired electron being localized on one of the copper centres. Unfortunately, we could not investigate e.s.r. spectral characteristics of the Cu<sup>II</sup>Cu<sup>I</sup>L<sup>+</sup> ions of the compounds under consideration due to lack of facilities.

In the light of the above discussion it is clear that in order to correlate the magnitude of  $\Delta G_c$  with intramolecular electron transfer rates the role of solvent molecules should be considered along with the structural factor ( $\Delta G_{\text{struct}}$ ) of the species. The X-ray crystal structure of the one-electron reduction product of (1a), [Cu<sup>II</sup>Cu<sup>I</sup>L][ClO<sub>4</sub>], provided<sup>28</sup> the following information. The co-ordination environment about the Cu<sup>II</sup> centre is square planar, with Cu–N and Cu–O bond lengths of ca. 1.98 and 1.96 Å respectively. The Cu<sup>I</sup> site is statistically distributed in a 65:35 ratio. The 65% site is displaced 0.15 Å from the O<sub>2</sub>N<sub>2</sub> plane in which the Cu–O distances are ca. 2.12 Å and the Cu–N distances are ca. 1.96 Å; the co-ordination geometry can be described as distorted square planar. The 35% site is displaced 0.65 Å from the ligand plane with considerable increase in Cu–N (2.03 Å)

and Cu-O (2.26 Å). The overall geometry of Cu<sup>I</sup> in this case is square pyramidal; the fifth bond is formed with a carbon atom of the aromatic ring in the adjacent molecule. The two distinct geometric forms observed in the solid state are likely to be lost in solution. Since e.s.r. spectra gave no indication<sup>1</sup> of molecular association in solution, it is probable that the co-ordination environment around the metal centres fluctuates between square planar and distorted square planar arrangements. It is conceivable that although the molecule will be structurally less stable when both the copper atoms are in the square planar configuration, the intramolecular electron transfer rate will be faster under this condition. Intuitively one may argue that in mixed-valent complexes derived from (1b)–(1i) (the derivatives having peripheral substituents) the dynamics of conformational changes in a non-co-ordinating solvent such as CH<sub>2</sub>Cl<sub>2</sub> will be slower and so the barrier height of electron transfer will be greater. In the extreme, localized spectra on the e.s.r. time-scale may be observed. On the other hand, solvents like MeCN having a strong affinity for copper(I) are likely to stabilize the system structurally through bond formation. Here, as a consequence of availing a square pyramidal geometry for copper(I), a localized situation will probably arise. E.s.r.-localized spectra may also arise through a distorted tetrahedral configuration about copper(I). It may be pointed out that in the Cu<sup>II</sup>Cu<sup>I</sup> complexes of the macrocyclic ligands obtained by condensing 4-t-butyl-2,6-diformylphenol with diamines, in the three cases which gave localized spectra one of the condensed diamines was either 1,1'-biphenyl-2,2'-diamine or 1,4-diaminobutane. There is structural evidence that the introduction of 1,1'-biphenyl-2,2'-diamine<sup>29</sup> and 1,4-diaminobutane<sup>30</sup> in ligand systems produces tetrahedral distortion in copper(II) complexes, which undoubtedly could be more pronounced with copper(I).

On the basis of the above information one may correlate the difference of ΔG<sub>c</sub> values in MeCN and CH<sub>2</sub>Cl<sub>2</sub> for any particular compound as in equations (6) and (7). In other words, the gain in energy through structural stabilization in a co-ordinating solvent is partially offset by loss in electron delocalisation energy.

$$\Delta G_c^{\text{MeCN}} - \Delta G_c^{\text{CH}_2\text{Cl}_2} = (\Delta G_{\text{struct}}^{\text{MeCN}} - \Delta G_{\text{struct}}^{\text{CH}_2\text{Cl}_2}) - (\Delta G_{\text{del}}^{\text{CH}_2\text{Cl}_2} - \Delta G_{\text{del}}^{\text{MeCN}}) \quad (6)$$

$$\Delta\Delta G_s = \Delta\Delta G_{\text{struct}} - \Delta\Delta G_{\text{del}} \quad (7)$$

In the mixed-valent complexes of the partially saturated macrocyclic systems, the stereochemistry of the metal centres will deviate more from square planar due to greater flexibility of one-half of the chelate rings. A localized situation is likely to be observed in these cases. Finally it may be noted that the ΔG<sub>c</sub> values of the compounds (1) and (2) show similar changes with solvent variation. Thus, the difference in ΔG<sub>c</sub> for the pair (1f) and (2b) is 1.9 kcal mol<sup>-1</sup> in MeCN, and 1.5 kcal mol<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>. The corresponding differences between the pair (1g) and (2c) are 1.8 and 1.7 kcal mol<sup>-1</sup>, respectively. These values indicate that the mixed-valent compounds of the unsaturated macrocyclic systems have stabilization energies at least 1.5 kcal mol<sup>-1</sup> greater than the partially saturated analogues.

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