Dinuclear Metal Complexes. Part 2.† Synthesis, Characterisation, and Electrochemical Studies of Macrocyclic Dicopper(II) Complexes ‡

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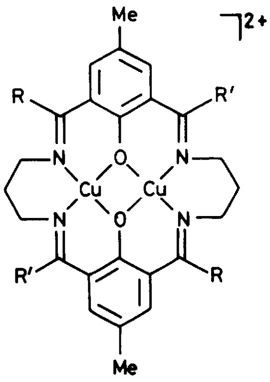
The synthesis, characterisation, and electrochemical studies of dicopper(II) complexes $[Cu_2L^1][ClO_4]_2{\cdot}nH_2O$ of the macrocycle 7,11;19,23-dimetheno-9,21-dimethyl[1,5,13,17]-tetra-azacycloicosa-5,7,9,12,17,19,21,24-octaene-25,26-diol (H_2L^1), and of some 6,12,18,24-substituted (Me_4; $Pr^n{}_4$; Ph_4; Ph, Me, Ph, Me) derivatives have been carried out. These compounds undergo sequential one-electron transfers at two different potentials. For all of these compounds, except for $[Cu_2L^1][ClO_4]_2{\cdot}2H_2O$, two reversible or almost reversible reduction steps have been observed in acetonitrile medium using a hanging mercury drop electrode. In the case of $[Cu_2L^1][ClO_4]_2{\cdot}2H_2O$, the second couple became obscured due to the presence of an adsorption phenomenon or secondary electrode reaction. However, in *NN*-dimethylformamide (dmf) medium, satisfactory voltammograms have been obtained only with $[Cu_2L^1][ClO_4]_2{\cdot}2H_2O$. The mixed-valent complexes are considerably more stable in acetonitrile than is $[Cu^{II}Cu^{I}L^1]^+$ in dmf. The potentials of the first reduction step (E_1) remain practically invariant throughout the series and are independent of the extent of magnetic interactions in the dicopper(II) complexes. The potentials of the second reduction step (E_2) vary with the alkyl and aryl groups present, and a linear plot has been obtained for E_2 *vs.* the Hammett function σ_m. On the basis of previously reported observations and the present study it is inferred that in acetonitrile medium the unpaired electron in the mixed-valent complexes remains localised on one of the copper atoms.

The electron-transfer behaviour of binuclear copper(II) complexes is a subject of considerable interest from the point of view of understanding and replicating the redox function of 'type 3' copper proteins.[1] Compounds that contain two copper centres with identical geometries and have very low or no magnetic interactions (that is, the metal centres are remotely located) undergo either one-step two-electron transfers [2,3] or overlapping sequential one-electron reductions.[3] In the case of strongly coupled binuclear complexes, electron transfers generally take place in the following ways: either (*i*) two sequential one-electron reductions at different potentials [4-7] yielding the mixed-valent species Cu^{II}/Cu^{I} as the intermediate product; or (*ii*) the transfer of two electrons at the same potential [8,9] producing Cu^{I}/Cu^{I} species as the sole product. While mechanism (*i*) is expected on statistical grounds and indeed has been observed in the majority of cases,[4-7] mechanism (*ii*) is more intriguing and has been reported so far in bis(1,3,5-triketonato)dicopper complexes by Fenton *et al.*[8] and more recently in $[Cu_2L'_2][ClO_4]_2{\cdot}2H_2O$ by us.[9]

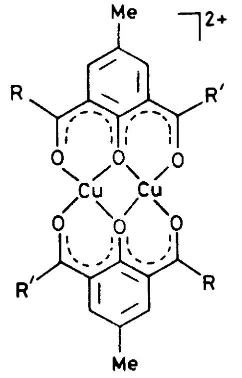
Here we report the synthesis, characterisation, and electrochemical behaviour of the dicopper macrocyclic complexes $[Cu_2L][ClO_4]_2{\cdot}nH_2O$.

The electron-transfer, magnetic, and spectroscopic properties of $[Cu^{II}{}_2L^1][ClO_4]_2{\cdot}2H_2O$ and $[Cu^{II}Cu^{I}L^1][ClO_4]$ have been investigated by Gagne *et al.*[6] Crystal structure analysis [10] and delocalisation energy determination [11] of the mixed-valent complex have also been accomplished by this group. Several years ago Addison [5] briefly reported the electrochemistry of $[Cu_2L^2][ClO_4]_2$, although the synthesis and characterisation of this compound were not reported. Our motivation for studying several derivatives of $[Cu_2L]^{2+}$ stems from the fact that because a wide range of redox potentials can be obtained by subtle and cumulative variations in macrocyclic ligand structure,[12] a varying degree of stabilisation of the mixed-valent complexes of these derivatives can be expected. We also wished to know whether the potentials for the addition of the first electron would be dependent on the extent of magnetic interactions in the dicopper(II) complexes.



$[Cu_2L]^{2+}$

$[Cu_2L^1]^{2+}$: R = R' = H
$[Cu_2L^2]^{2+}$: R = R' = Me
$[Cu_2L^3]^{2+}$: R = R' = Pr^n
$[Cu_2L^4]^{2+}$: R = R' = Ph
$[Cu_2L^5]^{2+}$: R = Ph, R' = Me



$[Cu_2L'_2]^{2+}$

$[Cu_2L^{1'}{}_2]^{2+}$: R = R' = H
$[Cu_2L^{2'}{}_2]^{2+}$: R = R' = Me
$[Cu_2L^{3'}{}_2[^{2+}$: R = R' = Pr^n
$[Cu_2L^{4'}{}_2]^{2+}$: R = R' = Ph
$[Cu_2L^{5'}{}_2]^{2+}$: R = Ph, R' = Me

Experimental

Materials.—All chemicals were reagent grade and used as received. For electrochemical work acetonitrile was treated successively with CaH_2 and P_4O_{10}, and *NN*-dimethylformamide (dmf) was dried over $CuSO_4$ and 4A molecular sieves.

Preparation of the Ligands.—2-Hydroxy-5-methylbenzene-1,3-dicarbaldehyde (1) was prepared by a literature method [13] (m.p. 131 °C, lit.[13] 133.5 °C). ^1H N.m.r. ([$^2H_1$]chloro-

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† Part 1 is ref. 9.
‡ *Non-S.I. units employed:* 1 B.M. = 9.27×10^{-24} J T^{-1}; G = 10^{-4} T.

form): δ 2.40 (s, 3 H, CH_3), 7.73 (s, 2 H, phenyl), 10.20 (s, 2 H, CHO), and 11.38 p.p.m. (s, 1 H, OH). I.r. (KBr): ν(C=O) 1 670s and 1 655s, $\nu(C-C)_{ring}$ 1 600s cm^{-1}. U.v. (MeCN): 350 (ε = 5 500), 232 nm (ε = 27 800 dm^3 mol^{-1} cm^{-1}).

1,3-*Diacetyl*-2-*hydroxy*-5-*methylbenzene* (2). In a 3-dm^3 three-necked flask fitted with a mercury-sealed overhead stirrer, a reflux condenser, and a pressure equalising addition funnel, $AlCl_3$ (200 g, 1.5 mol) was dissolved in dry nitrobenzene (300 cm^3) by stirring. To the resulting solution was added freshly distilled *p*-cresol (27 g, 0.25 mol). The reaction vessel was then placed in an ice–water bath to adjust the temperature to *ca.* 15 °C and acetyl chloride (60 g, 0.75 mol) was added dropwise over a period of 1.5 h. After the addition of acetyl chloride the bath temperature was slowly raised to 60 °C over 3 h, and the reaction was continued at 60 °C for a further 3 h. The reaction container was then cooled by surrounding it with crushed ice and ice-cooled HCl (400 cm^3, 6 mol dm^{-3}) was slowly added (**CAUTION:** brisk evolution of HCl gas occurred at this stage). When about 100 cm^3 of the acid was added the reaction mixture became highly viscous due to the separation of an aluminium complex. The speed of the stirrer was increased, and with the addition of more acid a thin slurry resulted. After the complete addition of the acid solution the contents of the flask were transferred to a separating funnel and allowed to stand overnight. The organic layer thus separated was collected and steam distilled to remove nitrobenzene and some 2-hydroxy-5-methylacetophenone which formed. The brown solid which remained was extracted with chloroform and dried over Na_2SO_4. The chloroform solution, after treatment with activated charcoal, was allowed to crystallise at ambient temperature by slow evaporation. The needle-shaped crystals which separated were collected by filtration and recrystallised from light petroleum (b.p. 60—80 °C). Yield, 20 g; m.p. 82 °C (Found: C, 69.1; H, 6.15. $C_{11}H_{12}O_3$ requires C, 68.75; H, 6.25%). ^{1}H N.m.r. (CCl_4): δ 2.28 (s, 3 H, CH_3), 2.58 (s, 6 H, COMe), 7.63 (s, 2 H, aromatic), and 13.05 p.p.m. (s, 1 H, OH). I.r. (KBr): ν(C=O) 1 665s and 1 635s, $\nu(C-C)_{ring}$ 1 600s cm^{-1}. U.v. (MeCN): 350 (ε = 5 600), 230 nm (ε = 24 200 dm^3 mol^{-1} cm^{-1}).

1,3-*Dibutyryl*-2-*hydroxy*-5-*methylbenzene* (3). This compound was obtained by a similar method to that described above for (2). Yield, 25 g; m.p. 46 °C (Found: C, 72.35; H, 8.2. $C_{15}H_{20}O_3$ requires C, 72.6; H, 8.05%). ^{1}H N.m.r. (CCl_4): δ 2.28 (s, 3 H, CH_3), 0.98 (t, 6 H, $CH_2CH_2CH_3$), 1.72 (m, 2 H, $CH_2CH_2CH_3$), 2.96 (t, 2 H, $CH_2CH_2CH_3$), 7.65 (s, 2 H, aromatic), and 13.16 p.p.m. (s, 1 H, OH). I.r. (KBr): ν(C=O) 1 600s and 1 625s, $\nu(C-C)_{ring}$ 1 590s cm^{-1}. U.v. (MeCN): 345 (ε = 5 500), 230 nm (ε = 22 000 dm^3 mol^{-1} cm^{-1}).

1,3-*Dibenzoyl*-2-*hydroxy*-5-*methylbenzene* (4). A reaction mixture containing nitrobenzene (300 cm^3), $AlCl_3$ (200 g, 1.5 mol), *p*-cresol (27 g, 0.25 mol), and benzoyl chloride (105 g, 0.75 mol) was heated at 80 °C for 8 h. After decomposition of the reaction mixture with HCl (400 cm^3, 6 mol dm^{-3}), the nitrobenzene layer was collected and washed with a saturated aqueous solution of $NaHCO_3$ (3 × 50 cm^3) to remove any benzoic acid formed. The nitrobenzene layer was then steam distilled and the product was isolated from the residue by extracting with $CHCl_3$. The $CHCl_3$ solution was dried over Na_2SO_4, treated with activated charcoal, filtered, and the filtrate allowed to crystallise. Yield, 24 g; m.p. 160 °C (Found: C, 79.85; H, 4.85. $C_{21}H_{16}O_3$ requires C, 79.75; H, 5.05%). ^{1}H N.m.r. ([$^2H_1$]chloroform): δ 2.33 (s, 3 H, CH_3), 7.3—7.9 (m, 12 H, aromatic), 12.02 (s, 1 H, OH). I.r. (KBr): ν(C=O) 1 655s and 1 620s, $\nu(C-C)_{ring}$ 1 600s cm^{-1}. U.v. (MeCN): 350 (ε = 6 000), 250 nm (ε = 24 700 dm^3 mol^{-1} cm^{-1}).

3-*Benzoyl*-2-*hydroxy*-5-*methylacetophenone* (5). This compound was obtained by a two-stage Friedel-Crafts reaction. In the first step 2-hydroxy-5-methylacetophenone was prepared by reacting *p*-cresol, $AlCl_3$, and acetyl chloride (molar ratio 1 : 2 : 1) in nitrobenzene in the same way as described for 1,3-diacetyl-2-hydroxy-5-methylbenzene. On steam distillation, the product (with nitrobenzene) was collected as the distillate, which was then extracted with NaOH (4 × 50 cm^3, 2 mol dm^{-3}). The alkaline solution was acidified with HCl (*ca.* 70 cm^3, 6 mol dm^{-3}) and then extracted with chloroform (2 × 50 cm^3). The compound crystallised out from the chloroform solution in 80% yield (m.p. 50 °C). This was then reacted with benzoyl chloride and $AlCl_3$ (1 : 1 : 2) in the same way as described for the dibenzoyl derivative (4). The overall yield was 40%; m.p. 101—102 °C (Found: C, 75.3; H, 5.6. $C_{16}H_{14}O_3$ requires C, 75.6; H, 5.5. ^{1}H N.m.r. (CCl_4): δ 2.30 (s, 3 H, CH_3), 2.60 (s, 3 H, COMe), 7.38 (m, 5 H, benzoyl), 7.60 (m, 2 H, phenyl), 12.32 (s, 1 OH). I.r. (KBr): ν(C=O) 1 660s and 1 630s, $\nu(C-C)_{ring}$ 1 590s cm^{-1}. U.v. (MeCN): 340 (ε = 5 700), 250 nm (ε = 24 000 dm^3 mol^{-1} cm^{-1}).

Preparation of the Complexes $[Cu_2L][ClO_4]_2\cdot nH_2O$.—The general procedure described here is a modified version of the one reported by Pilkington and Robson [14] for the preparation of $[Cu_2L^1][ClO_4]_2\cdot 2H_2O$. 1,3-Diaminopropane (0.45 g, 6 mmol) diluted with methanol (5 cm^3) was added to a solution of $Cu[ClO_4]_2\cdot 6H_2O$ (1.48 g, 4 mmol) in methanol (50 cm^3). The solution was heated to boiling. To this was added dropwise a hot methanol solution (50 cm^3) of compounds (1)—(5) (4 mmol). The resulting solution was refluxed for 6 h. During this period, for the reactions involving compounds (1) and (2), crystalline copper(II) complexes began to separate out, while the solution remained clear for the other three ligands. The mixture was cooled to room temperature, filtered, and the filtrate was allowed to evaporate slowly. Additional crops of crystals were obtained in the reactions with compounds (1) and (2), and in the remaining cases needle-shaped crystals deposited over a period of 24 h. The products were filtered off, washed several times with water, and dried over $CaCl_2$. The compounds were recrystallised from a large volume of boiling methanol, except for $[Cu_2L^1][ClO_4]_2\cdot 2H_2O$, which was recrystallised from boiling water.

Alternatively, these complexes may be obtained by condensing the binuclear complexes $[Cu_2L'_2][ClO_4]_2\cdot 2H_2O$ [9] with 1,3-diaminopropane. Typically, 1.72 g (2 mmol) of $[Cu_2L^{3\prime}_2][ClO_4]_2\cdot 2H_2O$ was suspended in dry methanol (75 cm^3), and a solution of 1,3-diaminopropane (0.3 g, 4 mmol) in dry methanol (5 cm^3) was added. The mixture was boiled under reflux for 5 h. During this period all the solid dissolved. The solution was filtered, the filtrate was concentrated to *ca.* 25 cm^3, and left for crystallisation at room temperature. The compound was collected after 24 h by filtration and recrystallised from methanol.

$[Zn_2L^4][ClO_4]_2\cdot 2H_2O$.—This compound was prepared by a similar method to that described previously for $[Zn_2L^1][ClO_4]_2\cdot 2H_2O$.[6]

Physical Measurements.—Infrared spectra were recorded on a Beckman IR-20 i.r. spectrophotometer in KBr pellets. Electronic spectra in solution were obtained with a Pye-Unicam SP8-150 spectrophotometer. ^{1}H N.m.r. spectra were obtained with a Varian T-60 n.m.r. spectrometer using $SiMe_4$ as the standard. A PAR model 155 vibrating sample magnetometer, operated at 9.5 kG, was used to measure magnetic susceptibility of the compounds. Calibration of the magnetometer was made with $Hg[Co(SCN)_4]$. A diamagnetic correction, estimated from Pascal constants,[15] was used to calculate molar susceptibilities. Analyses (C, H, N) were carried out by the Australian Mineral Development Laboratories, Melbourne.

Table 1. Analytical data for the binuclear copper(II) complexes

		Analysis (%) *			
Complex	Colour	C	H	N	Cu
$[Cu_2L^1][ClO_4]_2{\cdot}2H_2O$	Bright green	37.9 (37.7)	4.0 (3.9)	7.2 (7.3)	16.55 (16.65)
$[Cu_2L^2][ClO_4]_2$	Brown	43.15 (42.85)	4.55 (4.35)	7.35 (7.15)	15.6 (15.5)
$[Cu_2L^3][ClO_4]_2{\cdot}2H_2O$	Dull green	46.85 (46.35)	5.45 (5.8)	6.05 (6.0)	13.8 (13.65)
$[Cu_2L^4][ClO_4]_2{\cdot}2H_2O$	Dull green	53.8 (53.95)	4.1 (4.3)	5.4 (5.25)	12.0 (11.9)
$[Cu_2L^5][ClO_4]_2{\cdot}2H_2O$	Dull green	48.55 (48.3)	4.3 (4.45)	6.15 (5.95)	13.3 (13.45)

* Calculated values are in parentheses.

Table 2. Infrared and electronic spectral data and magnetic moments for the binuclear copper(II) complexes

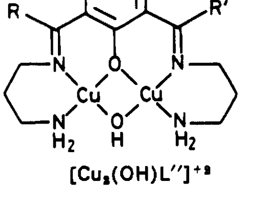
	I.r. data [a] (cm^{-1})				
Complex	ν(C═N)	ν(C–C) [c]	ν(C═O)	Electronic spectral data [b] λ/nm (ε/dm^3 mol^{-1} cm^{-1})	$\mu_{eff.}$/ B.M. [d]
$[Cu_2L^1][ClO_4]_2{\cdot}2H_2O$	1 635	1 610	1 565	350 (12 000), 600 (90), 700 (sh) (60)	0.74
$[Cu_2L^2][ClO_4]_2$	1 590	1 610	1 545	350 (14 200), 580 (170)	0.66
$[Cu_2L^3][ClO_4]_2{\cdot}2H_2O$	1 580	1 610	1 540	350 (14 500), 590 (170)	0.81
$[Cu_2L^4][ClO_4]_2{\cdot}2H_2O$	1 590	1 610	1 550	360 (15 800), 580 (165)	0.42
$[Cu_2L^5][ClO_4]_2{\cdot}2H_2O$	1 580	1 605	1 540	355 (14 200), 580 (160)	0.70

[a] All strong bands. [b] In MeCN. [c] Benzene rings. [d] At 298 K.

Electrochemistry.—Cyclic voltammetry was performed using a PAR model 174A polarographic analyser, PAR model 175 universal programmer, and RE 0074 *x*-*y* recorder. The three-electrode cell consisted of a Metrohm E410 hanging mercury drop electrode (h.m.d.e.), a platinum wire auxiliary electrode, and a saturated calomel electrode (s.c.e.). In the h.m.d.e. the size of the mercury drop was held constant by adjusting the vernier scale of the Metrohm device to the same extent. Constant-potential electrolysis was performed in a mercury pool using a PAR 173 potentiostat and a PAR 179 digital coulometer. All measurements were carried out at ambient temperature under an atmosphere of nitrogen, and tetraethylammonium perchlorate (0.1 mol dm^{-3}) was used as the supporting electrolyte. Potentials were uncorrected for junction potentials.

Results and Discussion

Synthesis and Characterization.—The binuclear macrocyclic complexes, $[Cu_2L][ClO_4]_2{\cdot}nH_2O$, were synthesised by template condensation of either bis(1,3-diaminopropane)copper(II) perchlorate with compounds (1)—(5) or by reacting the complexes $[Cu_2L'_2][ClO_4]_2{\cdot}2H_2O$ with 1,3-diaminopropane. The yields obtained by these two methods were comparable (80% or better). However, when dilute aqueous solutions containing $Cu[ClO_4]_2{\cdot}6H_2O$, 1,3-diaminopropane, and each of compounds (1)—(5) neutralized with NaOH were boiled for several hours, the complexes $[Cu_2(OH)L'']^{2+}$ (R = R′ = H, Me, Pr^n, or Ph; R = Ph, R′ = Me) were obtained as the major products instead of $[Cu_2L]^{2+}$ which formed only in small quantities.[16]



$[Cu_2(OH)L'']^{+2}$

Analytical data of the complexes (Table 1) show that all of them, except the diacetyl derivative, were obtained as the dihydrates, $[Cu_2L][ClO_4]_2{\cdot}2H_2O$. The diacetyl derivative was devoid of water molecules. In the case of $[Cu_2L^5][ClO_4]_2{\cdot}2H_2O$, two isomeric species in which the two methyl/phenyl groups are in *syn* or *anti* positions were expected. However, the products obtained through the two synthetic routes were identical, and t.l.c. characterised them as a unique compound. We presume that in this compound the substituents are in the *anti* position.

The room-temperature magnetic moments of these complexes (Table 2) vary from 0.4 to 0.8 B.M.; $[Cu_2L^3][ClO_4]_2{\cdot}2H_2O$ and $[Cu_2L^4][ClO_4]_2{\cdot}2H_2O$ have the highest and lowest values, respectively. The antiferromagnetic coupling constants (J) of these compounds have not yet been determined, but an estimate can be made by considering the value reported[17] for $[Cu_2(L^1)Cl_2]{\cdot}6H_2O$ [$J = -294$ cm^{-1} and $\mu_{eff.}$ (285 K) = 0.8 B.M.]. *X*-Ray structure determination[18] of $[Cu_2(L^1)Cl_2]{\cdot}6H_2O$ showed that the chloride ions occupy the fifth apical co-ordination sites on the opposite sides of the plane of the macrocycle, and both the copper(II) ions are somewhat displaced from the plane. Bearing in mind that the σ overlap in $d_{x^2-y^2}$ orbitals of the two copper(II) ions and *s* and *p* orbitals of the ligand oxygens (which are involved in the exchange pathway) will be reduced for out-of-plane copper(II) ions, it has been suggested[17] that the effectiveness of the magnetic interaction is somewhat reduced in $[Cu_2(L^1)Cl_2]{\cdot}6H_2O$. No correlation has been reported between the room-temperature magnetic moments and J values in dicopper(II) complexes. However, in several closely related binuclear copper(II) complexes obtained from the condensation products of 3-formylsalicylic acid and substituted diamines, an approximate linear relationship can be obtained between the reported[19] J values and room-temperature magnetic moments. On the basis of these facts it may be concluded that there is considerable variation in the singlet–triplet separation energies of the five compounds under consideration and probably $-J \geqslant 290$ cm^{-1}.

In the u.v. region all of the complexes have similar spectral features (Table 2). However, in the visible region, the di-

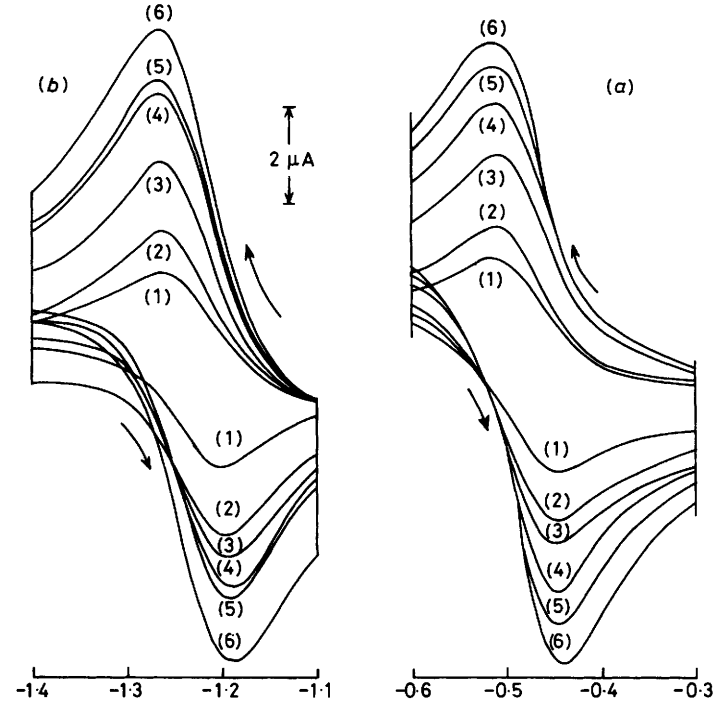


Figure 1. Cyclic voltammograms of [Cu$_2$L^2][ClO$_4$]$_2$ in acetonitrile at different scanning rates. (*a*) Cu^{II}/Cu^{I} couple; (*b*) Cu^{I}/Cu^{I} couple: scan rate (1) 50, (2) 100, (3) 200, (4) 300, (5) 400, and (6) 500 mV s^{-1}

carbaldehyde complex [Cu$_2$L^1]$^{2+}$ differs somewhat from the others. This compound shows a band of relatively weaker intensity at 600 nm and a shoulder at 700 nm, while the others have a broad absorption maximum at *ca.* 600 nm.

The i.r. spectra in the region 1 650—1 500 cm^{-1} show three strong bands (Table 2). It may be noted that $\nu(\text{C}\overset{\cdots}{-}\text{N})$ of [Cu$_2$L^1][ClO$_4$]$_2$·2H$_2$O appears at a considerably higher frequency (1 635 cm^{-1}) compared with the other compounds (1 585 cm^{-1}). The band observed at *ca.* 1 550 cm^{-1} has been assigned due to $\nu(\text{C}\overset{\cdots}{-}\text{O})$. This is a consequence of delocalisation of double bonds in the chelate rings that has increased the bond order of the phenolic C–O. The above conclusion has been confirmed by synthesising binuclear macrocyclic complexes in which all azomethine linkages have been reduced.[16] Since in the reduced system there is no room for delocalisation, accordingly the band at 1 550 cm^{-1} was also absent.

Electrochemistry.—The cyclic voltammograms of [Zn$_2$L][ClO$_4$]$_2$·2H$_2$O (R = R′ = H or Ph) in dmf lacked waves at potentials positive of −1.5 V, showing that azomethine groups are reduced at more negative potentials. The electrochemical behaviour of [Cu$_2$L^1][ClO$_4$]$_2$·2H$_2$O reported by Gagne *et al.*[6] has been corroborated by us. In dmf using the h.m.d.e., two quasi-reversible reduction processes at −0.515 and −0.854 V were observed. These are due to the formation of [Cu^{II}Cu^{I}L^1]$^+$ and [Cu^{I}Cu^{I}L^1]. In acetonitrile the first redox couple is almost reversible having a difference (ΔE_p) of 65 mV between the cathodic ($E_{p,c}$) and anodic ($E_{p,a}$) peak potentials at a scanning rate of 50 mV s^{-1}.

The potential of the second couple could not be determined with certainty; in the range −0.7 to −1 V a peak which consumed a large amount of current was observed during both cathodic and anodic sweeps. The second wave did not have the characteristic shape of a diffusion-controlled process. In acetonitrile medium the same adsorption problem was encountered also with [Cu$_2$L^2][ClO$_4$]$_2$, [Cu$_2$L^3][ClO$_4$]$_2$·2H$_2$O, and to a lesser extent with [Cu$_2$L^5][ClO$_4$]$_2$·2H$_2$O. Only in the case of [Cu$_2$L^4][ClO$_4$]$_2$·2H$_2$O was this problem absent. However, we found that if the two redox couples were scanned separately between 0 and −0.6 V, and −1.1 and −1.4 V, highly satisfactory voltammograms can be obtained. This is illustrated in Figure 1 by the reversible cyclic voltammograms of [Cu$_2$L^2][ClO$_4$]$_2$ for both the couples obtained in this way. Figure 2 shows a continuous voltammogram of [Cu$_2$L^4][ClO$_4$]$_2$·2H$_2$O from −0.2 to −1.2 V. When the voltammograms of the same compound were recorded separately for the two reduction steps, exactly the same redox potentials were obtained. The quality of voltammograms for all these compounds in dmf was poor and therefore they were not investigated further. The electrochemical results summarized in Table 3 show that the ΔE_p

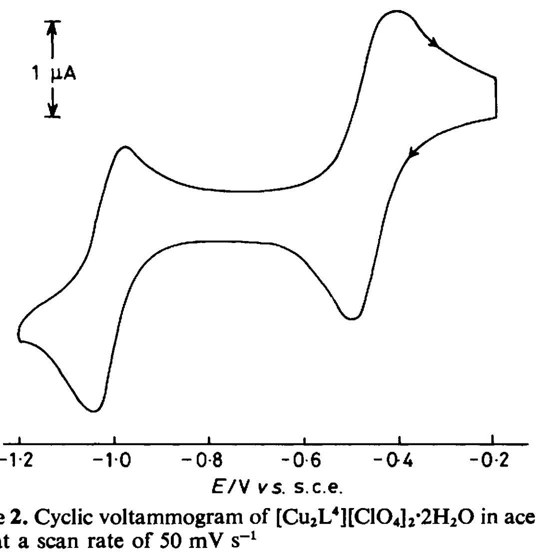


Figure 2. Cyclic voltammogram of [Cu$_2$L^4][ClO$_4$]$_2$·2H$_2$O in acetonitrile at a scan rate of 50 mV s^{-1}

Table 3. Electrochemical data for the binuclear copper(II) complexes

	$Cu^{II}/Cu^{II} \rightleftharpoons Cu^{II}/Cu^{I}$				$Cu^{II}/Cu^{I} \rightleftharpoons Cu^{I}/Cu^{I}$					
Complex	ΔE_p/mV [a]	E_1/V [b]	$I_{p,c}/I_{p,a}$	$(I_{p,c}/c\sqrt{v})$/A $s^{\frac{1}{2}}$ dm^3 mol^{-1} $V^{-\frac{1}{2}}$	ΔE_p/mV [a]	E_2/V [b]	$I_{p,c}/I_{p,a}$	$(I_{p,c}/c\sqrt{v})$/A $s^{\frac{1}{2}}$ dm^3 mol^{-1} $V^{-\frac{1}{2}}$	ΔE/V [c]	$K_{con.}$
$[Cu_2L^1][ClO_4]_2 \cdot 2H_2O$ [d]	70	−0.515	0.95		100	−0.855	0.92		0.34	5.6×10^5
$[Cu_2L^1][ClO_4]_2 \cdot 2H_2O$ [e]	65	−0.463	0.98							
$[Cu_2L^2][ClO_4]_2$ [e]	60	−0.459	1.02	14.2 ± 0.4 [f]	60	−1.232	0.98	14 ± 0.1 [f]	0.773	1.2×10^{13}
$[Cu_2L^3][ClO_4]_2 \cdot 2H_2O$ [e]	60	−0.47	0.98	13.5 ± 0.2 [g]	60	−1.25	1.04	15 ± 0.5 [g]	0.78	1.6×10^{13}
$[Cu_2L^4][ClO_4]_2 \cdot 2H_2O$ [e]	75	−0.467	0.97		60	−1.015	0.99	10 ± 0.3 [h]	0.547	1.8×10^9
$[Cu_2L^5][ClO_4]_2 \cdot 2H_2O$ [e]	70	−0.48	1.04		60	−1.183	0.98	9.6 ± 0.4 [i]	0.703	7.8×10^{11}

[a] $\Delta E_p = E_{p,c} - E_{p,a}$. Scanning rate 50 mV s^{-1}. [b] $E_j = 0.5(E_{p,c} + E_{p,a})$. [c] $\Delta E = E_1 - E_2$. [d] In dmf. [e] In CH_3CN. [f] Concentration = 0.68 mmol dm^{-3}. [g] Concentration = 0.2 mmol dm^{-3}. [h] Concentration = 0.72 mmol dm^{-3}. [i] Concentration = 0.39 mmol dm^{-3}.

values for both the couples are *ca.* 60 mV, or slightly greater. The ratios of the cathodic to anodic peak currents ($I_{p,c}/I_{p,a}$) are all *ca.* 1. These are in accord with a Nernstian $n = 1$ process.[20] The reversible nature of these couples (when ΔE_p = 60 mV) was further verified by observing strictly linear plots of i_p/c *vs.* $\sqrt{v}$,[20] where i_p is the peak current, c is the concentration of the complex, and v is the scanning rate. The values obtained for $i_{p,c}/c\sqrt{v}$ are shown in Table 3 for comparison.

Two mechanisms [3,11] have been proposed for the electron transfers in binuclear copper(II) complexes having moderately strong antiferromagnetic interaction ($J \leqslant -300$ cm^{-1}). The mechanism [3] suggesting that the first electron transfer occurs at the lowest unoccupied orbital of the singlet state predicts that the complex with the greatest antiferromagnetic interaction should have the lowest-potential first reduction step. The addition of the second electron will be also at the lowest potential for the one having greatest J. According to the other proposal [11] electron transfer occurs at the triplet state. It was shown that the observed potential for a system having J *ca.* −300 cm^{-1} differed by only 6 mV from the potential calculated for a hypothetical system with $J = 0$. This would predict that for related compounds the potentials for the first reduction step would be virtually independent of the extent of magnetic interaction. It has been already pointed out that the J values of the five compounds described here should vary significantly ($J \geqslant -290$ cm^{-1}). These, therefore, provide an opportunity to test the mechanisms of electron transfer. From Table 3 it may be noted that the potentials of the first couple (E_1) remain practically invariant throughout the series. This clearly supports the mechanism involving triplet copper(II) ion reduction.

Since the magnitude of singlet–triplet separation energy in a Cu^{II}/Cu^{II} complex has no influence on the energy levels of its reduced form, *i.e.* Cu^{II}/Cu^{I}, the addition of the second electron should be also independent of J. The second electron transfer will be more difficult for electrostatic reasons and will also depend on the nature of the substituents present. Electron-releasing substituents will shift the potential to a more negative value. This is shown in a plot of Hammett σ_m values [21] against E_2 (Figure 3). A fairly good linear fit indicates that the electron-density change on the ligand is transmitted directly to the metal ion.

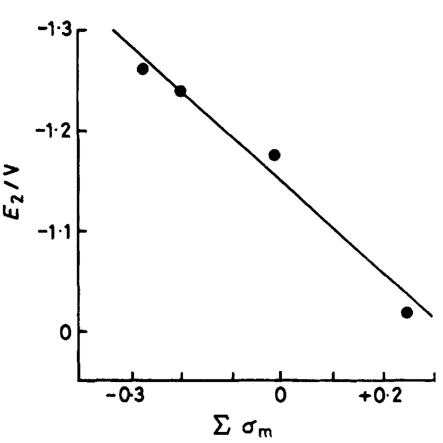


Figure 3. Plot of E_2 *vs.* Hammett σ_m for $[Cu_2L][ClO_4]_2 \cdot nH_2O$

The relation between the conproportionation constant, $K_{con.}$, and the reduction potentials of a binuclear copper(II) complex is given below, where $\Delta E = E_1 - E_2$. Thus the

$$K_{con.} = \frac{[Cu^{II}Cu^{I}L^{+}]^2}{[Cu^{II}Cu^{II}L^{2+}][Cu^{I}Cu^{I}L]} = \exp(nF.\Delta E/RT)$$

larger the separation between the potentials of the couple, the greater is the stability of the mixed-valent species with respect to conproportionation. The values of ΔE and $K_{con.}$ for all of the complexes in Table 3 reveal that in acetonitrile medium the mixed-valent complexes $[Cu^{II}Cu^{I}L]^+$ ($L = L^2 - L^5$) are more stable relative to $[Cu^{II}Cu^{I}L^1]^+$ in dmf.

Some discussion can be made at this stage about the odd-electron delocalisation behaviour in the mixed-valent complexes. According to the classification made by Robin and Day [22] these would belong either to the Class I or II, that is, either both the copper atoms are in sites of different symmetry and valences are trapped, or they have nearly identical symmetry and the electron is delocalised between the two metal centres. The Class I Cu^{II}/Cu^{I} compounds are characterised by the lack of intervalence transfer (i.t.) transition and by four-line e.s.r. spectra, while in the Class II compounds one or more i.t. bands and seven-line hyperfine splitting in the e.s.r. spectra are expected. $[Cu^{II}Cu^{I}L^1]^+$, in a non-co-ordinating solvent like dichloromethane, exhibited [6] a seven-line spectrum at room temperature that reverted to a four-line pattern at $T \leqslant 200$ K. The electronic spectrum showed [6] three strong absorptions at 600, 1 175, and 1 725 nm. However, a solution of $[Cu^{II}Cu^{I}(CO)L^1]^+$ in dichloromethane gave [6] a four-line spectrum at ambient and low temperatures, and showed a single relatively weaker band at 600 nm. The greater conproportionation constant of $[Cu^{II}Cu^{I}(CO)L^1]^+$ (1.9×10^8) relative to that of $[Cu^{II}Cu^{I}L^1]^+$ (4×10^6) in dmf indicates that the former belongs to Class I and has acquired greater stability by virtue of its more compatible steric environment for copper(I), namely square pyramidal. It appears that in dichloromethane $[Cu^{II}Cu^{I}L^1]^+$ is stereochemically non-rigid

$$\underset{\text{Class II}}{[\mathrm{Cu^{II}(planar)/Cu^{I}(planar)}]^+} \rightleftharpoons \underset{\text{Class I}}{[\mathrm{Cu^{II}(planar)/Cu^{I}(apically\ distorted\ planar)}]^+}$$

and probably there is an equilibrium of the type shown above. The equilibrium shifts more to the right with decrease in temperature. When the thermal energy is sufficiently low, the electron becomes trapped into the energetically lower state, that is, in the more stable conformation. *X*-Ray structure analysis[10] of $[\mathrm{Cu^{II}Cu^{I}L^1}][\mathrm{ClO_4}]\cdot0.5\mathrm{MeOH}$ showed the presence of two types of copper(I), namely that which is essentially planar and another with an overall square-pyramidal geometry arising due to axial interaction with the adjacent aromatic ring.

We now turn our attention to the situation that prevails in the acetonitrile solutions of $[\mathrm{Cu^{II}Cu^{I}L}]^+$. We have observed a single absorption band for $[\mathrm{Cu^{II}Cu^{I}L^2}]^+$ and $[\mathrm{Cu^{II}Cu^{I}L^3}]^+$ at *ca.* 600 nm; this was also reported by Gagne *et al.*[6] for $[\mathrm{Cu^{II}Cu^{I}L^1}]^+$. Addison[5] reported a four-line e.s.r. spectrum for an acetonitrile solution of $[\mathrm{Cu^{II}Cu^{I}L^2}]^+$ at room temperature. The values of $K_{\mathrm{con.}}$ for all these compounds in acetonitrile medium (except for the dicarbaldehyde derivative, $[\mathrm{Cu_2L^1}]^{2+}$, for which there are no data) are significantly greater relative to that of $[\mathrm{Cu^{II}Cu^{I}L^1}]^+$ in dmf (see Table 3). Since acetonitrile is a strong donor for copper(I) it is reasonable to believe that in this solvent copper(I) becomes solvated and acquires a square-pyramidal geometry. The net effect is the formation of Class I compounds. We believe that the acetonitrile solutions of all mixed-valent copper complexes reported here, including the dicarbaldehyde derivative, should exhibit four-line e.s.r. spectra (we are unable to verify this at present) from low temperatures to room temperature.

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