Dinuclear Metal Complexes. Part 8.† Effect of Remote Substituents on the Redox Potentials of Mono- and Di-nuclear Copper(II) Complexes‡

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A number of mono- and di-nuclear copper(II) complexes have been synthesized from the Schiff bases obtained by condensing 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde (HA) with p-$H_2NC_6H_4X$ (X = H, Me, OMe, Cl, COMe, or NO_2) alone or in combination with 1,3-diaminopropane. Three types of Schiff bases have been prepared by condensing (*a*) one of the CHO groups of the dicarbaldehyde with the aromatic amines, (*b*) both CHO groups with the same or different arylamines, and (*c*) one CHO with 1,3-diaminopropane and the other with p-$H_2NC_6H_4X$. The e.s.r. spectra of the mononuclear complexes show the absence of tetrahedral distortion. The formal redox potentials (E_f^1, E_f^2) of the complexes are influenced by the nature of X, the reduction taking place more easily with electron-withdrawing substituents. The linear free-energy relation obtained by plotting E_f^1 or E_f^2 *vs.* $\Sigma\sigma_p$ (Hammett parameters) indicates that the electron-transfer reactions are governed by inductive and resonance effects. The free energy of stabilization of the mixed-valence species, ΔG_c, also has a similar correlation with $\Sigma\sigma_p$. The difference between E_f^1 and E_f^2 for the complexes with the ligands of type (*c*) are considerably greater than those obtained with type (*b*). The electrochemical behaviour of the dicopper(II) complexes of type (*a*) ligands shows the prevalence of adsorption, demetallation, and slow electrode kinetics. The dicationic Cu^{II}–Cu^{II} and cationic Cu^{II}–Cu^{I} species are respectively 0.59 and 0.18 V easier to reduce than the corresponding neutral mononuclear complexes.

In the past few years electrochemical studies have been made for a fairly large number of acyclic and macrocyclic dinuclear copper(II) complexes[1–13] derived from Schiff bases of 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde and its derivatives. These studies have provided useful information regarding factors affecting the stabilities of mixed-valence species, electron delocalization in the mixed-valence state, stereochemical change brought about by electron transfer, and the mechanism involved therein.

It is known that the redox properties of mononuclear copper(II) complexes are markedly influenced by structural and electronic factors,[14–19] but it is not known to what extent remote substituent effects mediated through ligand bridges can modify the redox potentials of dicopper(II) complexes. For this reason, the present study is concerned with the synthesis, characterization, and electrochemistry of mononuclear (**1**)—(**11**) and dinuclear (**12**)—(**30**) copper(II) complexes of Schiff bases of 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde. As outlined in the Scheme, the three types of dinuclear complexes (**12**)—(**17**), (**18**)—(**25**), and (**26**)—(**30**) differ in their co-ordination environment. We demonstrate here that both inductive and resonance effects influence the redox potentials in a cumulative manner, and the potentials vary linearly with the summation of the Hammett σ values of the *para* substituents. It is also shown that the $[Cu^{II}(N_4O_2)Cu^{II}]^{2+}$ and $[Cu^{II}(N_4O_2)Cu^{I}]^{+}$ species are respectively *ca.* 0.6 and *ca.* 0.18 V easier to reduce than the neutral complexes $[Cu^{II}(N_4O_2)]$ carrying the same substituents.

Experimental

Materials.—All chemicals were reagent grade and used as received. 2-Hydroxy-5-methylbenzene-1,3-dicarbaldehyde was prepared by a literature method.[20] Dimethylformamide (dmf) used for electrochemical measurements was dried successively over $MgSO_4$, $CuSO_4$, and 4-Å molecular sieves and vacuum distilled prior to use. The supporting electrolyte tetraethylammonium perchlorate was recrystallized from ethanol and dried exhaustively in vacuum before use.

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer model 783 spectrophometer in KBr pellets, electronic spectra in solution 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. The magnetometer was calibrated with $Hg[Co(NCS)_4]$. E.s.r. spectra were obtained on a Varian XL-E109 spectrometer at room temperature using a microwave frequency of 9.525 GHz. The spectra of complexes (**1**), (**3**), (**5**), and (**7**)—(**11**) were recorded both in polycrystalline form (5% of the complex cocrystallized with 95% of the corresponding free ligand) and in chloroform solution.

The electrochemical measurements were carried out under a nitrogen atmosphere at room temperature using a BAS CV-27 voltammograph and a Houston Omnigraph 2000 *xy* recorder. A three-electrode system consisting of a glassy carbon (g.c.) or platinum working electrode, a platinum auxiliary electrode, and a saturated calomel reference electrode (s.c.e.) was used. The complexes were $(1 \pm 0.2) \times 10^{-3}$ mol dm^{-3} in dmf and NEt_4ClO_4 had a fixed concentration, 0.1 mol dm^{-3}. The potentials measured are uncorrected for junction potentials and were compared to those for the ferrocene–ferrocenium couple, which was used as the internal reference.

Preparation of the Mononuclear Complexes.—*Compounds* (**1**)—(**6**). The monosubstituted Schiff bases, HL^1, were prepared by refluxing equimolar (10 mmol) quantities of 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde and *para*-substituted anilines in methanol (50 cm^3) for 4 h. Concentration of the solution, followed by cooling in ice gave orange crystals, which were filtered off and recrystallized from ethanol. Yield 70—80%.

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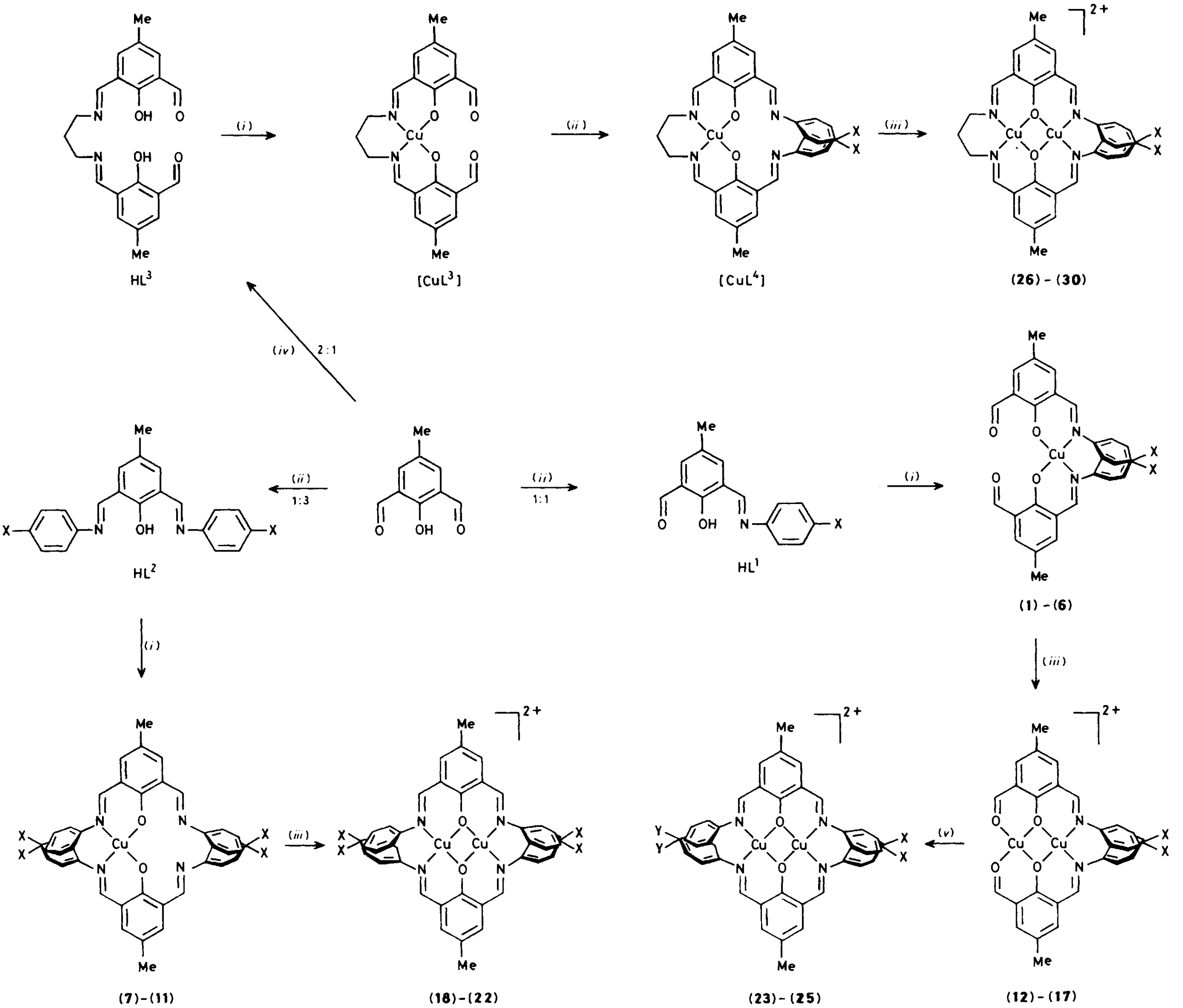
† Ref. 13 is to be considered as Part 7.

‡ *Non-S.I. unit employed:* cal = 4.184 J.



Scheme. X = H [(**1**), (**7**), (**12**), (**18**), or (**26**)], Me [(**2**), (**8**), (**13**), (**19**), or (**27**)], OMe (**3**), (**9**), (**14**), (**20**), or (**28**)], Cl [(**4**), (**10**), (**15**), (**21**), or (**29**)], COMe [(**5**), (**11**), (**16**), (**22**), or (**30**)], NO_2 [(**6**) or (**17**)]; X = H, Y = OMe [(**23**)]; X = H, Y = NO_2 [(**24**)]; X = NO_2, Y = OMe [(**25**)]. (*i*) $Cu(O_2CMe)_2$; (*ii*) *p*-$XC_6H_4NH_2$; (*iii*) $Cu(ClO_4)_2$; (*iv*) $H_2N(CH_2)_3NH_2$; (*v*) *p*-$YC_6H_4NH_2$

To an acetone solution (30 cm^3) of a particular HL^1 (2.5 mmol) an aqueous solution (10 cm^3) of $Cu(O_2CMe)_2 \cdot 2H_2O$ (2 mmol) was added dropwise with stirring. After stirring for 2 h, the brown product that deposited was collected by filtration, washed with water, and dried in vacuum ($CaCl_2$). All the complexes, except for (**6**), were recrystallized from chloroform; the latter was recrystallized from hot dmf (100 °C). Yield 70—75%.

Compounds (**7**)—(**11**). The disubstituted Schiff bases, HL^2, were obtained similarly to HL^1 in 75—80% yield using a 1:3 molar ratio of 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde and aniline derivatives. The chocolate coloured complexes (**7**)—(**11**) were also obtained as described above in 50—60% yield. These compounds were recrystallized from methanol–acetone mixtures.

Preparation of the Dinuclear Complexes.—Compounds (**12**)—(**17**). To a stirred suspension of complexes (**1**)—(**6**) (2 mmol) in dry acetone (50 cm^3) was added solid $Cu(ClO_4)_2 \cdot 6H_2O$ (3 mmol). In a few minutes the mononuclear complex dissolved resulting in a deep green colour, which on refluxing deposited deep green crystals. These were filtered off, washed successively with dry acetone and chloroform, and finally air dried. Yield 70%.

Compounds (**18**)—(**22**). Using the ligands HL^2, these complexes were obtained as greenish yellow crystals in *ca.* 80% yield by adopting the procedure described above.

Compounds (**23**)—(**25**). An appropriate dicopper(II) complex (1 mmol) of the series (**12**)—(**17**) in dry methanol (25 cm^3) was mixed with the required *para*-substituted aniline in excess (6 mmol). The mixture was heated under reflux, whereupon the green complex gradually dissolved and eventually a chocolate coloured product was deposited. This was filtered off, washed with methanol, and air dried. Yield *ca.* 80%.

Compounds (**26**)—(**30**). Ligand HL^3 was obtained as orange crystals (m.p. 146 °C) by refluxing a mixture of 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde (6 mmol) and 1,3-diaminopropane (3 mmol) in ethanol (150 cm^3) followed by partial removal of the solvent in a rotary evaporator. The complex [CuL^3] was obtained straightforwardly from HL^3 (4 mmol) in

Table 1. Analytical and electronic spectral data and magnetic moments for some of the complexes

	Analysis (%)[b]					
Complex[a]	C	H	N	Cu	Electronic spectral data[c] λ/nm (ε/dm^3 mol^{-1} cm^{-1})	$\mu_{eff.}$[d]
(2)	65.8 (65.6)	5.1 (5.1)	4.85 (4.8)	10.95 (10.85)	425 (46 000), 720 (sh)	1.95
(5)	61.1 (63.6)	4.5 (4.7)	4.15 (4.35)	9.8 (9.9)	425 (46 900), 730 (sh)	1.89
(6)	55.8 (55.6)	3.6 (3.7)	8.7 (8.65)	9.65 (9.8)	425 (22 000), 720 (sh)	1.81
(7)	70.45 (70.35)	5.1 (5.15)	7.7 (7.8)	8.6 (8.85)	425 (21 500), 780 (90)	1.89
(8)	72.05 (72.3)	5.7 (5.75)	7.45 (7.35)	8.45 (8.3)	425 (22 300), 780 (90)	1.92
(10)	58.75 (59.2)	3.7 (3.85)	6.35 (6.55)	7.6 (7.45)	425 (20 500), 800 (80)	1.96
(11)	69.0 (68.55)	5.1 (5.0)	6.4 (6.4)	7.1 (7.25)	425 (31 600), 770 (110)	2.02
(13)	45.6 (45.3)	3.65 (3.55)	3.35 (3.3)	14.85 (15.0)	425 (26 900), 710 (160)	1.08
(16)	45.4 (45.15)	3.15 (3.3)	3.2 (3.1)	13.95 (14.05)	420 (25 800), 710 (145)	1.12
(17)	39.3 (39.55)	2.75 (2.65)	6.25 (6.15)	14.0 (13.95)	425 (25 500), 715 (140)	1.15
(18)	52.25 (51.95)	3.65 (3.7)	5.7 (5.75)	13.2 (13.1)	425 (25 400), 710 (200), 810 (sh)	1.16
(19)	54.2 (53.8)	4.25 (4.3)	5.3 (5.45)	12.2 (12.4)	425 (26 600), 700 (205), 800 (sh)	1.2
(22)	53.0 (52.7)	3.8 (3.85)	4.85 (4.9)	11.0 (11.15)	435 (32 800), 720 (180), 810 (sh)	1.15
(23)	51.4 (51.25)	4.0 (3.9)	5.55 (5.45)	12.2 (12.3)	440 (35 400), 710 (195)	1.18
(24)	47.2 (47.55)	3.2 (3.2)	8.0 (7.9)	11.9 (12.0)	430 (28 900), 715 (170)	1.19
(26)	46.3 (46.15)	3.6 (3.75)	6.6 (6.55)	14.9 (14.8)	410 (16 800), 640 (155), 750 (sh)	0.85
(27)	47.15 (47.4)	4.15 (4.05)	6.2 (6.3)	14.1 (14.35)	400 (14 000), 640 (145), 750 (sh)	0.88
(29)	43.0 (42.7)	3.2 (3.25)	5.9 (6.05)	13.5 (13.7)	425 (18 500), 660 (160), 750 (sh)	0.82

[a] See the Scheme for the numbering of the complexes. All the complexes are monohydrates, except for **(7)** and **(10)** which contain 1.5 H_2O molecules. [b] Calculated values are given in parentheses. [c] In dmf. [d] At 298 K.

Table 2. E.s.r. spectral parameters for the mononuclear copper(II) complexes

Complex	$g_{\parallel}$	$g_{\perp}$[a]	g_{iso}[b]	$10^4A_{\parallel}$/cm^{-1}	$10^4A_{\perp}$[a]/cm^{-1}	A_{iso}[b]	$g_{\parallel}A_{\parallel}^{-1}$/cm
(1)	2.230	2.070	2.123	178	23.5	75	125
(3)	2.227	2.074	2.125	177	22.5	74	126
(4)	2.230	2.065	2.120	172	22	72	129
(5)	2.231	2.069	2.123	177	22.5	74	126
(7)	2.236	2.083	2.134	171	25	74	131
(8)	2.233	2.081	2.132	167	25.5	72	134
(9)	2.238	2.086	2.137	171	27	75	131
(10)	2.234	2.081	2.132	172	25	74	130

[a] $g_{\perp} = (3g_{iso} - g_{\parallel})/2$; $A_{\perp} = (3A_{iso} - A_{\parallel})/2$. [b] In $CHCl_3$ solution.

ethanol (100 cm^3) and an aqueous solution (10 cm^3) of $Cu(O_2CMe)_2 \cdot 2H_2O$ (2.5 mmol). A mixture of [CuL^3] (2 mmol) and a *para*-substituted aniline (6 mmol) in methanol (30 cm^3) gave on refluxing a crystalline product [CuL^4]. The desired compounds **(26)**—**(30)** were then obtained by stirring [CuL^4] (1 mmol) in methanol (30 cm^3) with $Cu(ClO_4)_2 \cdot 6H_2O$ (1.5 mmol) and heating under reflux for 2 h. The solution on concentration and standing gave chocolate, **(26)**—**(28)**, or yellow crystals, **(29)** and **(30)**. Overall yield *ca.* 50%. **CAUTION**. The perchlorate salts of the dinuclear complexes are stable at room temperature for an indefinite period, but are potentially explosive when heated.

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer model 240C elemental analyser in our department. Copper was estimated gravimetrically with α-benzoin oxime.[21] Analytical data for a few selected complexes are given in Table 1.

Results and Discussion

Synthesis and Characterization.—The reaction sequences involved in the preparation of the mono- and di-nuclear complexes (1)—(30) are illustrated in the Scheme. All the complexes are obtained as monohydrates, except for (7) and (10), which contain 1.5 water molecules. The i.r. spectra of complexes (1)—(6) exhibit three strong bands at 1 660, 1 620, and 1 535 cm^{-1} which are due to free ν(C=O), metal-bound ν(C=N), and $\nu(C\overset{\cdots}{-}O)$ of the phenoxo moiety, respectively. For complexes **(7)**—**(11)**, again three bands are observed at 1 660, 1 610, and 1 535 cm^{-1}, differing from the previous series in that the band at 1 660 cm^{-1} is of moderate intensity and is due to the free carbaldimine moiety. The metal-bound C=N and C=O stretchings overlap to give a strong broad band centred at 1 625 cm^{-1} for the dinuclear complexes **(12)**—**(17)**, while a single ν(C=N) band at 1 620 cm^{-1} is observed for the remaining dinuclear complexes. For all the dinuclear complexes the $\nu(C\overset{\cdots}{-}O)$ vibration appears at a slightly higher frequency (1 550 cm^{-1}) than that of the mononuclear complexes (1 535 cm^{-1}). The dinuclear complexes are further characterized by the presence of bands due to ionic perchlorate at about 1 100 and 625 cm^{-1}. Because of the appearance of a number of bands due to the ligand in the range 700—250 cm^{-1}, no attempt has been made to identify the ν(Cu–N) and ν(Cu–O) frequencies. Finally we note that complexes **(5)**, **(11)**, **(16)**, **(22)**, and **(30)** display an additional strong band between 1 685 and 1 670 cm^{-1} due to ν(C=O) of the *para*-substituted COMe group present in these compounds.

The electronic spectral features of the deeply coloured complexes are dominated by a strong absorption band at 420 nm. As a result, the longer wavelength *d–d* transitions (650—800 nm) are usually observed in the form of one or two shoulders (Table 1). The band at 420 nm appears to be due to a combination of intra-ligand and ligand-to-metal charge-transfer transitions. Additional ligand-based bands are observed at shorter wavelengths. The general spectral characteristics of the copper(II) complexes are indicative of square-planar based geometry and the absence of pseudo-tetrahedral distortion, in which case a spectral shift occurs to a considerably lower energy (< 10 000 cm^{-1}). The room-temperature effective magnetic moments per copper atom for the dinuclear complexes lie between 0.8 and 1.2 (Table 1), showing that antiferromagnetic interactions of varying intensities are operative in these compounds.

Since the redox potential of a copper(II) complex is greatly dependent on its steric environment,[15–19,22] an assessment of the inductive influence of substituents in a series of complexes with the same donor atoms requires that no change in stereochemistry takes place throughout the series. We have examined the e.s.r. spectra of the mononuclear complexes as they are quite responsive to changes in co-ordination geometry.[16,18,22–26] Table 2 lists the e.s.r. parameters for some of these complexes. The line shapes of these complexes doped in the corresponding free ligands are typical of a $d_{x^2-y^2}$ ground state with D_{4h} symmetry. It is well known that pseudo-tetrahedral distortion leads to a greatly reduced value of $A_{\parallel}$ and an increased value of $g_{\parallel}$. Often the quotient $g_{\parallel}/A_{\parallel}$ is empirically treated[27] as an index of tetrahedral distortion; for square-planar structures the usual range is 105—135 and 150—250 cm for tetrahedrally distorted complexes. The range of our values, 125—135 cm, clearly indicates the absence of tetrahedral distortion from D_{4h} symmetry. An important implication of this observation is that in order to avoid steric repulsion the phenyl rings of the azomethine linkages should be perpendicular to the plane of the metal atom. Consideration of molecular models showed that this should be the case also for the dinuclear complexes (as shown in the Scheme). Although $g_{\parallel}$ is known to increase as the electron-withdrawing power of a ligand substituent increases,[28] the lack of such a trend in the compounds considered (Table 2) indicates that the remote substituents are not strong enough to perturb the bonding parameters of the complexes.

Table 3. Electrochemical data[a] for the mononuclear copper(II) complexes in dmf

Complex	$E_f{}^b$/V	$\Delta E_p{}^c$/mV	$I_{p,c}/I_{p,a}$
(1)	−0.52	100	1.05
(2)	−0.54	100	1.1
(3)	−0.545	110	1.15
(4)	−0.505	90	1.05
(5)	−0.49	100	1.15
(6)	−0.46	100	1.15
(7)	−0.56	140	1.15
(8)	−0.58	140	1.15
(9)	−0.585	130	1.05
(10)	−0.54	100	1.05
(11)	−0.50	100	1.1

[a] Values obtained by using a g.c. electrode *vs.* s.c.e. at a scan rate of 200 mV s^{-1}. [b] $E_f = 0.5\ (E_{p,c} + E_{p,a})$. [c] $\Delta E_p = E_{p,c} - E_{p,a}$.

Electrochemistry.—As already mentioned, the ferrocene–ferrocenium couple was used as the internal redox standard as a measure of the consistency of the potentials recorded. This couple was observed at + 0.455 ± 0.005 V *vs.* s.c.e., and the peak-to-peak separation ($\Delta E_p = E_{p,c} - E_{p,a}$) was 75 ± 5 mV, which remained unchanged with variation of the scan rate (v). The deviation of ΔE_p from the expected value (60 mV) is due to the presence of uncompensated solution resistance. Thus, redox couples for which ΔE_p was found to lie between 70 and 80 mV were considered as reversible systems.

The cyclic voltammograms for the ligands HL^2 showed that while irreversible oxidation takes place at about + 1.1 V, no reduction occurs at potentials positive of − 1.5 V, except for the ligand having a *p*-nitro substituent. In the case of the *p*-$O_2NC_6H_4$ derivative, a quasi-reversible redox process with the formal potential $E_f = 1.16$ V [$E_f = 0.5\ (E_{p,c} + E_{p,a})$] and $\Delta E_p = 100$ mV (at $v = 100$ mV s^{-1}) was observed, presumably due to the electron-transfer reaction $\text{-NO}_2 + e^- \rightleftharpoons \text{-NO}_2{}^{\bullet -}$.

The mononuclear complexes **(1)**—**(6)** and **(7)**—**(11)** undergo electrode reaction (1) quasi-reversibly. The electrochemical data

$$[CuL_2] \underset{E_f}{\overset{e^-}{\rightleftharpoons}} [CuL_2]^- \qquad (1)$$

for these compounds are given in Table 3. In general, measurements carried out at a platinum electrode showed considerably slow electrode kinetics compared to that observed with a g.c. electrode. For example, the ΔE_p for complex **(1)** at the g.c. and platinum electrodes (at $v = 200$ mV s^{-1}) are 100 and 180 mV, respectively and the corresponding values for **(7)** are 140 and 240 mV.

The typical cyclic voltammetric response for the dinuclear

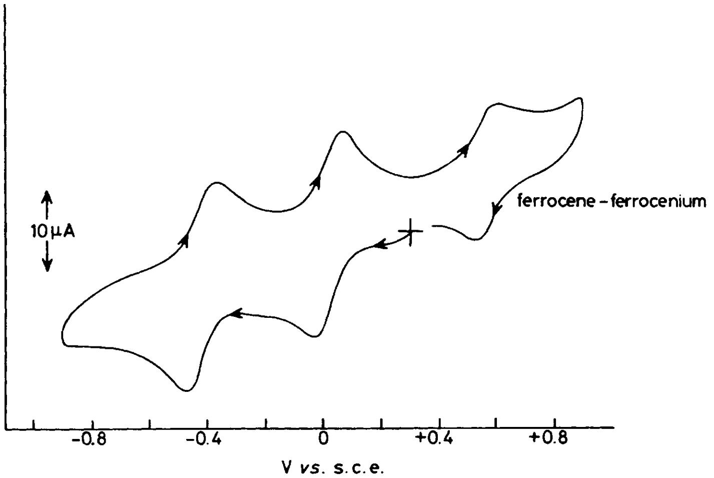


Figure 1. Cyclic voltammogram of complex **(20)** (0.96 mmol dm^{-3}) mixed with ferrocene in dmf using a glassy carbon electrode. Concentration of NEt_4ClO_4: 0.1 mol dm^{-3}. Scan rate: 200 mV s^{-1}

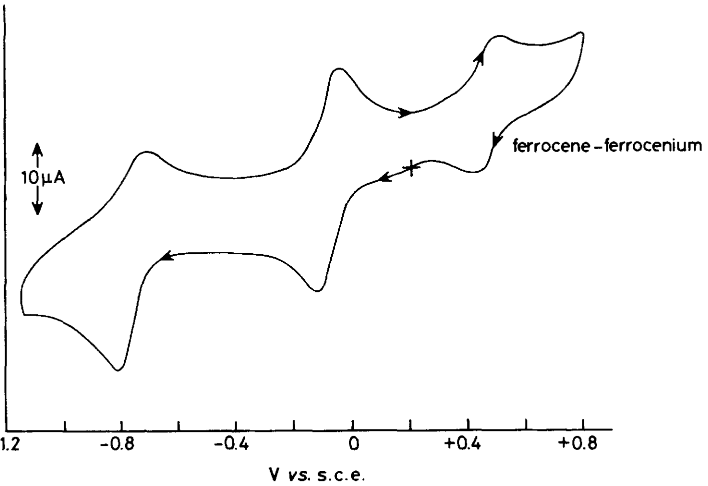


Figure 2. Cyclic voltammogram of complex (**26**) (1.01 mmol dm^{-3}) mixed with ferrocene in dmf using a glassy carbon electrode. Details as in Figure 1

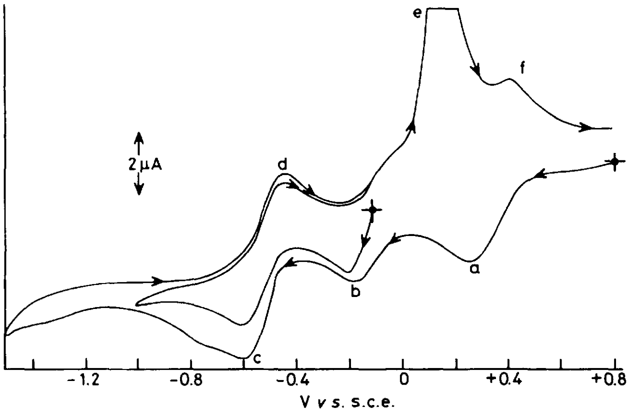


Figure 3. Cyclic voltammogram of complex (**12**) (1.09 mmol dm^{-3}) in dmf using a platinum electrode. Concentration of NEt_4ClO_4: 0.1 mol dm^{-3}. Scan rate: 100 mV s^{-1}. Insert shows the cyclic voltammogram of the same solution in the potential range −0.1 to −1.0 V

complexes (**18**)—(**25**) is shown in Figure 1 for complex (**20**) at a g.c. electrode. The data given in Table 4 show that two one-electron transfers (2) and (3) occurred almost reversibly or quasi-reversibly.

$$[Cu^{II}Cu^{II}L_2]^{2+} \underset{E_f^1}{\overset{e^-}{\rightleftharpoons}} [Cu^{II}Cu^{I}L_2]^+ \qquad (2)$$

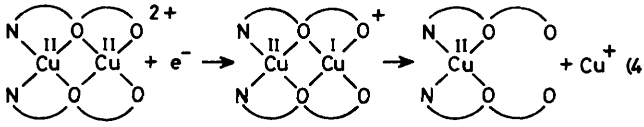
$$[Cu^{II}Cu^{I}L_2]^+ \underset{E_f^2}{\overset{e^-}{\rightleftharpoons}} [Cu^{I}Cu^{I}L_2] \qquad (3)$$

Figure 2 shows the cyclic voltammogram complex (**26**) at a g.c. electrode, and is typical of those for compounds (**26**)—(**30**). Similar to the mononuclear complexes, the dinuclear complexes also undergo slow electron transfers at a platinum electrode. Table 4 indicates that the separations between the two redox couples ($\Delta E = E_f^1 - E_f^2$) in the series (**26**)—(**30**) are considerably greater than those for (**18**)—(**25**).

The electrochemical behaviour of the dicopper(II) complexes (**12**)—(**17**) in which the two copper atoms have different co-ordination sites (CuN_2O_2 and CuO_4) is exemplified by the voltammogram of (**12**) at a platinum electrode (Figure 3). This voltammogram is complex in nature because it is associated with adsorption, chemical reaction following electron transfer, slow electrode kinetics, anodic stripping, *etc.*

The peak a observed at quite a positive potential, +0.26 V in the cathodic sweep, shows its counterpart f in the reverse scan at +0.44 V. The peak b at −0.2 V does not show a corresponding peak in the return potential sweep. The redox couple c/d is observed at −0.60/−0.44 V. In addition, the anodic sweep shows strong current absorption between 0 and +0.3 V (e). Figure 3 also shows that when the cyclic voltammogram is recorded in the potential range −0.1 to −1.0 V (see insert), only the peak b and the couple c/d are observed. The electrochemical responses of these compounds at a g.c. electrode are essentially the same with minor shifts in potential, but more importantly, the peaks a and f are either less conspicuous or absent.

The redox couple a/f probably involves strong adsorption of the product of charge transfer encountered in the electrochemical reduction of the dicopper(II) complex. When both adsorption and diffusion control are significant, a response prior to the diffusion-controlled one is obtained for the reduction to the adsorbed state; the reverse potential scan also contains a response related to the adsorption process following the diffusion-controlled response.[29,30] The peak b for which the anodic response is lacking is due to electron transfer followed by demetallation reaction (4).



(4)

We recently reported[31] that a similar (e.c.) mechanism is operative with related hetero-dinuclear complexes. Evidence in favour of reaction (4) was obtained from the redox potentials for the couple c/d in complexes (**12**)—(**17**) which are identical to those for the corresponding member of the series (**1**)—(**6**). The copper(I) ion released in reaction (4) is irreversibly reduced at a more negative potential (not seen clearly in the voltammogram) and causes electrode poisoning. The surge of current at e is probably due to anodic stripping of the deposited metal.

The effect of *para*-substituents on redox potentials can be evaluated in terms of the Hammett linear free-energy equation (5),[32–34] where ΔE_f represents the shift in redox potential

$$\Delta E_f = \Sigma\sigma_p\rho \qquad (5)$$

consequent upon a change in substituents, $\Sigma\sigma_p$ is a summation

Table 4. Electrochemical data[a] for the dinuclear copper(II) complexes in dmf

	$Cu^{II}–Cu^{II} + e^- \overset{E_f^1}{\rightleftharpoons} Cu^{II}–Cu^{I}$			$Cu^{II}–Cu^{I} + e^- \overset{E_f^2}{\rightleftharpoons} Cu^{I}–Cu^{I}$				
Complex	E_f^1/V	ΔE_p/mV	$I_{p,c}/I_{p,a}$	E_f^2/V	ΔE_p/mV	$I_{p,c}/I_{p,a}$	$\Delta E_f{}^b$/V	$K_c{}^c$
(18)	+0.035	70	1.0	−0.385	90	0.95	0.42	1.28×10^7
(19)	+0.02	80	0.95	−0.41	100	1.05	0.43	1.89×10^7
(20)	+0.015	90	0.95	−0.42	100	1.1	0.435	2.29×10^7
(21)	+0.055	80	0.9	−0.36	80	0.9	0.415	1.05×10^7
(22)	+0.075	110	1.15	−0.315	110	1.1	0.39	3.98×10^6
(23)	+0.015	90	1.0	−0.425	110	1.15	0.44	2.79×10^7
(24)	+0.065	90	1.2	−0.34	80	1.15	0.405	7.08×10^6
(25)	+0.055	90	1.1	−0.36	100	0.9	0.415	1.05×10^7
(26)	−0.08	80	0.9	−0.76	80	1.15	0.68	3.20×10^{11}
(27)	−0.09	80	0.95	−0.775	90	1.1	0.685	3.89×10^{11}
(28)	−0.11	80	1.0	−0.785	90	1.15	0.675	2.64×10^{11}
(29)	−0.07	80	0.9	−0.745	90	1.1	0.675	2.64×10^{11}
(30)	−0.05	80	1.05	−0.725	110	1.2	0.675	2.64×10^{11}

[a] Values obtained by using a g.c. electrode *vs.* s.c.e. at a scan rate of 200 mV s^{-1}. [b] $\Delta E_f = E_f^1 - E_f^2$. [c] $K_c = 10^{\Delta E_f/0.0591}$.

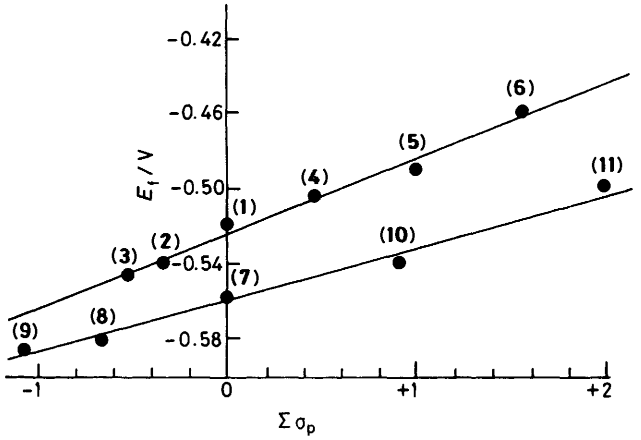


Figure 4. Plot of E_f *vs.* $\Sigma\sigma_p$ for the mononuclear complexes **(1)**—**(11)**

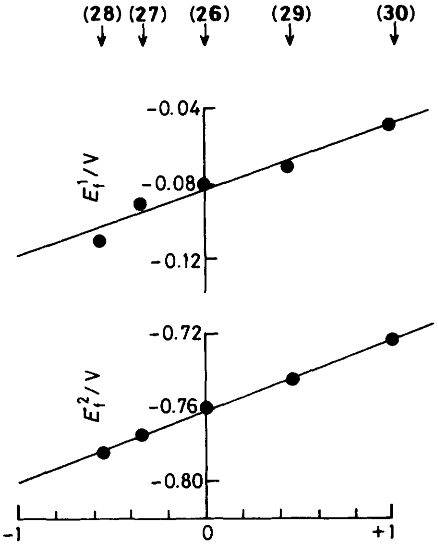


Figure 6. Plots of E_f^1 and E_f^2 *vs.* $\Sigma\sigma_p$ for the dinuclear complexes **(26)**—**(30)**

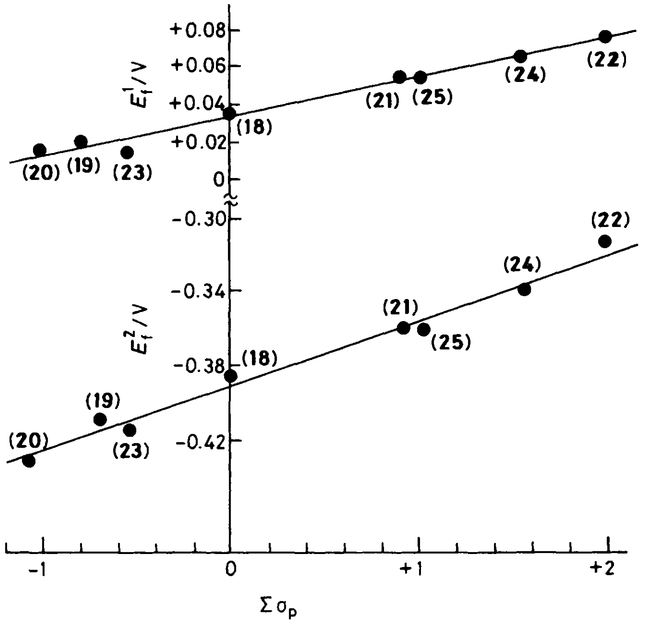


Figure 5. Plots of E_f^1 and E_f^2 *vs.* $\Sigma\sigma_p$ for the dinuclear complexes **(18)**—**(25)**

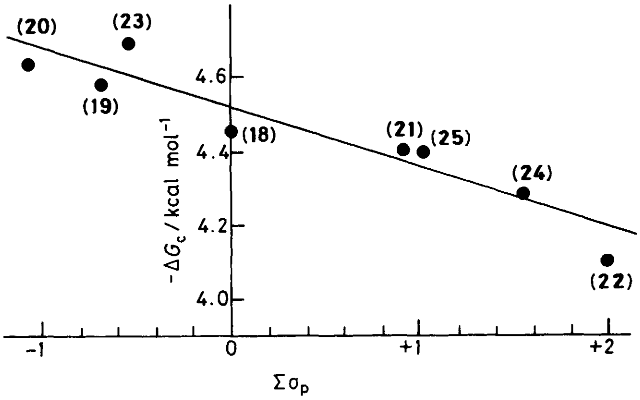


Figure 7. Plot of ΔG_c *vs.* $\Sigma\sigma_p$ for the dinuclear complexes **(18)**—**(25)**

of the inductive and resonance effects of all the *para* substituents,[35] and ρ, the reaction constant (in volts), gives a measure of the susceptibility of the electrode reaction to the polar effect of the substituents.

As shown in Figure 4, the linear free-energy relation gives an excellent correlation between E_f and $2\sigma_p$ for complexes (**1**)—(**6**) (correlation coefficient, $r = 0.99$, $\rho = 0.039$ V), and E_f and $4\sigma_p$ for (**7**)—(**11**) ($r = 0.99$, $\rho = 0.028$ V). Although the choice of the number of *para* substituents was limited by the availability of reagents, the point is clearly made. The implication of this correlation is that in all cases the electron-transfer mechanism is the same, *viz.* the electron-density change at the ligand is transmitted directly to the metal and no stereochemical change takes place across the series. On the other hand, when E_f was plotted *vs.* $\Sigma\sigma^0$, where σ^0 is the Taft substituent parameter,[35] which does not take into consideration the resonance effect, no correlation was obtained.

The E_f values for mononuclear complexes (Table 3) show that the monoaldimine complexes are more easily reduced than their dialdimine analogues. Thus, a constant difference of 40 mV between E_f of complexes (**1**) and (**7**), (**2**) and (**8**), and (**3**) and (**9**) gives an indication of the electron-withdrawing power of the free CHO group in (**1**)—(**3**). This difference decreases with the introduction of electron-withdrawing *para* substituents, but even then the inductive influence of p-$MeCOC_6H_4$ is 10 mV less than that of CHO [compare (**5**) and (**11**)].

The applicability of the linear free-energy relation is firmly established for the dinuclear complexes (**18**)—(**25**), which contain various combinations of electron-repelling and -attracting *para* substituents. The plots of E_f^1 *vs.* $\Sigma\sigma_p$ ($r = 0.99$, $\rho = 0.021$ V) and E_f^2 *vs.* $\Sigma\sigma_p$ ($r = 0.98$, $\rho = 0.034$ V) are shown in Figure 5. Again no such correlations were observed with $\Sigma\sigma^0$ values.

The linear free-energy relation is also valid for the dinuclear complexes (**26**)—(**30**) (Figure 6). It is to be noted that in these compounds although the two copper centres have the same donor atoms, the chelate effect is different. The redox potentials given in Table 4 indicate that the first electron transfer occurs to the metal centre that has aryl azomethine donor sites. Another noteworthy feature of these compounds is that the ρ values for the electron-transfer reactions $Cu^{II}Cu^{II} + e^- \overset{E_f^1}{\rightleftharpoons} Cu^{II}Cu^{I}$ ($\rho = 0.035$ V) and $Cu^{II}Cu^{I} + e^- \overset{E_f^2}{\rightleftharpoons} Cu^{I}Cu^{I}$ ($\rho = 0.038$ V) are practically the same. This means, that regardless of the nature of the *para* substituents, ΔE_f remains virtually unchanged for these compounds.

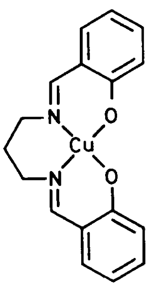
The question whether the relative stability of the mixed-valence species $[Cu^{II}Cu^{I}L_2]^+$ is affected by the remote substituents has been considered in the light of the conproportionation constant K_c for reaction (6). The values of K_c obtained

$$[Cu^{II}Cu^{II}L_2]^{2+} + [Cu^{I}Cu^{I}L_2] \overset{K_c}{\rightleftharpoons} 2[Cu^{II}Cu^{I}L_2]^+ \quad (6)$$

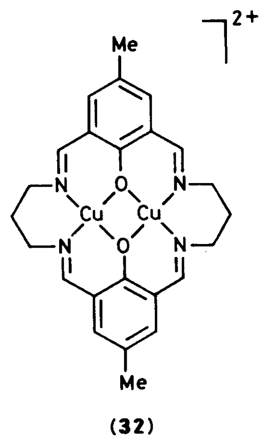
from the relation $K_c = 10^{\Delta E_f/0.0591}$ are given in Table 4 for all the dinuclear complexes. The free energy of stabilization of $[Cu^{II}Cu^{I}L_2]^+$, ΔG_c, in turn can be obtained according to the relation (7). The magnitude of ΔG_c depends on several

$$\Delta G_c = -(RT/2)\ln(K_c/4) \quad (7)$$

factors,[2,36–38] *viz.* the delocalization energy, structural change, electrostatic effect, and magnetic superexchange interaction. We recently pointed out[11] that in a homomorphic series the major factors contributing to the variation of ΔG_c are the energies related to delocalization and structural changes. In the series (**18**)—(**25**), since no abrupt change in geometry is anticipated to take place, ΔG_c is expected to vary linearly with $\Sigma\sigma_p$. Figure 7 shows that a reasonable least-squares fit ($r = 0.95$) of ΔG_c *vs.* $\Sigma\sigma_p$ has been obtained. This indicates that the delocalization energy increases with the electron-releasing power of the *para* substituents.



(**31**)



(**32**)

The extent to which the redox potential of a mononuclear complex is modified in the corresponding dinuclear species can be evaluated by comparing the E_f value of a particular compound in the series (**7**)—(**11**) with the E_f^1 and E_f^2 values for the dinuclear analogue in the series (**18**)—(**22**). It may be noted that in all the cases the $[Cu^{II}Cu^{II}L_2]^{2+}$ and $[Cu^{II}Cu^{I}L_2]^+$ species are respectively 0.59 and 0.18 V easier to reduce than the neutral $[Cu^{II}L_2]$. Incidentally, almost identical values (0.58 and 0.19 V) were obtained for complex (**31**) *vis-à-vis* the dicopper macrocycle (**32**). Undoubtedly, the observed differences are mainly due to the molecular charge, but the electron delocalization energy also plays an important role.

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