Autoxidation of a Dicopper(I) Macrocyclic Complex: Evidence for a Mixed-valence Intermediate†

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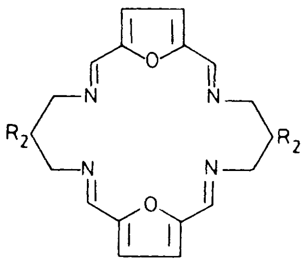
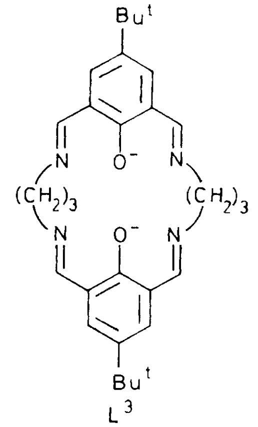
Interaction of O_2 with dicopper(I) complexes of 20-membered N_4 macrocycles L^1 and L^2 {23,24-dioxa-3,7,14,18-tetra-azatricyclo[18.2.1.1^{9,12}]tetracosa-1(22),2,7,9,11,13,18,20-octaene and its 5,5,16,16-tetramethyl derivative} proceeds *via* an intermediate red-brown species, whose electronic and e.s.r. spectra suggest a mixed-valence formulation. This red-brown species can also be generated by conproportionation between dicopper(I) and dicopper(II) complexes of these macrocycles. The mixed-valence product cannot be isolated in the solid state, as concentration of the solutions leads to disproportionation with precipitation of a solid $[Cu_4L^1_2(OH)]^{3+}$ cluster. Cyclic voltammetry revealed that all redox processes associated with the copper centres in these complexes are irreversible, probably due to a chemical process such as transfer of the hydroxo bridging ligand at each redox stage. It is believed that the pair of irreversible reduction waves observed in the cyclic voltammogram of the di-μ-hydroxo-dicopper(II) complex of L^1 correspond to sequential one-electron reductions of the dicopper centre.

The binuclear copper site is of widespread occurrence in biology, having particular importance in proteins which deal with the transport and reduction of oxygen. These include the oxygen-transport protein haemocyanin and the mono-oxygenase tyrosinase. Tyrosinase utilises O_2 in the hydroxylation of monophenols, and also functions as a dehydrogenating agent when converting the diphenol formed into a quinone. The similarity in the properties of the active site in haemocyanin and tyrosinase extends to the existence[1] of both enzymes in a semi-oxidised form. In this form both sites are capable of tightly binding a bridging exogenous ligand in such a way as to generate an intervalence charge-transfer absorption in the near i.r., so that the assembly exhibits class II mixed-valence[2] character. In the oxidised form of both haemocyanin and tyrosinase, the active site is e.s.r.-silent, showing that the copper(II) centres undergo strong antiferromagnetic exchange mediated by a bridging ligand of type RO^-. However, although polypeptide chain recognition has now been achieved for haemocyanin in the 3.2-Å resolution *X*-ray crystal structure, identifying three histidine ligands per copper, the study fails to identify any bridging ligand of major electron density,[3] and raises the possibility of hydroxide acting as a bridging ligand, despite the apparent hydrophobicity of the site. There is thus some interest in models where sizeable antiferromagnetic interaction between copper(II) centres is mediated by hydroxide bridges, particularly where, as in the present system,[4] this property is accompanied by catalytic activity in oxidation reactions.

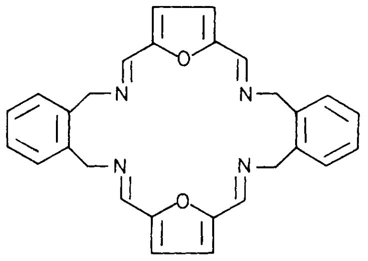
Our earlier investigations into the catalytic properties of dicopper(I) and dicopper(II) derivatives of the macrocyclic ligand L^1 reveal activity in the dehydrogenation of a wide range of substrates with replaceable hydrogen,[4,5] and the oxidative coupling of others.[6] In the hope of adding to our understanding of the redox changes which are involved in the catalytic cycle, we have undertaken a study of the autoxidation of dicopper(I) complexes of L^1 and the related ligand L^2. The reactions were followed spectrophotometrically in solution by means of electronic and e.s.r. spectroscopy, and the solid products obtained from the reaction mixture were also investigated. In addition, we examined the electrochemical behaviour of dicopper(I) and dicopper(II) complexes of L^1, as well as of its mixed-valence complex.



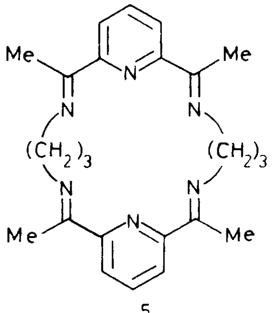
L^1 R = H
L^2 R = Me



L^3



L^4



L^5

Results and Discussion

Reaction Stoicheiometry.—In the case of the enzymes haemocyanin and tyrosinase, an oxygen uptake of 1 mol O_2 per every two copper(I) ions is observed in a reversible process. This

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† *Non-S.I. unit employed*: G = 10^{-4} T.

Table 1. Analytical, conductivity, and i.r. data for the dicopper complexes

Complex	Colour	Analysis[a]/%			Conductivity, Λ_m/S cm^{-2} mol^{-1}	Selected i.r. data[b]/cm^{-1}		
		N	C	H		ν(OH)	ν(C=N)	ν(ClO_4^-)
(**1**) $[Cu_2L^1(MeCN)_2][ClO_4]_2$[c]	Yellow	11.7 (11.5)	35.8 (36.1)	2.8 (3.6)	270[d]		1 625ms	1 090vs 620s
(**2**) $[Cu_2L^2(MeCN)_2][ClO_4]_2$[c]	Yellow	10.6 (10.7)	39.8 (39.6)	4.3 (4.3)	275[d]		1 625ms	1 090vs 620s
(**3**) $[Cu_2L^1(OH)_2(H_2O)][ClO_4]_2$[c]	Green	8.1 (8.0)	31.0 (30.8)	3.3 (3.4)	260[d]	≈3 500br	1 640ms	1 090vs 625s
(**4**) $[Cu_2L^1(OH)_2(MeCN)_2][ClO_4]_2$	Green	10.8 (10.9)	34.9 (34.5)	3.7 (3.9)	252[d]	≈3 400br	1 640ms	1 095vs 630s
(**5**) $Cu_4L^1_2(OH)(ClO_4)_3$	Brick	9.1 (9.2)	35.5 (35.5)	3.5 (3.4)	101[e]	3 570sp	1 630ms	1 095vs 630ms
(**6**) $[Cu_2L^1(OH)_2(dma)_{1.5}][ClO_4]_2$	Green	9.1 (9.4)	35.2 (35.4)	4.2 (4.4)	288[d]	≈3 300br	1 635ms	1 090vs 625ms

[a] Calculated values in parentheses. [b] s = Strong, v = very, m = medium, br = broad, and sp = sharp. [c] Included in the Table for completeness but has been described elsewhere.[5,15] [d] 10^{-3} mol dm^{-3} in MeCN. [e] 10^{-3} mol dm^{-3} in dmso.

Table 2. Oxygen uptake data under different conditions

Deoxygenated dma[a]		O_2-Saturated dma[a]		dmso[b]	
10^3[Complex]/ mol dm^{-3}	O_2 Uptake[c] per mol Cu^I_2	10^3[Complex]/ mol dm^{-3}	O_2 Uptake[c] per mol Cu^I_2	10^3[Complex]/ mol dm^{-3}	O_2 Uptake[c] per mol Cu^I_2
1.16	0.48	1.71	0.92	4.31[d]	0.85
1.24	0.48	4.77	0.79		
2.37	0.49	5.07	0.78	5.14[e]	0.86
5.02	0.53	7.43	0.75	6.44[e]	0.83
6.55	0.50	8.55	0.71	6.82[d]	0.87
6.61	0.52	17.40	0.68		
9.52	0.48	18.80	0.63		

[a] Dried over $CuSO_4$. [b] Dried over CaH_2. [c] Uptake stoicheiometries ±0.03. [d] Deoxygenated dmso. [e] O_2-Saturated dmso.

stoicheiometry has also been achieved in the binucleating model compound recently developed by Karlin *et al.*,[7] where reversible oxygenation is observed at −50 °C in dichloromethane. A number of other copper(I) compounds take up oxygen at least quasireversibly[8] in a 1:2 O_2:Cu^I ratio, and this stoicheiometry is also observed where the ligand is oxidised in the course of the reaction,[9] although in these cases the oxygen uptake is irreversible.

However, in other catalytically active dicopper systems, oxygen uptake is limited to the O_2:Cu^I ratio 0.5:2, which is explained[10] in terms of rapid and irreversible reaction of an initially formed peroxo-adduct with unreacted Cu^I, this consumption of reactant making it unavailable for uptake of O_2.

We have used manometric methods to study the O_2 uptake of the macrocyclic complexes $[Cu_2L(MeCN)_2][ClO_4]_2$ (L = L^1 or L^2) in dimethylacetamide (dma) and dimethyl sulphoxide (dmso) over the concentration range 10^{-3}–10^{-2} mol dm^{-3}. The complexes studied are characterised in Table 1, and the results obtained listed in Table 2. When O_2 was admitted to a degassed dma solution of $[Cu_2L^1(MeCN)_2][ClO_4]_2$ (**1**) (see Table 1) the uptake lay within 0.5 ± 0.03 mol O_2 per mol of dicopper(I) complex. It was noted, however, that if the dicopper(I) complex was added to an O_2-saturated solution so that O_2 was always in excess, uptakes significantly greater than 0.5 per mol of complex were observed, suggesting transient formation of a 1:1 species. Nevertheless, bleeding in the copper(I) solution over a period of minutes so that it remained always in deficit did not generate a spectroscopically detectable amount of any new species, nor could we find, by gas chromatography–mass spectrometry (g.c.–m.s.), any evidence for solvent oxygenation or coupling. It seems that any initially formed dioxo- or peroxo-species is rapidly destroyed in subsequent reactions.

In dmso solution, uptakes in excess of 0.5 O_2 per mol of dicopper(I) complex are routinely observed under conditions either of an initial excess or initial deficit of O_2. Mass spectral examination of the solvent after reaction shows that this is due to the formation of dimethyl sulphone, Me_2SO_2, suggesting that complex (**1**) has the capacity to act as an oxygenation, as well as dehydrogenation, catalyst.

Spectroscopic Monitoring of the Reaction.—In the course of the autoxidation reaction of complex (**1**) or $[Cu_2L^2(MeCN)_2][ClO_4]_2$ (**2**) in dma, dimethylformamide (dmf), or dmso it was noticed that the orange copper(I) solution passed through an intense red-brown colour before attaining the final green colour typical of Cu^{II}. Electronic spectra (Table 3) of these solutions show a fairly strong near-i.r. absorption, centred at 11 900 cm^{-1} for the solution obtained from (**1**) and 12 400 cm^{-1} for that obtained from (**2**). This absorption is not present either in the spectrum of the starting material (**1**) or (**2**) or of the final oxidation products. Variation of the ratio of O_2:Cu^I_2 reveals that the near-i.r. absorption maximised (Figure 1) at a ratio of O_2:Cu^I_2 of ≈0.25:1, indicating 50% oxidation of the copper(I) centres.

Both the position and intensity of the bands at ≈12 000 cm^{-1} suggest an intervalence charge-transfer (i.c.t.) copper(II)–copper(I) transition. Such transitions are observed in the solution spectra of established mixed-valence dicopper complexes of the type $[Cu_2L^3]^{2+}$, which have been isolated in the solid state[11] and in some cases structurally characterised.[12]

Table 3. Electronic and e.s.r. spectral data

Complex	$\lambda_{max.}$/cm^{-1}	Solvent	ε/dm^3 mol^{-1} cm^{-1}	g_{iso}[a]	A_{iso}/G	D_{iso}/G	Signal intensity[b]
(**1**) $[Cu_2L^1(MeCN)_2][ClO_4]_2$	34 500	MeCN	40 000				
	28 000 (sh)						
(**2**) $[Cu_2L^2(MeCN)_2][ClO_4]_2$	34 000	MeCN	40 000				
	29 500 (sh)						
(**3**) $[Cu_2L^1(OH)_2(H_2O)][ClO_4]_2$	34 700	MeCN	30 000	2.16	33	215	0.10
	21 000 (sh)		190				
	16 200						
(**4**) $[Cu_2L^1(OH)_2(MeCN)_2][ClO_4]_2$	34 000	MeCN	30 000	2.16	32	215	0.11
	22 000br (sh)		230				
	15 700						
	14 800	dma	175				
(**5**) $Cu_4L^1{}_2(OH)(ClO_4)_3$	33 000br		*c*				
	25 000 (sh)						
(**6**) $[Cu_2L^1(OH)_2(dma)_{1.5}][ClO_4]_2$	34 000	MeCN	30 000	2.16	33	215	0.08
	22 000br (sh)						
	15 900		240				
	14 800	dma	177				
(**7**) $[Cu_2L^1(MeCN)_2]^{2+}:0.25\ O_2$	11 900	dma	425[d]	2.16	33	*e*	0.85
(**8**) $[Cu_2L^1(MeCN)_2]^{2+}:0.5\ O_2$	14 800	dma	175	2.16	33	215	0.08
(**9**) $[Cu_2L^2(MeCN)_2]^{2+}:0.25\ O_2$	12 400	dma	437[d]	2.15	33	*f*	0.85
(**10**) $[Cu_2L^2(MeCN)_2]^{2+}:0.5\ O_2$	15 300	dma	154	2.16	34	220	0.08

[a] Assuming the fourth line to be the centre of a seven-line pattern. All e.s.r. spectra in fluid dmf solution. [b] Relative to 0.02 mol dm^{-3} $CuSO_4\cdot 5H_2O$ in dma solution. [c] Nujol mull. [d] ε_{app} per Cu_2. [e] Additional component around $g = 2.12$. [f] Additional component $g = 2.11$.

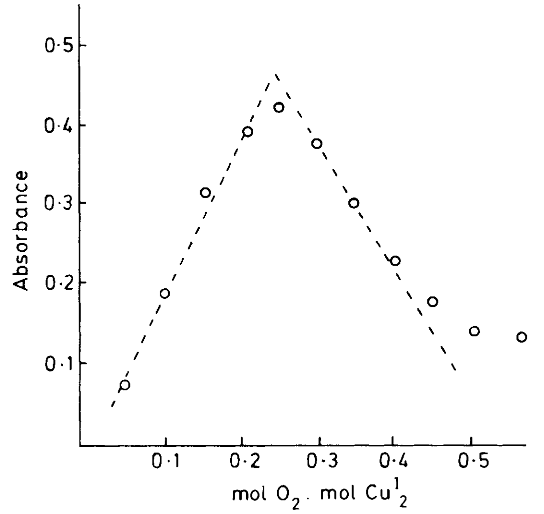


Figure 1. Dependence of the intensity of the peak at 11 900 cm^{-1} for $[Cu_2L^1]^{2+}$–O_2 mixtures on the O_2:Cu^I_2 ratio (10^{-3} mol dm^{-3} $[Cu_2L^1]^{2+}$ in dma in 1-mm cell)

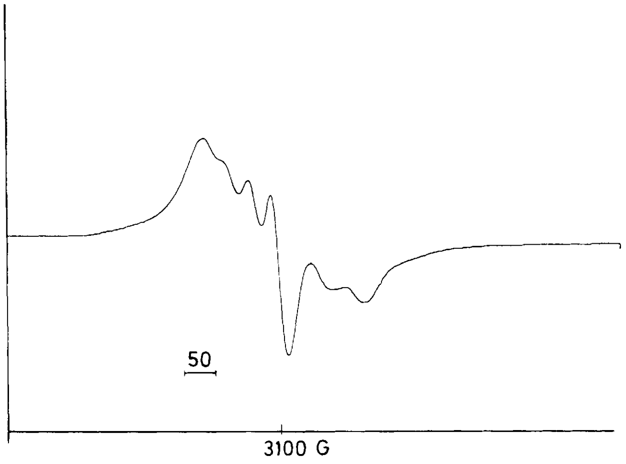


Figure 2. E.s.r. spectrum of complex (**7**) in fluid dmf solution (O_2:Cu^I_2 ratio of <0.25 : 1)

Here the copper ions are bridged *via* an endogenous phenoxy oxygen. In an earlier example[13] an acetate oxygen is thought to bridge a pair of copper ions in methanol solution. The mixed-valence intermediate observed in the course of oxidation of complexes (**1**) and (**2**) seems likely also to incorporate a bridging oxygen donor.

E.s.r. spectroscopy was also used to follow the course of the autoxidation of complex (**1**) in dma and dmf solvents. The integrated intensity of the signal was monitored at various ratios of O_2:Cu^I_2, using $CuSO_4\cdot 5H_2O$ as standard. When the O_2:Cu^I_2 ratio is ≈0.25:1 the signal has maximum intensity, equivalent to 0.85 times the intensity of the copper(II) standard (*i.e.* with reference to a $CuSO_4\cdot 5H_2O$ solution of equal concentration). At higher or lower O_2:Cu^I_2 ratios the signal intensity diminishes, decreasing towards zero at <0.25:1 and falling off more slowly at >0.25:1. The completely oxidised solution has a signal intensity less than 0.1 times the intensity of the copper(II) standard, evidently as a result of strong antiferromagnetic interaction between a pair of Cu^{2+} ions.

The simplest e.s.r. spectrum (Figure 2) is obtained in the presence of an excess of the dicopper(I) complex. At ratios O_2:Cu^I_2 of ⩾0.25:1 new components appear which render the pattern very complex. Even the simpler spectrum of Figure 2 exhibits a signal around $g = 2.12$ superimposed on the seven-line 33-G hyperfine splitting (h.f.s.) pattern which suggests the existence of a paramagnetic impurity (possibly rapidly exchanging Cu^{II}). Although both signals are difficult to saturate, indicating rapid relaxation, the $g = 2.12$ component loses intensity somewhat, relative to the main signal, at microwave powers above 60 mW.

Long and Hendrickson[11] observed an irregular seven-line pattern in some cases where an intermediate state of exchange operates in mixed-valence $[Cu_2L^3]^+$ systems, so that both localised copper(II) and delocalised copper(II)–copper(I) signals appear in the spectrum. In their rigidly co-ordinated system, increase of temperature accelerates the rate of electron exchange and enhances the delocalised spectrum; in the present system, however, increase of temperature produced a broad, poorly defined four-line signal suggesting accelerated decomposition of the sample to an effectively mononuclear copper(II) species. If the brown mixed-valence dmf solution is kept for some days at ambient temperature, the four-line pattern progressively replaces the pattern in Figure 2. The decomposition suggested by this alteration of the e.s.r. spectrum is particularly troublesome in the presence of an excess of O_2; one possible explanation of the change (see later) is a macrocyclic ring opening which relaxes the steric contraints operating to hold the copper atoms within μ-OH bridging distance.

The e.s.r. signal arising from the mixed-valence form of complex (**2**) in fluid dmf solution at 20 °C is very similar to that shown in Figure 2. It shows a 33-G hyperfine splitting pattern with a stronger unsplit signal $g = 2.11$ superimposed. Following the spectrum with time shows the development of a 70-G pattern at the expense of the 33-G one. The 70-G pattern represents a non-interacting copper(II) system, perhaps a ring-opened derivative.

The e.s.r. spectra of the final oxidation products of complexes (**1**) and (**2**), *i.e.* green solutions obtained by bubbling an excess of O_2 for 5—10 min, are complex and of low intensity. The main feature is a pair of sharp signals separated by ≈200 G, which are flanked by less intense broad features indicating poorly resolved hyperfine splitting of ≈33 G. We suggest that the 200-G separation of the central peaks is due to zero-field splitting, indicating sizeable interaction between copper(II) ions. Zero-field splitting, D_{iso}, approaching this magnitude, is seen together with a 35-G hyperfine splitting in the fluid dmf solution spectra of other interacting copper(II) dimers we have studied.[14] Comparison of the e.s.r. spectrum of fully oxidised complex (**1**) with the fluid dmf solution spectra of $[Cu_2L^1(OH)_2(H_2O)][ClO_4]_2$ (**3**) and $[Cu_2L^1(OH)_2(MeCN)_2][ClO_4]_2$ (**4**) reveals that these are very similar, but not identical, the main difference in pattern being the appearance in the case of (**3**) and (**4**) of an additional weak component of variable intensity close to $g = 2.0$. The electronic spectrum of a dma or dmf solution of fully oxidised (**1**) is however identical with that of (**3**) or (**4**) in the same solvent, which suggests that the additional e.s.r. component may be due to the presence of a small amount of paramagnetic mononuclear impurity, such as is indicated by the form of the temperature dependence of the magnetic susceptibility of (**3**).[15]

Attempted Isolation of Solid Product from the Mixed-valence Solution: Formation of $[Cu_4L^1{}_2(OH)]^{3+}$.—We tried to isolate, as a solid, the dark red-brown mixed-valence intermediate product obtained by partial oxidation of dma or dmf solutions of complex (**1**). However, concentration of the solution or addition of diethyl ether resulted only in disproportionation with precipitation of the brick-red insoluble copper(I) product $Cu_4L^1{}_2(OH)(ClO_4)_3$ (**5**) from a green copper(II) solution. An identical brick-red product precipitates out from concentrated O_2-free solutions of (**1**) in dma or dmf, even when the solvents have been dried over anhydrous copper sulphate and molecular sieves, emphasising, as do other results, the avidity of these systems for water. This material, which analyses for $[Cu_4L^1{}_2(OH)][ClO_4]_3$, has an i.r. spectrum showing it to contain intact macrocycle and ionic perchlorate. In addition, there is a sharp, medium-weak ν(OH) absorption at 3 570 cm^{-1} indicating the presence of an isolated hydroxyl group remote from any hydrogen-bond acceptor. In dmso solution, complex (**5**) behaves as a 3:1 electrolyte in agreement with these inferences. The compound does not exhibit near-i.r. absorption around 12 000 cm^{-1}, nor any *d–d* band in the visible region. It is e.s.r.-silent, and has a well defined ^1H n.m.r. spectrum in $(CD_3)_2SO$ (see Experimental section). The most notable feature of the spectrum is a splitting of the macrocyclic methylene proton signal. This suggests either severe folding of the macrocyclic skeleton[6] or a low-symmetry arrangement of the two macrocyclic units, leading to inequivalence of the methylene protons. With the related macrocycle L^4, an ion of analogous stoicheiometry $[Cu_4L^4{}_2(OH)]^{3+}$ has been shown[16] to contain a square plane of copper(I) atoms with a disordered μ_3-OH^- in the centre. It seems possible that a similar arrangement is present in this cluster, although without *X*-ray crystallographic data we are unable to say whether the bridging oxygen is three- or four-co-ordinate. Inequivalence of methylene protons is likely to result in either case.

The fast atom bombardment (f.a.b.) mass spectrum of complex (**5**) in dmso shows a weak feature (at 1—2% base peak) in the range *m/e* = 1 240—1 244. This corresponds to a Cu_4L_2 ion {apparently a protonated derivative $[Cu_4L^1{}_2(OH)(ClO_4)_3 \cdot 2H_2O + 3H^+]$ in which all copper ions have been oxidised to the +2 state}. Stronger peaks corresponding to dicopper fragments are observed, but no tetracopper fragments. Apparently the four-copper unit is easily dissociated in the f.a.b. process.

Preparation of the Mixed-valence Solution by Conproportionation.—Isolation of complex (**5**) provides some weakish indirect evidence for the existence of a μ-OH bridge in the mixed-valence intermediate. Stronger evidence is supplied by formation of this intermediate when equimolar quantities of complexes (**1**) and (**3**) are mixed under inert-atmosphere conditions. The electronic and e.s.r. spectra of the dark red-brown solution produced in this way are identical with those of the solution of O_2:$Cu^I{}_2$ ratio 0.25:1.

Investigation of the stoicheiometry of the reaction confirms the 1:1 Cu^{II}:Cu^I ratio in the mixed-valence form, as inferred from the O_2:$Cu^I{}_2$ ratio of 0.25:1 observed in the autoxidation experiment. The rate of reaction of complex (**1**) with (**3**) is moderately slow, complete formation of the mixed-valence form (as judged by ε_{app}, the absorption coefficient of the near-i.r. band at 11 900 cm^{-1}) being attained after 0.5—2 h over the concentration range 2×10^{-3}—2×10^{-2} mol dm^{-3}. Use of an excess (200—400%) of reagent, either (**1**) or (**3**), results in a 10—20% increase in ε_{app}, so it seems that equilibrium in the reaction of (**1**) with (**3**) does not lie completely to the mixed-valence side.

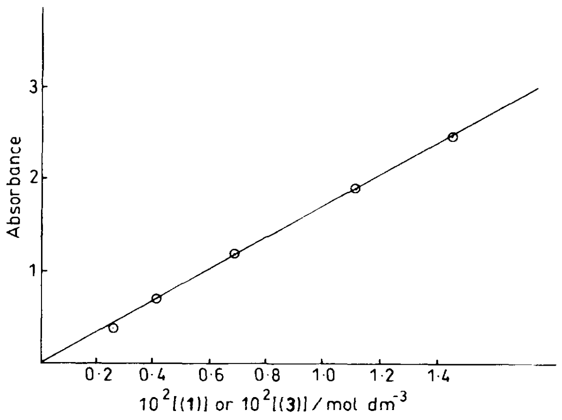


Figure 3. Absorbance of the 11 900 cm^{-1} i.c.t. absorption of complex (**7**) at 11 900 cm^{-1} (made by conproportionation) *versus* the concentration of reagents (**1**) and (**3**) (equimolar ratio)

Table 4. Cyclic voltammetric data for L^1 complexes[a]

Complex	Ep_c/mV	Ep_a/mV	ΔEp/mV	$E_{\frac{1}{2}}$/V
(**11**) $[SrL^1][ClO_4]_2$	−990	−860	130	−0.925
(**12**) $[BaL^1][ClO_4]_2\cdot EtOH$	−1 040	−880	160	−0.960
(**1**) $[Cu_2L^1(MeCN)_2][ClO_4]_2$	−145[b]	+590[b]		
	−240[c]	+50[c]		
(**7**) $[Cu_2L^1(MeCN)_2][ClO_4]_2{:}0.25\ O_2$	−290[c]	0[c]		
(**7′**) $[Cu_2L^1(MeCN)][ClO_4]_2{:}[Cu_2L^1(OH)_2(H_2O)][ClO_4]_2$	−350[c]	+30[c]		
(**8**) $[Cu_2L^1(MeCN)_2][ClO_4]_2{:}0.5\ O_2$	−190, −440	+530		
(**3**) $[Cu_2L^1(OH)_2(H_2O)][ClO_4]_2$[d]	−220, −380	+520		

[a] $\approx 10^{-3}$ mol dm^{-3} solutions in dma, scan rate 50 mV s^{-1}, potentials *vs.* s.c.e. [b] First scan, started in anodic direction. [c] Second and subsequent scans. [d] Voltammogram develops slowly; these potentials were observed in the tenth scan.

Variation of the concentration of reagents [for an equimolar ratio of (**1**) to (**3**)] reveals (Figure 3) a linear, rather than higher power, dependence of absorbance on concentration, which argues for the formation of 2 mol of a simple binuclear cation as in equation (1). Conductivity measurements on the mixed-valence product in dmf support this interpretation, as they lie in the range typical[17] of 1:2 electrolytes (although it is not possible, on conductivity data alone, to rule out a 1:4 electrolyte at half the assumed concentration).

$$[Cu^I{}_2L^1]^{2+} + [Cu^{II}{}_2(OH)_2L^1]^{2+} \longrightarrow 2[Cu^I(OH)Cu^{II}L^1]^{2+} \quad (1)$$

An attempt was made to obtain a f.a.b. spectrum of the mixed-valence solution in dma. The spectrum was weak but showed peaks centred at *m/e* 467 and 549 corresponding respectively to $[Cu^I{}_2L^1(OH)]^+$ and $[Cu^I{}_2L^1(ClO_4)]^+$. Reduction of transition-metal ions with an accessible lower oxidation state is frequently observed[18] in the course of the ionization process in positive-ion f.a.b. m.s. A weaker peak around *m/e* 604 is also observed, corresponding presumably to $[Cu^ICu^{II}L^1(OH)(ClO_4)\cdot 2H_2O]^+$. No peaks were observed at higher mass number.

If the mixed-valence intermediate is a simple binuclear reduction product of the μ-hydroxy dimer (**3**) then it should be generated by treatment of (**3**) with reducing agents. Carrying out this reduction with 1 mol equivalent of $[Cu(MeCN)_4]^+$ to 1 of (**3**) did generate the mixed-valence product, as characterised by the electronic absorption spectrum, while use of 2 mol equivalents of $[Cu(MeCN)_4]^+$ effected complete reduction to (**1**). Sodium tetraphenylborate, which is known[19] to act as a mild reducing agent, also reduces the mixed-valence product quantitatively to (**1**) but does not succeed in reducing (**3**) under ambient conditions in dma. These results suggested an electrochemical investigation of the system, which is described in the next section.

Generation of spectroscopically identical forms of the mixed-valence product by reduction of complex (**3**) or oxidation of (**1**) strongly suggests that the formulation of $[Cu^I(OH)Cu^{II}L^1]^{2+}$ applies whatever the source. The implication of this for the oxidation route is that bridging hydroxo does not derive solely from oxygen, but involves the intervention of water. One may speculate on the transient existence of a reactive four-copper mixed-valence μ-oxo species which is subsequently hydrolysed to produce two molecules of the μ-hydroxo-dimer [equation (2)].

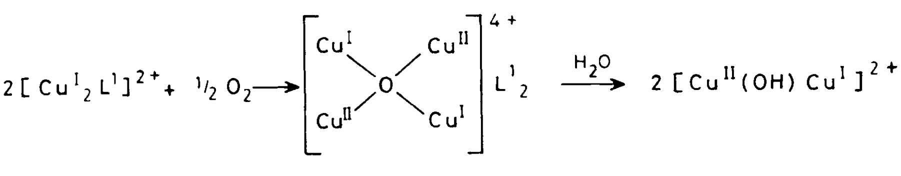
Electrochemical Investigations.—Isolation of the mixed-valence species (**7**) led us to hope that cyclic voltammetry would provide information on the thermodynamics of its one-electron oxidation and reduction. Disappointingly, however, the electrochemical behaviour in all three copper redox states, dicopper(I), mixed-valence, and dicopper(II), was irreversible, leading with any certainty only to the conclusion that rapid chemical change accompanies redox transformations of copper in these systems.

Cyclic voltammetry was carried out under the conditions described in the Experimental section on complexes (**1**), (**3**), and (**7**) as prepared either by conproportionation or the action of O_2 on (**1**). Also for comparison, measurements were made on the strontium(II) and barium(II) complexes of L^1. Selected data are reported in Table 4.

The ligand L^1 is electrochemically active, giving with both $[SrL^1][ClO_4]_2$ and $[BaL^1][ClO_4]_2\cdot EtOH$ complexes a quasi-reversible one-electron wave close to −1 V, corresponding presumably to ligand reduction. The solutions showed no sign of decomposition within 48 h, indicating that the ligand is stable in dma solution so long as the metal centres are not affected by redox processes. Freshly prepared solutions of the dicopper complexes (**1**), (**3**), and (**7**) also exhibited electrochemical activity around −1 V, although in these cases the wave was less reversible, having a broadened anodic component. On examination, the electrode showed signs of copper deposition. To prevent interference from this ligand-centred redox process, then, cathodic scans reported in Table 4 for (**1**), (**3**), and (**7**) were restricted to potentials less negative than −700 mV.

Although solutions of complex (**1**) in dma were stored under N_2, the initial orange colour was replaced after about 1 h by a more intense reddish brown, then by greenish brown, and finally after about 24 h by a pure green colour. These colour changes replicate the behaviour of (**1**) as it reacts with O_2 to give first (**7**) and then (**8**) and so it must be assumed that the nitrogen protection is inadequate to prevent these redox changes. Accordingly, we will consider only the freshly prepared solution as (**1**), the red-brown solution as (**7**), and the green solutions as (**8**).

The first scan of complex (**1**) with clean platinum electrodes showed an irreversible oxidation at +590 mV followed on the reverse scan by an irreversible reduction at −145 mV. However, these processes were not subsequently observed, as the second and following scans showed instead [Figure 4(*a*)] an oxidation process at +50 mV and a reduction at −240 mV, both

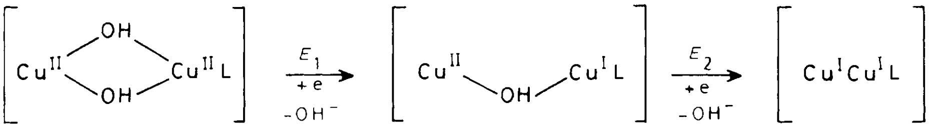


(2)

irreversible. It appears that the electrode surface is modified by deposition of some product of a redox process from the first cycle (see Experimental section). The large difference between the oxidation and reduction potential in both the initial and subsequent scans indicates a chemical change associated with electron transfer.

After some time in solution when the orange-red colour had changed to red-brown, presumably now representing the mixed-valence state (**7**), cyclic voltammograms on their second and subsequent scans [following electrode modification presumably similar to that noted with (**1**)] showed a broad cathodic peak around −300 to −350 mV and a similar ill defined anodic peak in the vicinity of 0 V. These two irreversible waves were seen, although more clearly defined [Figure 4(*b*)], in the mixed-valence solution prepared (as described in the Experimental section) by conproportionation of complexes (**1**) and (**3**). Because of the irreversible nature of the processes, it cannot be expected that the potential at which (**1**) is oxidised will coincide with that at which (**7**) is reduced. It is curious but probably accidental, however, that the reduced forms of (**1**) and (**7**) are oxidised at much the same potential.

When the solution of complex (**1**) had changed colour to green representing the fully oxidised dicopper(II) state, the cyclic voltammograms were again recorded. It was noticed now that two reduction processes were occurring at fairly similar potentials, *i.e.* around −200 mV (E_1) and around −400 mV (E_2). This observation mirrored that made [after an initial 'inert' period, see Figure 4(*c*) and Experimental section] on dma solutions of complex (**3**). A poorly defined anodic peak, at +500 mV, was also seen for both (**3**) and (**8**). It seems at least possible, in light of the chemical evidence, that the reduction processes at −200 and −400 mV correspond to sequential one-electron reductions of the metal centre, as outlined schematically in equation (3). Both chemical evidence and the irreversibility of the cyclic voltammetric waves suggest that each reduction is associated with loss of ligand, probably hydroxo. In order to check for any loss of bridging ligand unassociated with the redox process, we monitored the conductivity of freshly made 10^{-3} mol dm^{-3} dma and dmf solutions of complex (**3**) over a few hours and found no change. Similarly, the conductivity of dma or dmf solutions of (**1**) remained virtually unaffected as these underwent the sequence of colour changes orange to red-brown to green, which supports the hypothesis of equation (3), that bridging ligand is transferred in each redox process. The separation of E_1 and E_2 by ≈200 mV does indicate appreciable stability for the mixed-valence species, but the poor quality of the electrochemical data does not permit any estimate of the conproportionation constant. The ineffectiveness of BPh_4^- as reducing agent for (**3**) under ambient conditions cannot be explained on thermodynamic grounds, and must be related to kinetic factors, possibly concerned with loss of bridging ligand. One might expect this step in the mechanism of the redox process to be facilitated to a greater extent by copper(I) reagent than by BPh_4^-.



(3)

The lack of coulometric data and the ill defined nature of the cyclic voltammograms combine to prohibit speculation on the precise nature of the products of the redox processes illustrated in Figure 4. However, the suggestion that loss of hydroxo-ligand is responsible for the irreversibility of the reductions of complexes (**3**) and (**7**) receives support from electrochemical investigations[20,21] on other μ-hydroxo-copper(II) dimers where irreversibility is associated with loss of bridging ligand and reduction eventually leads to copper metal.

Comparison with the analogous $[Cu^{II}{}_2L^3]^{2+}$ complexes studied by Long and Hendrickson,[11] where reversible waves are observed at −0.77 and −1.17 V *vs.* s.c.e. for the sequential one-electron reductions of the rigidly held copper(II) ions (*via* an isolable mixed-valence form) to copper(I), indicates lower stability for the +2 oxidation state in $[Cu_2L^1]$ than in $[Cu_2L^3]$ complexes. The chemical behaviour of $[Cu^{II}{}_2L^1]$ complexes has already established their ready reduction to the +1 state, which is attributed[4,22] to geometric factors, particularly the preference of L^1 for tetrahedral rather than planar co-ordination. The μ-hydroxo-dicopper(II) complex of L^5, $[Cu_2L^5(OH)]^{3+}$, shows a reversible reduction wave[23] more negative by ≈80 mV than E_1 (despite the smaller number of co-ordinated anions, a factor which would be expected to destabilise the +2 state). The planar pyridylmethylimino N_3 donor set in L^5 makes regular tetrahedral geometry unachievable so presumably here also the greater stability of Cu^{II} is attributable to geometric factors. Unfortunately these same factors which favour the +1 state and thus make $[Cu_2L^1]$ complexes suitable redox catalysts also generate the steric strain[22] which is presumed responsible for the ring-opening reactions observed within hours in solutions of dicopper(II) L^1 complexes. A better redox catalyst would have this built-in preference for copper(I) co-ordination uncomplicated by any steric strain which could stimulate macrocyclic ring opening in the +2 state. We hope that the cryptand ligands which we[24,25] are presently developing will have these characteristics.

Isolation of Solid from the Fully Oxidised Reaction Mixture.— Addition of dry diethyl ether to a concentrated dma solution of fully oxidised complex (**3**) resulted in the isolation of crystals of a green solid (**6**). The i.r. spectrum shows that this product contains intact macrocycle, ionic perchlorate, and co-ordinated dma. It behaves in both dma and MeCN solution as a 2:1 electrolyte, and has a *d–d* spectrum suggesting square-based co-ordination of Cu^{II}. Because of the care taken to dry the solvent and apparatus used in its preparation (see Experimental section) and the absence of a clearly defined sharp ν(OH) absorption in the i.r. spectrum, it was initially believed that this might be a μ-oxo derivative $[Cu_2L^1(O)(dma)][ClO_4]_2$. However, the available analytical data provide an acceptable fit either for this formulation or for alternative formulations. The analytical data are intermediate between that expected for $[Cu_2L^1(OH)_2(dma)_2][ClO_4]_2$ and $[Cu_2L^1(OH)_2(dma)][ClO_4]_2$, and the compound does not show i.r. absorption above 3 500 cm^{-1} [*cf.* (**3**) where such absorption is attributed to ν(OH) in solvated H_2O]. Careful inspection of the mull spectrum in sodium-dried Nujol does reveal a very broad hydrogen-bonded absorption spread out over the region 3 400—3 000 cm^{-1}. A broad hydrogen-bonded ν(OH) is also observed in the mull spectrum of complexes (**3**) and (**4**).

Positive-ion f.a.b. mass spectra of complexes (**4**) and (**6**) carried out in dry dma with added 3-nitrobenzyl alcohol are identical, showing peaks of medium intensity clustered around *m/e* 855 and 756 and stronger peaks clustered around *m/e* 703 and 604. Computer simulation of the isotopic cluster for these stronger peaks confirms their origin in the ions $[Cu_2L^1(OH)(ClO_4)_2\cdot 2H_2O]^+$ and $[Cu_2L^1(OH)(ClO_4)\cdot 2H_2O]^+$. The peak at *m/e* 855 appears to arise from a rearrangement producing the

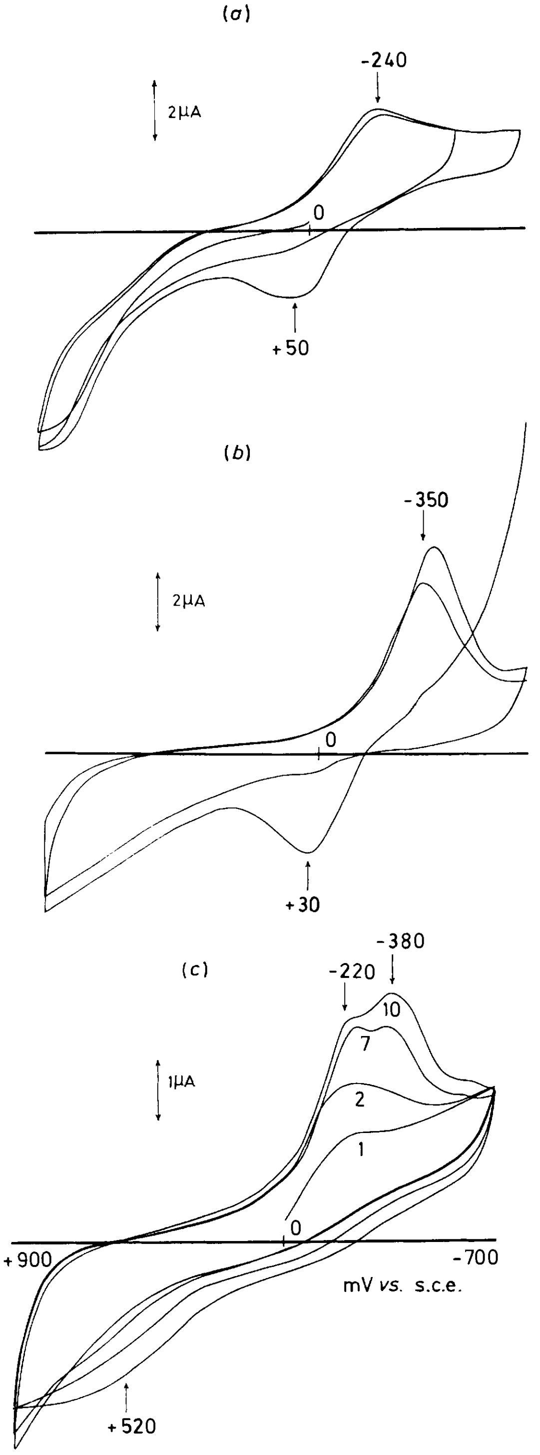


Figure 4. Cyclic voltammograms of complexes (**1**), (**7**), and (**3**) in 10^{-3} mol dm^{-3} dma solution: (*a*) second and subsequent scans of (**1**); (*b*) second and subsequent scans of (**7**) (made by conproportionation); and (*c*) development of the voltammogram of (**3**) over the first 10 cycles (first, second, seventh and tenth)

protonated species $Cu_2L^1(Hdma)(ClO_4)_3 \cdot H_2O$ (to judge from the isotopic cluster simulation) and likewise that at *m/e* 754 from $Cu_2L^1(Hdma)(ClO_4)_2 \cdot H_2O$, though of course we have no direct information on the protonation site. Observation of the peaks at *m/e* 604, 754, and 855 confirms the tendency[18] of the copper ion in these systems to undergo redox change in the course of the f.a.b. ionisation process.

The green crystals deteriorate in air, which could be explained either as addition of water or as replacement of co-ordinated solvent. This deterioration prevented solution of the problem by *X*-ray crystallographic structure determination. Deliberate addition of an excess of water to solutions of complex (**6**) results in spectroscopic changes which are associated with formation of ring-opened products to judge by the isolation of green solids showing $\nu(NH_2)$ and $\nu(C{=}O)$ absorptions in the i.r. region. In fact such absorptions are normally observed for solids isolated from > 1 d old dma solutions of (**3**) or oxidised (**1**) suggesting that ring opening is the cause of the mononuclear e.s.r. spectra observed for such aged solutions.

When fresh dma solutions of this green solid are mixed in equimolar concentration with (**1**) the red-brown mixed-valence solution is generated, thus replicating the behaviour of (**3**) and (**4**). On balance, and particularly in the light of results obtained in our study of the mixed valence product, we now believe that the green oxidation product (**6**) has a di-μ-hydroxo-formulation $[Cu_2L^1(OH)_2(dma)_n][ClO_4]_2$. In general, the best fit with analytical data is found with $n = 1.5$, and this is the formulation used in Tables 1 and 2.

The source of protons for the μ-hydroxo-bridge is uncertain. These systems are known,[4,5] to act as dehydrogenation catalysts, so proton abstraction from solvent or ligand appears to be a possibility. Alternatively, and we have already noted the hygroscopicity of these systems, it may be that sufficient water was picked up during handling or on standing to provide the necessary protons.

The mechanism of formation of complex (**6**) may possibly involve the existence of a reactive μ-oxo form in solution in the early stages of reaction, which acts as a powerful proton abstractor. However, spectroscopic monitoring did not reveal any electronic or e.s.r. spectral features attributable to such an intermediate. Whatever the mechanism, it is remarkable that (**6**) should form even when stringent precautions have been taken to dry the solvent. Its formation illustrates the avidity with which both pairs of copper(II) or copper(II), copper(I) ions accept a hydroxo bridge. A further illustration of the preference of Cu^I for the hydroxo-bridge in apparently inappropriate surroundings is the μ_3-OH link observed[16] at the heart of the hydrophobic cavity formed by the pair of interlocked L^4 macrocycles. These observations may have some relevance to the question of the identity of the bridging ligand in haemocyanin. Hydrophobicity or a low concentration of water in the environment of the dicopper unit was unable to prevent formation of the hydroxo-bridge in these macrocyclic systems. This observation seems to increase the credibility of the suggestion that the bridging ligand in haemocyanin may indeed be hydroxide.

Experimental

Preparation of the Complexes.—The complex $[Cu_2L^1(OH)_2(H_2O)][ClO_4]_2$ (**3**) was prepared, as described elsewhere[15] by transmetallation of the $[BaL^1][ClO_4]_2 \cdot EtOH$ template condensation product with $Cu(ClO_4)_2 \cdot 6H_2O$ in ethanol; $[Cu_2L^1(OH)_2(MeCN)_2][ClO_4]_2$ (**4**) was prepared analogously by transmetallation in a mixed MeCN–EtOH solvent. The dicopper(I) complexes $[Cu_2L(MeCN)_2][ClO_4]_2$ [$L = L^1$ (**1**) or L^2 (**2**)] were obtained by transmetallation[5] of the Group 2 metal complex $ML(ClO_4)_2$ with $[Cu(MeCN)_4]ClO_4$ in MeCN–EtOH under an inert atmosphere.

$Cu_4L^1_2(OH)(ClO_4)_3$ (**5**). A solution of $[Cu_2L^1(MeCN)_2][ClO_4]_2$ (0.25 mmol, 150 mg) in dry dmf (10 cm^3) was oxidised by bubbling O_2 gas for 10—15 min. The resulting green solution was degassed under Ar and a further 150 mg of solid

$[Cu_2L^1(MeCN)_2][ClO_4]_2$ were added under Ar. After a couple of hours under an inert atmosphere, deposition of the brick-coloured insoluble product from the dark brown mixed-valence solution was noticed. After 1—2 d under Ar, the brick solid was filtered off leaving a green filtrate ($\lambda_{max.}$ = 660 nm). The ^1H n.m.r. spectrum of (**5**) in $(CD_3)_2SO$ shows two singlets of equal intensity at 8.41 and 7.33 from relative $SiMe_4$, corresponding to imino and furan protons respectively, and a pair of signals at 4.03 (d) and 3.97 (t) corresponding to the methylene protons α to the imino N. The signal from the methylene protons β to the C=N group is obscured by solvent absorption.

Mixed-valence solutions (**7**) *and* (**9**). (*i*) Complex (**7**) could be prepared in dma, dmf, or dmso by a similar procedure to that described above for (**5**), but using less than 12 mg (**1**) in 1 cm^3 solvent on each occasion.

(*ii*) It could also be obtained by adding complex (**1**) (14.9 mg, 2.0×10^{-5} mol) to O_2-saturated dma (1 cm^3, 5.1×10^{-6} mol) and rapidly degassing under Ar.

(*iii*) A degassed solution of complex (**3**) (10 mg, 1.42×10^{-2} mmol) in dmf or dma (1 cm^3) was treated with an equimolar quantity (10.4 mg) of solid (**1**) under an inert atmosphere. An equimolar quantity of solid $[Cu(MeCN)_4]ClO_4$ is equally effective in this reduction, generating (**7**) in 0.7×10^{-2} mol dm^{-3} concentration; Λ_m = 139 S cm^2 mol^{-1} in 10^{-3} mol dm^{-3} dmf solution.

Complex (**9**) was prepared by method (*i*) or (*ii*) using (**2**) (16 mg, 2.0×10^{-5} mol) and O_2-saturated dma (1 cm^3): Λ_m = 120 S cm^2 mol^{-1} in 10^{-3} mol dm^{-3} solution.

$[Cu_2L^1(OH)_2(dma)_n][ClO_4]_2$ (**6**). Complex (**1**) (150 mg, 0.137 mmol) was dissolved in dry dma (2 cm^3) and O_2 gas was bubbled for 30 min at ambient temperature until the colour change to green was complete. Dry diethyl ether ($\approx$0.5 cm^3) was added dropwise until the first sign of turbidity, and the solution was allowed to stand at room temperature for a few hours until dark green crystals of the product appeared. The solvent was syringed off and product washed with dma–Et_2O mixtures of diminishing dma content and finally with pure Et_2O.

Oxidised solutions (**8**) *and* (**10**). These were prepared by bubbling O_2 through solutions of complexes (**1**) and (**2**) in the appropriate solvent for 10—15 min until the colour change to green was complete: in 10^{-3} mol dm^{-3} dmf solution Λ_m = 143 S cm^2 mol^{-1} for (**8**) and 115 S cm^2 mol^{-1} for (**10**).

Oxygen-uptake Experiments.—Oxygen uptakes were monitored by measuring the pressure change observed in a thermostatted vessel using a Langham–Thompson transducer as described earlier.[26] The solid complex was dissolved either in deoxygenated or in O_2-saturated solvent, and stirred under 1 atm (101 325 Pa) of oxygen. The uptakes in dma were complete within 10 min; however, in dmso 70—80 min were required for completion, presumably owing to the slower rate of solution of O_2 in this solvent.

Solvent Purification.—Dimethylacetamide and dmf were dried over anhydrous $CuSO_4$, distilled under vacuum, and stored over freshly dried molecular sieves (3A). Karl-Fischer analysis showed the water content of solvents used for the preparation of complex (**6**) to be less than 0.008% before use. Glassware and syringes used in handling solutions of (**6**) were flamed before use. Dimethyl sulphoxide was dried over CaH_2, distilled in vacuum, and stored over molecular sieves.

Physical Measurements.—E.s.r. spectra were recorded using a Varian *X*-band E-109 spectrometer, electronic spectra using a Perkin-Elmer λ 9 instrument, and i.r. spectra on a Perkin-Elmer 498 instrument as mulls in sodium-dried Nujol or as KBr discs. Conductivities were measured with a Metrohm 660 conductometer using a cell constant of 7.50 cm^{-1}. Proton n.m.r. spectra were obtained using a 270-MHz Bruker spectrometer. F.a.b. spectra were obtained either at Queens University, Belfast, with a Spartan Ion Tech Saddle Field Source using argon, on an AEI MS902 updated by V. G., or at the S.E.R.C. Mass Spectrometry Centre at Swansea.

Electrochemical experiments were performed as previously described,[19] with a platinum bead as working electrode. Solutions in dma (kept over molecular sieves 4A) were 0.1 mol dm^{-3} in tetraethylammonium perchlorate and 10^{-3}—10^{-4} mol dm^{-3} in complex. This combination of working electrode, solvent, and supporting electrolyte gave the most reproducible results. Under these experimental conditions, the ferrocenium–ferrocene couple at 50 mV s^{-1} gave cyclic voltammograms with $E_{\frac{1}{2}} = +0.410$ V *vs.* s.c.e. and ΔE = 100 mV.

In the cyclic voltammetry of solutions of complexes (**1**) and (**7**) there was evidence for modification of the electrode during the first scan, the peaks observed in the first scan being different from those in the second and subsequent scans. However, with (**3**) the modifications appeared to require 6—10 scans for completion, as the peak intensity built up over this sequence, being virtually unobservable during the first three scans. Such a build up is not uncommon [21,27] in complex redox systems where the electrochemical behaviour is dominated by irreversibility.

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