

# Electrochemical Reversibility of the Cu<sup>I</sup>–Cu<sup>0</sup> Couple in Bis[2,9-di(*o*-substituted phenyl)-1,10-phenanthroline]-copper(I) complexes. Stability of the Corresponding Copper(0) Species

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Copper(I) complexes of 1,10-phenanthroline disubstituted at the 2,9 positions or monosubstituted at the 2 position by phenyl moieties having *ortho* substituents have been prepared and investigated by spectral and electrochemical methods. The bis[2,9-di(*o*-substituted phenyl)-1,10-phenanthroline]-copper(I) complexes, where Cu<sup>I</sup> is surrounded by two disubstituted phenanthroline units, undergo reversible electrochemical reduction at about –1.72 V vs. saturated calomel electrode, whereas bis[2-(*o*-substituted phenyl)-1,10-phenanthroline]copper(I) complexes, where Cu<sup>I</sup> is surrounded by two monosubstituted phenanthroline units, undergo quasireversible/irreversible electrochemical reduction at about –1.68 V. The electrochemical reversibility of the former complexes is related to the dual effect of stabilization of copper(0) species and the steric involvement of the *ortho* substituents on the phenyl ring.

In recent years, interlocking macrocyclic ligands, catenands, have been used to obtain complexes of lower-oxidation-state transition-metal ions.<sup>1,2</sup> Stabilization of these oxidation states by catenands obtained from 1,10-phenanthroline has been ascribed to interaction of  $\pi^*$  orbitals of the ligand and metal-ion orbitals. The special topology of the catenands is a major structural factor preventing the complexes from dissociating into metal and ligand when reduced at an electrode surface, thereby imparting a high degree of electrochemical reversibility. Thus the copper(I) catenates of 1,10-phenanthroline show reversible Cu<sup>I</sup>–Cu<sup>0</sup> voltammetric behaviour at *ca.* –1.67 V vs. saturated calomel electrode (SCE) and are shown to have highly distorted tetrahedral geometries. On the other hand, copper(I) complexes obtained from 1,10-phenanthroline ligands like 2,9-di(*p*-methoxyphenyl)-1,10-phenanthroline readily decompose into metal and the free ligand on electrochemical reduction.<sup>3</sup> These complexes are thus electrochemically irreversible and are known to have tetrahedral/pseudo-tetrahedral geometries.<sup>4</sup>

The question which arises from these observations is whether the electrochemical reversibility of the copper(I) catenates is due to the special topology and topography of the catenands, which are invariably related to geometrical distortions, or due to the high distortion of the co-ordination polyhedron from tetrahedral geometry coupled with steric repulsions and electronic attractions, or a combination of both. To understand the effect of distortion on electrochemical reversibility on copper(I) systems, we have synthesized a number of new ligands such as 2,9-di(*o*-substituted phenyl)-1,10-phenanthroline and 2-(*o*-substituted phenyl)-1,10-phenanthroline and prepared their copper(I) complexes. Steric crowding due to the *ortho* substituents of the phenyl group at the 2,9 positions of 1,10-phenanthroline is expected to distort the co-ordination polyhedron around the Cu<sup>I</sup>. These complexes should show electrochemical reversibility similar to that observed in the case of copper(I) catenates. On the other hand, they would be expected to be electrochemically irreversible if the structural features of the catenands are primarily responsible for reversibility.

## Experimental

**Materials.**—All the solvents were of reagent grade and distilled either over CaH<sub>2</sub> or sodium wire and stored over

molecular sieve prior to use. 2-Bromotoluene, 2-bromoanisole and *o*-phenetidine were obtained from Fluka. *o*-Phenetidine was converted into bromo-2-ethoxybenzene by the usual method of diazotization followed by coupling with copper(I) bromide.

**Preparation of the Ligands.**—All ligands were prepared by the method described earlier.<sup>5</sup> A typical modified preparation for one of the ligands, 2,9-di(*o*-tolyl)-1,10-phenanthroline is as follows. *o*-Bromotoluene (8.6 g, 50 mmol) in dry diethyl ether (20 cm<sup>3</sup>) was added dropwise under nitrogen to freshly cut lithium metal pieces (0.765 g, 0.111 mol) at such a rate that the reaction mixture boiled briskly. The amount of lithio reagent formed was estimated through titration with 1,3-diphenyl-2-propanone tosyl hydrazone.<sup>6</sup> This reagent was then transferred by a double-ended needle to a two-neck round-bottom flask under argon, containing 1,10-phenanthroline (1.08 g, 6 mmol) in toluene (25 cm<sup>3</sup>)–benzene (100 cm<sup>3</sup>) and was allowed to stir for 10 h. The reaction mixture was cooled below 10 °C and hydrolysed under argon by addition of distilled water (25 cm<sup>3</sup>). The organic layer was collected and oxidized by stirring over MnO<sub>2</sub> (60 g) for 2 h followed by stirring for 1 h over anhydrous MgSO<sub>4</sub> (60 g). The solution was filtered and the solvent stripped off under reduced pressure to leave a dark brown, highly impure, ligand. This solid was purified by eluting on a silica gel column using CH<sub>2</sub>Cl<sub>2</sub>–hexane (1:4 v/v).

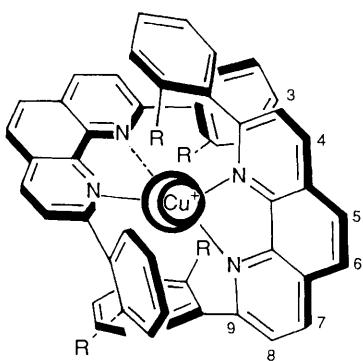
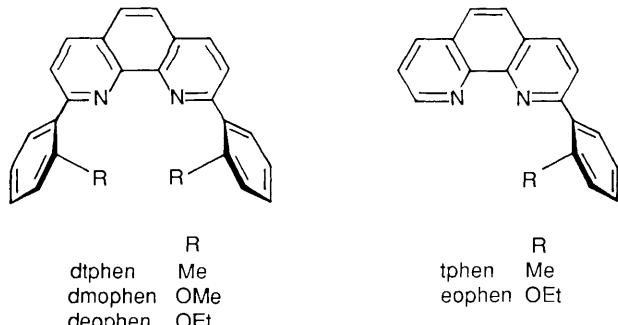
The procedure for the preparation of 2-(*o*-tolyl)-1,10-phenanthroline was the same except that 2.16 g (12 mmol) of 1,10-phenanthroline were taken. The ligands synthesized were 2,9-di(*o*-tolyl)-1,10-phenanthroline (dtphen), 2,9-di(2-methoxyphenyl)-1,10-phenanthroline (dmophen), 2,9-di(2-ethoxyphenyl)-1,10-phenanthroline (deophen), 2-(*o*-tolyl)-1,10-phenanthroline (tphen) and 2-(2-ethoxyphenyl)-1,10-phenanthroline (eophen). Spectral and analytical data are given in Table 1.

**Preparation of Copper(I) Complexes.**—The complexes were prepared according to a procedure similar to that for catenates<sup>7</sup> which involved reaction of ligands with [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub>,<sup>8</sup> in acetonitrile. In a typical reaction dtphen (0.18 g, 0.5 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) and mixed with [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> (0.078 g, 0.25 mmol) suspended in MeCN (5 cm<sup>3</sup>). Immediately a deep red coloration developed. The reaction mixture was

**Table 1** Analytical and spectral data for the ligands

Ligand	Yield (%)	M.p./°C	Analysis <sup>a</sup> (%)			IR <sup>b</sup> /cm <sup>-1</sup>	$\lambda_{\max}$ /nm (log ε/dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )	<sup>1</sup> H NMR <sup>c</sup> (δ)
			C	H	N			
dtphen	70	164–165	85.30 (86.65)	5.60 (5.60)	7.50 (7.75)	3000, 1358 <sup>d</sup> 1475 <sup>e</sup> , 1580 <sup>f</sup>	291(4.65), 252(4.66)(sh), 236(4.86)	2.46 (s, 6 H), 7.34–9.2 (14 H)
dmophen	71	190–191	78.10 (79.55)	5.10 (5.15)	7.10 (7.15)	2975, 1362 <sup>d</sup> 1485 <sup>e</sup> , 1240 <sup>g</sup> 1025 <sup>h</sup> , 1585 <sup>f</sup>	307(4.56), 260(4.63), 237(4.79)	3.84 (s, 6 H), 6.76–9.0 (14 H)
deophen	35	160–161	79.70 (79.95)	5.75 (5.75)	6.85 (6.65)	2980, 1360 <sup>d</sup> 1485 <sup>e</sup> , 1245 <sup>g</sup> 1035 <sup>h</sup> , 1575 <sup>f</sup>	309(4.58), 260(4.67), 235(4.79)	1.3–1.44 (t, 6 H), 4.0–4.2 (q, 4 H), 6.96–8.24 (14 H)
tphen	78	158–159	84.00 (84.45)	5.20 (5.20)	10.30 (10.35)	2975, 1380 <sup>d</sup> 1480 <sup>e</sup> , 1580 <sup>f</sup>	276(4.63), 233(4.89)	2.47 (s, 3 H), 7.4–9.24 (11 H)
cophen	80	128–130	78.65 (79.95)	5.40 (5.35)	9.55 (9.35)	2980, 1385 <sup>d</sup> 1480 <sup>e</sup> , 1230 <sup>g</sup> 1035 <sup>h</sup> , 1580 <sup>f</sup>	309(4.42)(sh), 277(4.59), 235(4.90)	1.28–1.43 (t, 3 H), 4.0–4.2 (q, 2 H), 6.96–9.22 (11 H)

<sup>a</sup> Calculated values in parentheses. <sup>b</sup> Only selected peaks are presented. <sup>c</sup> Recorded in CDCl<sub>3</sub> with SiMe<sub>4</sub> as internal standard. <sup>d</sup> R stretch. <sup>e</sup> Aromatic. <sup>f</sup> C=N stretch. <sup>g</sup> Aryl C–O stretch. <sup>h</sup> Alkyl O–R stretch.



R = Me, OMe, or OEt

stirred for 15 min and cooled in a refrigerator to get deep red crystals of the complex. The copper(II) complexes synthesized and investigated are [Cu(dtphen)<sub>2</sub>]BF<sub>4</sub>, [Cu(dmophen)<sub>2</sub>]BF<sub>4</sub>, [Cu(deophen)<sub>2</sub>]BF<sub>4</sub>, [Cu(tphen)<sub>2</sub>]BF<sub>4</sub> and [Cu(eophen)<sub>2</sub>]BF<sub>4</sub>. Spectral and analytical data are given in Table 2.

**Physical Measurements.**—Melting points were recorded on a Büchi 510 apparatus and are uncorrected. The analyses of C, H and N were carried out on Perkin-Elmer 240C analyser. Conductivity measurements were done on a CM-82T Elico conductivity meter at 25 °C in CH<sub>2</sub>Cl<sub>2</sub> and the solutions were 0.001 mol dm<sup>-3</sup>. Infrared spectra were recorded on Perkin-Elmer IR 1310 or 297 spectrophotometers in the range 4000–600 cm<sup>-1</sup> in KBr pellets, electronic spectra on a Perkin-Elmer Lambda 3B UV/Vis spectrophotometer in CH<sub>2</sub>Cl<sub>2</sub> using 1 × 10<sup>-4</sup> mol dm<sup>-3</sup> solutions for the visible range and 1 × 10<sup>-5</sup> mol dm<sup>-3</sup> solutions for the UV range, and <sup>1</sup>H NMR spectra on

a JEOL JEL 980B JNM-FX 100 FT spectrometer. Cyclic voltammetry experiments were carried out on a PAR electrochemistry system consisting of a 174A polarographic analyser and a single-compartment cell. Solutions of the copper(II) complexes (1 × 10<sup>-3</sup> mol dm<sup>-3</sup>) in dimethylformamide (dmf) were used. The supporting electrolyte was 0.1 mol dm<sup>-3</sup> tetraethylammonium perchlorate. The working electrode was a hanging mercury drop electrode, the auxiliary electrode was a coiled platinum wire and the reference electrode was a standard calomel electrode (SCE). All potentials are referred to the SCE. All the experiments were performed at room temperature, ca. 27 ± 1 °C, under an atmosphere of dry nitrogen.

## Results and Discussion

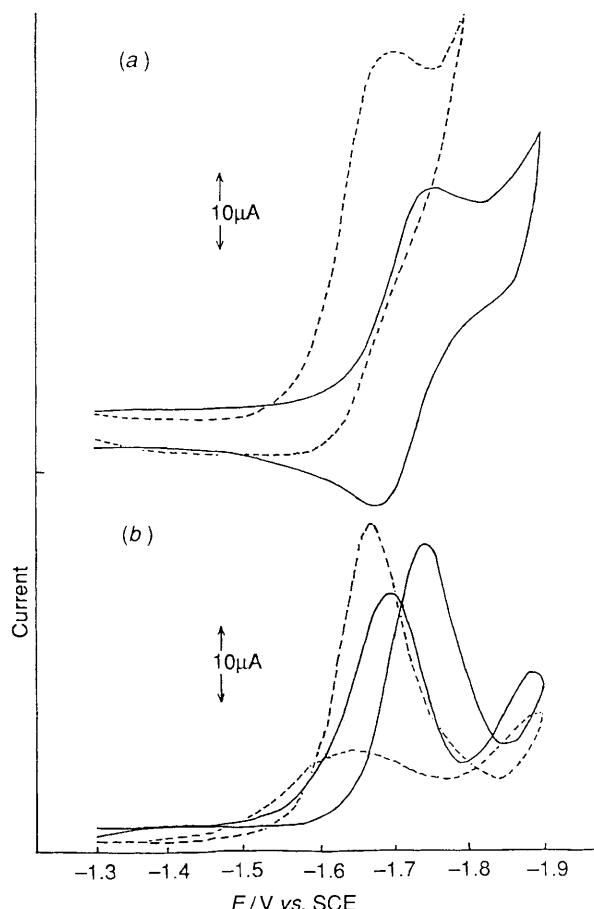
The 2,9-di(o-substituted phenyl)-1,10-phenanthroline ligands and their copper(II) salts were characterized by analytical and spectral methods. The complexes absorb in the range 450–470 nm and their solutions on standing at room temperature for 24 h do not show any variation in absorbance, indicating that the complexes are stable. Conductance values in CH<sub>2</sub>Cl<sub>2</sub> at room temperature are in the range of 67–70 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Room-temperature solid magnetic susceptibility measurements show that the complexes are diamagnetic. Selected IR data for the ligand and the fluoroborate peak positions of the complexes are presented in Tables 1 and 2, respectively. All the complexes gave well defined NMR spectra and some important proton signals are presented in Table 2.

In cyclic voltammetric experiments both the positive and negative potential ranges were scanned. Reduction peaks for Cu<sup>1</sup> → Cu<sup>0</sup> are in the potential range of -1.64 to -1.76 V for different disubstituted complexes. During the reverse scan, anodic peaks were observed at -1.58 to -1.67 V, thus showing electrochemical reversibility. The magnitude of the separation of these cathodic and anodic peaks is ca. 60–80 mV and the potentials do not change with scan rate. The ratio of the peak currents, *i<sub>c</sub>/i<sub>a</sub>* is ca. 1:1 and remains constant on successive scans. The monosubstituted copper(II) complexes show only the reduction peak in the range -1.67 to -1.69 V and either have weak or no corresponding oxidation peak in the reverse scan, showing quasireversible/irreversible nature. Cyclic voltammograms and differential pulse voltammograms of reversible and irreversible complexes are shown in Fig. 1 and data are presented in Table 3. All ligands are found to be electrochemically inactive in the range 0 to -1.8 V. In the positive potential range the oxidation peak for the process Cu<sup>1</sup> → Cu<sup>II</sup> was observed at about +0.7 V for disubstituted and at about +0.3 V for monosubstituted copper(II) complexes. The

**Table 2** Analytical and spectral data for the copper(i) complexes as their  $\text{BF}_4^-$  salts

Complex	Analysis <sup>a</sup> (%)			IR/cm <sup>-1</sup> for $\text{BF}_4^-$	Conductivity/ ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	$\lambda_{\max}/\text{nm}$ ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	<sup>1</sup> H NMR <sup>b</sup> ( $\delta$ )
	C	H	N				
$[\text{Cu}(\text{dtphen})_2]^+$	70.55 (71.70)	4.80 (4.65)	6.45 (6.45)	1065	70	467 (4765)	1.6 (s, 12 H), 8.5 (s, H <sup>4</sup> ), 8.08 (s, H <sup>3</sup> ), 8.12 (s, H <sup>5</sup> , H <sup>6</sup> ), 8.58 (s, H <sup>7</sup> )
$[\text{Cu}(\text{dmophen})_2]^+$	66.70 (66.80)	4.25 (4.30)	6.10 (6.00)	1065	70	467 (4360)	3.56 (s, 12 H), 7.3 (s, H <sup>7</sup> , 4 H), 7.10–7.18 (q, H <sup>6</sup> , 4 H), 7.88 (s, H <sup>8</sup> ), 7.96 (s, H <sup>3</sup> ), 8.1 (s, H <sup>5</sup> , H <sup>6</sup> ), 8.41 (s, H <sup>4</sup> ), 8.48 (s, H <sup>7</sup> )
$[\text{Cu}(\text{deophen})_2]^+$	66.35 (67.85)	4.85 (4.90)	5.65 (5.65)	1040	69	472 (4595)	1.2–1.32 (t, 12 H), 3.7–3.92 (q, 8 H), 7.0–7.08 (q, H <sup>6</sup> , 4 H), 7.29 (s, H <sup>7</sup> , 4 H), 7.9 (s, H <sup>8</sup> ), 7.98 (s, H <sup>3</sup> ), 8.02 (s, H <sup>5</sup> , H <sup>6</sup> ), 8.4 (s, H <sup>4</sup> ), 8.48 (s, H <sup>7</sup> )
$[\text{Cu}(\text{tphen})_2]^+$	66.00 (66.05)	4.25 (4.05)	8.25 (8.10)	1060	67	452 (5385)	c
$[\text{Cu}(\text{eophen})_2]^+$	63.05 (63.95)	4.40 (4.30)	7.60 (7.45)	1040	69	451 (5125)	c

<sup>a</sup> Calculated values in parentheses. <sup>b</sup> Spectra recorded in  $\text{CDCl}_3$  with  $\text{SiMe}_4$  as internal standard; only selected signals are presented. <sup>c</sup> Spectra not clearly resolved.



**Fig. 1** Cyclic voltammetric (a) and differential pulse voltammetric (b) profiles of  $[\text{Cu}(\text{deophen})_2]^+$  (—) and  $[\text{Cu}(\text{eophen})_2]^+$  (---). Scan rates are 50 and 10  $\text{mV s}^{-1}$  respectively.

separation of the redox peaks is large. These peaks were not further investigated since the emphasis of the present study is on the electrochemistry of lower oxidation states.

From the analytical data, it is clear that the copper(i) complexes have a 1:2 metal to ligand ratio with the general composition bis[2,9-di(*o*-substituted phenyl)-1,10-phenanthroline]copper(i) fluoroborate or bis[2-(*o*-substituted phenyl)-1,10-phenanthroline]copper(i) fluoroborate. Conductivity measurements show that they are 1:1 electrolytes. In the IR spectra strong peak characteristic of ionic  $\text{BF}_4^-$  is observed in the range

1065–1040  $\text{cm}^{-1}$ . Various proton signals are clearly identified and their integration is in accord with the number of protons expected from the proposed structure.

It is known that copper(i) bis(2,9-disubstituted phenanthroline) complexes have a tetrahedral/pseudo-tetrahedral geometry.<sup>9</sup> In the case of complexes of interlocking catenands containing phenanthroline subunits the co-ordination polyhedron is highly distorted as compared to the tetrahedral geometry. This strong distortion has been partly ascribed to charge-transfer interaction between the phenanthroline nucleus of one macrocyclic unit and phenyl groups of the other. The present complexes are expected to have an even higher degree of distortion arising from charge-transfer type interactions and steric interactions due to the *ortho* groups of phenyl rings substituted at the 2,9 positions of the phenanthroline ligand system. The high distortion is reflected in the shift of the  $\lambda_{\max}$  values of the complexes to higher wavelengths. This spectral spread, though narrow, is attributed to enhanced splitting among the  $d_{x^2-y^2}$ ,  $d_{xy}$  and  $d_{yz}$  orbitals, and arises due to the  $e(xz, yz) \rightarrow e(\psi^*)$  and  $b_1(x^2 - y^2) \rightarrow a_2(\chi^*)$  transitions. Thus, the band is of metal-to-ligand charge transfer (m.l.c.t.) origin and is observed at about 465 nm, while copper(i) catenates exhibit the m.l.c.t. band at 454 nm and bis[2,9-di(*p*-methoxyphenyl)-1,10-phenanthroline]copper(i) at 440 nm.<sup>10,11</sup> The molar absorption coefficient of the present set of complexes varies from 4360 to 5385  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , in the range observed for 2,9-diphenyl-1,10-phenanthroline complexes.<sup>12</sup>

The electrochemical reversibility of the copper(i) complexes parallels the distortions observed in them. For instance, copper(i) catenates can be electrochemically reduced without demetallation (reversible) while bis[2,9-di(*p*-methoxyphenyl)-1,10-phenanthroline]copper(i) is first reduced followed by rapid dissociation to copper metal and free ligand. These results show that highly distorted copper(i) catenates with special topology have greater electrochemical reversibility. Cyclic voltammetric and differential pulse voltammetric results on bis[2,9-di(*o*-substituted phenyl)-1,10-phenanthroline]copper(i) show that they can be electrochemically reduced and oxidized (reversible). No evidence for demetallation is observed at various scan rates and the redox couple is found to be reversible even after several scans. The  $\Delta E_p$  values and the ratio  $-i_c/i_a$  show that the redox process is reversible and involves a one-electron transfer, *i.e.* reduction of copper(i) to copper(0) and reoxidation of copper(0) to copper(i). It is also observed that as the *ortho* substituent of the phenyl ring is varied from methyl to methoxy or ethoxy the reduction shifts to more negative values. This is due to the weak interaction of the oxygen atom of the methoxy or ethoxy substituent of the phenyl ring with  $\text{Cu}^{1+}$ <sup>13</sup> thus stabilizing the complex. The complexes  $[\text{Cu}(\text{tphen})_2]\text{BF}_4$  and  $[\text{Cu}(\text{eophen})_2]\text{BF}_4$

**Table 3** Cyclic voltammetric and differential pulse voltammetric data for the copper(i) complexes<sup>a</sup>

Complex	Scan rate/ (V s <sup>-1</sup> )	Cyclic voltammetry					Differential pulse voltammetry	
		Cathodic <i>E</i> <sub>p</sub> /V	Anodic <i>E</i> <sub>p</sub> /V	Δ <i>E</i> <sub>p</sub> /V	̄ <i>E</i> <sub>p</sub> /V	− <i>i</i> <sub>c</sub> / <i>i</i> <sub>a</sub>	Cathodic <i>E</i> <sub>p</sub> /V	Anodic <i>E</i> <sub>p</sub> /V
[Cu(dtphen) <sub>2</sub> ] <sup>+</sup>	0.01	−1.64	−1.58	0.06	−1.61	1.06	−1.63	−1.58
	0.02	−1.64	−1.58	0.06	−1.61	1.06	−1.64	−1.57
	0.05	−1.64	−1.57	0.07	−1.61	1.08		
	0.10	−1.65	−1.58	0.07	−1.61	1.06		
[Cu(dmophen) <sub>2</sub> ] <sup>+</sup>	0.01	−1.76	−1.68	0.08	−1.72	1.02	−1.73	−1.68
	0.02	−1.76	−1.68	0.08	−1.72	1.03	−1.74	−1.67
	0.05	−1.75	−1.68	0.07	−1.72	1.02		
	0.10	−1.75	−1.67	0.08	−1.71	1.00		
[Cu(deophen) <sub>2</sub> ] <sup>+</sup>	0.01	−1.76	−1.68	0.08	−1.72	1.05	−1.73	−1.69
	0.02	−1.76	−1.68	0.08	−1.72	1.06	−1.75	−1.68
	0.05	−1.76	−1.68	0.08	−1.72	1.07		
	0.10	−1.76	−1.68	0.08	−1.72	1.01		
[Cu(tphen) <sub>2</sub> ] <sup>+</sup>	0.01	−1.68	<i>b</i>	—	—	—	−1.66	<i>b</i>
	0.02	−1.67	<i>b</i>	—	—	—	−1.65	<i>b</i>
	0.05	−1.67	−1.59	0.08	−1.63	1.18		
	0.10	−1.67	−1.59	0.08	−1.63	1.13		
[Cu(eophen) <sub>2</sub> ] <sup>+</sup>	0.01	−1.68	<i>b</i>	—	—	—	−1.67	<i>b</i>
	0.02	−1.69	<i>b</i>	—	—	—	−1.68	<i>b</i>
	0.05	−1.69	<i>b</i>	—	—	—		
	0.10	−1.70	−1.60	0.10	−1.65	1.35		

<sup>a</sup> As BF<sub>4</sub><sup>−</sup> salts, recorded in dmso at 27 ± 1 °C with NEt<sub>4</sub>ClO<sub>4</sub> as supporting electrolyte (see Experimental section). <sup>b</sup> Peaks not observed.

(eophen)<sub>2</sub>]BF<sub>4</sub>, where only the 2 position of the phenanthroline moiety is substituted, show quasireversible behaviour at higher scan rates and irreversible behaviour at slow scan rates. These complexes are expected to have less distortion because of reduced steric interaction due to the presence of only one *ortho*-substituted phenyl ring per phenanthroline.

The electrochemical reversibility of the bis[2,9-di(*o*-substituted phenyl)-1,10-phenanthroline]copper(i) complexes can be compared with that of bis[2,9-di(*p*-methoxyphenyl)-1,10-phenanthroline]copper(i), which in the absence of *ortho* substituents in the phenyl ring is much less distorted from the tetrahedral geometry and is electrochemically irreversible. The reversibility exhibited by the former complexes implies that the Cu<sup>0</sup> generated by electrochemical reduction is very stable. Stability in the present context signifies that this reduced species is retained within the co-ordination sphere and does not decompose into metal and free ligand. Thus the cyclic voltammetric and differential pulse voltammetric results for these complexes indicate that they mimic the electrochemical reversibility of copper(i) catenates obtained from topologically suited catenands. Since the present complexes do not have the topological features of copper(i) catenates, the electrochemical reversibility should be the combined result of the appreciable geometrical distortion of the co-ordination polyhedron resulting from *ortho* substitution of the phenyl groups of the ligand system, the particular topography, charge-transfer interaction between the phenanthroline nucleus of one unit and phenyl groups of the other, and the weak interaction mediated through the alkoxy group of the phenyl with the central metal ion. The spectral results discussed earlier have also shown evidence for increased distortion in these complexes.

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