Electrochemical and Mössbauer Studies on Iron(II) Complexes of a New Series of Entwining Ligands: Stabilization of Uni- and Zero-valent Oxidation States

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Iron(II) complexes of 1,10-phenanthroline ligands (L) disubstituted at the 2,9 positions or monosubstituted at the 2 position by phenyl moieties having *ortho* substituents were prepared and investigated by spectral, Mössbauer and electrochemical techniques. The 2,9-di(*o*-alkoxyphenyl)-1,10-phenanthroline ligands readily form stable bis complexes $[FeL_2]^{2+}$. Owing to the particular entwining arrangement of the co-ordinating sub-units, their topography together with the large tetrahedral distortions they induce, and the influence of the alkoxy group at the *ortho* position of the phenyl ring of the ligand system, these iron(II) complexes display novel electrochemical properties and exceptional stability of their lower oxidation states.

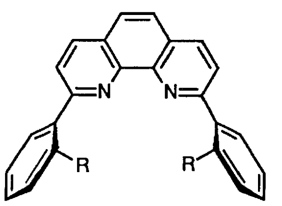
In recent years, interest in aromatic polyimine ligands such as 2,2′-bipyridyl, 1,10-phenanthroline (phen) and their substituted derivatives has been renewed because of their interesting redox,[1] photoredox[2-5] and catalytic properties.[6] Further, the tendency of these ligands to stabilize the lower oxidation states of various transition metals provides an additional interesting feature.[7-10]

Another class of interlocking macrocyclic ligand, the catenands, has been synthesised recently and used to obtain complexes containing metals in lower oxidation states.[1,11,12] The stabilization of these oxidation states by either aromatic polyimines or catenands derived from 1,10-phenanthroline type ligands has been ascribed to the interaction of π^* orbitals of the ligand and metal ion orbitals. For the catenands, their special topology stabilizes their complexes to dissociation into the metal and free ligand upon electrochemical reduction. The complexes are thereby imparted with a high degree of electrochemical reversibility. This is evidenced by comparing catenand complexes with those of 2,9-disubstituted-1,10-phenanthroline ligands, the latter complexes being decomposed readily into the metal and free ligand on electrochemical reduction.[13]

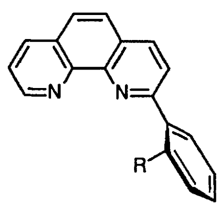
Very recently, however, we have prepared complexes of 1,10-phenanthroline ligands substituted at the 2,9 positions by large sterically constrained groups having sites that can interact with metal centres. These complexes show large geometrical distortions and can mimic the behaviour of catenands as observed in the bis ligand complexes of copper(I),[14] cobalt(II)[15] and nickel(II)[16]. In a preliminary report[17] we showed that the complex $[Fe(dmophen)_2]^{2+}$ [dmophen = 2,9-di(*o*-methoxyphenyl)-1,10-phenanthroline] also displayed similar behaviour. In the present study, this and further iron(II) complexes of various 2,9-di- and 2-(*o*-substituted phenyl)-1,10-phenanthroline ligands are investigated both from the point of view of their electrochemical behaviour in solution and their structural features in solution and in the solid state. Scarcely any literature data are available on the electrochemical properties of 2,9-disubstituted-1,10-phenanthroline iron(II) complexes[1] as they are highly unstable in solution and electrochemically inert. The present work therefore also extends the literature in this area.

Experimental

Preparation of the Ligands.—The ligands 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) were prepared as described earlier.[14]



	R
dtphen	Me
dmophen	OMe
deophen	OEt



	R
tphen	Me
eophen	OEt

Preparation of the Complexes.—The complexes were prepared by the following general procedure.

To the appropriate ligand L (2.1 mmol) dissolved in CH_2Cl_2–MeOH (5 cm^3, 1:2 v/v) was added a methanolic solution (10 cm^3) of $Fe(ClO_4)_2 \cdot 6H_2O$ (1 mmol) with stirring. A light- to deep-yellow coloration developed depending on the ligand used, followed by precipitation when the volume of the solution was reduced. The complexes were recrystallized from CH_2Cl_2–hexane (1:4 v/v). The complexes $[FeL_2][ClO_4]_2$ (L = dtphen, dmophen, deophen, tphen or eophen) were prepared in this manner.

For a comparative Mössbauer study the chloro complex $[Fe(dtphen)Cl_2]$ was also prepared by treating dtphen (1.1 mmol) with $FeCl_2$ (1 mmol) in MeOH (10 cm^3) under nitrogen. It should be noted that $[Fe(dtphen)_2][ClO_4]_2$ did not show consistent C, H and N analyses nor was it fully soluble in MeCN. Its properties (see below) were also found to differ significantly from those of the other complexes.

CAUTION: All perchlorates are hazardous and should be handled with care.

Physical Measurements.—The C, H and N analyses were carried out on a Perkin-Elmer 240C analyser. Conductivity measurements were done on a CM-82T Elico conductivity meter at 25 °C in nitromethane and the solutions were 0.001 mol dm^{-3}. Infrared spectra were recorded on a Perkin-Elmer

Table 1 Analytical and spectral data for the iron complexes

Complex	Analysis[a] (%)			Conductivity[b]/ ohm^{-1} cm^2 mol^{-1}	λ_{max}[c]/nm (ε/dm^3 mol^{-1} cm^{-1})	μ_{eff}
	C	H	N			
$[Fe(dtphen)_2]^{2+}$	63.10 (65.00)	4.30 (4.10)	6.00 (5.15)	148	*d*	5.16
$[Fe(dmophen)_2]^{2+}$	59.85 (60.05)	3.75 (3.85)	5.20 (5.40)	175	440(sh) (560)	5.28
$[Fe(deophen)_2]^{2+}$	61.65 (61.35)	4.50 (4.40)	5.05 (5.10)	180	448(sh) (550)	5.66
$[Fe(tphen)_2]^{2+}$	56.20 (57.35)	3.50 (3.50)	7.20 (7.05)	153	440 (540)	4.98
$[Fe(eophen)_2]^{2+}$	55.40 (56.15)	3.75 (3.75)	6.60 (6.55)	160	445 (460)	5.01

All complexes show $\nu(ClO_4)$ at 1090 cm^{-1} and IR bands consistent for co-ordinated ligands. [a] Calculated values in parentheses. [b] In nitromethane at 25 ± 1 °C. [c] UV spectra consistent with co-ordinated ligands. [d] Neither the shoulder or the peak is observed.

Table 2 Mössbauer and photoacoustic data for the iron complexes

Complex	Mössbauer		Photoacoustic wavenumber[b]/cm^{-1}
	Isomer shift[a]/ mm s^{-1}	Quadrupolar shift[a]/ mm s^{-1}	
$[Fe(dtphen)_2]^{2+}$	0.37	0.72	—
$[Fe(dmophen)_2]^{2+}$	1.06	3.43	8695
$[Fe(deophen)_2]^{2+}$	1.01	3.33	8000
$[Fe(tphen)_2]^{2+}$	1.03	2.44	—
$[Fe(eophen)_2]^{2+}$	0.98	1.13	—
$[Fe(dtphen)Cl_2]$	0.83	2.53	—

[a] Relative to iron foil. [b] Internal standard carbon black.

IR 283 spectrophotometer in the range 4000–200 cm^{-1} in KBr pellets, electronic spectra on a Perkin-Elmer Lambda 3B UV/VIS spectrophotometer in MeCN using 1×10^{-3} mol dm^{-3} solutions for the visible range and photoacoustic spectra for the solid samples on a PAR 6001 spectrophotometer in the range 250–1800 nm using carbon black as an internal standard. Magnetic susceptibilities were determined on a Bruker BM6 magnet with a Faraday magnetic balance and using $HgCo(NCS)_4$ as the calibrant. Mössbauer spectra were recorded at room temperature by employing a constant acceleration Elscint drive in conjunction with a multichannel analyser (Promeda) and a 10 mCi (3.7×10^8 Bq) Co^{57}/Rh source. Cyclic voltammetry (CV) experiments were carried out on a PAR electrochemistry system consisting of a 174A polarographic analyser and a single compartment cell. Solutions of the iron(II) complexes (1×10^{-3} mol dm^{-3}) in MeCN were used. The supporting electrolyte was 0.1 mol dm^{-3} tetraethylammonium perchlorate which was prepared as previously described,[18] recrystallised twice from H_2O–MeOH and dried under vacuum at 40 °C. All experiments were performed under a blanket of dry nitrogen at 27 ± 1 °C in a three-electrode configuration with a hanging mercury drop electrode (HMDE) as the working electrode, platinum wire as the auxiliary electrode and a standard calomel electrode (SCE) as the reference electrode. All potentials are referred to the SCE.

Results and Discussion

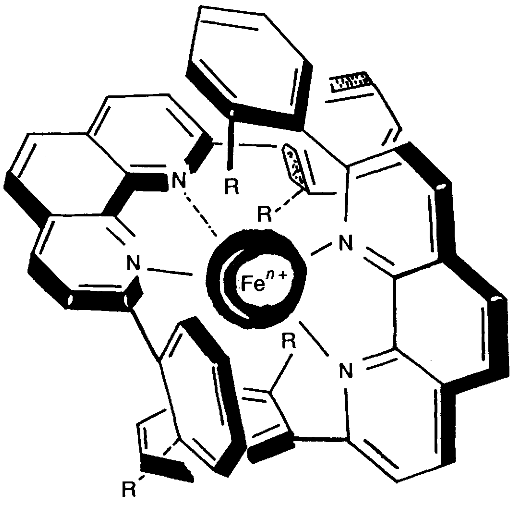
The iron(II) complexes $[FeL_2][ClO_4]_2$ [L = 2,9-di- or 2-(*o*-substituted phenyl)-1,10-phenanthroline] were characterized by analytical and spectral methods (Table 1). Their conductivities in nitromethane lie in the range 150–180 ohm^{-1} cm^2 mol^{-1} and are typical of 1:2 electrolytes.[19] Their IR spectra exhibit a strong band at 1090 cm^{-1} characteristic of ionic perchlorate[20] and consistent with the above formulation. The complex $[Fe(dtphen)Cl_2]$ shows an IR band at 363 cm^{-1} usually a Fe–Cl stretch.[21]

The 2,9-disubstituted iron(II) complexes exhibited a high-energy shoulder at *ca.* 22 400 cm^{-1} while the 2-monosubstituted iron(II) complexes exhibited a band at about 22 220 cm^{-1}, the former complexes being more sterically constrained than the latter. These absorptions are due to parity-allowed charge-transfer transitions from occupied d orbitals of the central metal ions to empty π^* orbitals of the substituted phenanthroline ligands.[22] The chloro complex $[Fe(dtphen)Cl_2]$ also exhibited a shoulder in the visible region at about 21 277 cm^{-1} (470 nm), the origin of which is similar to those for $[FeL_2]^{2+}$. Photoacoustic spectra (Table 2) of solid samples of $[Fe(dmophen)_2]^{2+}$ and $[Fe(deophen)_2]^{2+}$ gave reliable spectra with broad peaks centred at 8700 and 8000 cm^{-1} respectively while solution spectra of these complexes in MeCN also showed similar broad features in the same region. All the other complexes were found to give poorly characterized electronic spectra. For $[Fe(dmophen)_2]^{2+}$ and $[Fe(deophen)_2]^{2+}$ the low-energy absorptions are assigned to d–d transitions. Although lower in energy than expected for octahedral complexes[23] they are higher than expected for strictly tetrahedral complexes. This may be attributed to an intramolecular interaction of the alkoxy *ortho* substituents of the ligands with the iron(II) centre leading to a highly distorted octahedral geometry (see below).

Effective magnetic-moment (μ_{eff}) values (Table 1) for the complexes $[FeL_2][ClO_4]_2$ lie in the range 5.0–5.7, which are typical of high-spin iron(II) complexes and compare well with reported values for other tetrahedral iron(II)-substituted phenanthroline complexes.[22,24] The proposed structure for the bis[2,9-di(*o*-substituted phenyl)-1,10-phenanthroline]iron(II) complexes is shown in Fig. 1.

The divalent state of iron in the complexes $[FeL_2][ClO_4]_2$ was established unambiguously by Mössbauer spectroscopy (Table 2), except for $[Fe(dtphen)_2]^{2+}$. The isomer shift (i.s.) values lie in the range 0.98–1.06 mm s^{-1}, and are slightly higher than usually observed for tetrahedral iron ($\approx$0.8 mm s^{-1})[25] indicating the ligand disposition around the iron to be distorted from tetrahedral possibly as a result of an additional interaction of the co-ordinated ligands with the iron centre. Significantly where there is strictly no possibility for such an interaction as in [Fe(dtphen)Cl$_2$] the i.s. value is quite close to 0.8 mm s^{-1}, characteristic of tetrahedral iron. The slightly higher i.s. for [Fe(tphen)$_2$]$^{2+}$ may be attributed to a combination of lattice affects and the temperature dependence of isomer shifts.[25] Intramolecular interaction of *ortho* alkoxy substituents of the ligands is however certainly feasible for [FeL$_2$]$^{2+}$ (L = eophen, dmophen or deophen). The quadrupole splitting values lie in the wide range 1.12–3.42 mm s^{-1}. The data show that [Fe(eophen)$_2$]$^{2+}$ is least distorted while [Fe(dmophen)$_2$]$^{2+}$ and [Fe(deophen)$_2$]$^{2+}$ are most distorted from cubic symmetry. The large distortions observed apparently arise as a result of greater steric effects within these complexes.

The complex [Fe(dtphen)$_2$]$^{2+}$ gives anomalous results when compared to the other complexes. The magnetic susceptibility, Mössbauer isomer shift and quadrupole splitting clearly *suggest* the presence of high-spin trivalent iron and a large distortion from cubic symmetry. The quadrupole splitting suggests that the lattice is highly distorted since the electric field gradient contribution to Fe^{3+} (which has a half-filled 3d^5 shell con-



R = Me, OMe or OEt

Fig. 1 The proposed structure for the bis[2,9-di(*o*-substituted phenyl)-1,10-phenanthroline]iron(II) complexes

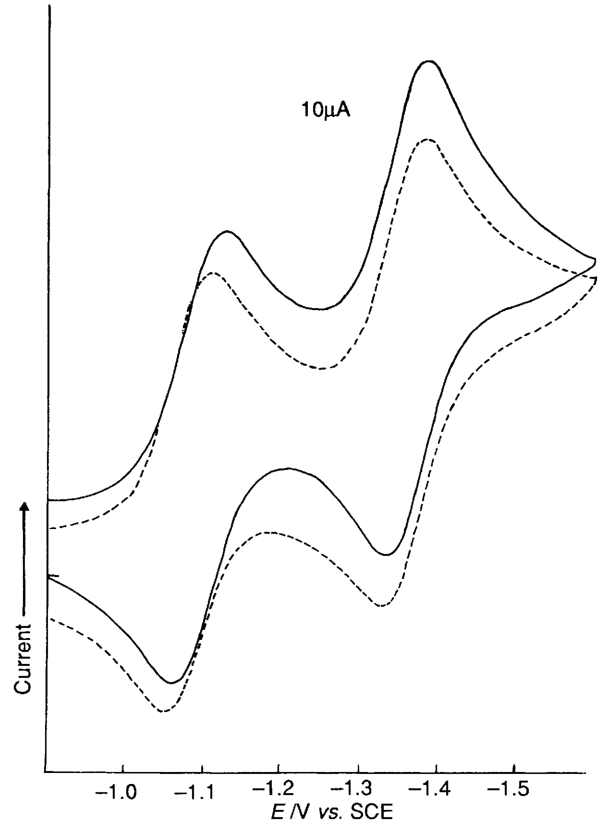


Fig. 2 Cyclic voltammetric profiles of [Fe(dmophen)$_2$]$^{2+}$ (——) and [Fe(deophen)$_2$]$^{2+}$ (– – –) at a scan rate of 100 mV s^{-1}

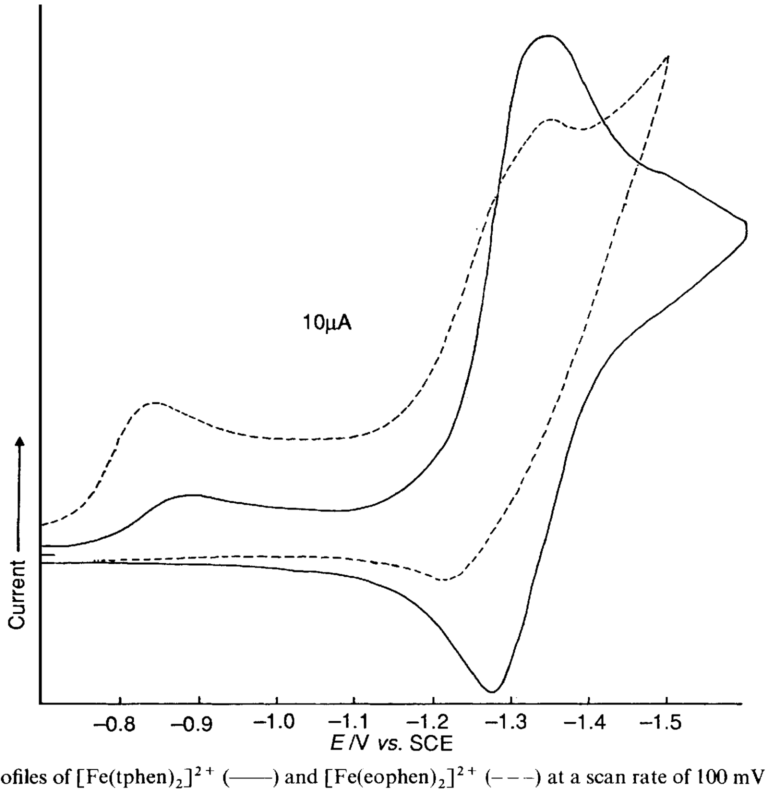


Fig. 3 Cyclic voltammetric profiles of [Fe(tphen)$_2$]$^{2+}$ (——) and [Fe(eophen)$_2$]$^{2+}$ (– – –) at a scan rate of 100 mV s^{-1}

Table 3 Cyclic voltammetric and differential pulse voltammetric data for the Fe^{2+}–Fe^{+} couple[a]

		Cyclic voltammetry					Differential pulse voltammetry	
Complex	Scan rate/V s^{-1}	Cathodic E_p/V	Anodic E_p/V	ΔE_p/V	$\bar{E}$/V	$-i_c/i_a$	Cathodic E_p/V	Anodic E_p/V
$[Fe(dmophen)_2]^{2+}$	0.02	−1.13	−1.07	0.06	−1.10	1.06	−1.12	−1.06
	0.05	−1.13	−1.07	0.06	−1.10	1.02		
	0.10	−1.14	−1.08	0.06	−1.11	1.01		
$[Fe(deophen)_2]^{2+}$	0.02	−1.10	−1.04	0.06	−1.07	1.04	−1.11	−1.04
	0.05	−1.10	−1.04	0.06	−1.07	1.00		
	0.10	−1.10	−1.04	0.06	−1.07	1.00		
$[Fe(tphen)_2]^{2+}$	0.02	−0.86	*b*					
	0.05	−0.88	*b*					
	0.10	−0.87	*b*					
$[Fe(eophen)_2]^{2+}$	0.02	−0.85	*b*					
	0.05	−0.85	*b*					
	0.10	−0.85	*b*					
$[Fe(dtphen)_2]^{2+}$	0.02	0.105[c]	0.17	0.065	0.138	1.12	0.12	0.18
	0.05	0.105[c]	0.17	0.065	0.138	1.03		
	0.10	0.105[c]	0.17	0.065	0.138	1.12		

[a] Recorded as 0.001 mol dm^{-3} solutions in acetonitrile at 27 ± 1 °C, with NEt_4ClO_4 as the supporting electrolyte. [b] Oxidation peak is not observed. [c] The potentials are for the Fe^{3+}–Fe^{2+} couple.

Table 4 Cyclic voltammetric and differential pulse voltammetric data for the Fe^{+}–Fe^{0} couple[a]

		Cyclic voltammetry					Differential pulse voltammetry	
Complex	Scan rate/V s^{-1}	Cathodic E_p/V	Anodic E_p/V	ΔE_p/V	$\bar{E}$/V	$-i_c/i_a$	Cathodic E_p/V	Anodic E_p/V
$[Fe(dmophen)_2]^{2+}$	0.02	−1.395	−1.335	0.06	−1.365	1.02	−1.395	−1.33
	0.05	−1.395	−1.335	0.06	−1.365	0.95		
	0.10	−1.405	−1.34	0.065	−1.373	1.04		
$[Fe(deophen)_2]^{2+}$	0.02	−1.38	−1.31	0.07	−1.345	1.04	−1.38	−1.35
	0.05	−1.38	−1.32	0.06	−1.35	1.00		
	0.10	−1.38	−1.32	0.06	−1.35	1.00		
$[Fe(tphen)_2]^{2+}$	0.02	−1.34	−1.26	0.08	−1.30	1.14	−1.345	−1.27
	0.05	−1.34	−1.26	0.07	−1.305	1.14		
	0.10	−1.34	−1.27	0.07	−1.31	1.10		
$[Fe(eophen)_2]^{2+}$	0.02	−1.35	−1.22	0.13	−1.285	*b*	*c*	
	0.05	−1.35	−1.22	0.13	−1.285	*b*	*c*	
	0.10	−1.35	−1.22	0.13	−1.285	*b*	*c*	
$[Fe(dtphen)_2]^{2+}$	0.02	−0.84[d]					−0.84	—
	0.05	−0.84						
	0.10	−0.84						

[a] Experimental conditions as in Table 3. [b] Because of the ill defined peak it was not possible to calculate $-i_c/i_a$. [c] Very ill defined peaks observed. [d] This irreversible peak is for the Fe^{2+}–Fe^{+} couple.

figuration) arises exclusively from the lattice. These observations are also supported by the absence of d–d transitions in the photoacoustic spectrum of the complex in the solid state or in the electronic spectrum in solution. The unusual behaviour of $[Fe(dtphen)_2]^{2+}$ is also reflected in its cyclic voltammogram, which shows a reversible peak for a one-electron process at $\bar{E}$ + 0.14 V *vs.* SCE. This value for the Fe^{3+}–Fe^{2+} couple can be compared with a value of +1.012 V *vs.* SCE[26] for octahedral $[Fe(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridyl). A completely irreversible peak at −0.84 V is also observed for $[Fe(dtphen)_2]^{2+}$ and suggests that the reduced monovalent species undergoes disproportionation.[27] Although this behaviour is consistent with previous observations for reduced 2,9-disubstituted phenanthroline iron complexes,[1] the newly prepared complexes $[Fe(dmophen)_2]^{2+}$ and $[Fe(deophen)_2]^{2+}$ (see below) show completely different behaviour.

The apparent trivalent oxidation state for iron in $[Fe(dtphen)_2]^{2+}$ does appear anomalous and thus, together with its uncertain purity, makes further discussion for this complex unwarranted.

It was previously reported that the iron(II) complex of 2,9-di(*p*-methoxyphenyl)-1,10-phenanthroline could not be prepared,[1] which is surprising considering that the iron complexes of the ligands studied here could be prepared readily. Further, hardly any literature is available on the electrochemical properties of bis complexes of iron(II) involving sterically hindered 2,9-disubstituted-1,10-phenanthroline ligands since such complexes are considered to be electrochemically inert. Thus the importance of the present ligands is realised as they are able to form stable iron(II) complexes which are electrochemically active and interesting.

Electrochemical Studies.—Electrochemical, cyclic voltammetric and differential pulse voltammetric studies were performed in acetonitrile.[28] All the ligands are electrochemically inactive up to −1.9 V. The cyclic voltammetric profiles at various scan rates and repeated scans were also investigated. These are shown in Figs. 2 and 3 and the electrochemical data are presented in Tables 3 and 4.

$[Fe(dmophen)_2]^{2+}$ *and* $[Fe(deophen)_2]^{2+}$. The complex $[Fe(deophen)_2]^{2+}$ exhibits two perfectly reversible one-electron reductions (Fig. 2) in the negative potential range at *ca.* −1.07

($Fe^{2+} \longrightarrow Fe^{+}$) and −1.35 V ($Fe^{+} \longrightarrow Fe^{0}$). For [Fe(dmophen)$_2$]$^{2+}$ these values are shifted to slightly more negative potentials, *viz.* −1.11 and −1.37 V respectively. The ΔE_p values of *ca.* 60 mV and $-i_c/i_a$ values of *ca.* 1 for both sets of redox peaks indicate both chemical and electrochemical reversibility for the two reduction processes. There was no shift in the potentials at various scan rates nor did the peaks alter on repeated scanning. The differential pulse voltammetric results are in general agreement with those obtained by cyclic voltammetry.

The above results can be compared with those obtained for related systems. The complex [Fe(phen)$_3$]$^{2+}$ has been shown to have redox couples at −1.39 and −1.55 V[8] while for [Fe(bipy)$_3$]$^{2+}$ these occur at −1.34 and −1.53 V.[29] More anodic potentials were however obtained for the iron(II) catenate derived from 2,9-di(*p*-methoxyphenyl)-1,10-phenanthroline, which exhibits $\bar{E}$ at −0.71 and −1.26 V for the corresponding Fe^{2+}–Fe^{+} and Fe^{+}–Fe^{0} couples. The iron(II) catenate is more tetrahedrally distorted and these topographical and topological effects together contribute to the stabilization of its univalent state by about 0.675 V relative to [Fe(phen)$_3$]$^{2+}$. The reduction potentials for the Fe^{2+}–Fe^{+} couple in [Fe(dmophen)$_2$]$^{2+}$ and [Fe(deophen)$_2$]$^{2+}$ are intermediate between these two cases occurring at a potential *ca.* 0.28 V more cathodic than that of the catenate. Despite this, both the mono- and zero-valent states of iron are quite accessible for these complexes. Furthermore the couples are perfectly reversible showing the remarkable stability of these reduced states in which the iron atom is presumably entrapped within the co-ordination polyhedron so preventing dissociation into the metal and free ligand. The observation of two perfectly reversible redox cycles on the formation of lower oxidation states, *viz.*, iron(I) and iron(0), is significant considering the fact that these ligands lack interlocked ring systems.

It should perhaps be noted that the iron(I), and particularly the iron(0) oxidation states, should be regarded as formal in these systems. Although the free ligands dmophen and deophen show no reduction processes down to −1.9 V *vs.* SCE, there remains the possibility that ligand-based orbitals can accept electron density from reduced iron(I) or iron(0) centres.

The absence of an oxidation ($Fe^{2+} \longrightarrow Fe^{3+}$) in the cyclic voltammetric studies for [Fe(dmophen)$_2$]$^{2+}$ and [Fe(deophen)$_2$]$^{2+}$ shows that the particular topography adopted by these complexes, which is marked by steric congestion inhibits the formation of octahedral complexes but favours a low co-ordination number, *i.e.* tetrahedral/pseudo-tetrahedral geometry. As a consequence, high oxidation states requiring strong ligand-field stabilization are markedly disfavoured relative to lower oxidation states.[30]

It is well established that electron-donating substituents on a ligand will strengthen σ bonding with a central metal ion resulting in a shift towards more negative reduction potentials.[8] On this basis [Fe(deophen)$_2$]$^{2+}$ would be expected to show more cathodic reduction potentials than [Fe(dmophen)$_2$]$^{2+}$. The opposite behaviour observed possibly arises from a larger geometrical distortion in the dmophen complex (see also Mössbauer) relative to the deophen complex, and a presumed greater degree of interaction of the methoxy group with the central metal ion. This feature has been reflected in previous studies with other transition-metal complexes of dmophen and deophen.[14–16]

[Fe(tphen)$_2$]$^{2+}$ *and* [Fe(eophen)$_2$]$^{2+}$. These monosubstituted complexes exhibit an irreversible hump at about −0.88 V and a quasireversible peak at *ca.* −1.3 V (Fig. 3) indicating that the reduced complexes are unstable and dissociate into the free metal and ligand on electrochemical reduction as a result of incomplete shielding of the central metal ion.

In conclusion, it can be stated that despite a decrease in thermodynamic stability[31] of iron–phenanthroline complexes upon substitution at the 2,9 or 2 positions of 1,10-phenanthroline, the presence of alkoxy groups as *ortho* substituents on the phenyl rings of 2,9-disubstituted-1,10-phenanthroline leads to a strong interaction with the central metal ion giving rise to stable iron(II) complexes. On subsequent electrochemical reduction these complexes form stable iron(I) and iron(0) complex species. Doubtless the 2,9-disubstitution or 2-monosubstitution in these ligands increases their σ-donation basicity through positive electron-releasing inductive and resonance effects; however steric effects dominate which lead to severely distorted-tetrahedral complexes the degree of which depends upon the nature of the *ortho* substituents of the ligand system.

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