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LETTER

Frontier and near-frontier orbitals
Part 2. Spectroelectrochemical studies of $[Fe(phen)_3]^{2+/+/0/-}$

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Fe(II) complexes with 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) have received increasing attention in recent years [1], but we are aware of no spectroscopic studies of the electrochemically reduced species. We have performed electrochemical and spectroelectrochemical studies on $[Fe(phen)_3]^{2+}$ (**I**) and $[Fe(bpy)_3]^{2+}$ (**II**) (phen = 1,10-phenanthroline; bpy = 2,2′-bipyridine) in DMF solution. Like previous workers [2], we find that the cyclic voltammograms of both complexes show a sequence of three reversible one-electron reductions, with spacings around 175 mV, in the range expected for reductions based on these ligands when attached to a divalent metal center, but electrochemical data alone cannot show whether the added electrons are localized or delocalized over the three equivalent ligands.

Comparison of the spectra of **I**, **II** [3] and their one-, two- and three-electron products shows that the reductions are ligand- rather than metal-based (despite the fact that in these complexes the lowest excited state of the parent ions is d–d in nature) and that the added electrons are indeed localized on separate ligands. The data for the reduction products of **I** give, for the first time, the spectrum of the coordinated phenanthroline anion radical ligand. In contrast to coordinated $[bpy]^-$, this spectrum differs substantially from that of the corresponding free radical anion.

The parent complex **II** shows MLCT transitions at 23000 cm^{-1}. This is moved to higher energy on reduction, while the characteristic [4] $\pi(6)\rightarrow\pi(7)$ (27030 cm^{-1}), $\pi(7)\rightarrow\pi(10)$ (18180 cm^{-1}) and $\pi(7)\rightarrow\pi(8,9)$ (10530 cm^{-1}) bands of coordinated $[bpy]^-$ appear on the addition of the first electron and increase in intensity at each further step, as in the related Ru(II) complex [5]. The assignments of the spectrum of reduced **I** are more difficult than those of **II**, although a pseudo-isosbetic point occurs for the series $\mathbf{I}^{0/-/2-/3-}$. The phen system is characterized by two low-lying unoccupied molecular orbitals of comparable energies [6c], so that the visible MLCT absorption of **I** [6] (and of $\mathbf{I}^{0/-/2-}$; Fig. 1 and Table 1) contain two kinds of very closely located MLCT transitions, $d\rightarrow\pi(8)$ and $d\rightarrow\pi(9)$, and the order of these in the complex relative to the free ligand is a matter of some interest [7].

The band at around 390 nm is presumably associated with the intra-ligand HOMO $[\pi(7)]\rightarrow$LUMOs$[\pi(8)$ and $\pi(9)]$ $(\pi\rightarrow\pi^*)$ transition of the coordinated $[phen]^-$. Transitions between the LUMOs and higher orbitals (e.g. $\pi(10)$–$\pi(14)$) are observed in the near IR and visible regions. Further studies are required for precise assignments of these bands, but the stepwise increase in intensity of the $[phen]^-$ $\pi^*\rightarrow\pi^*$ and, especially, $\pi\rightarrow\pi^*$ transition on progressive reduction is characteristic of localization of the added electrons.

We have found that the cathodic reduction product of phen (unlike that of bpy) is too short-lived for conventional spectroelectrochemistry; however, our data lead to the first spectroscopic characterization of the reduced coordinated phen ligand. The strong visible $\pi^*\rightarrow\pi^*$ band, at around 16700 cm^{-1}, is significantly shifted from that reported around 21000

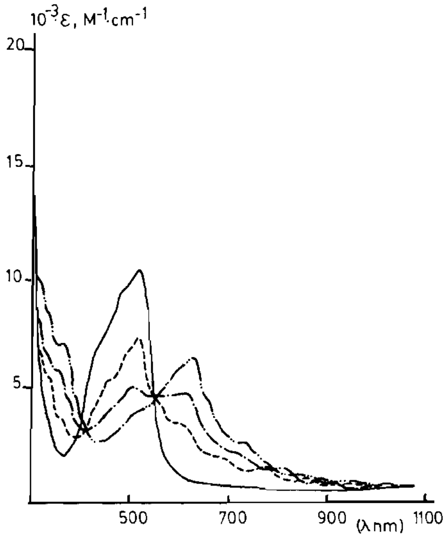

Fig. 1. Absorption spectra of $[Fe(phen)_3]^{2+/+/0/-}$ in DMF–$TBABF_4$ solution at 25 °C (V vs. ferrocene/ferrocenium$^+$). ——, parent; – – –, singly reduced species at −1.735 V; – · –, doubly reduced species at −1910 V; – · · –, triply reduced species at −2.089 V.

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TABLE 1. The main absorption bands and assignments of $\mathbf{I}^{0/-/2-/3-}$ ($\nu/10^3$ cm^{-1}) ($10^{-3}\times\epsilon$ (M^{-1} cm^{-1}))[a]

	$\pi\rightarrow\pi^*$ (L^{1-})	MLCT	MLCT	$\pi^*\rightarrow\pi^*$ (L$^-$)	$\pi^*\rightarrow\pi^*$ (L$^-$)
$\mathbf{I}$		23.0(7.3)	19.4(11.2)		
$\mathbf{I}^-$	26.0(4.2)	23.2[b](5.9)	19.7(7.7)	16.9(3.9)	11.7(2.4)
$\mathbf{I}^{2-}$	25.7(6.3)		19.9[b](5.1)	16.7(5.0)	11.5(2.5)
$\mathbf{I}^{3-}$	25.3(7.9)			16.5(7.1)	11.2(2.6)

[a] DMF–TBABF$_4$ solution at 25 °C. [b] Shoulder.

cm^{-1} in the pulse radiolysis data of Simic and coworkers [8] and Atherton [9]. Further experimental and theoretical studies are in progress, to see whether this difference corresponds to a shift within a uniform assignment, or to a more radical change in LUMO order.

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