Iron(II) Complex of Entwined 2,9-Bis(*o*-methoxyphenyl)-1,10-phenanthroline: Stabilization of its Iron(I) and Iron(0) Oxidation States

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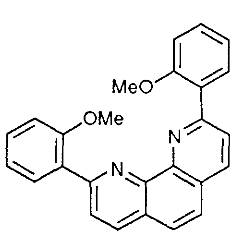
2,9-Bis(*o*-methoxyphenyl)-1,10-phenanthroline, L, readily forms the stable complex $[Fe(L)_2](ClO_4)_2$, which shows unusual electrochemical properties and exceptional stability of the lower oxidation states.

Although iron(II) complexes of 2,9-disubstituted-1,10-phenanthrolines are known,[1,2] their redox behaviour is virtually unknown. Examples of iron(I) complexes with nitrogen ligands are mainly restricted to tetraazamacrocylic compounds[3,4] and complexes with 2,2′-bipyridine,[5] 1,10-phenanthroline or substituted phenanthrolines,[6] or 2,2′ : 6′,2″-terpyridine,[7] in which steric hindrance does not stop octahedral coordination being attained. It has been reported that the iron(II) complex of 2,9-bis(*p*-methoxyphenyl)-1,10-phenanthroline (dap) cannot be prepared as it lacks the necessary topology and is unable to provide ligand field stabilization.[8] However, the corresponding cyclic iron(II) catenate[8] could be prepared easily because its geometry was favourable, and it showed unusual electrochemical properties in forming stabilized lower oxidation states. We have recently synthesized the new ligand 2,9-bis(*o*-methoxyphenyl)-1,10-phenanthroline (L) which has the necessary geometrical properties to enable it to mimic the catenate in complex formation,[9] because of the presence of the *ortho*-methoxy groups.



L

We have now prepared a stable complex of iron(II) and two L units by the reaction of $FeClO_4 \cdot 6H_2O$ (1 mmol) in MeOH with the ligand L (2 mmol) in CH_2Cl_2–MeOH (1 : 1). The yellow complex precipitated on evaporation of the solution. We suggest that the complex has the structure shown in Fig. 1. Satisfactory elemental analyses (C,H,N) were obtained and its IR spectrum shows a band at 1090 cm^{-1}

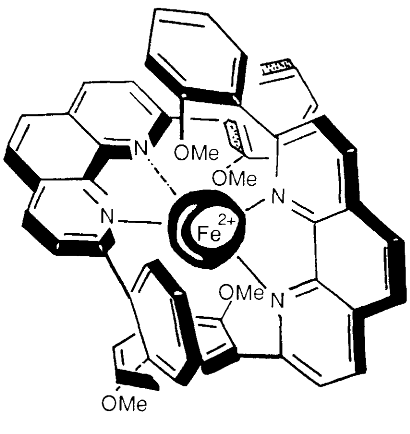


Fig. 1 Proposed structure of the complex $[Fe(L)_2]^{2+}$

Table 1 Cyclic voltammetric data

	Fe^{2+}/Fe^{1+}				Fe^{1+}/Fe^{0}			
Complex	$E_{p,c}$	$E_{p,a}$	ΔE_p	$E_{\frac{1}{2}}$	$E_{p,c}$	$E_{p,a}$	ΔE_p	$E_{\frac{1}{2}}$
$[Fe(dap)_2]^{2+}$	—	—			—	—		
$[Fe(L)_2]^{2+}$ [a]	−1.13	−1.07	0.06	−1.10	−1.39	−1.33	0.06	−1.36
$[Fe(catenate)]^{2+}$ [b]				−0.71				−1.26

[a] All potentials are in V with respect to a standard calomel electrode, and were recorded in MeCN with Et_4NClO_4 as supporting electrolyte, a hanging mercury drop as working electrode, and Pt wire as auxiliary electrode. The temperature was 27 ± 1 °C. [b] Data from ref. 8.

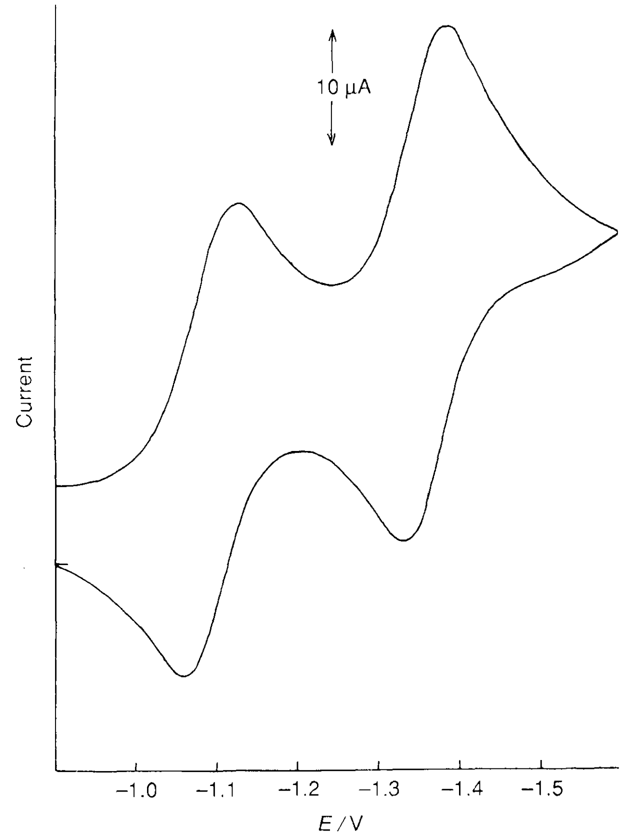


Fig. 2 Cyclic voltammogram of $[Fe(L)_2]^{2+}$ at a scan rate of 100 mV s^{-1}; potential *vs.* standard calomel electrode

indicating ionic perchlorate.[10] An isomer shift value of 1.059 mm s^{-1} with respect to iron foil in its Mössbauer spectrum shows it to be a high spin d^6 iron(II) complex in the $^5T_2$ ground state with the methoxy groups weakly interacting with the central metal ion.[11] Its magnetic susceptibility was 5.28 μ_B, while its photoacoustic spectrum showed a weak band at 1150 nm consistent with a distorted tetrahedral geometry. The quadrupolar Mössbauer shift of 3.43 mm s^{-1} showed that the tetrahedral coordination is highly distorted.

The complex $[Fe(L_2)]^{2+}$ shows unusual redox behaviour and generates stabilized lower oxidation states when reduced at a mercury drop electrode (Table 1). The Fe^{2+}/Fe^{1+} couple is reversible with a cathodic potential at −1.13 V, an anodic potential at −1.07 V and $E_{1/2}$ centred at −1.10 V. A second electron transfer also occurs, which is reversible, with a cathodic peak at −1.39 V, an anodic peak at −1.33 V, and $E_{1/2}$ centred at −1.36 V. The potentials are not affected by change in scan rate, while the peak separation of 0.06 V for both couples indicates that both reductions are one-electron reversible processes. The $-i_c/i_a$ value is *ca.* 1 for various scan rates as well as for repeated scans indicating that the Fe^I and Fe^0 complex species are stable. This implies that the coordination polyhedron around the central metal ion in the reduced states must also be pseudotetrahedral, thus facilitating the single-step electron transfers to Fe^{II} to form the reduced Fe^I and Fe^0 species. The cyclic voltammogram is shown in Fig. 2.

The redox behaviour of the complex is unusual, particularly since other tetrahedral sterically constrained 2,9-disubstituted-1,10-phenanthroline iron(II) complexes are usually unstable and electrochemically inert. The geometry of the complex leads to the unusual stability of the reduced oxidation states.

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