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Oxidative Dehydrogenation of an Iron–Tetraazacyclotetradecatriene Complex

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Abstract

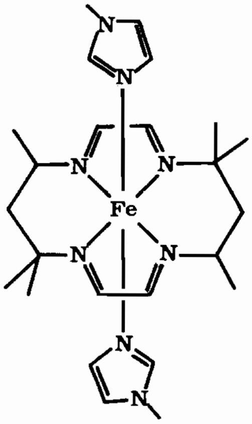
The oxidative dehydrogenation of the bis(*N*-methyl imidazole)(*meso*-5,5,7,12,12,14-hexamethyl-1 4,8 11-tetraazacyclotetradeca-1,3,8-triene)iron(II) complex, forming the corresponding 1 3,8,10-tetraene product was investigated by cyclic voltammetry, spectroelectrochemistry and stopped-flow kinetics with $[Fe(CN)_6]^{3-}$, at 25 °C, $I = 0.50$ M and pH 7–10. The results led to a mechanism consistent with a reversible one electron transfer process generating iron(III) species which lose a proton ($pK_a = 9.77$) and undergo induced electron transfer in the presence of the hexacyanoferrate(III) ion ($k = 4.2 \times 10^5$ M^{-1} s^{-1}). The intermediate precursor complex ($\lambda_{max} = 665$ nm) formed at this step, converted to the tetraene product according to a first order kinetics, with $k = 0.12$ s^{-1}.

Introduction

The oxidative dehydrogenation of coordinated amines has been frequently employed in the synthesis of conjugated macrocyclic imines [1–4]. In the case of simple amine complexes the reaction proceeds via a metal induced oxidation mechanism involving higher oxidation states [5–9]. However, in contrast with these systems, a detailed mechanistic study on the dehydrogenation of macrocyclic ligands has never been reported before.

In the present work we have investigated the kinetics of formation of the conjugated $[Fe(tetraene)(mim)_2]$ complex (**1**), starting from the corresponding triene species (tetraene = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene ligand, mim = *N*-methyl imidazole).

Our main interest was the elucidation of the several possible electron transfer pathways, as recently reported for some transition metal amine complexes [5–9].



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Experimental

The $[Fe(triene)(CH_3CN)_2](BF_4)_2$ compound and the corresponding tetraene complex were prepared according to the procedures previously published in the literature [1–3, 10, 11]. *Anal.* Calc. for $FeC_{20}N_6H_{36}B_2F_8$: C, 39.60; N, 13.85; H, 6.16. Found: C, 39.9; N, 13.4; H, 6.2%. Calc. for $FeC_{20}N_6H_{34}B_2F_8$: C, 40.87; N, 14.29; H, 5.78. Found: C, 41.2; N, 13.7; H, 5.9%. The *N*-methyl imidazole derivatives were freshly prepared by dissolving the acetonitrile complexes in an aqueous solution of the *N*-heterocyclic ligand (0.10 M) under argon atmosphere.

Cyclic voltammetry was performed with a Princeton Applied Research instrument consisting of a potentiostat and a universal programmer. A platinum working electrode was employed for the measurements, using the conventional Luggin capillary with theAg/AgCl (1 M KCl) reference electrode in a nonisothermic arrangement. A platinum wire was used as the auxiliary electrode.

The electrode spectra were recorded on a Cary 17 spectrophotometer. Spectroelectrochemical measurements were carried out with the PARC 173 potentiostat attached to a Hewlett-Packard 8451-A diode-array spectrophotometer. A three electrode system was designed for a thin layer cell of 0.028

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cm internal optical pathlength. A gold minigrid was used as transparent working electrode, in the presence of a small Ag/AgCl (1 M KCl) reference electrode and of a platinum auxiliary electrode. All the experiments were performed at 25 °C under semi-infinite diffusion conditions, as described by Kuwana and Winograd [12].

The kinetics of formation of the tetraene complex were carried out with a Durrum model D-110 stopped-flow apparatus, equipped with a Kel-F flow system. The data were obtained under pseudo-first order conditions, at 25 °C and $I = 0.50$ M in the presence of a high excess of the reactants over the macrocyclic complex.

Results and Discussion

The electronic spectrum of the bis(*N*-methyl imidazole)trieneiron(II) complex consists of a strong absorption band at 614 nm ($\epsilon = 4.0 \times 10^3$ M^{-1} cm^{-1}) associated with a metal-to-diimine charge-transfer transition [1]. This band is shifted to 692 nm in the corresponding tetraene complex ($\epsilon = 9.3 \times 10^3$ M^{-1} cm^{-1}), with a shoulder appearing at 640 nm.

The spectroelectrochemical behavior of the triene complex at pH 6 is illustrated in Fig. 1a. As we increased the applied potential from 0.2 to 0.5 V *versus* NHE, the charge-transfer band of the triene complex disappeared completely and about 20% of the starting complex was converted to the tetraene product. At pH 9, however, the dehydrogenation reaction was practically complete, as one can see in Fig. 1b.

Typical cyclic voltammograms of the triene complex, measured at 25 °C and $I = 0.50$ M NaCl, are shown in Fig. 2. Above pH 6, two successive anodic waves were observed around 0.45 and 0.8 V, corresponding to the monoelectronic oxidation of the trieneiron(II) and tetraeneiron(II) complexes, respectively. The reversibility was rather poor under alkaline conditions due to the decomposition of the oxidized products. However, in the range of pH from 5.5 to 6.0, the cyclic voltammograms of the triene complex were practically reversible, with $E_{1/2} = 0.42$ V. Only a small fraction of the starting complex was converted to the tetraene form, in agreement with the spectroelectrochemistry. Parallel measurements carried out for the tetraeneiron(II) complex at pH 5–6, resulted in reversible cyclic voltammograms with $E_{1/2} = 0.78$ V *versus* NHE and a diffusion coefficient of 5×10^{-6} cm^2 s^{-1}.

The oxidative dehydrogenation of the trieneiron(III) species forming the corresponding tetraene(II) complex should proceed within the interval of the applied potentials from 0.45 to 0.8 V, being probably responsible for the anodic shoulder around 0.7 V in the cyclic voltammograms. The yield was observed to increase with the pH, reaching a maximum around pH 9. Above this pH, however, parallel decomposition reactions led to a substantial decrease in the observed yields. The electrochemical response became very irreversible, with poorly defined waves, precluding reliable mechanistic studies.

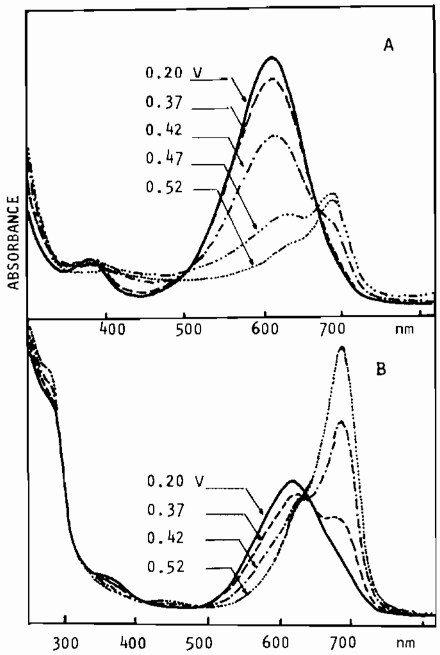


Fig. 1. Spectroelectrochemistry of the $[Fe(triene)(mim)_2]^{2+}$ complex. (a) pH 6, (b) pH 9; 25 °C and $I = 0.50$ M NaCl. Solid lines refer to the starting measurements at 0.20 V *versus* NHE.

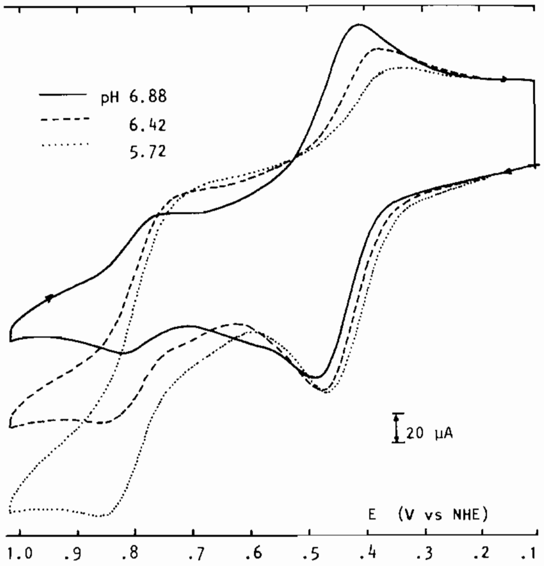


Fig. 2. Cyclic voltammograms of the $[Fe(triene)(mim)_2]^{2+}$ complex, 2.7×10^{-3} M, at several pHs, 25 °C and $I = 0.50$ M NaCl, obtained with a potential scan rate of 100 mV s^{-1}.

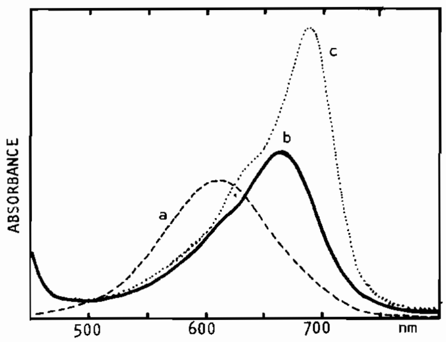


Fig. 3. Electronic spectra of (a) the starting complex $[Fe(triene)(mim)_2]^{2+}$, (b) the intermediate product *I*, (c) the final tetraene product, measured at $t = 3$ and 120 s, respectively, in the presence of $[Fe(CN)_6{}^{3-}] = 1.9 \times 10^{-4}$ M, $[Fe(CN)_6{}^{4-}] = 3.8 \times 10^{-4}$ M, pH 7.9, $I = 0.50$ M NaCl, 25 °C.

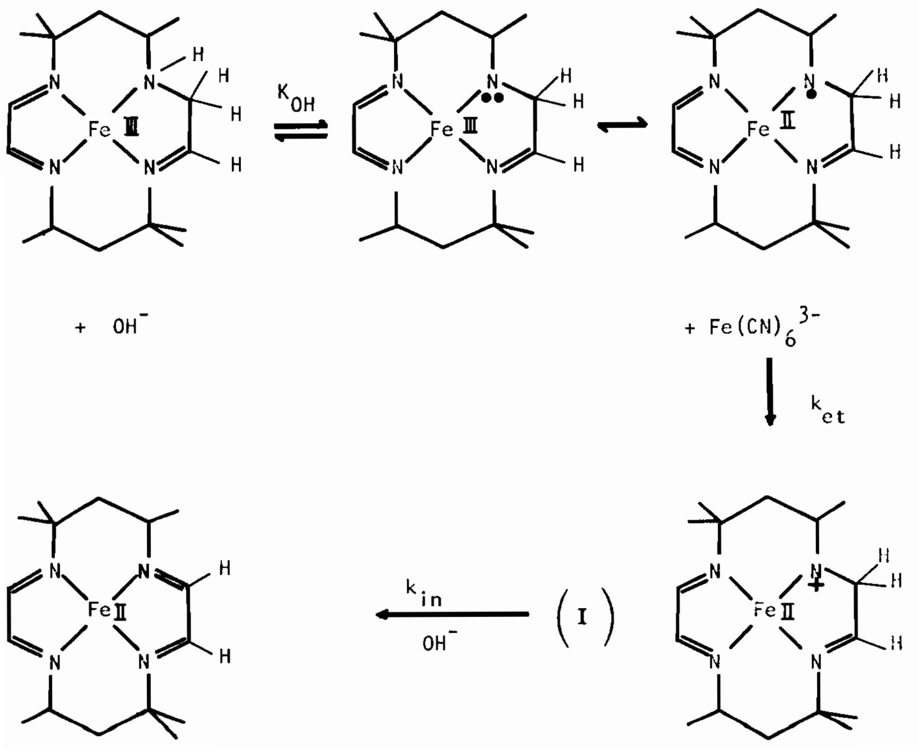
For this reason, the oxidative dehydrogenation process was investigated by an alternative approach, using the stopped-flow technique, in the presence of $[Fe(CN)_6{}^{3-}] = 0.13$–0.98 mM, $[Fe(CN)_6{}^{4-}] = 0.064$–$0.38$ mM, $[OH^-] = 1.8 \times 10^{-6}$–$4.4 \times 10^{-4}$ M, [mim] = 0.10 M at 25 °C and $I = 0.50$ M NaCl.

Under the conditions of this work, the overall reaction proceeded according to three consecutive steps. The first one was complete within the mixing time of the stopped-flow instrument (2 ms), leading to the decay of the characteristic absorption band of the triene complex at 614 nm. The second step followed a pseudo-first order kinetics, generating an intermediate product which absorbed at $\lambda_{max} = 665$ nm (Fig. 3). Then, the intermediate species converted to the tetraene complex with a half-life of about 6 s.

Based on the observed spectral changes and on the electrochemical results, we ascribed the first reaction to the reversible monoelectronic oxidation of the trieneiron(II) complex by the $[Fe(CN)_6]^{3-}$ ion.

$$[Fe(triene)(mim)_2]^{2+} + [Fe(CN)_6]^{3-} \overset{K_{ox}}{\rightleftharpoons} [Fe(triene)(mim)_2]^{3+} + [Fe(CN)_6]^{4-} \quad (1)$$

The second reaction exhibited an inverse dependence of the observed rate constants on the concentration of $[Fe(CN)_6]^{4-}$, and a non-linear dependence with respect to the concentration of the $[Fe(CN)_6]^{3-}$ and OH^- ions, as shown in Fig. 4a–c. These results can be explained in terms of a mechanism consisting of a rapid, reversible electron transfer step (eqn. (1)), followed by a deprotonation equilibrium and by a second electron transfer step, as in eqn. (2).



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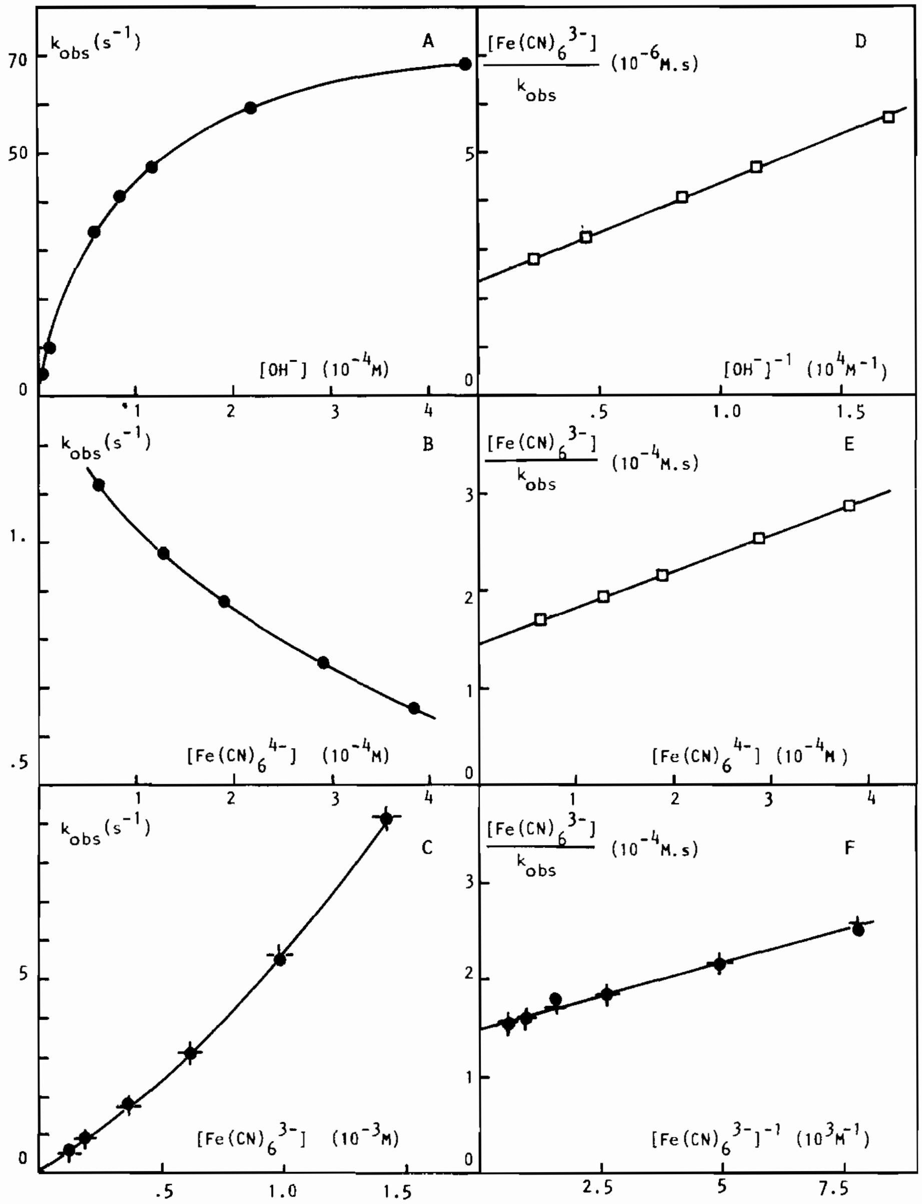

Fig. 4. Plots of the observed rate constants of oxidative dehydrogenation of the $[Fe(triene)(mim)_2]^{2+}$ complex, against the concentration of (a) OH^-, (b) $[Fe(CN)_6]^{4-}$, (c) $[Fe(CN)_6]^{3-}$; and of their corresponding reciprocals (d–f), in the presence of (a) $[Fe(CN)_6{}^{4-}] = 1.9 \times 10^{-4}$ M, $[Fe(CN)_6{}^{3-}] = 1.9 \times 10^{-4}$ M; (b) $[Fe(CN)_6{}^{3-}] = 1.9 \times 10^{-4}$ M, $[OH^-] = 9.5 \times 10^{-7}$ M; (c) $[Fe(CN)_6{}^{4-}] = 1.9 \times 10^{-4}$ M, $[OH^-] = 1.0 \times 10^{-6}$ M, at 25 °C and $I = 0.50$ M NaCl. The solid lines in plots (c) and (f) refer to the theoretical values.

The rate law for this mechanism can be expressed by

$$\frac{d[\mathbf{I}]}{[\mathbf{I}_\infty] - [\mathbf{I}]} = k_{obs}dt \qquad (3)$$

where **I** is the intermediate product, and

$$k_{obs} = \frac{k_{et}K_{OH}K_{ox}[Fe(CN)_6{}^{3-}]_2[OH^-]}{[Fe(CN)_6{}^{4-}] + K_{ox}[Fe(CN)_6{}^{3-}] + K_{ox}K_{OH}[Fe(CN)_6{}^{3-}][OH^-]}$$

The reciprocal form of eqn. (3) can be converted into the linear expression eqn. (4). The corresponding plots are shown in Fig. 4d–f.

$$\frac{[Fe(CN)_6{}^{3-}]}{k_{obs}} = \frac{1}{k_{et}} + \frac{1}{k_{et}K_{OH}[OH^-]} + \frac{[Fe(CN)_6{}^{4-}]}{k_{et}K_{OH}K_{ox}[Fe(CN)_6{}^{3-}][OH^-]} \qquad (4)$$

From the intercepts of the linear plots in Fig. 4d and 4e, k_{et} was evaluated as 4.2×10^5 M^{-1} s^{-1}, and $K_{OH} = 1.7 \times 10^4$ M^{-1} ($pK_a = 9.77$). By combining the linear and angular coefficients, the equilibrium constant for the electron transfer reaction, K_{ox}, was calculated as 2.2 in agreement with the theoretical value of 2 ± 1, based on the electrochemical data.

In the present case, only two sets of results, e.g. k_{obs} *versus* OH^-, and k_{obs} *versus* $[Fe(CN)_6{}^{4-}]$ are necessary to evaluate the individual K_{ox}, K_{OH} and k_{et} constants from eqn. (4). The third set, e.g. k_{obs} *versus* $[Fe(CN)_6{}^{3-}]$ can be used to check the internal consistency and the fitness of the mechanism. As we can see in Fig. 4c and f, the agreement between the experimental and theoretical points is excellent.

In eqn. (2), the uptake of a proton from the macrocyclic amine ligand led to a structure admitting two resonance forms. On the other hand, the oxidation of the deprotonated species produced an intermediate complex **I** presenting the characteristic charge-transfer band of the iron(II)-diimine chromophore. These observations imply that the oxidative dehydrogenation reaction proceeds via an induced electron transfer pathway, as in the cases previously reported by Taube [13].

The third reaction leading to the formation of the tetraene product, followed a typical first order kinetics for at least two half-lives. The observed rate constants (k_{in}) were practically independent on the concentration of the $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$ and OH^- ions, varying in the range of 0.11 to 0.13 s^{-1}, under the conditions employed in this work. This kind of behavior is consistent with an intramolecular process involving the species **I**.

The electronic spectrum of **I**, in Fig. 3, is intermediate between those of the 1,3,8-triene and 1,3,8,10-tetraene complexes. Based on the examples from the literature [1, 3], the observed spectra would be consistent with a species containing a diimine group and at least one isolated imine bond, such as the immediate product of the induced electron transfer step shown in eqn. (2). In this case, the third reaction would be associated with the elimination of a vicinal proton to form a diimine bond. On the other hand, the lower yields found above pH 10 would be coherent with the expected susceptibility of **I** to the nucleophilic attack of the OH^- ions. The elimination of a proton from **I**, however, could also lead to the 1,3,7,10-tetraene tautomer [3] containing one diimine group and two isolated imine bonds, with little change in the absorption spectra. This isomer has been obtained by a different route, starting from the 4,11-diene complex, in acetonitrile solutions, and is expected to be less stable than the 1,3,8,10-tetraene analog, because of the reduced number of diimine linkages [1, 4]. In this way, a parallel tautomerization process seems possible, analogous to that observed for the less conjugated 1,4,8,11-tetraene iron(II) complex [2].

The present work has elucidated many basic aspects of the mechanisms of the oxidative dehydrogenation of a typical macrocyclic amine complex [14]. The results were also consistent with those recently reported for diaminetetracyanoferrate(II) complexes [5–8]. However, in the preceding cases, a complete evaluation of the individual kinetic parameters has only been made for the (2-aminomethylpyridine)tetracyanoferrate(II) complex [6]. In spite of representing an isolate example, it is remarkable that the reported rate constant for the induced electron transfer step in this complex ($k_{et} = 6.3 \times 10^5$ M^{-1} s^{-1}), is comparable to that obtained in this work.

Acknowledgements

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References

1 J. C. Dabrowiak and D. H. Busch, *Inorg. Chem.*, *14*, 1881 (1975).
2 J. C. Dabrowiak, F. V. Lovecchio, V. L. Goedken and D. H. Busch, *J. Am. Chem. Soc.*, *94*, 5502 (1972).
3 V. L. Goedken and D. H. Busch, *J. Am. Chem. Soc.*, *94*, 7355 (1972).
4 V. L. Goedken, P. H. Merrell and D. H. Busch, *J. Am. Chem. Soc.*, *94*, 3397 (1972).
5 A. M. C. Ferreira and H. E. Toma, *J. Chem. Soc., Dalton Trans.*, 2051 (1983).
6 H. E. Toma, A. M. C. Ferreira and N. Y. M. Iha, *Nouv. J. Chim.*, *9*, 473 (1985).
7 M. Goto, M. Takeshita, N. Kanda, T. Sakai and V. L. Goedken, *Inorg. Chem.*, *24*, 582 (1985).
8 V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, 207 (1972).
9 M. J. Ridd and F. R. Keene, *J. Am. Chem. Soc.*, *103*, 5733 (1981).
10 N. F. Curtis and R. W. Hay, *J. Chem. Soc., Chem. Commun.*, 524 (1966).
11 J. C. Dabrowiak and D. H. Busch, *Inorg. Chem.*, *11*, 1979 (1972).
12 T. Kuwana and N. Winograd, in A. J. Bard (ed.), 'Electroanalytical Chemistry', Vol. 7, Marcel Dekker, New York, 1974, p. 1.
13 H. Taube, 'Electron Transfer of Complex Ions in Solution', Academic Press, New York, 1970, p. 73.
14 J. F. Endicott and B. Durham, in G. A. Melson (ed.), 'Coordination Chemistry of Macrocyclic Compounds', Plenum Press, New York, 1979, p. 432.