Contribution from the Department of Chemistry and Biochemistry,
University of Notre Dame, Notre Dame, Indiana 46556

Chiral Induction in Electron-Transfer Reactions of Iron(II) and Iron(III) Bis(oxime–imine) Complexes

Rosemary A. Marusak, Christopher Sharp, and A. Graham Lappin*

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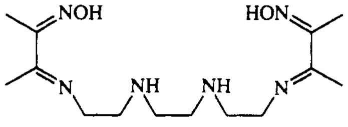
The kinetics and mechanisms of reductions of $[Co(edta)]^-$ and $[Co(phen)_3]^{3+}$ by the bis(oxime–imine) reagent $[Fe^{II}Me_2L(1)]$ ($Me_2L(1)H_2 = C_{14}H_{28}N_6O_2$) are reported over the pH range 6–9 at 0.10 M ionic strength and 25.0 °C. The reaction rates are dependent on pH, and pathways involving $[Fe^{II}Me_2L(1)]$ dominate with second-order rate constants 86.5 $M^{-1}\ s^{-1}$ for $[Co(edta)]^-$, and $8.3 \times 10^5\ M^{-1}\ s^{-1}$ for $[Co(phen)_3]^{3+}$. In the pH range 1–4, oxidation of $[Co(phen)_3]^{2+}$ by $[Fe^{III}Me_2L(1)]^+$ has been examined, and in this instance, it is the protonated form, $[Fe^{III}Me_2L(1)H]^{2+}$, with a rate constant of $1.09 \times 10^5\ M^{-1}\ s^{-1}$, which is more reactive than the unprotonated form. The reactions are outer sphere in nature, and the reactivity patterns reflect the thermodynamic driving forces for the individual pathways. The synthesis and characterization of a chiral iron(II) derivative, $[\Lambda\text{-}Fe^{II}(Me_2L(2))]$ ($Me_2L(2)H_2 = C_{16}H_{32}N_6O_2$), allows for investigations of chiral induction in these reactions and for comparisons with stereoselectivities obtained for the isostructural nickel(IV/III) oxime–imine complexes. Trends in the data indicate that where electrostatic interactions in the ion-pair precursor complex are favorable, they govern the magnitude and sense of the observed stereoselectivity. However, when the electrostatic interactions are less important, or repulsive, electronic factors may be predominant in determining the stereoselectivity.

Introduction

Over the past decade, there have been a number of studies[1-7] of stereoselectivity in outer-sphere electron-transfer reactions between metal ion complexes in solution. These observations suggest that there can be significant interactions between the reactants in outer-sphere electron-transfer reactions and have led to the deduction of models for intermediates along the reaction path. Despite this detail and the evolution of a number of structure–stereoselectivity relationships,[4-7] other features have proven much more difficult to investigate. One such potentially important factor is the role of electronic factors related to orbital overlap on stereoselectivity. Some idea of the importance of these factors is implied from the work of Geselowitz and Taube,[2] who investigated the reactions of a number of $[M(bpy)_3]^{3+}$ complexes with $[Co(edta)]^{2-}$. While the oxidants are of similar shape and configuration, the stereoselectivities appear random: a $\Delta\Delta$ preference for M = Co and Os and a $\Delta\Lambda$ preference for M = Fe and Ru are observed and show a marked lack of correlation with electronic structure. Clearly, there is as yet no satisfactory explanation for these data. One aim of this paper is to begin to decipher the importance of these factors and to discover limits for their detection.

Two of the most intensely investigated and best understood outer-sphere reactions from the point of view of stereoselectivity are the oxidations[4,5] of the cobalt(II) complexes $[Co(edta)]^{2-}$ and $[Co(phen)_3]^{2+}$ by the nickel(IV) system, $[Ni^{IV}Me_2L(1)]^{2+}$ ($Me_2L(1)H_2$ = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime, I) and its chiral analogue, $[\Lambda\text{-}Ni^{IV}Me_2L(2)]^{2+}$ ($Me_2L(2)H_2$ = (5*S*,12*S*)-3,5,12,14-tetramethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime, II). The $[Co(edta)]^{2-}$ reactions are characterized by relatively strong interactions between the reactant complexes so that it might be expected that any change in the electronic configuration of the metal-ion would have a minor effect on reaction stereoselectivity. This is borne out in the present paper where the characterization of the iron(III) and iron(II) derivatives $[Fe^{III/II}Me_2L(1)]^{+/0}$ and their chiral analogues $[\Lambda\text{-}Fe^{III/II}Me_2L(2)]^{+/0}$ are reported, together with a study of the kinetics and mechanisms of electron transfer with $[Co(edta)]^{2-}$ and $[Co(phen)_3]^{2+}$.



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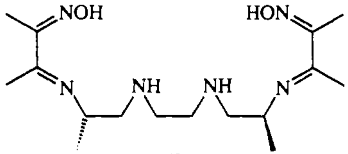

II

Experimental Section

(a) Preparation of Complexes. The preparations of $Na[Co(edta)]\cdot 4H_2O$[8] ($\epsilon_{535} = 331\ M^{-1}\ cm^{-1}$), $[Co(phen)_3][ClO_4]_3\cdot 2H_2O$[9] ($\epsilon_{280} = 6.7 \times 10^4\ M^{-1}\ cm^{-1}$), and $[Fe^{II}Me_2L(1)H_2][ClO_4]_2$[10] were carried out according to known literature procedures. Optically active $[\Lambda\text{-}Fe^{II}Me_2L(2)H_2][ClO_4]_2$ was prepared by the slow addition of 3.05 g (9 mmol) of (5*S*,12*S*)-3,5,12,14-tetramethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime[4a] ($Me_2L(2)H_2$) to a solution of 3.54 g (9 mmol) of ammonium ferrous sulfate in 60 mL of water with constant stirring. After the addition of an excess of $NaClO_4$, the reaction mixture was filtered rapidly and the product washed with portions of ice-cold ethanol[11] and dried under vacuum over anhydrous $Ca[SO_4]$ for 24 h. The iron(II) complexes were recrystallized from degassed 10^{-3} M $HClO_4$ at 60–70 °C. Solutions of the iron(II) complexes the air-sensitive at neutral pH and must be prepared under rigorous anaerobic conditions prior to each usage. The iron(III) complexes are generated by addition of a 3-fold excess of solid $K[IO_4]$ to degassed solutions of iron(II) at pH = 3 (HNO_3). The yellow iron(III) solution was used immediately after passage through a Dowex 1 anion-exchange column (7 × 3.5 cm) in the $[NO_3]^-$ form. Iron(II) and iron(III) extinction coefficients were determined by spectrophotometric titrations of the iron(III) complexes with standardized solutions of ascorbate. The extinction coefficients of the achiral

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(1) Kondo, S.; Sasaki, Y.; Saito, K. *Inorg. Chem.* **1981**, *20*, 429-433.
(2) Geselowitz, D. A.; Taube, H. *J. Am. Chem. Soc.* **1980**, *102*, 4525-4526.
(3) Kaiju, Y.; Mori, T.; Kobayashi, H. *J. Phys. Chem.* **1985**, *89*, 332-335.
(4) (a) Lappin, A. G.; Laranjeira, M. C. M.; Peacock, R. D. *Inorg. Chem.* **1983**, *22*, 786-791. (b) Martone, D. P.; Osvath, P.; Eigenbrot, C.; Laranjeira, M. C. M.; Peacock, R. D.; Lappin, A. G. *Inorg. Chem.* **1985**, *24*, 4693-4699. (c) Martone, D. P.; Osvath, P.; Lappin, A. G. *Inorg. Chem.* **1987**, *26*, 3094-3100.
(5) Lappin, A. G.; Martone, D. P.; Osvath, P.; Marusak, R. A. *Inorg. Chem.* **1988**, *27*, 1863-1868.
(6) Marusak, R. A.; Osvath, P.; Kemper, M.; Lappin, A. G. *Inorg. Chem.* **1989**, *28*, 1542-1548.
(7) Geselowitz, D. A.; Hammershoi, A.; Taube, H. *Inorg. Chem.* **1987**, *26*, 1842-1845.
(8) (a) Dwyer, F. P.; Gyarfas, E. C.; Mellor, D. J. *J. Phys. Chem.* **1955**, *59*, 296-297. (b) Osvath, P.; Lappin, A. G. *Inorg. Chem.* **1987**, *26*, 1842-1845.
(9) (a) Warren, R. M. L.; Lappin, A. G.; Mehta, B. D.; Neumann, H. M. Submitted for publication. (b) Mason, S. F.; Peart, B. J. *J. Chem. Soc., Dalton Trans.* **1973**, 949-955.
(10) (a) Mohanty, J. G.; Singh, R. P.; Chakravorty, A. *Inorg. Chem.* **1975**, *14*, 2178-2183. (b) Mohanty, J. G.; Chakravorty, A. *Inorg. Chem.* **1977**, *16*, 1561-1563.
(11) *Caution!* Washing these perchlorato species with ether as suggested in ref 10 has in one instance, led to detonation. This procedure should be carried out with extreme care.

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$[Fe^{II}Me_2L(1)H_2][ClO_4]_2$ complex were also determined by $K[IO_3]$ titration. Values of $\epsilon_{515} = 10\,500$ M^{-1} cm^{-1} and $\epsilon_{526} = 10\,000$ M^{-1} cm^{-1} were obtained for $[Fe^{II}Me_2L(1)H_2][ClO_4]_2$ and $[\Lambda\text{-}Fe^{II}Me_2L(2)H_2][ClO_4]_2$, respectively.

(b) Cyclic Voltammetry Studies. Cyclic voltammetry measurements for the $[Fe^{II}Me_2L(1)]^{3+/2+}$ couple were carried out on 10^{-3} M solutions of the iron(II) complex under an atmosphere of argon by using apparatus described previously.[5] The pH range from 1.4 to 9.3 was examined in the presence of 0.01 M buffer, at 0.10 M ionic strength ($NaNO_3$) and 25.0 ± 0.1 °C.

(c) pH Titrations of $[Fe^{II}Me_2L(1)H_2][ClO_4]_2$. Titrations of $[Fe^{II}Me_2L(1)H_2][ClO_4]_2$ (15 mL, 10^{-3} M) with standardized carbonate-free, degassed NaOH (0.05 M) were carried out under an atmosphere of argon at 0.10 M ionic strength ($NaNO_3$) and 25.0 ± 0.1 °C by using a Beckman Selectlon 2000 ion analyzer. The hydrogen ion concentrations were evaluated with the empirical relationship pH = $-\log_{10}$ $[H^+]$ + 0.02. Acidity constants were determined by standard least-squares fits obtained by the Speakman method.[12]

(d) Kinetic Measurements. The kinetics of the reduction of $[Fe(III)L]^+$ by $[Co(phen)_3]^{2+}$ and the oxidation of the corresponding iron(II) species by $[Co(phen)_3]^{3+}$ and $[Co(edta)]^-$ were carried out under anaerobic conditions, in the presence of 0.01 M buffer, at 0.10 M ionic strength ($Na[NO_3]$ unless noted otherwise) and at 25.0 ± 0.1 °C. Solution preparation for $[Co(phen)_3]^{2+}$ as reductant has been described previously.[5] The kinetics were carried out under pseudo-first-order conditions with, in all cases, the iron complex as the limiting reagent ($\leq 6 \times 10^{-5}$ M). The pH-dependence studies encompassed ranges from 1 to 5 for the $[Co(phen)_3]^{2+}$ reduction reaction and from 6 to 8 for the oxidation reactions with $[Co(edta)]^-$ and $[Co(phen)_3]^{3+}$. All reactions were monitored at approximately 515 nm where the decay and formation of the iron(II) species are readily observed. The reactions with the $[Co(phen)_3]^{3+/2+}$ couples were monitored on a Durrum D-110 stopped-flow spectrophotometer while the reaction with $[Co(edta)]^-$ was amenable to conventional analysis on a Varian DMS 100 UV/visible spectrophotometer.

The base hydrolysis of the iron(III) complex was monitored at 540 nm where the resulting product absorbs. Below pH ~ 9 the reaction is very slow, and competing reactions with trace amounts of oxygen complicate the reaction; therefore, most of the data were obtained over the pH range from 9.8 to 12.3. The base hydrolysis reaction is first order in the iron(III) complex concentration.

Rate constants are collected in Tables SI–SIV, available as supplementary material.

(e) Stereoselectivity Studies. Stereoselectivity experiments involving the reduction of $[\Lambda\text{-}Fe^{III}Me_2L(2)H]^{2+}$ by $[Co(phen)_3]^{2+}$ were carried out in 0.10 M HNO_3 in the presence of an excess of the reductant. Under these conditions, the rate for the electron-transfer process is much greater than the rate of product racemization, and the stereoselectivity was determined by measuring the decay in circular dichroism signal of the optically active cobalt(III) product at 405 nm. At this wavelength and over the time scale of the measurements, there is an unchanging circular dichroism signal from the iron(II) product that must be taken into account. Stereoselectivities in the reduction of $[\Lambda\text{-}Fe^{III}Me_2L(2)]^+$ by $[Co(edta)]^{2-}$ were examined briefly in 0.10 M nitrate media at pH ~ 3, by mixing 10 mL of 0.10 M $[Co(edta)]^{2-}$ with 100 mL of 10^{-4} M $[\Lambda\text{-}Fe^{III}Me_2L(2)]^+$. The reacted mixture was diluted (×10), loaded onto a Dowex 1 anion-exchange column (1 × 15 cm, NO_3^- form), and washed with water, 0.01 M HCl, and 0.05 M HCl, and the product, $[Co(edta)(H_2O)]^-$, was removed with 0.5 M HCl. Stereoselectivities in the oxidation of $[\Lambda\text{-}Fe^{II}Me_2L(2)]$ by $[Co(edta)]^-$ were determined from optical activity produced in an excess of the oxidant in degassed buffer at a variety of pH values and at 0.10 M ionic strength. After reaction, solutions were passed through a Dowex cation-exchange column (1 × 5 cm) to remove the optically active iron(III) product. Circular dichroism spectra were measured on an Aviv Model 60DS circular dichroism spectropolarimeter (Aviv Associates, Lakewood, NJ).

Results and Discussion

(a) Preparation and Characterization of $[Fe^{II}Me_2L(1)H_2]^{2+}$.

Preparation and characterization of the iron(II) complex, $[Fe^{II}Me_2L(1)H_2]^{2+}$, has been reported previously by Chakravorty and co-workers.[10] However, the conditions used in the present paper differ from those reported in the earlier work, and preliminary studies indicated significant discrepancies in values for some key parameters associated with the complex. The complex is diamagnetic, and the extinction coefficient of $[Fe^{II}Me_2L(1)H_2]^{2+}$ at the visible maximum, 515 nm, has been redetermined to be $10\,500$ M^{-1} cm^{-1} rather than 6300 M^{-1} cm^{-1} as reported previously.[10] Deprotonation with dissociation constants (4.88 ± 0.5) × 10^{-6} M and (3.8 ± 0.9) × 10^{-9} M results in shifts in the visible maximum to 525 and 535 nm respectively. In the previous work,[10] the dissociation constants were determined to be 1.78 × 10^{-5} and 3.55 × 10^{-8} M, but ionic strength apparently was not controlled.

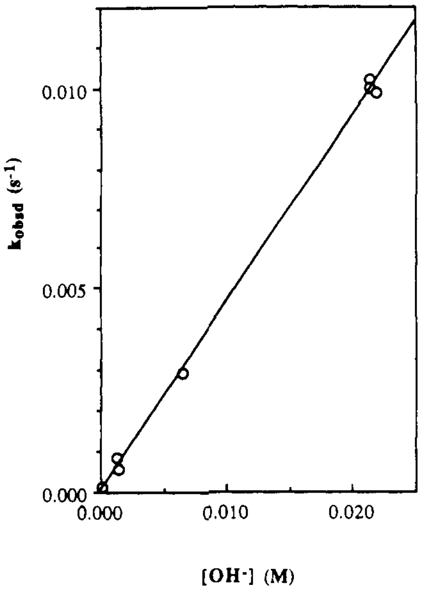

Figure 1. Plot of $k_{obsd}(1)$ against $[OH^-]$ for the base-catalyzed hydrolysis reaction of $[Fe^{III}Me_2L(1)]^+$ at 25.0 °C and 0.10 M ($NaNO_3$) ionic strength.

Periodate oxidation of the iron(II) complex results in formation of $[Fe^{III}Me_2L(1)]^+$, which has a visible absorption maximum at 309 nm ($\epsilon_{309} = 10\,000$ M^{-1} cm^{-1}), a shoulder at 400 nm (ϵ_{400} = 4300 M^{-1} cm^{-1}), and a well-defined isosbestic for the redox process at 428 nm. This species was not isolated as a solid. Above pH 8, $[Fe^{III}Me_2L(1)]^+$ is susceptible to slow hydrolysis to give an uncharacterized, air-sensitive product that has an absorption maximum at 540 nm. The hydrolysis reaction is first-order in $[[Fe^{III}Me_2L(1)]^+]$ and is catalyzed by base (Figure 1), and the observed rate constants obey the relationship in eq 1, where k_{H_2O}

$$k_{obsd} = k_{H_2O} + k_{OH}[OH^-] \qquad (1)$$

= 5.3 × 10^{-5} s^{-1} and k_{OH} = 0.46 M^{-1} s^{-1}. On exposure to oxygen, this hydrolysis product reacts to give the blue complex quoted by Chakravorty and co-workers,[10] absorbing at 580 nm.

The reduction potential of $[Fe^{III}Me_2L(1)]^+$ has been examined previously[10] in 0.10 M NaCl solutions and shows a strong dependence on pH consistent with the presence of all three protonated forms of the reduced complex and $[Fe^{III}Me_2L(1)]^+$ as the sole oxidized form over the pH range 1–9. The same general behavior describes the present work in nitrate media although the value of the potentials and acidity constants differ. The data are presented in diagrammatical form in Figure 2. Below pH 5.5, where $[Fe^{II}Me_2L(1)H_2]^{2+}$ is the dominant reduced species, the potential decreases by 120 ± 5 mV for each pH unit, indicative of a one-electron–two-proton process, eq 2, with a potential of 0.76

$$[Fe^{III}Me_2L(1)]^+ + e^- + 2H^+ \rightleftharpoons [Fe^{II}Me_2L(1)H_2]^{2+} \qquad (2)$$

V (vs NHE). Between pH 5.5 and 8.0, $[Fe^{II}Me_2L(1)H]^+$ is the dominant reduced complex, and the dependence of the potential on pH is 60 mV/unit, eq 3, with a formal potential of 0.51 V (vs

$$[Fe^{III}Me_2L(1)]^+ + e^- + H^+ \rightleftharpoons [Fe^{II}Me_2L(1)H]^+ \qquad (3)$$

$$[Fe^{III}Me_2L(1)]^+ + e^- \rightleftharpoons [Fe^{II}Me_2L(1)] \qquad (4)$$

NHE). Above pH 8.5, the potential is pH independent, eq 4, with a value of 0.10 V (vs NHE). The values of the acidity constants for $[Fe^{II}Me_2(1)H_2]^{2+}$ derived from the cyclic voltammetry study (pK_{h1}^{II} = 5.4, pK_{h2}^{II} = 8.3) are in reasonable agreement with those from the pH titration (pK_{h1}^{II} = 5.3, pK_{h2}^{II} = 8.5).

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(12) Speakman, J. C. *J. Chem. Soc.* **1940**, 855–859.

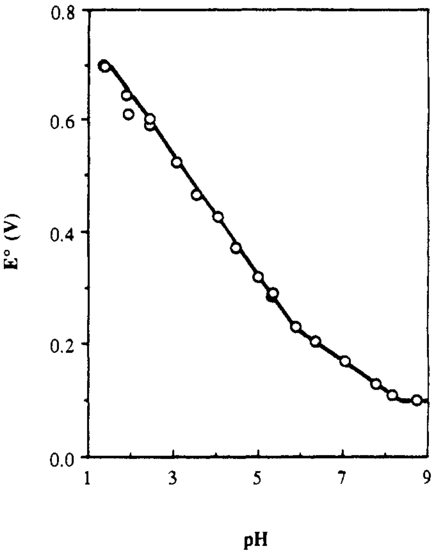

Figure 2. Plot of reduction potential (vs. NHE), $E°$ (V), against pH for $[Fe^{II}Me_2L(1)]$ at 0.10 M ($NaNO_3$) ionic strength and 25.0 °C.

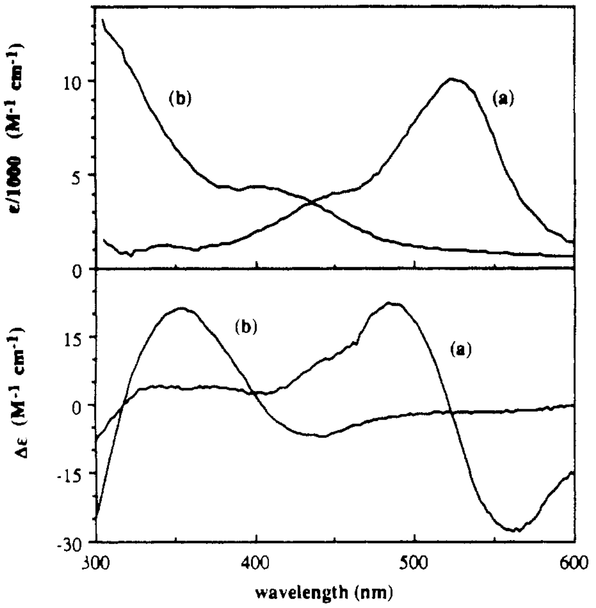

Figure 3. Absorption and circular dichroism spectra of the $[\Lambda\text{-}Fe^{II}Me_2L(2)H_2]^{2+}$ (a) and $[\Lambda\text{-}Fe^{III}Me_2L(2)]^{+}$ (b) species in a 10^{-3} M HNO_3 solution.

(b) Preparation and Characterization of $[Fe^{II}Me_2L(2)H_2]^{2+}$. The complex $[Fe^{II}Me_2L(2)H_2]^{2+}$ was prepared in a manner analogous to $[Fe^{II}Me_2L(1)H_2]^{2+}$ with use of the optically active ligand $Me_2L(2)H_2$. It was assumed that, as is the case[4b] with $[Ni^{II}Me_2L(2)H_2]^{2+}$, the single diastereomer $[\Lambda\text{-}Fe^{II}Me_2L(2)H_2]^{2+}$ is produced, thus affording a chiral analogue of the redox reagent. The circular dichroism and UV–visible spectroscopic characteristics of $[Fe^{II}Me_2L(2)H_2]^{2+}$ and its oxidized form $[Fe^{III}Me_2L(2)]^{+}$ are presented in Figure 3. This complex was used exclusively in stereoselectivity studies.

(c) Oxidation of $[Fe^{II}Me_2L(1)]$ by $[Co(edta)]^-$. The stoichiometric oxidation of $[Fe^{II}Me_2L(1)]$ by $[Co(edta)]^-$ ($E° = 0.37$ V)[13] is thermodynamically favored above pH = 4. Under conditions of excess oxidant, the reaction rate shows a first-order dependence on both $[[Fe^{II}Me_2L(1)]]_T$ and $[cobalt(III)]_T$ concentrations, and the second-order rate constant, k_{so}, has a pH dependence (Figure 4a) that can be described by eq 5, where $k_7 = 0.6 \pm 0.2$ M^{-1} s^{-1},

$$k_{so} = (k_7[H^+] + k_8K_{h2}^{II})/([H^+] + K_{h2}^{II}) \quad (5)$$

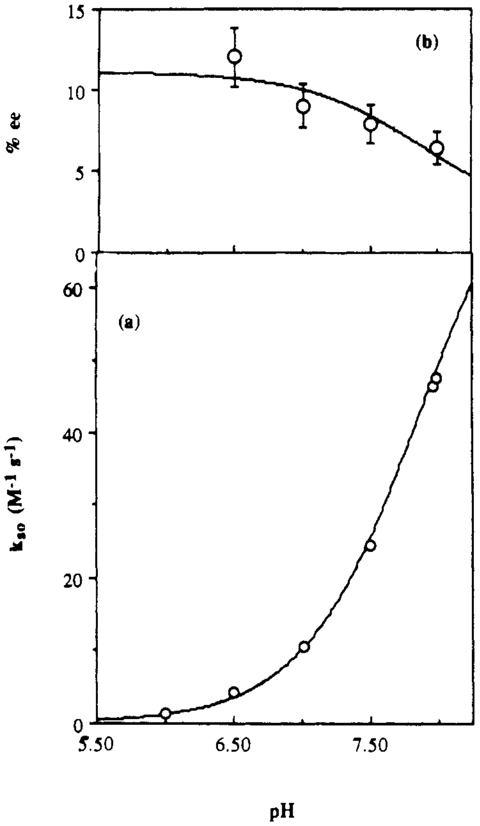

Figure 4. (a) Plot of the second-order rate constant $k_{so}(5)$ against pH for the oxidation of $[Fe^{II}Me_2L(1)]$ by $[Co(edta)]^-$ at 25 °C and 0.10 M ($NaClO_4$) ionic strength. (b) Plot of % enantiomeric excess against pH for the oxidation of $[\Lambda\text{-}Fe^{II}Me_2L(2)]$ by $[Co(edta)]^-$ at 25 °C and 0.10 M ($NaClO_4$) ionic strength. Stereoselectivity values are extrapolated to large excess $[[Co(edta)]^-]$ as indicated in text.

$k_8 = 86.5 \pm 0.9$ M^{-1} s^{-1}, and $K_{h2}^{II} = (1.3 \pm 0.4) \times 10^{-8}$ M at 25.0 °C and 0.10 M ionic strength. The corresponding mechanism, eqs 6–8, reveals that the unprotonated iron(II) complex,

$$[Fe^{II}Me_2L(1)H]^+ \rightleftharpoons [Fe^{II}Me_2L(1)] + H^+ \quad K_{h2}^{II} \quad (6)$$

$$[Fe^{II}Me_2L(1)H]^+ + [Co(edta)]^- \rightarrow [Fe^{III}Me_2L(1)]^+ + [Co(edta)]^{2-} + H^+ \quad k_7 \quad (7)$$

$$[Fe^{II}Me_2L(1)] + [Co(edta)]^- \rightarrow [Fe^{III}Me_2L(1)]^+ + [Co(edta)]^{2-} \quad k_8 \quad (8)$$

$[Fe^{II}Me_2L(1)]$, is much more reactive than its protonated form. The acidity constant for the iron(II) complex determined from this kinetic study is a factor of 3 larger than is obtained from the more reliable thermodynamic studies. While this discrepancy is outside the limits of the calculated errors, it does not significantly affect the interpretation of the mechanism.

Although the rates of the electron-transfer reactions are modest, the reaction is taking place between two complexes where the central ions have the inert low-spin d^6 configuration. Substitution reactions of $[Co(edta)]^-$ are much slower than the electron-transfer rates, and comparable sexidentate iron(II) oxime complexes are reported to have substitution rates on the order of 10^{-5} M^{-1} s^{-1}.[14] It thus seems likely that the reactions are outer sphere in nature.

Stereoselectivity in the reduction of $[Co(edta)]^-$ by these iron(II) complexes was investigated by using the chiral analogue $[\Lambda\text{-}Fe^{II}Me_2L(2)]$. Racemization of $[Co(edta)]^-$ is slow compared with the electron-transfer process, and so determinations were made by measuring the induction of optical activity in an unreacted excess of the oxidant over the course of the reaction. The stereoselectivity measured by this method is dependent on the ratio

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(13) Ogino, H.; Ogino, K. *Inorg. Chem.* **1983**, *22*, 2208–2211.

(14) Gardner, E. R.; Mekhail, F. M.; Burgess, J. *Int. J. Chem. Kinet.* **1974**, *6*, 133–142.

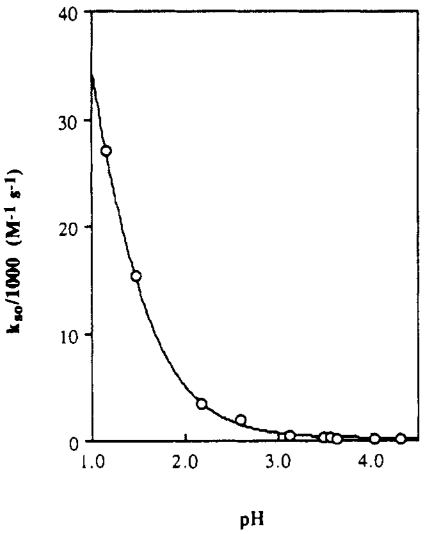

Figure 5. Plot of the second-order rate constant $k_{so}(11)$ against pH for the reduction of $[\mathrm{Fe^{III}Me_2L(1)}]^+$ by $[\mathrm{Co(phen)_3}]^{2+}$ at 25 °C and 0.10 M ($NaNO_3$) ionic strength.

of the two reactants and a corrected value, independent of concentration, is obtained by extrapolation to conditions of very large excess of $[\mathrm{Co(edta)}]^-$. This extrapolation was made with the use of data at a variety of different ratios of oxidant to reductant.

The stereoselectivity in the reaction is dependent on pH as shown in Figure 4b, decreasing with increasing pH. The limiting stereoselectivities are 11 ± 1% ΔΛ for the reaction of $[\Lambda\text{-}\mathrm{Fe^{II}Me_2L(2)H}]^+$, eq 7, and 2 ± 4% ΔΛ for the reaction of $[\Lambda\text{-}\mathrm{Fe^{II}Me_2L(2)}]$, eq 8, for a pK_a of 7.9. Clearly, the errors on this latter value do not allow meaningful discussion except that the stereoselectivity is smaller than the value for $[\Lambda\text{-}\mathrm{Fe^{II}Me_2L(2)H}]^+$. Below pH 4, $[\mathrm{Fe^{III}Me_2L(1)}]^+$ will oxidize $[\mathrm{Co(edta)}]^{2-}$, and this would appear to afford an opportunity to examine the stereoselectivity for eq 7 in the reverse direction. While no detailed kinetic studies were carried out for the reaction in this direction, the observed rate is an order of magnitude faster than expected on the basis of the reduction potentials and is comparable with the rate of hydrolysis of the iron(III) complex in neutral solution. Significantly, the cobalt(III) reaction product is identified as $[\mathrm{Co(edta)H_2O}]^-$, indicating that the observed process is not the reverse of the reaction in eq 7 but is most likely an inner-sphere process given by the sequence, in eqs 9 and 10, although an

$$[\mathrm{Fe^{III}Me_2L(1)}]^+ \rightarrow [\mathrm{Fe^{III}Me_2L(1)OH}] + \mathrm{H^+} \qquad (9)$$

$$[\mathrm{Fe^{III}Me_2L(1)OH}] + [\mathrm{Co(edta)}]^{2-} + \mathrm{H^+} \rightarrow [\mathrm{Fe^{II}Me_2L(1)}] + [\mathrm{Co(edta)H_2O}]^- \qquad (10)$$

outer-sphere oxidation of $[\mathrm{Co(edta)(H_2O)}]^{2-}$ cannot be ruled out. This reaction does exhibit stereoselectivity, 2.1 ± 1% ΛΛ, under conditions with pH 3.8 and 0.10 M ionic strength.

(d) Reduction of $[\mathrm{Fe^{III}Me_2L(1)}]^+$ by $[\mathrm{Co(phen)_3}]^{2+}$. Below pH 4, $[\mathrm{Fe^{III}Me_2L(1)}]^+$ is capable of oxidizing $[\mathrm{Co(phen)_3}]^{2+}$ (E° = 0.36 V).[9] The reaction was examined under pseudo-first-order conditions with an excess of $[[\mathrm{Co(phen)_3}]^{2+}]$ and is first order in both reactants. The second-order rate constant increases strongly with decreasing pH. The reductant is labile and requires a sufficient excess of free phen ligand for quantitative formation. Above pH = 3, and with a 1.0×10^{-3} M excess of the phen ligand, formation of the tris complex is almost quantitative (>90%).[15] A correction to the concentration was applied to take account of discrepancies, and this involves the not unreasonable assumption that $[\mathrm{Co(phen)_3}]^{2+}$ is the sole reactive reductant. Below pH 3, this correction is less reliable since $[\mathrm{Co(phen)_3}]^{2+}$ is increasingly thermodynamically unstable as the pH is lowered. However, the rate of dissociation of $[\mathrm{Co(phen)_3}]^{2+}$ is relatively slow, 0.16 s^{-1},[16] and conditions were chosen such that neutral solutions of $[\mathrm{Co(phen)_3}]^{2+}$ are mixed with acidic solutions of the iron(III) complex and the resulting electron transfer is an order of magnitude faster than the competing ligand dissociation. Thus, the electron-transfer rate can be determined from the initial part of the reaction trace. The results of these experiements are shown in Figure 5, in which the pH dependence of the second-order rate constant, k_{so}, is described by eq 11, with k_{13} = (1.09 ± 0.01) × 10^5 M^{-1} s^{-1} and k_{14}

$$k_{so} = (k_{13}[\mathrm{H^+}] + k_{14}K_h^{III})/([\mathrm{H^+}] + K_h^{III}) \qquad (11)$$

= 150 ± 1500 M^{-1} s^{-1}. The corresponding mechanism is given in eqs 12–14. A value of 0.22 M for the acid dissociation constant

$$[\mathrm{Fe^{III}Me_2L(1)H}]^{2+} \rightleftharpoons [\mathrm{Fe^{III}Me_2L(1)}]^+ + \mathrm{H^+} \quad K_h^{III} \qquad (12)$$

$$[\mathrm{Fe^{III}Me_2L(1)H}]^{2+} + [\mathrm{Co(phen)_3}]^{2+} \rightarrow [\mathrm{Fe^{II}Me_2L(1)H}]^+ + [\mathrm{Co(phen)_3}]^{3+} \quad k_{13} \qquad (13)$$

$$[\mathrm{Fe^{III}Me_2L(1)}]^+ + [\mathrm{Co(phen)_3}]^{2+} \rightarrow [\mathrm{Fe^{II}Me_2L(1)}] + [\mathrm{Co(phen)_3}]^{3+} \quad k_{14} \qquad (14)$$

of the monoprotonated form of the iron(III) complex is evaluated. This is consistent with the cyclic voltammetry data where it was concluded that there is no evidence for protonation of the iron(III) complex above pH 1. It is interesting to note that while the first protonation constants of $[\mathrm{Fe^{II}Me_2L(1)}]$ (8.49) and $[\mathrm{Ni^{II}Me_2L(1)}]$ (7.80) do not differ dramatically, the corresponding values for the trivalent complexes differ by almost 4 orders of magnitude and may reflect the additional driving force for distortion in low-spin d^7 nickel(III). The reduction potential of the protonated complex, $[\mathrm{Fe^{III}Me_2L(1)H}]^{2+}$, can be calculated as 0.57 V.

Stereoselectivity in the reduction of $[\Lambda\text{-}\mathrm{Fe^{III}Me_2L(2)H}]^{2+}$ by $[\mathrm{Co(phen)_3}]^{2+}$ can be investigated at low pH where the rate of the electron-transfer process exceeds the rate of dissociation of the $[\mathrm{Co(phen)_3}]^{2+}$ complex provided the reductant is in excess. The low pH conditions that cause dissociation of the labile cobalt(II) complex serve to slow the subsequent self-exchange catalyzed racemization of the $[\mathrm{Co(phen)_3}]^{3+}$ product. The stereoselectivity in the reaction is calculated to be 4% ΛΛ.

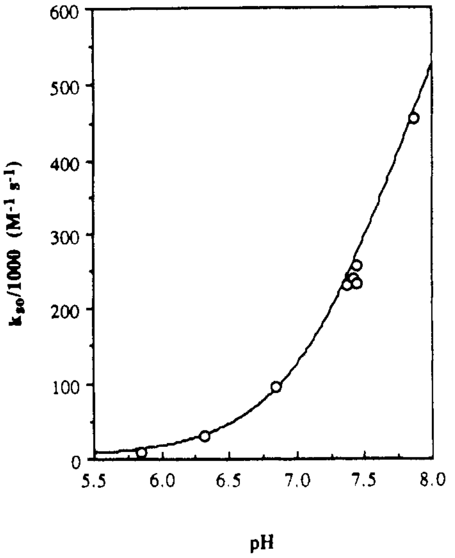

Figure 6. Plot of the second-order rate constant $k_{so}(15)$ against pH for the oxidation of $[\mathrm{Fe^{II}Me_2L(1)}]$ by $[\mathrm{Co(phen)_3}]^{3+}$ at 25 °C and 0.10 M ($NaNO_3$) ionic strength.

(e) Oxidation of $[\mathrm{Fe^{II}Me_2L(1)}]$ by $[\mathrm{Co(phen)_3}]^{3+}$. Above pH 5, $[\mathrm{Co(phen)_3}]^{3+}$ will oxidize the iron(II) complex $[\mathrm{Fe^{II}Me_2L(1)}]$. The reaction is first-order in both reagents and the second-order rate constants, k_{so}, show a pH dependence (Figure 6) consistent with eq 15, with best-fit parameters k_{-13} = (3 ± 3) × 10^3 M^{-1}

$$k_{so} = (k_{-13}[\mathrm{H^+}] + k_{-14}K_{h2}^{II})/([\mathrm{H^+}] + K_{h2}^{II}) \qquad (15)$$

s^{-1}, k_{-14} = (8.3 ± 0.1) × 10^5 M^{-1} s^{-1}, and K_{h2}^{II} = (1.7 ± 0.4) × 10^{-8} M at 25.0 °C and 0.10 M ionic strength. As with the

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[15] McBryde, W. A. E. *IUPAC Chem. Data Ser.* **1978**, *17*, 18–36.

[16] Ellis, P.; Wilkins, R. G. *J. Chem. Soc.* **1959**, 299–304.

Table I. Observed and Calculated Rate Constants for the Electron-Transfer Reactions between the Iron(II) and Iron(III) Complexes $[\mathrm{Fe^{III/II}Me_2L(1)}]^{+/0}$ and Cobalt Reagents at 25.0 °C and 0.10 M Ionic Strength

oxidant	reductant	k_{12}^{obsd}, $\mathrm{M^{-1}\,s^{-1}}$	$k_{12}^{\mathrm{calcd}\,a}$, $\mathrm{M^{-1}\,s^{-1}}$
$[\mathrm{Co(edta)}]^-$	$[\mathrm{Fe^{II}Me_2L(1)}]$	86.5	289
$[\mathrm{Co(edta)}]^-$	$[\mathrm{Fe^{II}Me_2L(1)H}]^+$	≤ 0.6	0.053
$[\mathrm{Co(phen)_3}]^{3+}$	$[\mathrm{Fe^{II}Me_2L(1)}]$	8.3×10^5	5.7×10^5
$[\mathrm{Co(phen)_3}]^{3+}$	$[\mathrm{Fe^{II}(Me_2L(1)H}]^+$	$\leq 3 \times 10^3$	309
$[\mathrm{Fe^{III}Me_2L(1)H}]^{2+}$	$[\mathrm{Co(phen)_3}]^{2+}$	1.09×10^5	1.1×10^5
$[\mathrm{Fe^{III}Me_2L(1)}]^+$	$[\mathrm{Co(phen)_3}]^{2+}$	≤ 150	23

[a] Values used for Marcus calculations include the following: k_{11}-($[\mathrm{Co(edta)}]^{-/2-}$) = 4×10^{-7} $\mathrm{M^{-1}\,s^{-1}}$, r = 5 Å; k_{11}($[\mathrm{Co(phen)_3}]^{3+/2+}$) = 12 $\mathrm{M^{-1}\,s^{-1}}$, r = 7 Å. For all iron(II/III) complexes, r = 5.5 Å. Other parameters are given in the text.

Table II. Stereoselectivities in the Reactions of Oxime–Imine Complexes with Cobalt Reagents at 0.10 M Ionic Strength and 25.0 °C

		stereo-selectivity		
oxidant	reductant	% ee[a]	type	ref
$[\mathrm{Co(edta)}]^-$	$[\Lambda\text{-}\mathrm{Fe^{II}Me_2L(2)}]^b$	2	ΔΛ	this work
$[\mathrm{Co(edta)}]^-$	$[\Lambda\text{-}\mathrm{Fe^{II}Me_2L(2)H}]^+$	11	ΔΛ	this work
$[\Lambda\text{-}\mathrm{Fe^{III}Me_2L(2)OH}]$	$[\mathrm{Co(edta)}]^{2-}$	2	ΛΛ	this work
$[\Lambda\text{-}\mathrm{Ni^{IV}Me_2L(2)}]^{2+}$	$[\mathrm{Co(edta)}]^{2-}$	11	ΔΛ	4a
$[\Lambda\text{-}\mathrm{Ni^{III}Me_2L(2)H}]^{2+}$	$[\mathrm{Co(edta)}]^{2-}$	10	ΔΛ	4a
$[\Lambda\text{-}\mathrm{Ni^{IV}Me_2L(2)}]^{2+}$	$[\mathrm{Co(phen)_3}]^{2+}$	19	ΛΛ	5
$[\Lambda\text{-}\mathrm{Fe^{III}Me_2L(2)H}]^{2+}$	$[\mathrm{Co(phen)_3}]^{2+}$	4	ΛΛ	this work

[a] Stereoselectivities are reported as enantiomeric excess. [b] $\mathrm{Me_2L(2)H_2}$ = (5*S*,12*S*)-3,5,12,14-tetramethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime.

reduction of $[\mathrm{Co(edta)}]^-$, the unprotonated iron(II) complex is significantly more reactive than its protonated form, and in this case also, it can be argued that the reactions are likely to be outer sphere in nature.

(f) Application of Marcus Theory. Reductions of the substitution-inert cobalt(III) complexes by the iron(II) complexes $[\mathrm{Fe^{III/II}Me_2L(1)}]^{+/0}$ and $[\mathrm{Fe^{III/II}Me_2L(1)H}]^{2+/+}$ are likely to be outer-sphere processes and as such may be described with use of the Marcus expression,[17,18] eqs 16 and 17, where ΔG^{**} is the

$$\Delta G_{12}^{**} = \tfrac{1}{2}(\Delta G_{11}^{**} + \Delta G_{22}^{**} + \Delta G^\circ(1 + \alpha^{**})) \quad (16)$$

$$\alpha^{**} = \Delta G^\circ / 4(\Delta G_{11}^{**} + \Delta G_{22}^{**}) \quad (17)$$

electrostatically corrected free energy of activation and ΔG° is the electrostatically corrected free energy for the reaction. Observed rate constants are collected in Table I, where they can be compared with rate constants calculated by using eqs 16 and 17. Self-exchange rates for the $[\mathrm{Fe^{III/II}Me_2L(1)}]^{+/0}$ and $[\mathrm{Fe^{III/II}Me_2L(1)H}]^{2+/+}$ complexes are calculated to be 1×10^6 $\mathrm{M^{-1}\,s^{-1}}$ and 4×10^5 $\mathrm{M^{-1}\,s^{-1}}$, respectively, for the conditions of the study. There is fairly consistent agreement between the observed and calculated data, lending credence to outer-sphere mechanisms. The self-exchange rates for the d^5/d^6 iron(III)/(II) are significantly faster than those for the isostructural complexes of d^6/d^7 nickel(IV)/nickel(III), 2.4×10^4 $\mathrm{M^{-1}\,s^{-1}}$, and d^7/d^8 nickel(III)/nickel(II), 2×10^3 $\mathrm{M^{-1}\,s^{-1}}$.[19] Interestingly, the effect of protonation on the rate constant, a factor of 5 reduction, is comparable in both the iron(III)/iron(II) and nickel(III)/nickel(II) systems.

(g) Stereoselectivity Results. In Table II, the stereoselectivity results obtained in this paper are summarized together with those for the corresponding reactions of the isostructural nickel(IV) and nickel(III) complexes. In the reactions of the cationic oxime–imine complexes with $[\mathrm{Co(edta)}]^-$ or $[\mathrm{Co(edta)}]^{2-}$ where there are strong favorable electrostatic interactions and the structure of the electron transfer precursor complex is well-defined,[4] the stereoselectivity appears to be insensitive to whether the electron transfer is $d^6 \rightarrow d^6$, $d^7 \rightarrow d^6$, or $d^7 \rightarrow d^7$. However, with the neutral iron(II) complex, $[\mathrm{Fe^{II}Me_2L(2)}]$, as reductant for $[\mathrm{Co(edta)}]^-$ there is a marked reduction in the stereoselectivity, presumably as a result of reduced electrostatic interactions in the precursor complex. Interestingly, for the inner-sphere reaction between $[\mathrm{Fe^{III}Me_2L(2)(H_2O)}]^+$ and $[\mathrm{Co(edta)}]^{2-}$, the stereoselectivity is comparable in magnitude but in the opposite sense.

Whereas stereoselectivities in the oxidations of $[\mathrm{Co(phen)_3}]^{2+}$ by both $[\Lambda\text{-}\mathrm{Ni^{IV}Me_2L(2)}]^{2+}$ and $[\Lambda\text{-}\mathrm{Fe^{III}Me_2L(2)H}]^{2+}$ are in the same sense, the magnitudes of the effects differ significantly, by a factor of 5. In this instance, the reactant pairs are similarly charged and there is no possibility of stabilization of the electron-transfer precursor complex by electrostatic forces. The difference in stereoselectivity may be a manifestation of an electronic effect.

In summary, changing the nature of the metal ion center appears to have a much larger effect on the electron-transfer stereoselectivity in systems where there is no significant stabilization of the electron-transfer precursor complex. It is noteworthy that although electrostatic interactions should be strong in reactions of $[\mathrm{M(bpy)_3}]^{3+}$ with $[\mathrm{Co(edta)}]^{2-}$, the high symmetry of the oxidant precludes formation of a unique precursor structure and this may allow domination of the stereoselectivity by electronic effects.

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Supplementary Material Available: Listings of observed rate constants for the base hydrolysis and electron-transfer reactions (Table SI–SIV) (3 pages). Ordering information is given on any current masthead page.

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(17) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155–196.

(18) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437–480.

(19) (a) Lappin, A. G.; Martone, D. P.; Osvath, P. *Inorg. Chem.* **1985**, *24*, 4187–4191. (b) Marusak, R. A.; Sharp, C.; Lappin, A. G. To be submitted for publication.