Affinities of Imidazolate and Imidazole Ligands for Pentacyanoiron(III)

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Abstract: Association constants for the reaction $(CN)_5FeH_2O^{2-} + L^n \rightleftharpoons (CN)_5FeL^{n-2} + H_2O$ have been measured in μ = 1.00 NaCl for L^n = imidazole (Him), imidazolate (im^-), and 1-methylimidazole (1-CH_3im). The thermodynamic parameters are as follows (L, K_f(298 K), $\Delta H°$, $\Delta S°$): (Him, 3.4×10^5 M^{-1}, -15.8 ± 0.6 kcal/mol, -27 ± 2 eu); (1-CH_3im, 3.0×10^5 M^{-1}, -13.1 ± 0.2 kcal/mol, -18.8 ± 0.5 eu); (im^-, 8.8×10^8 M^{-1}, -25.4 ± 2.3 kcal/mol, -45 ± 8 eu). The affinity of im^- for $(CN)_5Fe^{2-}$ exceeds that of CN^- ($K_f = 5 \times 10^8$); the origin of ligand affinity order toward $(CN)_5Fe^{2-}$ is discussed. Comparisons are made for the affinities of imidazolate vs. imidazole as a ligand for the transition-metal complexes of series I: $(CN)_5Fe^{2-}$, ferrimyoglobin, cobalamin, CH_3Hg^+, and $(NH_3)_5Ru^{3+}$. Imidazolate serves as a better σ donor than imidazole by about 7 kcal/mol toward transition-metal complexes compared to 10 kcal toward H^+. The pK_a of the pyrrole hydrogen of imidazole in $(CN)_5Fe(Him)^{2-}$ was studied as a function of temperature: pK_a(299 K) = 10.93 ± 0.03, $\Delta H° = 8.8 \pm 0.8$ kcal/mol, $\Delta S° = -21 \pm 3$ eu (μ = 1.00). The results are compared to pK_as for series I. The effects of imidazole ring substituents at C-5 on the pK_a of $(CN)_5Fe(RimH)^{n-2}$ complexes were studied in μ = 4.0 NaCl (R, pK_a): H, 10.4; CH_3, 10.4; $CH_2CH_2CO_2^-$, 10.5; $CHCHCO_2^-$, 8.6; $CH_2CH_2NH_3^+$, ca. 9.2; $CH_2CN(CO_2^-)NH_3^+$, ca. 9.7. The dissociation of the imidazolate ligand from $(CN)_5Fe(im)^{3-}$ occurs with parallel solvent-assisted and proton-assisted pathways ($k_d = k_0 + k_1[H_3O^+]$; $k_0 = (3.63 \pm 0.13) \times 10^{-4}$ s^{-1}, $k_1 = (3.28 \pm 1.07) \times 10^8$ M^{-1} s^{-1}, μ = 1.00, t = 25.0 °C). Activation parameters for the k_0 pathway are $\Delta H^‡ = 26.6 \pm 2.0$ kcal/mol, $\Delta S^‡ = 13.6 \pm 6.6$ eu. Formation of the imidazolate complex from $(CN)_5FeOH^{3-}$ and Him occurs by a first-order path in [Him] with k_f(298 K) = 0.141 ± 0.009 M^{-1} s^{-1}, $\Delta H^‡ = 20.2 \pm 2.0$ kcal/mol, $\Delta S^‡ = 5.1 \pm 6.6$ eu. The mechanism for dissociation of im^- from $(CN)_5Fe(im)^{3-}$ and formation of $(CN)_5Fe(im)^{3-}$ from $(CN)_5FeOH^{3-}$ and Him are discussed in terms of an I_d mechanism.

Introduction

Imidazole (Him) and the imidazolate ion (im^-) are of considerable interest in their role as ligands for transition metal ion centers. The imidazole ligand is particularly important as a potential bridging ligand between metal ion centers in metalloenzymes. Imidazolate bridges are a known structural feature of bovine erythrocyte superoxide dismutase (Cu_2Zn_2(SOD)).[1] The existence of an imidazolate bridge between heme a_3 and Cu(β) protein components of cytochrome oxidase has been proposed by Palmer to account for antiferromagnetic coupling between the Fe(III)-Cu(II) oxidation state level of the enzyme.[2] The degree to which imidazolate as a ligand can propagate antiferromagnetic coupling between adjacent sites is a matter of current interest and of some scientific dispute.[3-7] The binding of imidazolate to ferric porphyrins has been known for many years to cause formation of insoluble polymers. Recently $Fe(TPP)(Him)_2^+$ was titrated with tetrabutylammonium hydroxide in CH_2Cl_2 but no pK_a data were obtained.[8] The pK_a of imidazole coordinated to ferrimyoglobin$^+$ and cobalamin$^+$ has been reported by George et al. to be 10.34 and 10.25, respectively.[9,10] We previously observed that $(CN)_5Fe(Him)^{2-}$ exhibits a pK_a of 10.5 ± 0.1 in saturated NaCl solution.[12] Although a reasonable amount of current research has been aimed at studying magnetic interactions between two metal centers bridged by imidazolate,[4-7,11] there have been very few studies of the equilibrium constants for formation of metal imidazolate complexes and few of the pK_as for the coordinated imidazole complexes have been determined as a function of temperature. Since both the $(CN)_5Fe^{2-}$ and ferrimyoglobin complexes increase the acidity of coordinated imidazole by nearly the same 4 log units amount, it is of interest to compare their affinities of imidazole and imidazolate and the pK_a values as a function of temperature at equal ionic strengths. Association constants for $(CN)_5Fe(Him)^{2-}$ and $(CN)_5Fe(1\text{-}CH_3im)^{2-}$ have now been determined by competition of the respective ligands with NCS^- and pK_as by titration. Useful comparisons can be made from the evaluated constants to the corresponding data for the ferrimyoglobin$^+$ and cobalamin$^+$ macrocycles, CH_3Hg^+, which has a closed-shell configuration, and $(NH_3)_5Ru^{3+}$, a second-row analogue of $(CN)_5Fe^{2-}$.

Our data suggest that imidazolate is a better σ donor relative to imidazole by about 10 kcal/mol based on the enthalpies of formation of both ligands toward $(CN)_5Fe^{2-}$, and 6 kcal/mol for ferrimyoglobin$^+$ and cobalamin$^+$. Also $(CN)_5Fe^{2-}$ forms the stronger bonds to either Him or im^- of these three metal centers.

The chemical labilities of metal-ion centers coordinated to the imidazolate ligand are of current interest. The Zn(II) ions in Cu_2Zn_2(SOD) are labilized by lowering the pH; the competition of H^+ and M^{n+} for the terminal position of a coordinated imidazolate is suggested.[11] It was recently shown that the addition rate of CO on Fe(TPP)L (L = Him or im^-) is a factor of 320 slower for the imidazolate complex, presumably by stabilizing the five-coordinate complex relative to six-coordinate CO adduct in the transition state.[29] From the data we report here it is not surprising that imidazolate ion will influence ligand labilities of trans ligands more than imidazole. Although the influence on trans ligand labilities is of interest, the imidazolate lability is also an important issue. In this regard it is essential to study the lability of imidazolate with a trans ligand partner, such as CN^-, which does not exchange competitively. The processes by which imidazolates may form or dissociate from a metal site have not been studied in much detail in aqueous solution. We report here the mechanism of dissociation of the $(CN)_5Fe(im)^{3-}$ complex by solvent-assisted and proton-assisted pathways. The re-formation

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reaction has been found to be first order in the neutral imidazole, Him, species. A proton transfer between the entering pyrrole hydrogen of the imidazole ring to the hydroxy complex, $(CN)_5FeOH^{3-}$, is suggested as the logical pathway of chemical microscopic reversibility consistent with the dominant solvent-assisted dissociation route.

Experimental Section

Reagents. $Na_3[(CN)_5FeNH_3]\cdot 3H_2O$ was prepared from $Na_2[(CN)_5FeNO]\cdot 2H_2O$ as described previously.[12,13] Imidazole was used as supplied by Matheson Coleman and Bell. Other ligands used as supplied by the manufacturer included 4-methylimidazole (K & K), urocanic acid (Eastman), histamine and L-histidine (Sigma), and 1-methylimidazole (Aldrich). Aldrich 2-methylimidazole was sublimed in vacuo. 4-Imidazolepropionic acid was prepared previously[14] as was 2,5-dimethylimidazole.[12] Solutions of NaSCN were prepared within 3 days of their use; the solutions were stored in the dark. Solutions were prepared in distilled, deionized water with the ionic strength controlled by analytically pure NaCl (J. T. Baker AR). Buffer standards were prepared from premixed buffer salt packets available from Fisher Scientific Co.

Preparation of Complexes. Two methods were used to prepare $(CN)_5Fe(Him)^{2-}$ (Him = imidazole) and substituted derivatives, $(CN)_5Fe(RimH)^{2-}$.

Method A. At least a tenfold excess of the free ligand (imidazole, 4-methylimidazole, urocanic acid, 4-imidazolepropionic acid, histamine, histidine, 1-methylimidazole, 2-methylimidazole, or 2,5-dimethylimidazole) was dissolved in ca. 15 mL of water; 0.30 g of $Na_3[(CN)_5FeNH_3]\cdot 3H_2O$ was added slowly. Stirring was maintained with a rice-sized magnetic stirring bar. A reaction time of 5 min was allowed to assure the formation of the desired $(CN)_5Fe(RimH)^{3-}$ complex. The sample was diluted to about 30 mL. The pH was adjusted to between 8 and 9 with 1 M HCl. The pH was monitored on an Orion 701 digital pH meter calibrated with commercial buffers; 10 mL of 1 M H_2O_2 was added dropwise with magnetic stirring. The pH was maintained in the range of 8–9 throughout the addition of H_2O_2. The room was kept dark while the oxidation process proceeded to completion in about 90–120 min. The solution was treated with small amounts of AG-X4 anion exchange resin in the chloride form. When the settled solution phase was markedly diminished in the color of the respective $(CN)_5Fe(RimH)^{2-}$ species, the resin was filtered from the solution in a 30-mL medium glass frit. The resin appeared dark red to purple depending on the ligand; the resin was washed several times with H_2O. It was found essential to allow several minutes for H_2O_2 entrapped within the resin bead to exchange completely with the H_2O solvent. The beads were filtered to near dryness. A solution in the range of 10^{-3} M of the product $(CN)_5Fe(RimH)^{2-}$ complex was then eluted by several 30-mL equilibrations with 4.0 M NaCl, followed by filtration into a clean filter flask. The filtrate was transferred to a 100-mL volumetric flask and diluted to the mark at 25.0 °C for spectrophotometric analysis. The concentration of $(CN)_5Fe(RimH)^{2-}$ was determined from its visible spectrum. Spectra were obtained in 1.00-cm cells on a Varian-Cary 118 C spectrophotometer. The amount of Fe(III) complex was immediately calculated so that a known five- to tenfold excess of the free ligand could be added. The presence of the additional free ligand is necessary to suppress the dissociation of the substituted imidazole (RimH) or imidazole itself (Him) from the isolated $(CN)_5Fe(RimH)^{2-}$ complex. Solutions at other ionic strengths were prepared by dilution of solutions obtained by the ion-exchange method. The 4.0 M NaCl and other stock solutions were stored in the dark in a refrigerator at 4 °C to retard the dissociation processes. Solutions were used within 1 week of preparation. On longer periods of storage changes in the absorption spectrum were detectable and the samples were considered to be unreliable.

Method B. In the second method a known amount of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ and a known excess of imidazole or 1-methylimidazole were combined in a solution of the desired ionic strength. A known weight of KIO_4 was added to the solution and 10 min was allowed for the oxidation process forming $(CN)_5Fe(RimH)^{2-}$ to be complete. The spectra of the products prepared either by the H_2O_2 method or the IO_4^- method were identical. In the presence of excess IO_4^-, equilibrium studies gave equivalent results to those obtained on samples isolated by ion exchange.

Spectrophotometric Titrations. A flow cell was designed such that solution from an external temperature-equilibrated titration vessel could be passed by means of a peristaltic pump through a spectrophotometric cell in the temperature-controlled sample compartment of the Varian-Cary 118 unit. Separate tests on solution of known absorbance had shown that in ca. 30 s the entire solution volume included in the cell, the pumping tubing, and the titrator is equilibrated. In this time injection of a dye or colored metal complex produced a constant value for the absorbance of the flow-cell sample. The pH of the sample in the titration was monitored by a combination glass and SCE probe. Additions of NaOH titrant or other titrants were made and measured with a Gilmont microburet attached to a syringe needle through a septum in the top of the titration vessel cover. The solution was continually purged with N_2 to exclude CO_2. The same titration apparatus was used to determine the pK_as of the free ligands under an inert atmosphere. The titration of $(CN)_5Fe(RimH)^{2-}$ solutions was carried out by adjusting the pH to convenient values in the presence of a large excess of free ligand (usually 1.0 M). The excess ligand is necessary to prevent dissocation and formation of $(CN)_5FeOH^{3-}$ in the high-pH region. Spectra were obtained as a function of the recorded pH. Data from the pH vs. volume titration curves of the free ligands and the spectrophotometric titrations were treated by computer methods in order to extract the desired pK_a values. In early work some titrations of a wide variety of $(CN)_5Fe(RimH)^{2-}$ complexes were carried out at 4.0 ionic strength. These samples were manipulated in a more tedious way by adding titrant NaOH to samples separated by ion exchange, measuring the pH, and mechanically filling 1.00-cm cells for analysis. The problems with temperature control, dilution factors, and sometimes with ligand dissociation on the time scale of the transfers prompted the flow-cell method. The pK_a was extracted from the midpoint absorbance pH of the long-wavelength band of the imidazolate complex for the $\mu = 4.0$ runs. When the pK_as are corrected for ionic-strength effects on the complexes, ligands, and buffers, the values found by this method are in excellent agreement with flow-cell data at room temperature.

Competition Equilibrium Methods. The association constants for imidazole (Him) and 1-methylimidazole (1-CH_3im) were determined by competition with NCS^-. The affinity of NCS^- for $(CN)_5Fe^{2-}$ has been measured previously.[15] In these experiments a known concentration of the $(CN)_5Fe(Him)^{2-}$ or $(CN)_5Fe(1\text{-}CH_3im)^{2-}$ complex was combined with varying known concentrations of NaSCN. The total ionic strength was maintained at 1.00 and 4.00 such that $\mu = \sum([NaCl] + [NaSCN])$. In each sample the total amount of free ligand and the hydrogen ion were determined from the pH and the total ligand present. The pH was maintained within ±0.03 unit of the ligand pK_a in any series of experiments at a given temperature.

Volumetric flasks containing equal amounts of the Fe(III) complex and various amounts of NCS^- were suspended in temperature baths controlled to ±1 °C for 20 h. The solution spectra were recorded in order to determine the equilibrium amounts of $(CN)_5Fe(Him)^{2-}$ or $(CN)_5Fe(1\text{-}CH_3im)^{2-}$ and $(CN)_5FeSCN^{3-}$. Plots of $\ln (A/A_\infty - A)$ vs. $\ln [SCN^-]$ were made where A is the absorbance at 590 nm of the $(CN)_5FeSCN^{3-}$ species corrected to subtract the minor contribution of the imidazole or 1-methylimidazole complex at 590 nm. A_∞ is the value for total conversion to the $(CN)_5FeSCN^{3-}$ complex. The value of A_∞ was calculated using $\epsilon = 2.70 \times 10^3$ M^{-1} cm^{-1} at 590 nm.[12]

Samples were returned to the temperature baths for longer equilibration times in excess of the initial 20-h period. After an additional 24 h, the spectra showed no change from the equilibrium spectra at 20 h. In solutions at the highest $[SCN^-]$ and for $t > 40$ °C a small amount of precipitate was observed at the end of the initial 20-h equilibration period. The precipitate appeared to be $Fe(OH)_3$. Data was not used for the samples with $t > 40$ °C. Other studies in our laboratory have shown that $(CN)_5FeSCN^{3-}$ is unstable with respect to replacement of CN^- by SCN^-. This process would appear to be the route for formation of $Fe(OH)_3$ from the labilized $(CN)_5FeSCN^{3-}$ complex at high $[SCN^-]$ and high temperature.

Data Analysis. The equilibrium spectra for $(CN)_5Fe(Him)^{2-}/(CN)_5FeSCN^{3-}$ or $(CN)_5Fe(1\text{-}CH_3im)^{2-}/(CN)_5FeSCN^{3-}$ were treated mathematically by two procedures. A computer least-squares treatment of $\ln (A/A - A_\infty)$ vs. $\ln [SCN^-]$, referred to here as the graphical method, was used to find the intercept value for the relationship described by eq 11 of the Results section. The intercept of these plots is related to $\ln (K_{eq}/[L])$ where L = Him or 1-CH_3im and K_{eq} is the ratio of the formation constants of the $(CN)_5Fe^{2-}$ complexes: K_{SCN^-}/K_L. The concentration of [L] was calculated from the total ligand concentration, the amount bound by $Fe(CN)_5^{2-}$, and the hydrogen ion concentration as shown for Him in eq 12 of the Results section. The necessity to have accurate values for [L] requires a careful determination of the effective pK_as of imidazole and 1-methylimidazole as a function of temperature at $\mu = 1.00$. These pK_a values are given in Table IV of the Results section. A second procedure (designated here as the numerical method)

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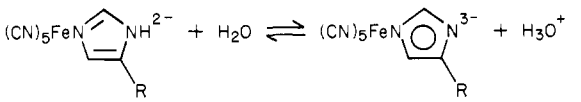
involved the fitting of the absorbance spectrum to simultaneous equations in a number equal to the individual species in solution. In the NCS^-/Him or NCS^-/1-CH_3im competition studies only the corresponding $(CN)_5FeL^{n-}$ complexes were necessarily considered. However, the spectral fitting program was also used in studies of the competition of 1-CH_3im for imidazolate (im^-) and OH^- for $(CN)_5FeOH_2^{2-}$. These spectra require three wavelengths for analysis. The values and wavelength used for the simultaneous-equation method at three wavelengths are given in Table VI. The value of K_{eq} was evaluated directly for the NCS^- competition experiments from the analytical concentrations of L and SCN^- and the concentrations of $(CN)_5FeSCN^{3-}$ and $(CN)_5FeL^{2-}$. Similarly the equilibrium data for the 1-CH_3im/im^- competition were obtained from the $[(CN)_5FeOH^{3-}]$, $[(CN)_5Fe(im)^{3-}]$, $[(CN)_5Fe(1\text{-}CH_3im)^{2-}]$, and $[OH^-]$. The pK_as of the ligands and of the coordinated complexes were determined by a program designed to fit the curve to a monoprotic weak acid dissociation equilibrium from the total moles of ligand and $[H_3O^+]$ or from the total moles of $(CN)_5FeL^{2-}$ complex, the amount of the imidazolate form at any pH, determined from the absorbance of $(CN)_5Fe(im)^{3-}$, and the $[H_3O^+]$.

Kinetic Studies. Displacement of the imidazolate ligand from $(CN)_5Fe(im)^{3-}$, forming $(CN)_5FeOH^{3-}$, obeyed approach-to-equilibrium kinetics. Air-exposed, temperature-equilibriated aliquots of the $(CN)_5Fe(Him)^{3-}$ complex and aliquots of OH^- containing controlled amounts of the free ligand were combined and transferred to 1.00-cm cells for repetitive scanning of spectra. The spectra of the progress of the reaction were determined from 700 to 350 nm with time. The inherent release of imidazole as the reaction proceeds accelerates the reverse reaction. The secondary attack of OH^- on $(CN)_5FeOH^{3-}$ causes the value of A_∞ for the final solutions to differ from the proper value as it relates to the initial part of the reaction. A program was used to forecast an A_∞ suitable for the early 20–30% of the net change to correct for the back-reaction enhancement (cf. text) and to avoid the hydrolysis side reaction. The value of A_∞ is reiterated until agreement is obtained for the k_{obsd} calculated throughout the initial test region. Convergence was usually achieved in three to four reiterations.

Results

Spectra of Imidazolates of $(CN)_5Fe^{2-}$. When solutions of $(CN)_5Fe(Him)^{2-}$ are raised in pH, the deprotonated imidazolate complex, $(CN)_5Fe(im)^{3-}$, forms by a shift of the equilibrium shown in eq 1.[12] The same imidazolate equilibrium occurs for imidazole

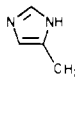


(1)

and derivatives in which a substituent group R is attached to the ring structure. It has been shown previously that the favored mode of coordination occurs when the R group is remotely placed with respect to the coordinated $(CN)_5Fe^{3-}$ moiety.[12,16] The $(CN)_5Fe(im)^{3-}$ complex has a maximum at 438 nm and a weaker intensity broad band centered at 625 nm. Two spectral bands in comparable regions of the visible spectrum have been reported for $(CN)_5Fe(RimH)^{2-}$ complexes. For the coordinated imidazoles the band between 400 and 404 nm, depending on the nature of R, is attributed to a ligand field transition while the longer wavelength band, whose position is much more sensitive to the nature of R, is attributed to a ligand to metal charge transfer transition (LMCT).[12] The imidazolate form (Rim^-) should be a better π donor than the parent RimH ligand. The position of the long-wavelength maximum, from 140 to 270 nm toward lower energy of the LMCT maximum of the parent $(CN)_5Fe(RimH)^{2-}$ complex, is consistent with a similar LMCT assignment for the imidazolate complex. Spectral maxima for both RimH and Rim^- coordinated to $(CN)_5Fe^{2-}$ are given in Table I.

Dissociation and Formation of $(CN)_5Fe(im)^{3-}$. At high pH ($\gtrsim$12) a solution of the imidazolate complex dissociates until an equilibrium mixture of $(CN)_5Fe(im)^{3-}$ and $(CN)_5FeOH^{3-}$ is reached. The rate of approach to equilibrium for these species is dependent on the concentration of free imidazole and OH^- in the solution. The progress of this reaction is shown with representative conditions in Figure 1. The initial maximum at 438 nm shifts to the equilibrium value at 420 nm for the example conditions. The 420-nm position is the weighted average spectral maximum of the $(CN)_5Fe(im)^{3-}$ species and $(CN)_5FeOH^{3-}$ (λ_{max} 390 nm). An isosbestic point is found at 407 nm which is maintained through $\gtrsim$90% of the reaction. At long times the attack of OH^- on $(CN)_5FeOH^{3-}$ to displace CN^- causes a loss of the isosbestic point. Rates measured at a constant value of free imidazole ($[Him]_0 = 1.83 \times 10^{-3}$ M) reveal that a modest 10% decrease in rate is noticed as $[OH^-]$ increases from 0.050 to 0.200

Table I. Spectra of $(CN)_5FeL^{2-}$ Complexes (maxima in nm)

$(CN)_5Fe^{III}$ complex	imidazole form λ_{LF}	imidazole form λ_{CT}	imidazolate form λ_{LF}	imidazolate form λ_{CT}	$\mu = 4.0$ pK_a
	402	485 (sh)	438	625	(10.44)
	401	530	444	~800	(10.39)
	403 ($pK_{a_2} \sim 4.5$)	575 550	435	~800	(8.64)
	402	528	447	~800	(10.50)
	400	489	443		(≥9.23)
	400	485 (sh)	445	~800	(≥9.74)
	403	515	445		
	404	585			

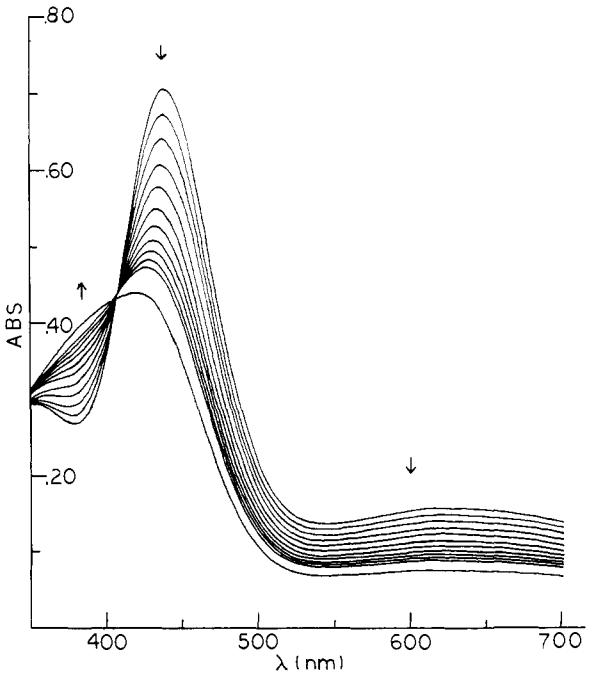


Figure 1. A representative repetitive scan of the approach to the $(CN)_5Fe(im)^{3-}/(CN)_5FeOH^{3-}$ equilibrium: $[(CN)_5Fe(im)^{3-}]_0 = 2.68 \times 10^{-4}$ M, $[Him]_0 = 1.03 \times 10^{-3}$ M, $[OH^-]_0 = 0.10$ M, $\mu = 1.00$ (NaCl, NaOH), $t = 25.0$ °C. Scans are at 450-s intervals.

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Table II. OH^- Dependence on the $(CN)_5Fe(im)^{3-}/(CN)_5FeOH^{3-}$ Approach to Equilibrium Rate[a]

$[OH^-]$	$k_{obsd} \times 10^4$, s^{-1}	$[OH^-]$	$k_{obsd} \times 10^4$, s^{-1}
0.050	3.29	0.150	2.70
0.075	3.03	0.200	2.87
0.100	3.10		

[a] μ = 1.0 (NaCl, NaOH), t = 25.0 °C, $[(CN)_5Fe(im)^{3-}]_0 = 2.69 \times 10^{-4}$ M, $[Him]_0 = 1.83 \times 10^{-3}$ M.

Table III. Approach to Equilibrium Kinetics for the $(CN)_5Fe(im)^{3-}/(CN)_5FeOH^{3-}$ Equilibrium[a]

t, °C	k_f, M^{-1} s^{-1}	$10^5 k_d$, s^{-1} kinetic	$10^4 k_d$ equilibrium
25.0	0.141 ± 0.009	2.7 ± 1.3	1.80
30.5	0.250 ± 0.014	5.6 ± 2.1	4.50
33.5	0.329 ± 0.019	29.1 ± 2.7	5.90
36.2	0.526 ± 0.040	18.1 ± 5.9	10.00

[a] $[OH^-] = 0.10$ M, $[(CN)_5Fe(im)^{3-}]_0 = 2.68 \times 10^{-4}$ M, $[Him]_0$ = (1.03, 1.29, 1.55, 1.81) $\times 10^{-3}$ M.

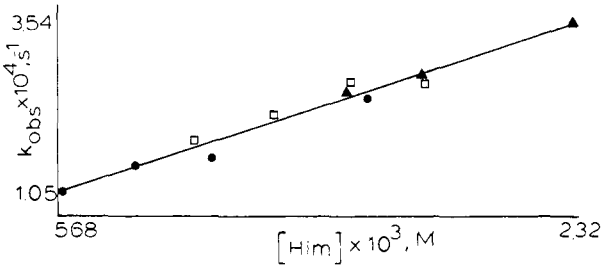


Figure 2. Approach to equilibrium dependence on imidazole for the $(CN)_5Fe(im)^{3-}/(CN)_5FeOH^{3-}$ reaction: solid circles, μ = 0.90 (NaCl, NaOH); open squares, μ = 1.00 (NaCl, NaOH); solid triangles, μ = 1.50 (NaCl, NaOH): t = 25.0 °C. (x and y axes are scaled for the largest expansion by the graphic subroutines of our computer programs.)

M at μ = 1.00 (NaCl, NaOH), t = 25.0 °C (Table II). The data obtained in the high $[OH^-]$ region conform to a $[OH^-]$- or $[H_3O^+]$-independent term plus a first-order term in $[H_3O^+]$:

$$k_d = k_0 + k_1[H_3O^+] \quad (2)$$

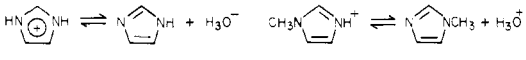
with $k_0 = (2.63 \pm 0.13) \times 10^{-4}$ s^{-1} and $k_1 = (3.28 \pm 1.07) \times 10^8$ M^{-1} s^{-1}. A complementary study for the approach to equilibrium at 0.10 M NaOH as a function of the free imidazole level reveals that the approach to equilibrium rate is first order in the neutral ligand, Him, form. The reaction is also independent of ionic strength. All data from μ = 0.90 to 1.50 at $[OH^-]$ = 0.10 and t = 25 °C for the approach to equilibrium as a function of [Him] obey a linear relationship as shown by Figure 2. The independence of the dissociation on $[OH^-]$ itself, the independence of the rate on the ionic strength, and the dependence of the approach to equilibrium on the neutral free ligand specify the equation

$$(CN)_5Fe(im)^{3-} + H_2O \underset{k_f}{\overset{k_d}{\rightleftharpoons}} (CN)_5FeOH^{3-} + Him \quad (3)$$

as the approach to equilibrium reaction. The values of the dissocation rate constant, k_d, and the formation constant, k_f, are the intercepts and slopes of the data as in Figure 2. Values of k_f and k_d were determined at 25.0, 30.5, 33.5, and 36.2 °C for $[OH^-]$ = 0.100 M, μ = 1.00 (NaCl), by varying the free imidazole concentration (Table III). The minor dependence of k_d on $[H_3O^+]$ contributes only a 10% correction to the dominant dissociative path, independent of acid or base. The path involving the k_0 term of k_d would appear to involve addition of H_2O to strained $(CN)_5Fe(im)^{3-}$ species. The $[H_3O^+]$-dependent term, k_1, suggests a H_3O^+-catalyzed parallel path. The values of k_d and k_f at various temperatures are given in Table III.

The errors in the intercept value, k_d, are large for several reasons. The ligand Him is released as the reaction proceeds, altering its concentration with time and accelerating the reverse rate. As a consequence of this experimental difficulty, a computer program was used to find the initial rate value of k_{obsd} as the best fit, using an adjustable infinite time value for the equilibrium absorbance (cf. Experimental Section). Errors accumulated from this procedure and the least-squares fitting of k_{obsd} vs. [Him] are largely placed in the intercept value. As a consequence we do not regard these values of k_d to be more reliable than a factor of 10. However, equilibrium studies to be described later allowed us to evaluate k_d from the kinetic k_f values and the equilibrium constant for formation of $(CN)_5Fe(im)^{3-}$. These values are recorded in Table III. The temperature dependence of k_d and k_f allows the evaluation of Eyring parameters as follows: (k_f) $\Delta H^\ddagger$ = 20.2 ± 2.0 kcal/mol, $\Delta S^\ddagger$ = 5.1 ± 6.6 eu; (k_d) $\Delta H^\ddagger$ = 26.6 ± 2.0 kcal/mol, $\Delta S^\ddagger$ = 13.6 ± 6.6 eu. The values given for the activation parameters correspond to the temperature dependencies for the k_0 path alone because the anticipated term of k_f in $[HimH^+]$, which would correspond to the reverse process of the $k_1[H_3O^+]$ dissociation step, is too small to be detected experimentally.

Table IV. pK_as of Imidazolium and 1-Methylimidazolium Ions at μ = 1.00 NaCl



t, °C	pK_a	t, °C	pK_a
7.2	7.62	5.6	7.86
16.5	7.37	15.2	7.61
25.0	7.20	25.0	7.39
35.2	6.99	35.2	7.14
44.0	6.81	44.7	6.93

pK_as of Imidazolium and 1-Methylimidazolium Ions. The values of the pK_as for $HimH^+$ and 1-CH_3imH^+ were essential for the data reduction of subsequent experiments. Various values have been reported for the pK_a of imidazolium ion but none appear under the conditions of μ = 1.00 NaCl as a function of temperature. We obtained the data in Table IV as described in the Experimental Section.

The temperature dependencies for eq 4 and 5 have been treated by the standard ln K vs. $1/T$ method to provide values of $\Delta H°'$ and $\Delta S°'$ where the prime refers to the conditions of the measurements at μ = 1.00 (NaCl). The values established are as follows: ($HimH^+$) $\Delta H_4°'$ = 8.7 ± 0.2 kcal/mol, $\Delta S_4°'$ = −3.7 ± 0.5 eu; (1-CH_3imH^+) $\Delta H_5°'$ = 9.6 ± 0.2 kcal/mol, $\Delta S_5°'$ = −1.5 ± 0.6 eu.

$$HimH^+ + H_2O \rightleftharpoons Him + H_3O^+ \quad (4)$$

$$1\text{-}CH_3imH^+ + H_2O \rightleftharpoons 1\text{-}CH_3im + H_3O^+ \quad (5)$$

pK_a of $(CN)_5Fe(Him)^{2-}$. A representative spectrophotometric titration of $(CN)_5Fe(Him)^{2-}$ to form $(CN)_5Fe(im)^{3-}$ is shown in Figure 3. The titration was carried out in a continuously flowing 1.00-cm spectrophotometric cell and titrator assembly as described in the Experimental Section. The titration allows the determination of the pK_a of $(CN)_5Fe(Him)^{2-}$. This equilibrium is shown in eq 1 with R = H. Equation 7 can be derived from the mass-balance expression (eq 6), Beer's law, and the acid dissociation expression for $(CN)_5Fe(Him)^{2-}$.

$$[Fe(III)]_{tot} = [(CN)_5Fe(Him)^{2-}] + [(CN)_5Fe(im)^{2-}] \quad (6)$$

$$\frac{[Fe(III)]_{tot}}{(\Delta A)_\lambda} = \frac{[H_3O^+]}{K_a \Delta\epsilon_\lambda} + \frac{1}{\Delta\epsilon_\lambda} \quad (7)$$

ΔA_λ is the difference in absorbance between the measured absorbance, A_{obsd}, at a given wavelength and the calculated value of the absorbance, A_{Him}, if all [Fe(III)] were present as $(CN)_5Fe(Him)^{2-}$. $\Delta\epsilon_\lambda$ equals $(\epsilon_{(CN)_5Fe(im)^{3-}} - \epsilon_{(CN)_5Fe(Him)^{2-}})$ at the given wavelength. The data were analyzed at two wavelengths (700 and 438 nm). For the 700-nm calculations both A_{Him} and $\epsilon_{(CN)_5Fe(Him)^{2-}} = 0$ and eq 7 simplifies to $([Fe(III)]_{tot}/A_{obsd}) = ([H_3O^+]/\epsilon_{(CN)_5Fe(im)^{3-}}) + (1/\epsilon_{(CN)_5Fe(im)^{3-}})$. At 438 nm both species

Table V. pK_a of $(CN)_5Fe(Him)^{3-}$ [a]

t, °C	pK'(700 nm)	pK'(438 nm)	ϵ_{700}	$\Delta\epsilon_{438}$	pK_a
21.2	11.15 ± 0.03	11.18 ± 0.01	402 ± 10	1850 ± 16	11.00 ± 0.04
26.0	11.08 ± 0.02	11.10 ± 0.01	397 ± 7	1850 ± 22	10.93 ± 0.03
30.2	11.00 ± 0.03	11.01 ± 0.02	390 ± 10	1840 ± 22	10.85 ± 0.03
38.4	10.79 ± 0.02	10.88 ± 0.02	385 ± 8	1880 ± 18	10.68 ± 0.07

[a] μ = 1.00 (NaCl), [Him] = 1.0 M.

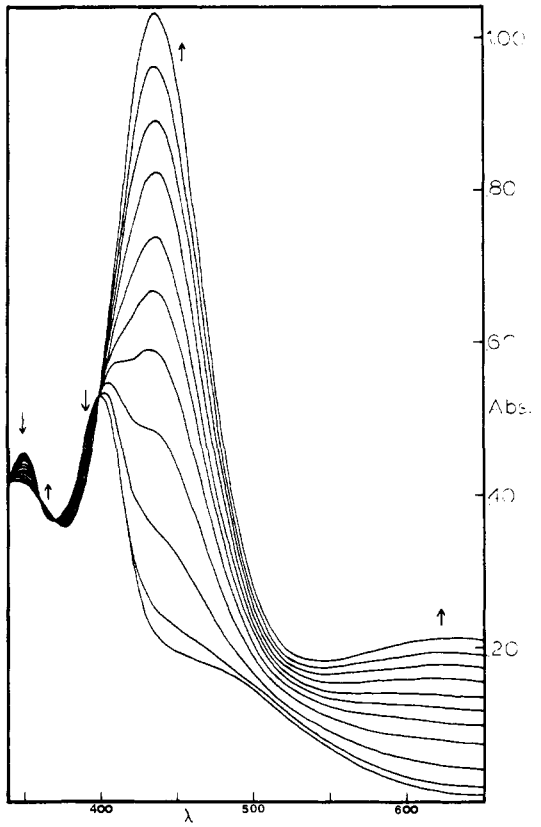


Figure 3. Spectrophotometric titration of $(CN)_5Fe(Him)^{2-}$: $[(CN)_5Fe(Him)^{2-}]_i = 4.63 \times 10^{-4}$ M, $[Him]_i = 1.00$ M, $\mu = 1.00$ (NaCl), $t = 21.2$ °C. pH recorded for descending curves in the range of 400–650 nm: 12.40, 12.10, 11.73, 11.56, 11.37, 11.24, 11.07, 10.83, 10.45, 9.79, 8.12. (Arrows show order of spectra with increasing pH.)

absorb and the more complete eq 7 applies.

Plots of $[Fe(III)]_{tot}/\Delta A_\lambda$ vs. $[H_3O^+]$ are found to be linear with a common intercept as predicted by eq 7. Data obtained at 700 nm at four temperatures are shown in Figure A of the microfilm edition. Values of K_a' and $\Delta\epsilon$ were evaluated from the slopes and intercepts of the plot of eq 7 at these temperatures. The pK_a values were corrected for the ionic strength effect on the measured hydrogen ion activity (cf. Table V). Agreement in the data at both wavelengths is excellent. The ln K vs. $1/T$ analysis provides the following thermodynamic parameters: (700 nm) $\Delta H°' = 8.8 \pm 0.8$ kcal/mol, $\Delta S°' = -21 \pm 3$ eu; (438 nm) $\Delta H°' = 7.5 \pm 0.3$ kcal/mol, $\Delta S°' = -26 \pm 1$ eu. Values for the ϵ_{700} and $\Delta\epsilon_{438}$ were used to evaluate extinction coefficients for $(CN)_5Fe(im)^{3-}$ at other wavelengths. Extinction coefficients at several wavelengths are used in the spectral fitting programs for equilibrium studies described in subsequent sections. Useful extinction coefficients at 390, 409, and 438 nm are given in Table VI.

Association Constants of $(CN)_5Fe(Him)^{2-}$. The affinity of OH^- for $(CN)_5Fe^{2-}$ is known to be 4×10^5.[15] The fact that the imidazolate ligand (im^-) competes with OH^-, when its absolute concentration at 0.10 M OH^- is 10^5 lower, points toward a very interesting fact about the $(CN)_5Fe(im)^{3-}$ complex: imidazolate has an unusually high association constant for $(CN)_5Fe^{2-}$ that exceeds even that of CN^-. In order to determine the association constant for $(CN)_5Fe(im)^{2-}$ we were forced to determine the association constant of imidazole (Him) and *N*-methylimidazole (I-CH_3im) in competition with NCS^-. The affinity of NCS^- for

Table VI. Extinction Coefficients for Species Used in Equilibrium Studies[a]

complex	ϵ_{390}	ϵ_{409}	ϵ_{438}
$(CN)_5Fe(im)^{3-}$	920	1.55×10^3	2.30×10^3
$(CN)_5Fe(1\text{-}CH_3im)^{2-}$	1.43×10^3	1.82×10^3	675
$(CN)_5FeOH^{3-}$	1.75×10^3	1.42×10^3	680

[a] μ = 1.00 (NaCl).

Table VII. Association Constants for $(CN)_5Fe(Him)^{2-}$

	KIO_4 oxidation $10^{-5}K$			H_2O_2 oxidation $10^{-5}K$	
t, °C	graphical method (μ = 1.00)[a]	numerical method (μ = 1.00)[a]	t, °C	graphical method (μ = 1.00)[b]	graphical method (μ = 4.00)[c]
19.6	5.85	5.51	20.0		8.6
24.8	3.46	3.47	25.0	4.66	
29.3	2.30	2.29	26.0		3.6
35.4	1.46	1.44	30.0	2.37	
			32.5		2.9
			35.0	1.25	
			37.5		2.6

[a] $[(CN)_5Fe(Him)^{2-}] = 4.00 \times 10^{-4}$ M, $[Him]_{tot} = 3.00 \times 10^{-3}$ M, pH 7.20 ± 0.5 (24.8 °C). [b] $[(CN)_5Fe(Him)^{2-}]_i = 4.23 \times 10^{-4}$ M, $[Him]_{tot} = 3.73 \times 10^{-3}$ M, pH 7.00 ± 0.05 (25.0 °C). [c] $[(CN)_5Fe(Him)^{2-}]_i = 1.58 \times 10^{-4}$ M, $[Him]_{tot} = 3.00 \times 10^{-2}$ M, pH 7.00 ± 0.05 (26.0 °C).

$(CN)_5Fe^{2-}$ has been studied by Espenson.[15] The absorbance spectrum of $(CN)_5FeNCS^-$ (λ_{max} 590 nm) gave the useful visible band for determining an equilibrium by competition between Him and NCS^- or 1-CH_3im and NCS^- for $(CN)_5Fe^{2-}$.

Consider the equations

$$(CN)_5FeOH_2^{2-} + Him \overset{K_8}{\rightleftharpoons} (CN)_5Fe(Him)^{2-} + H_2O \quad (8)$$

$$(CN)_5FeOH_2^{2-} + NCS^- \overset{K_9}{\rightleftharpoons} (CN)_5FeSCN^{3-} + H_2O \quad (9)$$

$$NCS^- + (CN)_5Fe(Him)^{2-} \overset{K_{10}}{\rightleftharpoons} (CN)_5FeSCN^{3-} + Him \quad (10)$$

Equilibrium measurements carried out on equilibrium 10 obey the relationship of eq 11 as described in the Experimental Section. In this expression $K_{eq} = K_{10}$. Since $K_{10} = K_9/K_8$, values of K_8 may be evaluated from the intercept of eq 11. The [Him] was calculated from the pH measurement and the conservation equation 12.

$$\ln\left(\frac{A}{A_\infty - A}\right) = \ln [SCN^-] + \ln\left(\frac{K_{eq}}{[Him]}\right) \quad (11)$$

$$[Him] = \frac{K_a([Him]_{tot} - [(CN)_5Fe(Him)^{2-}])}{K_a + [H_3O]^+} \quad (12)$$

This procedure was carried out at various temperatures for μ = 1.0 (NaCl/NaSCN) and 4.0 (NaCl/NaSCN). The pH was maintained constant by the buffering action of Him/$HimH^+$ or 1-CH_3im/1-CH_3imH^+ pairs at the pK_a value of the ligands. The values used for K_9 were determined from Espenson's temperature data for the $(CN)_5FeSCN^{3-}$ formation reaction.[15] The literature values are $\Delta H_9° = -8.8 \pm 0.6$ kcal/mol and $\Delta S_9° = -18.7 \pm 1.8$ eu for the NCS^- association constant (K_9); these thermodynamic parameters were used to evaluate K_9 at the desired temperatures.

Table VIII. Association Constants for $(CN)_5Fe(1\text{-}CH_3im)^{2-}$ [a]

t, °C	$10^{-5}K$ graphical method (μ = 1.00)	$10^{-5}K$ numerical method (μ = 1.00)
19.5	4.53	3.96
24.8	3.04	2.78
28.5	2.31	1.87
32.1	1.77	1.53
34.8	1.50	1.24

[a] μ = 1.00 (NaCl/NaSCN), $[(CN)_5Fe(1\text{-}CH_3im)^{2-}]_0 = 5.20 \times 10^{-4}$ M, H_2O_2 preparation, $[1\text{-}CH_3im]_{tot} = 2.58 \times 10^{-3}$ M.

Table IX. Equilibrium between $(CN)_5Fe(im)^{3-}$ and $(CN)_5Fe(1\text{-}CH_3im)^{2-}$ [a]

t, °C	K_{13}	t, °C	K_{13}
24.8	806 ± 28	34.8	461 ± 13
28.5	568 ± 28	40.2	394 ± 12
32.1	521 ± 10		

[a] $[OH^-] = 0.052$ M, $[Fe(CN)_5^{2-}]_{tot} = 4.29 \times 10^{-4}$ M, $[Him]_{tot} = 5.45 \times 10^{-3}$ M, μ = 1.00 (NaCl), $[1\text{-}CH_3im]_{tot}$ = 0.0625, 0.125, 0.250, 0.375, and 0.500 M.

Values for K_8 of the $(CN)_5Fe(Him)^{3-}$ complex are given in Table VII. Equilibrium solutions of $(CN)_5Fe(Him)^{2-}$ and $(CN)_5FeSCN^{3-}$ have an isosbestic point at 456 nm.

A second method, referred to here as the numerical method, was used to evaluate $[(CN)_5Fe(Him)^{2-}]$ and $[(CN)_5FeSCN^{3-}]$ by the use of simultaneous equations using the solution absorbances and the ϵ's at 590 and 403 nm. Coupled with the analytical value of $[SCN^-]$ and [Him] in each solution, values of K_{10} were calculated directly from the equilibrium expression. Separate values of K_8 were determined from the values of K_{10} and K_9 at each temperature. The validity of the equilibrium results was tested by using H_2O_2 or KIO_4 to oxidize $(CN)_5Fe(Him)^{3-}$ in the synthetic step to prepare $(CN)_5Fe(Him)^{2-}$ for equilibration with varying $[SCN^-]$. In the main method the source of the Fe(III) complex, $(CN)_5Fe(Him)^{2-}$, was the ion-exchanged complex formed by H_2O_2 oxidation of the Fe(II) complex, $(CN)_5Fe(Him)^{3-}$. The second set of equilibrium measurements were carried out in the presence of $[IO_4^-] = 4.7 \times 10^{-5}$ M after the oxidation of $(CN)_5Fe(Him)^{3-}$ by 1 equiv of IO_4^- forming IO_3^-. The values of the association constant for $(CN)_5Fe(Him)^{2-}$ are given in Table VII. The agreement in K_8 at μ = 1.00 is quite reasonable between the data sets where KIO_4 or H_2O_2 serves as the oxidant. Agreement between the numerical and graphical data reduction procedures dependence of K_8 was evaluated for μ = 1.00 with KIO_4 as the oxidant. Agreement between the numerical and graphical evaluated values for the enthalpy and entropy of the formation reaction is quite good: (graphical) $\Delta H_8° = -15.8 \pm 0.6$ kcal/mol, $\Delta S_8° = -27 \pm 2$ eu; (numerical) $\Delta H_8° = -15.3 \pm 0.4$ kcal/mol, $\Delta S_8° = -26 \pm 2$ eu.

Association Constants for $(CN)_5Fe(1\text{-}CH_3im)^{2-}$. The same procedures were used to determine the analogous association constant of 1-CH_3im for $(CN)_5Fe^{2-}$ (using the absorbances at the 409-nm maximum of $(CN)_5Fe(1\text{-}CH_3im)^{2-}$ and 590-nm maximum of $(CN)_5FeSCN^{3-}$). Equilibrium solutions containing the $(CN)_5Fe(1\text{-}CH_3im)^{2-}$ and $(CN)_5FeSCN^{3-}$ complexes show an isosbestic point at 457 nm. (See spectrum B of microfilm edition.) Values are given in Table VIII. The thermodynamic parameters calculated for the association reaction of 1-CH_3im and $(CN)_5FeOH_2^{2-}$ are as follows: (graphical) $\Delta H° = -13.1 \pm 0.2$ kcal/mol, $\Delta S° = -18.8 \pm 0.5$ eu; (numerical) $\Delta H° = -13.8 \pm 0.7$ kcal/mol, $\Delta S° = -21 \pm 3$ eu.

Competition of Imidazolate and 1-Methylimidazole for $(CN)_5Fe^{2-}$. The approach to equilibrium between $(CN)_5Fe(im)^{3-}$ and $(CN)_5FeOH^{3-}$ at 0.10 M NaOH and ca. 1×10^{-3} M Him implied that the association constant for the imidazolate complex was much larger than that for the OH^- ligand. Side reactions are caused when large amounts of the total Fe(III) are present as $(CN)_5FeOH^{3-}$ at high $[OH^-]$ for prolonged equilibration times. This problem prompted the use of 1-CH_3im as a suitable competitor ligand for im^-. A distribution of the total Fe(III), initially present as the $(CN)_5Fe(Him)^{2-}$ complex, was achieved in 20 h under conditions of $[1\text{-}CH_3im]_0 = 0.0625$–0.500 M, $[Him]_0 = 5.45 \times 10^{-3}$ M, and $[OH^-] = 0.052$ M.

The equilibrium spectra as a function of [1-CH_3im] were clearly distinct from one another in accordance with equilibrium 13. The spectra of the individual complexes are so overlapped that only the numerical method could be used. A representative set of spectra is shown in Figure C of the microfilm edition. Using the ϵ's provided in Table VI for the species $(CN)_5FeOH^{3-}$, $(CN)_5Fe(im)^{3-}$, and $(CN)_5Fe(1\text{-}CH_3im)^{2-}$ a convergence was achieved that gave the concentrations of each species (cf. Experimental Section). The results for the equilibrium constant of eq 13 as a function of temperature are given in Table IX. Using the ln K vs. $1/T$ treatment of the equilibrium constants, the values for $\Delta H°$ and $\Delta S°$ for reaction 13 are found to be -8.1 ± 1.3 kcal/mol and -14 ± 5 eu, respectively.

$$(CN)_5Fe(1\text{-}CH_3im)^{2-} + Him + OH^- \overset{K_{13}}{\rightleftharpoons} (CN)_5Fe(im)^{3-} + 1\text{-}CH_3im + H_2O \quad (13)$$

Association Constant for $(CN)_5Fe(im)^{3-}$. The data collected in the previous sections allows the calculation for the formation constant of $(CN)_5Fe(im)^{3-}$

$$(CN)_5FeH_2O^{2-} + im^- \overset{K_{14}}{\rightleftharpoons} (CN)_5Fe(im)^{3-} + H_2O \quad (14)$$

by two procedures: (1) based on the pK_a of $(CN)_5Fe(Him)^{2-}$ and the association constant of $(CN)_5Fe(Him)^{2-}$ or (2) based on equilibrium 13 and the association constant of $(CN)_5Fe(1\text{-}CH_3im)^{2-}$. These are shown by the sums in Table X.

From the free-energy equation the formation constant of $(CN)_5Fe(im)^{3-}$ may be calculated from either set of $\Delta H°$ and $\Delta S°$ values. The smaller error in $\Delta S°$ for eq 14 calculated by the determination of the pK_a of $(CN)_5Fe(Him)^{3-}$ would appear to be the slightly more reliable set of values. At 298 K the value of the association constant of $(CN)_5Fe(im)^{3-}$ is calculated to be 8.8×10^8; this value is entered in Table XI for comparison with various

Table X

	$\Delta H°$	$\Delta S°$	eq
Approach 1			
$(CN)_5Fe(Him)^{2-} \rightleftharpoons (CN)_5Fe(im)^{3-} + H_3O^+$	7.5 ± 0.3	−26 ± 1[a]	1
$(CN)_5FeH_2O^{2-} + Him \rightleftharpoons (CN)_5Fe(Him)^{2-} + H_2O$	−15.3 ± 0.4	−26 ± 2[a]	8
$im^- + H_3O^+ \rightleftharpoons Him$	−17.6 ± 1.6	7 ± 5[b]	15
$(CN)_5FeH_2O^{2-} + im^- \rightleftharpoons (CN)_5Fe(im)^{3-} + H_2O$	−25.4 ± 2.3	−45 ± 8	14
Approach 2			
$(CN)_5Fe(1\text{-}CH_3im)^{2-} + Him + OH^- \rightleftharpoons (CN)_5Fe(im)^{3-} + 1\text{-}CH_3im + H_2O$	−8.1 ± 1.3	−14 ± 5[a]	13
$(CN)_5FeH_2O^{2-} + 1\text{-}CH_3im \rightleftharpoons (CN)_5Fe(1\text{-}CH_3im)^{2-} + H_2O$	−13.8 ± 0.7	−21 ± 3[a]	8′
$im^- + H_2O^+ \rightleftharpoons Him$	−17.6 ± 1.6	7 ± 5[b]	15
$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$	13.8 ± 0.2	−17.9 ± 0.7	K_W
$(CN)_5FeH_2O^{2-} + im^- \rightleftharpoons (CN)_5Fe(im)^{3-} + H_2O$	−25.7 ± 3.8	−46 ± 19	14

[a] This work. [b] Reference 9.

Table XI. Affinities of Selected Ligands for the $(CN)_5Fe^{2-}$ Moiety (μ = 1.0)

ligand	K_{298K}, M^{-1}	$\Delta H°$, kcal/mol	$\Delta S°$, eu	ref
	8.8×10^8	-25.4 ± 2.3	-45 ± 8	this work
CN^-	5×10^8			17
OH^-	4×10^5			15, 17
	3.4×10^5	-15.8 ± 0.6	-27 ± 2	this work
	3.0×10^5	-13.1 ± 0.2	-18.8 ± 0.5	this work
NH_3	7.5×10^3			18
	6.5×10^3			17
N_3^-	1.9×10^3			18
SCN^-	2.3×10^2	-8.8 ± 0.6	-18.7 ± 1.8	15

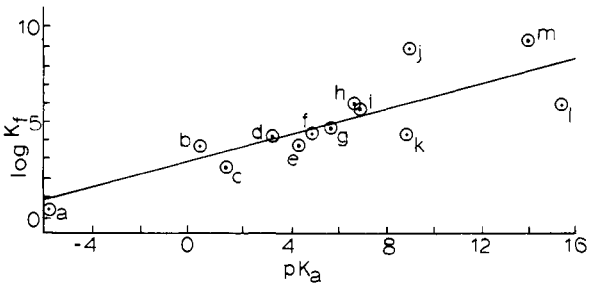


Figure 4. Affinities of ligands for $Fe(CN)_5^{2-}$. Ligands: (a) *N*-methylpyrazinium; (b) pyrazine; (c) SO_3H^-; (d) isonicotinamide; (e) N_3^-; (f) pyridine; (g) 4-methylpyridine; (h) imidazole; (i) *N*-methylimidazole; (j) CN^-; (k) NH_3; (l) OH^-; (m) imidazolate.

other ligand affinities for $(CN)_5Fe^{2-}$.

Discussion

The affinities of various ligands L for $(CN)_5Fe^{2-}$ relative to displacement of water (eq 16) are listed in Table XI.

$$(CN)_5FeH_2O^{2-} + L^{n-} \rightleftharpoons (CN)_5FeL^{(2+n)-} + H_2O \quad (16)$$

The value for the imidazole complex (3.4×10^5) is in reasonable agreement with a value of 8.3×10^5 calculated by Toma and Creutz from the redox potential of the $(CN)_5Fe(Him)^{2-/3-}$ couple in 1.00 M NaCl and an association constant for $(CN)_5Fe(Him)^{3-}$ determined in 0.5 M $LiClO_4$.[19] Imidazole is capable of serving as a σ donor, a π donor, and a π acceptor. Since the $(CN)_5Fe^{2-}$ center is not particularly electron rich the ability of imidazole to serve as a π acceptor is not likely to be important.

The failure of the isonicotinamide complex or the pyrazine complex to show any enhanced affinity relative to pyridine (see Figure 4) also suggests that the π-acceptor property is minimized as contributing to the bonding of ligands to $(CN)_5Fe^{2-}$. Also the π-acceptor character of NH_3, Him, and py would predict an order of stabilities of $(CN)_5FeL^{2-}$ complexes of $NH_3 \ll$ Him < py, which is not found. The observed order, py $\simeq NH_3$ < Him, is a commonly observed order of affinities toward transition-metal centers.[20] If σ basicity alone is considered, the predicted order would be NH_3 > Him > py. As π donors the ligand order is Him > py $\gg NH_3$. The observed order suggests that a combination of σ-donor and π-donor properties influences the magnitude of the association constants of $(CN)_5FeL^{(2+n)-}$ complexes. Toma and Creutz have suggested a correlation between the association constants of L for $(CN)_5Fe^{2-}$ and the pK_a of the ligand. In Figure 4 a linear representation of log K_f (formation constant) and the ligand pK_a is shown, including the imidazolate data of this report. The linear correlation is reasonably accurate over 20 orders of magnitude as specified by the equation

$$\log K_f = (0.36 \pm 0.07)pK_a + (2.38 \pm 0.60) \quad (17)$$

This relationship emphasizes the σ-donor strength of the ligand as reflected by the pK_a of the protonated form. The σ-donor capacity is clearly the dominant factor in affinities of ligands for $(CN)_5Fe^{2-}$. The value for log K_{NCS^-} was not included in Figure 4 because of the uncertainty of the pK_a for HNCS. HNCS is a strong acid; its pK_a should be ca. −7.0. The value for log K_f of the NCS^- complex (2.41) will fall well above the line for log K_f. The log K_f of the CN^- and imidazolate complexes are less deviant from the value suggested by eq 17 but these also are larger than the predicted value. NCS^-, CN^-, and im^- are three of the best potential π donors of the ligands whose affinities for $(CN)_5Fe^{2-}$ are known. The unusually high affinity of NCS^- for $(CN)_5Fe^{2-}$ is complicated by the fact that HNCS has the protonation site at nitrogen while the value for $(CN)_5FeSCN^{3-}$ reflects NCS^- coordination at sulfur. CN^- deviates by ca. 10^3 in K_f and im^- by 25-fold from the value predicted by eq 17. The influence of the π component would appear to be in the order $NCS^- \gg CN^-$ > im^- with the σ component dominant for CN^- and im^- contributing at least 80% of the bond strength. Hydroxide ion, which is a reasonably good π donor, is also much more strongly bound by 4×10^5 than H_2O. Hydroxide ion is the better σ base and π donor of HO^- and H_2O. Log K_f of OH^- falls below the line established by eq 17 and the spectral properties of $(CN)_5FeOH_2^{2-}$ and $(CN)_5FeOH^{3-}$ are similar. The σ-donation advantage of OH^- is sufficient to account for these observations.

Table XI suggests that the increased affinity of one ligand over another for $(CN)_5Fe^{2-}$ is largely attributed to the enthalpy of the formation reaction. The entropy of formation does not change a great amount from NCS^- through Him as ligands. The value for $\Delta S_f°$ of the imidazolate is significantly more negative while the $\Delta H_f°$ of $(CN)_5Fe(im)^{3-}$ is also about 10 kcal/mol more exothermic than for the other ligands. One explanation for the much lower value for $\Delta S_f°$ of the imidazolate complex is that $(CN)_5Fe(im)^{3-}$ has a much tighter solvation shell than most of the other complexes listed in Table XI. The potential origin of the tighter solvation for $(CN)_5Fe(im)^{3-}$ would likely be due to two factors: (1) the charge of the complex is more negative than on $(CN)_5FeH_2O^{2-}$; (2) the ligand (im^-) may be strongly hydrogen bonded to the solvent. Of these two factors the first would appear to be less important. If $\Delta S_f°$ of NCS^- is taken to be an estimate of a normal entropy term in the absence of strong hydrogen bonding, its value might be taken as an estimate of the charge effects. The increase in H bonding of imidazolate in $(CN)_5Fe(im)^{3-}$ is paralleled by a similar but more modest effect on the formation entropy of $(CN)_5Fe(Him)^{2-}$ compared to $(CN)_5Fe(1\text{-}CH_3im)^{2-}$. Both possess the same net charge on the complex, yet $\Delta S_f°$ is 9–10 eu more negative for the $(CN)_5Fe(Him)^{2-}$ species than when the *N*-methyl group prevents any strong interaction by H bonding to the remote nitrogen of the ring. It also appears that the pK_a of coordinated imidazoles is lowered if a ring substituent can form an H-bonded internal chelate ring within the resultant imidazolate. This effect is discussed later.

The pK_a value and thermodynamic parameters for some related coordinated imidazole complexes are entered in Table XII. The importance of coordination to the metal ion center in overcoming the endothermicity of the dissociation of the pyrrole hydrogen is evident for the $(CN)_5Fe(Him)^{2-}$, ferrimyoglobin(Him)$^+$, and cobalamin(Him)$^+$ data. The values of association constants for the same series of imidazolate complexes have been calculated by approach 1 from the pK_a of the coordinated imidazole and the affinity of imidazole for the corresponding ferrimyoglobin, cobalamin, methylmercury, and $(NH_3)_5Ru^{3+}$ aquo complexes. These entries are shown in Table XIII. The values of the log ratio of association constants of the imidazolate:imidazole are also given for these complexes. The values of association constants and pK_as

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Table XII. Pyrrole Hydrogen pK_as of Imidazoles, μ = 1.0 and t = 25 °C, and Acid Dissociation Enthalpies and Entropies

reaction	pK_a	$\Delta H°$	$\Delta S°$	ref
Him $\rightleftharpoons$ H_3O^+ + im^-	14.44	17.6 ± 1.6	−7 ± 5	9
$(CN)_5Fe(Him)^{2-} \rightleftharpoons H_3O^+ + (CN)_5Fe(im)^{3-}$	10.94	8.8 ± 0.8	−21 ± 3	this work
$(CN)_5Co(Him)^{2-} \rightleftharpoons H_3O^+ + (CN)_5Co(im)^{3-}$	~13.0			26
[ferrimyoglobin(Him)$^+$] $\rightleftharpoons$ H_3O^+ + [ferrimyoglobin(im)]	10.34	11.4 ± 1.0	−9 ± 4	9
[cobalamin(Him)]$^+$ $\rightleftharpoons$ H_3O^+ + [cobalamin(im)]	10.25	10.5 ± 1.0	−12 ± 3	10
$(NH_3)_5Co(Him)^{3+} \rightleftharpoons H_3O^+ + (NH_3)_5Co(im)^{2+}$	10.02			27
$CH_3Hg(Him)^+ \rightleftharpoons H_3O^+ + CH_3Hg(im)$	9.61			21
$(NH_3)_5Ru(Him)^{3+} \rightleftharpoons H_3O^+ + (NH_3)_5Ru(im)^{2+}$	8.9			22

Table XIII. Comparison of Imidazole and Imidazolate Association Parameters (μ = 1.0)

reaction	$\Delta H_f°$	$\Delta S_f°$	log (K_{im}/K_{Him})
$(CN)_5FeH_2O^{2-}$ + im^- $\rightleftharpoons$ $(CN)_5Fe(im)^{3-}$ [a]	−25.4 ± 2.3	−45 ± 8	3.41
$(CN)_5FeH_2O^{2-}$ + Him $\rightleftharpoons$ $(CN)_5Fe(Him)^{2-}$	−15.8 ± 0.6	−27 ± 2	
ferrimyoglobin$(H_2O)^+$ + im^- $\rightleftharpoons$ ferrimyoglobin(im) [b]	−10.3 ± 3.3	−5.9 ± 2.5	4.02
ferrimyoglobin$(H_2O)^+$ + Him $\rightleftharpoons$ ferrimyoglobin(Him)$^+$	−4.1 ± 0.7	−3.5 ± 2.5	
cobalamin$(H_2O)^+$ + im^- $\rightleftharpoons$ cobalamin(im) [c]	−13.4 ± 2.9	−8.5 ± 7.3	4.05
cobalamin$(H_2O)^+$ + Him $\rightleftharpoons$ cobalamin(Him)$^+$	−7.2 ± 0.6	−3.2 ± 2.0	
CH_3Hg^+ + im^- $\rightleftharpoons$ $CH_3Hg(im)$ [d]			4.75
CH_3Hg^+ + Him $\rightleftharpoons$ $CH_3Hg(Him)^+$			
$(NH_3)_5RuOH_2^{3+}$ + im^- $\rightleftharpoons$ $(NH_3)_5Ru(im)^{2+}$ [e]			10.8
$(NH_3)_5RuOH_2^{3+}$ + Him $\rightleftharpoons$ $(NH_3)_5Ru(Him)^{3+}$			

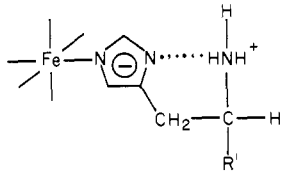
[a] This work. [b] Reference 9. [c] Reference 10. [d] Reference 21. [e] Reference 22.

are available only at 25 °C for CH_3Hg^+ and $(NH_3)_5Ru^{3+}$. The values of $\Delta H_f°$ in Table XIII show that ($\Delta H_f°_{(Him)}$ − $\Delta H_f°_{(im)}$) is close to 10 kcal/mol for $(CN)_5Fe^{2-}$ and 6 kcal/mol for ferrimyoglobin and cobalamin centers. This is consistent with im^- acting as a better donor than Him toward the low-spin Fe(III) and Co(III) complexes of this limited series. If the electrostatic factor that destabilizes $Fe(CN)_5(im)^{3-}$ relative to the next four pairs where an electrostatic attraction favors complexation is included, a corrected value of log (K_{im}/K_{Him}) of 4.6 is obtained. This correction was made from ratios of outer-sphere association constants where electrostatic effects are dominant. The relative affinities for im^- vs. Him are then approximately constant for $(CN)_5Fe^{2-}$, ferrimyoglobin, cobalamin, and CH_3Hg^+. CH_3Hg^+ has a closed-shell configuration; therefore, im^- is not likely to serve as a π donor toward the CH_3Hg^+ center. The log (K_{im}/K_{Him}), ca. 4.75, would reflect relative σ-donor abilities of im^- and Him. If any of the other complexes participated to large degree in accepting π bonding from im^-, the relative ratio of log (K_{im}/K_{Him}) would be anticipated to be larger than the 4.75 value for CH_3Hg^+. In Table XIII only $(NH_3)_5Ru^{3+}$ shows this effect with a 10.8 log units difference. The pK_a of $(NH_3)_5Ru(Him)^{3+}$ is also the lowest value consistent with a larger degree of π donation between Ru(III) and Him and even stronger interaction between im^- and Ru(III). The trends in the data in Table XIII suggest that for either im^- or Him the order of the metal center acting as an acceptor for the combined σ and π basic properties of the coordinated ligand is $(CN)_5Fe^{2-}$ > cobalamin$^+$ ≳ ferrimyoglobin$^+$ as shown by $\Delta H_f°$ values. The pK_a approximately follows this order with $(CN)_5Fe(Him)^{2-}$ > ferrimyoglobin(Him)$^+$ ≳ cobalamin(Him)$^+$. Since the order reflected in the $\Delta H_f°$ values suggests that the Fe(III) center in $(CN)_5Fe^{2-}$ is more positive than Co(III) in cobalamin$^+$ or Fe(III) in ferrimyoglobin$^+$, one might expect that the $(CN)_5Fe(Him)^{2-}$ would be the most acidic of the three. However, the unfavorable entropy caused by the separation of charge of H_3O^+ from the incipent $(CN)_5Fe(im)^{3-}$ anion overrides the stronger Fe(III)–imidazolate bonding in $(CN)_5Fe(Him)^{2-}$ or $(CN)_5Fe(im)^{3-}$. The $\Delta S°$ for the acid dissociation appears to be about 10 eu more negative for $(CN)_5Fe(Him)^{2-}$ compared to the cationic complexes in Table XII. If it were not for the anionic charge factor, the pK_a of $(CN)_5Fe(Him)^{2-}$, owing to bonding and electronic effects on the coordinated imidazole, would be nearly 2 units lower (8.9) and comparable to the value of $(NH_3)_5Ru(Him)^{3+}$. This is consistent with the conclusion of George et al. that electronic effects are more important than electrostatic repulsion between the effective positive charge of a coordinated metal center and the pyrrole hydrogen across the ring,[9,20] but it also shows that overall electrostatic charge and solvation of the species have strong effects on the pK_a. We have found that most of the observed pK_as of coordinated imidazole complexes can be fit by the equation

$$pK_a \text{ complex} = 14.44 - 2.07\chi_m - 0.20\delta \qquad (18)$$

wherein χ_m is the Pauling electronegativity of a given metal in a given oxidation state[28] and δ is the net charge on the complex ion. It is informative that coordination of most transition-metal centers will lower the pK_a of the coordinated imidazole by about 4 units with minor variations as a function of the oxidation state and metal ion involved. Although eq 18 is empirical, it does suggest that electronic effects on the ring orbitals as perturbed by the metal center (via χ_m) are a factor of about 10 more pronounced in comparing a unit change in χ_m to a unit change in net charge on the complex. However, when two metal ion complexes in which the metal centers have comparable χ_m values are compared, the net charge term can contribute the major difference between the observed pK_as. Equation 18 does not hold for pK_as of Cu(II) and Zn(II) imidazole complexes. Work in our laboratory is addressing the nature of the enhancement shown by these particular ions.

In the spectra of $(CN)_5Fe(RimH)^{2-}$ complexes, the presence of an electron-releasing group R on the ring shifts the charge-transfer band to lower energy relative to $(CN)_5Fe(Him)^{2-}$. The presence of an R group attached to the ring in $(CN)_5Fe(Rim)^{3-}$ complexes also shifts the MLCT band to longer wavelength. The parent complex $(CN)_5Fe(im)^{3-}$ has the long-wavelength maximum centered at 625 nm. With various R groups the band shifts to ca. 800 nm. The presence of a saturated R group causes little change in the pK_a of the $(CN)_5Fe(RimH)^{2-}$ complex. At μ = 4.0 the pK_a values are very similar: R = H, pK_a = 10.4; R = CH_3, pK_a = 10.4; R = $-CH_2CH_2CO_2^-$, pK_a = 10.5. However, the complex with R = $-CH{=}CHCO_2^-$ conjugated with the ring exhibits a pK_a at 8.64. This suggests that the imidazolate anion form is stabilized by delocalization of the π system. The isomer of urocanic acid (R = $-CH{=}CHCO_2^-$) in the experiment has previously been shown to be the trans isomer such that any chelation between the carboxylate and free imidazolate nitrogen is prevented. The imidazolate form of histidine and histamine is stabilized relative to imidazole. The ligand dissociation rate of imidazolate formed from histamine and histidine is much more rapid than that of imidazole itself. This feature caused difficulties in obtaining good spectrophotometric titration data to determine the pK_as of these complexes. However, the pK_as are apparently lowered relative to Him by 0.5–1.0 pK unit. The lowering of the pK_a suggests stabilization of the anion form by means of internal H bonding to the amine hydrogens:



Minor perturbations of the ligand field band of the imidazolate complexes are also observed. The LF transition of the $(CN)_5Fe(im)^{3-}$ complex occurs at 438 nm; this transition is shifted up to 9 nm to lower energy by electron-releasing groups. The opposite effect is observed for the imidazolate with R = $-CH{=}CHCO_2^-$; this complex has its LF maximum at 435 nm (3 nm to higher energy). The strength of the bonding between $(CN)_5Fe^{2-}$ and the R-substituted imidazoles is affected by a few kilocalories per mole as shown by the $\Delta H°$ parameters for $(CN)_5Fe(Him)^{2-}$ vs. $(CN)_5Fe(1\text{-}CH_3im)^{2-}$ when their σ basicities vary by only 0.2 log unit. These small changes make it nearly impossible to ascertain whether the shifts in the LF maxima are due to alteration in the bonding character of ground state, excited state, or both. However, the direction of the shifts is opposite to an effect largely due to σ donation alone. Perhaps the results are indicative of a greater degree of π bonding in the excited state of the substituted imidazolates relative to imidazolate.

The dissociation of ligands from $(CN)_5FeL^{2-}$ (L = a neutral ligand) is prone to catalysis from the corresponding $(CN)_5FeL^{3-}$ complexes. The ligand exchange of $(CN)_5Fe(Him)^{2-}$ is complicated by electron transfer catalyzed exchange with traces of $(CN)_5Fe(Him)^{3-}$ in the system; the intrinsic rate of exchange measured in the presence of excess IO_4^- is very slow in contrast to the rates observed when ion-exchanged samples of $(CN)_5Fe(Him)^{2-}$, prepared by H_2O_2 oxidation, are mixed with a labeled imidazole.[23] The seemingly thorough kinetic results on the substitution of NCS^- for OH^- in $(CN)_5FeOH^{3-}$ have been shown to be in error for the same catalytic problems.[15,24]

In order to be sure that the values of k_d measured for the dissociation of imidazolate at $[OH^-] = 0.10$ M were of the intrinsic pathway rather than one catalyzed by Fe(II) in the system, parallel runs were made. In one there was no added sources of Fe(II) other than that which is present by the separation or synthetic procedure. In the second run $Fe(CN)_6^{4-}$ was added at a level equal to the $(CN)_5Fe(im)^{3-}$ at initial mixing. No enhancement of the value for approach to equilibrium was detected in the presence of added $Fe(CN)_6^{4-}$. Under similar conditions exchange of $(CN)_5Fe(Him)^{2-}$ is markedly accelerated by several orders of magnitude in rate. We conclude that the observed values of k_d are reliable estimates, within experimental error, of the intrinsic dissociation rate constants rather than a redox catalyzed exchange pathway. In support of this view the value measured for k_d at 298 K is tenfold lower than the rate of dissociation of imidazole from $(CN)_5Fe^{3-}$;[12] also the re-formation pathway, which would have to involve substitution for H_2O on $(CN)_5FeH_2O^{3-}$ if a redox path were operative, exhibits activation parameters of 5 kcal/mol higher than $\Delta H^‡$ for displacement of H_2O by pyridines and pyrazines on $(CN)_5FeH_2O^{3-}$.[25]

The approach to equilibrium kinetics for the dissociation and re-formation of the $(CN)_5Fe(im)^{3-}$ complex obeys a kinetic rate law with terms $k_d + k_f[Him]$. The k_d term is a composite of an acid- or base-independent term and a term in $[H_3O^+]$ (eq 2). The term which corresponds to the reverse of the k_1 component of k_d is not observed. The concentration of $HimH^+$ is much too low to provide a detectable term. Therefore values of "k_d" calculated from the association constant of $(CN)_5Fe(im)^{3-}$ and the measured value of k_f reflect the value of k_0 alone. The detection of an acid-catalyzed component of k_d suggests that the k_0 pathway is the solvent serving in the general acid role.

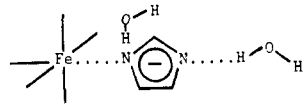


Figure 5. A possible orientation of k_0 component of dissociation reaction.

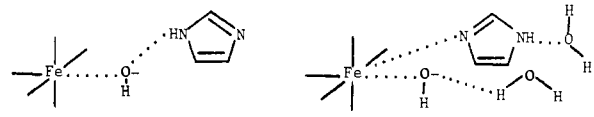


Figure 6. Possible orientations for the k_f pathway.

The values for $\Delta H^‡$ for dissociation and formation of $(CN)_5Fe(im)^{3-}$ are both larger positive terms while the corresponding $\Delta S^‡$ values are small but positive quantities. These parameters implicate a largely dissociative transition state in which the $(CN)_5Fe(III)\cdots L$ bond is strongly weakened for either L = im^- or OH^-. It is likely that the entering neutral H_2O molecule begins to transfer a proton to the leaving imidazolate ligand as initial bond formation to the oxygen of the incipient coordinated OH^- takes place. In this way the separation of charge is minimized and a pathway for the loss of a neutral imidazole is achieved. The reverse path is shown to involve the neutral free ligand. This supports the previous statement as the law of microscopic reversibility is obeyed. It is an interesting question as to whether the pyrrole imidazole hydrogen is transferred to coordinated OH^- or whether a solvent molecule serves this purpose. A strict adherence to the microscopic reversibility would favor the H end on attack of imidazole (see Figures 5 and 6) rather than the Lewis base end of the imidazole molecule. Because of the rapid exchange of protons with the solvent there is no way to test this system to discern between ligand entering orientations. The major result is that ligand addition of OH^- or im^- involves the protonated form (H_2O or Him) and the mechanism is largely a dissociative one of the opposite anion partner, im^- or OH^-. The origin of the $k_1[H_3O^+]$ component of k_d is readily accommodated by an activated complex similar to the one shown in Figure 5. However, for the H_3O^+-promoted path the remote water molecule, which is shown as being strongly hydrogen bonded in Figure 5, would be replaced by H_3O^+. The advantage for the H_3O^+-promoted path is again that separation of charge is minimized as the leaving group's negative charge is reduced by protonation.

The value determined for $\Delta H^‡$ for the loss of imidazolate by the solvent-assisted path is 26.6 ± 2.0 kcal/mol. $\Delta H^‡$ for dissociation of imidazolate is within experimental error of the value of the $\Delta H_f°$ of the association reaction of $(CN)_5Fe(im)^{3-}$. The dissociative transition state would appear to have very weak bonding between $(CN)_5Fe^{2-}$ and im^- in order that a second-sphere solvent molecule may insert into the greatly diminished bond. This process is equivalent to an I_d mechanism with proton transfer between H_2O and im^- at the rate-determining step. The "looseness" of the transition state for dissociation of im^- is supported by the $\Delta S^‡$ of +14 eu.

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Supplementary Material Available: Spectrophotometric determination of the K_a of $(CN)_5Fe(Him)^{2-}$ (Figure A), the $(CN)_5Fe(1\text{-}CH_3im)^{2-}/(CN)_5FeSCN^{3-}$ equilibrium at 19.5 °C (Figure B), and the $(CN)_5Fe(1\text{-}CH_3im)^{2-}/(CN)_5Fe(im)^{3-}/(CN)_5FeOH^{3-}$ equilibrium at 24.8 °C (Figure C) (3 pages). Ordering information is given on any current masthead page.

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