rous-ferric porphyrin dimer. This is not unique to tetraphenylporphyrin but has been observed in deuterioporphyrin, aetioporphyrin, protoporphyrin IX, and other similar dimeric species. In the latter species, marked differences in stability exist depending on the ring substitution positions. Results of this will be presented in a separate study.

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Hydrate–Carbonyl Equilibrium in the Complex Pentacyano(4-formylpyridine)iron(II) and the Kinetics of Some Related Electron Exchange Reactions[1a]

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Abstract: The influence of the pentacyanoiron(II) substituent on the ligand hydration equilibrium in the complex pentacyano(4-formylpyridine)iron(II) has been studied spectrophotometrically by following the shifts with temperature of the $\pi^* \leftarrow d\pi$ electron transfer bands in the visible–uv region. In the complex, the hydration constant, 0.48, measured at 37°, pH 7, and $\mu = 0.10\ M$ $LiClO_4$, is lower than those reported both for free and for protonated 4-formylpyridine, yet higher than that known for the pentaammine(4-formylpyridine)ruthenium(II) species. The observation is attributable to moderate stabilization of the aldehydo, relative to the hydrated form of the ligand by back-donation from the $Fe(CN)_5^{3-}$ moiety. The first-order rate constant for the hydration process is 2.4×10^{-2} sec^{-1} at 25°, pH 4.7, and $\mu = 0.10$. An investigation of the kinetics of electron transfer between pentacyano(pyridine)iron(II) and -(III) with hexacyanoiron(III) and -(II) has also been performed. Using the Marcus theory, the rate constant for self-exchange in pentacyano(pyridine)iron(II) and -(III) is calculated to be $2.4 \times 10^6\ M^{-1}$ sec^{-1} at 25°.

The properties of metal ions are modified by synthesizing complexes among which the charge, coordination geometry, or ligand field strength varies. Special significance arises when a ubiquitous ion, *e.g.*, iron(II), can be made to mimic the reactivity of the interesting but costly ruthenium(II). Octahedral, low spin complexes of the latter have attracted considerable attention because of their ability to interact with suitable ligands *via* metal-to-ligand back-donation.[2-6]

An example of this was provided by Zanella and Taube,[6] who showed that coordination of 4-formylpyridine to pentaammineruthenium(II) results in a marked stabilization of the ligand's aldehydo group with respect to hydration. Our interest in the similarity between substituted pentaammineruthenium(II) complexes and analogous pentacyanoiron(II) species[7] led to an investigation of the effect of the N-coordinated $Fe(CN)_5^{3-}$ substituent on the aqueous hydration equilibrium of 4-formylpyridine.

Data on the kinetics of dehydration of the coordinated ligand were obtained by reducing the pentacyano(4-formylpyridine)iron(III) complex, which exists predominantly in the hydrated form, to the iron(II) species. Rapid reaction with the reducing agent, ferrocyanide ion, produces an iron(II) complex which is spontaneously dehydrated at a measurable rate. An investigation of the kinetics of electron exchange between hexacyanoiron(II) and -(III) with pentacyano(pyridine)iron(III) and -(II) was important to this study and is presented herein.

Experimental Section

Reagents. All commonly available substances were of reagent grade and were used without further purification. Potassium hexacyanoiron(II) and -(III) were freshly prepared and standardized before each set of experiments. 4-Formylpyridine (Aldrich Chemical Co.) was converted to its hydrate form by dissolving it in water at 50° and cooling to ice bath temperature. The solid obtained was recrystallized several times yielding a white, crystalline material. *Anal.* Calculated for $C_6H_7O_2N$: C, 57.6; H, 5.6. Found: C, 57.3; H, 5.8. Organic amines and their pentacyanoiron(II) complexes were prepared and purified according to procedures described previously.[7] For the spectrophotometric measurements, the pentacyanoiron(II) complex of 4-formylpyridine was prepared in solution by treatment of the dissolved salt $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ with a tenfold or greater excess of the purified ligand.

Instruments and Techniques. Visible spectra were obtained employing a Cary Model 14 recording spectrophotometer fitted with thermostated cell compartments. Rapid kinetics measurements were made using a Durrum Model D-150 stopped flow apparatus. Reactions with half-lives greater than 15 sec were followed using the Cary instrument. Temperature control within the cell compartments of the two spectrophotometers was accurate within ±0.3°.

The hydration equilibrium of the pentacyano(4-formylpyridine)iron(II) complex was studied spectrophotometrically in the 7.3–41.1° range. Slow decomposition of the complex precluded measurements at higher temperatures. Ionic strength was maintained at 0.10 *M* by addition of lithium perchlorate. Experiments in buffered solutions at pH 6.7 (NaH_2PO_4–Na_2HPO_4, 10^{-2} *M*) gave results identical with those obtained in the absence of buffer at pH 9.

For the nmr measurements a Varian A 60 spectrometer was employed. The complex was prepared in solution as follows. A 0.125-g sample of solid 4-formylpyridine was treated with 3 ml of D_2O. Concentrated HCl was added dropwise until the solid dissolved at pH 4. While stirring, 0.30 g of solid $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ was added slowly to the solution, which became dark red-violet in color. The nmr spectrum showed peaks corresponding to the protonated form of the ligand, present in excess, and also to the $Fe(CN)_5^{3-}$ complex of the two forms of 4-formylpyridine. The spectrum confirmed that free nonprotonated 4-formylpyridine was not present. Under the experimental conditions the complex was stable in solution for at least 90 min. However, at higher pH or over longer time periods the color of the solutions changed, possibly because of the reaction of the small amount of free NH_3 present with the carbonyl group of bound 4-formylpyridine.

The rates of electron transfer reactions were studied starting with the pentacyano(pyridine)iron complex in either the (II) or the (III) oxidation state. Pentacyanoiron(III) complexes were prepared by oxidation of the pentacyanoiron(II) species with stoichiometric amounts of Ce(IV) (aqueous). The solutions were passed subsequently through a cationic resin column (AG 50W-X2, Bio-Rad) which removed Ce(III). Ionic strength and pH of solutions used in the electron transfer experiments were adjusted with potassium hydroxide and potassium nitrate solutions as necessary.

Probable errors quoted for enthalpy and entropy changes and for activation parameters were obtained by an analysis of variance about regression[8] employing Student's *t* values for 99% confidence limits.

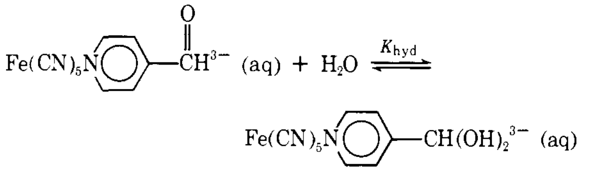
Results

Hydration Equilibrium. The aqueous pentacyano(4-formylpyridine)iron(II) complex shows two strong absorption bands (log $\epsilon \simeq 3$) in the visible region with maxima at 385 and 504 nm. Because the ion pentacyano(4-acetylpyridine)iron(II) as well as other pentacyanoiron(II) complexes of aromatic N heterocycles show only one band in the visible region, the spectrum in question could not be assigned to a single species.

To characterize the system, proton nmr spectra were obtained. The spectrum of a saturated solution made from solid, hydrated 4-formylpyridine in D_2O includes peaks located 10.0 and 6.0 ppm downfield from that of external tetramethylsilane. These peaks represent the aldehydo proton in the carbonyl and hydrate forms of the compound, respectively.[6,9-12] Multiplets due to the ring protons are observed at 8.75, 8.5, 7.8, and 7.45 ppm. The two signals at low field arise from protons lying α to the nitrogen in the carbonyl and hydrate forms. The higher field absorptions are due to the β protons of those two forms.

In the nmr spectrum of the pentacyanoiron(II) complex the α proton peaks are shifted downfield to 9.3 and 9.0 ppm while those due to the β protons move upfield to 7.6 and 7.3 ppm. The aldehydo proton signal in the complex is observed to be unshifted relative to the free aqueous ligand in both the carbonyl and hydrate forms.[13] The strength of the signals due to the carbonyl form relative to the hydrate is somewhat greater in the $Fe(CN)_5^{3-}$ complex than in the aqueous ligand.

The results indicate that the hydration equilibrium of 4-formylpyridine is responsible for the two visible-uv absorption bands observed in the pentacyanoiron(II) complexes. The system is described by eq. 1. In analogy with the pentaammineruthenium(II) complex[2,6] of this ligand, the band at 385 nm is assigned to the hydrate form while the 504-nm band is ascribed to the aldehyde form.



(1)

Figure 1 shows the variation with temperature of the spectrum of a solution containing the ion pentacyano(4-formylpyridine)iron(II). Although the isosbestic point at 420 nm is consistent with the presence of only two chromophores in equilibrium, direct spectrophotometric determination of the hydrate–carbonyl equilibrium quotient (K_{hyd} = [hydrate]/[carbonyl]) is impossible without knowledge of the molar extinction coefficients of at least one of the two species.

A solution to this problem resulted from two observations. First, in the visible region the extinction coefficients of pentacyanoiron(II) complexes of aromatic N heterocycles are virtually independent of temperature within the range employed here. Therefore the absorbance changes in Figure 1 must stem from variations in K_{hyd}. Second, although the visible absorption bands of pentacyanoiron(II) complexes incorporating aromatic N heterocycles are slightly asymmetric on the reciprocal centimeter (energy) scale, the asymmetry is negligible when plotting absorbance

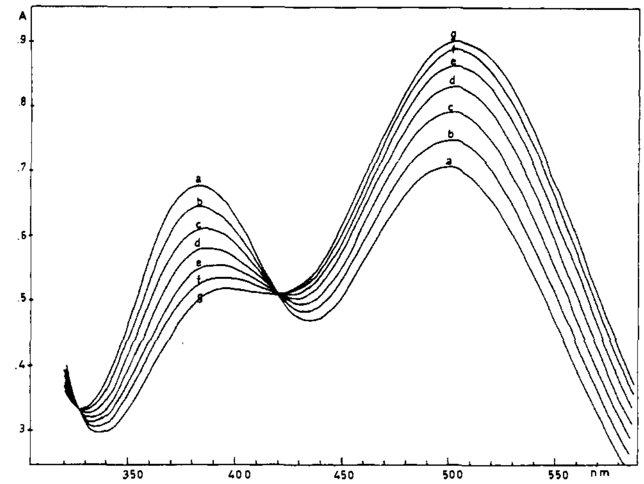


Figure 1. Variation with temperature of the visible spectrum of aqueous pentacyano(4-formylpyridine)iron(II), 2.20 × 10^{-4} *M*, pH 6.7, and 1.00-cm cuvette. Curves a–g refer to 7.3, 13.0, 19.0, 25.0, 31.0, 37.0, and 41.1°.

vs. wavelength. In this case the absorption curve can be generated by a simple Gaussian function. For example, an excellent fit was obtained for the spectrum of the pentacyano(4-acetylpyridine)iron(II) complex.

Applying Gaussian analysis to the spectra in Figure 1, one can show that the contribution of the hydrate form to the absorption band at 504 nm is very small. Neglecting this contribution and employing the usual conservation relationships, eq 2 is derived. In the equation C_{Fe} is the total

$$A_{385} = A_{504}\frac{(\epsilon_{A,385} - \epsilon_{B,385})}{\epsilon_{A,504}} + C_{Fe}\epsilon_{B,385} \qquad (2)$$

concentration of iron(II) species, A_λ is the measured absorbance at wavelength λ, and $\epsilon_{A,\lambda}$ is the extinction coefficient of the complex in the carbonyl form at that wavelength. Subscript B refers to the complex in the hydrate form.

Excellent straight lines of identical slope were obtained at several values of C_{Fe} by plotting A_{385} *vs.* A_{504} in the 7–41° temperature interval. From the slope of these lines the quotient $(\epsilon_{A,385} - \epsilon_{B,385})/\epsilon_{A,504} = -0.79 \pm 0.01$. Introducing these considerations into the mass-law expression for the hydration constant, one obtains

$$K_{hyd} = \frac{(A_{385}/A_{504})\epsilon_{A,504} - \epsilon_{A,385}}{0.79\epsilon_{A,504} + \epsilon_{A,385}} \qquad (3)$$

From the Gaussian form of the absorption band the ratio $\epsilon_{A,385}/\epsilon_{A,504} = 0.12 \pm 0.02$ was calculated. On substitution in eq 3, K_{hyd} could be found from measured values of A_{385}/A_{504}. The dependence of K_{hyd} on temperature is given in Table I.

Table I. Temperature Dependence of K_{hyd}[a]

Temp (°C)	K_{hyd}	Temp (°C)	K_{hyd}
7.3	0.89	31.0	0.54
13.0	0.78	37.0	0.48
19.0	0.68	41.1	0.45
25.0	0.61		

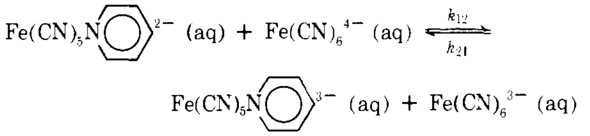
[a] μ = 0.1 *M* $LiClO_4$, pH 6.7.

Using the values of the hydration constants and the original spectra the extinction coefficients $\epsilon_{A,504}$ and $\epsilon_{B,385}$ were found to be 5.2 × 10^3 and 4.4 × 10^3 M^{-1} cm^{-1}, respectively. The latter is in excellent agreement with the value 4.5 × 10^3 M^{-1} cm^{-1} taken from the ordinate intercepts of plots of eq 2, demonstrating the validity of the assumptions employed.

From the temperature dependence of K_{hyd} the parameters ΔH and ΔS were found to be −3.5 ± 0.2 kcal/mol and −12.7 ± 2.2 cal °K^{-1} mol^{-1}, respectively.

Kinetics of Dehydration. Aqueous reduction of the pentacyano(4-formylpyridine)iron(III) complex with ferrocyanide ion at 25°, pH 4.7 (0.05 *M* sodium acetate-acetic acid), gives a very rapid absorbance increase at 504 nm, followed by another, much slower increase. The first reaction can be assigned to reduction of the pentacyanoiron(III) species. The second, which takes place at a first-order rate which is independent of excess $[Fe(CN)_6^{4-}]$, corresponds to dehydration of the coordinated ligand. For this step, k_{obsd} equals (6.8 ± 0.3) × 10^{-2} and (6.5 ± 0.3) × 10^{-2} sec^{-1} at pH 4.0 and 4.7, respectively. The plots of ln $|A - A_\infty|$ *vs.* time from which k_{obsd} was obtained were linear over at least three half-lives. Although the kinetics of the initial electron-transfer reaction were not studied extensively, the rate was found to be first order in the concentration of each of the reacting iron species, with a rate constant of (3.5 ± 0.4) × 10^5 M^{-1} sec^{-1} at pH 4.7, μ = 0.10 *M* and 25°.

Electron Transfer Kinetics in the Pentacyano(pyridine)iron(III)-Ferrocyanide Reaction. The result described above led to the investigation of the electron transfer kinetics of a simpler system. The reactions between pentacyano(pyridine)iron(II) and -(III) and ferri-ferrocyanide were chosen because the oxidation potentials of the two couples are nearly equal under the conditions employed. Therefore it was possible by adjusting the concentrations of reactants to measure independently the specific rates k_{12} and k_{21} for the process



(4)

Results for the forward and reverse reactions, obtained at μ = 0.05 *M* (KNO_3) and pH 6–8, are given in Tables II and III. At 25°, k_{12} = (8.8 ± 0.4) × 10^4 M^{-1} sec^{-1} with ΔH_{12}^* = (4.6 ± 0.8) kcal/mol and ΔS_{12}^* = −21 ± 3 cal deg^{-1} mol^{-1}. k_{21} = (3.4 ± 0.2) × 10^4 M^{-1} sec^{-1} with ΔH_{21}^* = 5.5 ± 0.9 kcal/mol and ΔS_{21}^* = −19 ± 3 cal deg^{-1} mol^{-1}.

Table II. Specific Rates (k_{12}) of Reduction of $Fe(CN)_5py^{2-}$ by $Fe(CN)_6^{4-}$ [a]

Temp (°C)	$10^3[Fe(CN)_6^{4-}]$, *M*	$10^{-1}k_{obsd}$, sec^{-1}	$10^{-4}k_{12}$, M^{-1} sec^{-1}
9.5	1.10	5.9	5.3
10.8	1.10	6.2	5.6
16.4	1.10	7.5	6.8
22.5	1.10	8.9	8.1
25.0	0.57	5.3	9.2
25.0	1.10	9.6	8.7
25.0	1.50	12.8	8.5
25.0	2.20	19.5	8.8
31.0	1.10	11.3	10.3

[a] μ = 0.050 *M* (KNO_3), pH 6–8, $[Fe(CN)_5py^{2-}(aq)]$ = 5.0 × 10^{-5} *M*.

Effect of Potassium Ion Concentration. Wahl and coworkers[14] have shown that association of potassium ion with ferri- and ferrocyanide ions causes significant catalysis of the iron(II) and -(III) self-exchange process. The effect of the potassium ion concentration on the reactions under

Table III. Specific Rates (k_{21}) of Oxidation of $Fe(CN)_5py^{3-}$ by $Fe(CN)_6^{3-}$ [a]

Temp (°C)	$10^3[Fe(CN)_6^{3-}]$, M	$10^{-1}k_{obsd}$, sec^{-1}	$10^{-4}k_{21}$, M^{-1} sec^{-1}
9.4	1.00	1.9	1.9
15.5	1.00	2.5	2.5
21.5	1.00	3.1	3.1
25.0	1.00	3.4	3.4
25.0	1.50	5.0	3.3
25.0	2.00	6.7	3.4
33.5	1.00	4.6	4.6

[a] μ = 0.050 M, pH 6–8, $[Fe(CN)_5py^{3-}(aq)]$ = 5.0 × 10^{-5} M.

discussion here was measured and is given in Figure 2. Values of $k_{12}{}^0$ and $k_{21}{}^0$, found by extrapolation of the specific rates to $[K^+(aq)] = 0$ are (1.2 ± 0.1) × 10^4 and (0.5 ± 0.05) × 10^4 M^{-1} sec^{-1}, respectively, at 25° and μ = 0.

Spectra of Pentacyanoiron(III) Complexes of Aromatic N Heterocycles. As reported previously[7] the pentacyanoiron(II) complexes of aromatic N heterocycles can be oxidized reversibly to the oxidation state (III) with complete disappearance of their strong metal-to-ligand electron transfer bands. However, the resulting iron(III) complexes present interesting spectra in and near the ultraviolet region. Besides the absorption due to the aromatic ligand, the complexes exhibit two characteristic peaks in the 340–420-nm range. These are illustrated for the pyridine and 4-formylpyridine complexes in Figure 3. The wavelengths of maximum absorption for these and several other complexes are given in Table IV.

Table IV. Maxima for the Absorption Bands of Pentacyanoiron(III) Complexes of Aromatic N Heterocycles in the Near-Uv Region[a]

Ligand	Band maxima, nm	
4-Picoline	418 (1.4 × 10^3)	362 (1.1 × 10^3)
Pyridine	414 (1.1 × 10^3)	368 (0.8 × 10^3)
Isonicotinamide	418 (1.0 × 10^3)	364 (0.9 × 10^3)
4-Formylpyridine	416 (1.7 × 10^3)	366 (1.4 × 10^3)
N-Methylpyrazinium	422 (2.8 × 10^3)	340 (shoulder)

[a] Extinction coefficients in M^{-1} cm^{-1} given in parentheses.

Somewhat in analogy with the complexes studied by Gutterman and Gray,[15] we suggest that the lower energy band is due to cyanide-to-metal electron transfer. The weaker, higher energy transition may be a ligand field band. Electron-transfer excitation between the heterocycle and iron(III) can be excluded since similar spectra are observed for the ions $Fe(CN)_5NH_3{}^{2-}$ (aq) and $Fe(CN)_5H_2O^{2-}$ (aq). For most of the complexes in Table IV no changes in the spectra were seen over periods of at least 2 hr at pH values between 2 and 7, 25°. However, for the N-methylpyrazinium (MPz) and 4-formylpyridine complexes, variations were observed above pH 5 and 6, respectively. These were partly due to disproportionation, since formation of the iron(II) complexes was observed. In the case of the MPz iron(III) complex, aquation also took place at a measured specific rate of (3.1 ± 0.1) × 10^{-4} sec^{-1}, μ = 0.1 M, 25°, and pH 2–4.

Discussion

A principal result of this work concerns the effect of the $Fe(CN)_5{}^{3-}$ substituent on the aqueous carbonyl-hydrate equilibrium of 4-formylpyridine. Several groups of workers have investigated the hydration process for the free ligand in aqueous solution.[9–12] Their findings agree that at pH 1 the ligand exists primarily in the hydrated form ([carbonyl]/[hydrate] ≤ 0.10) at both 0° and 37°. In near-neutral solution at 37° the ratio was reported by Zanella and Taube[6] to be 1.4 while their extrapolation of the results of Pocker, *et al.*,[9] yielded a value of 1.25.

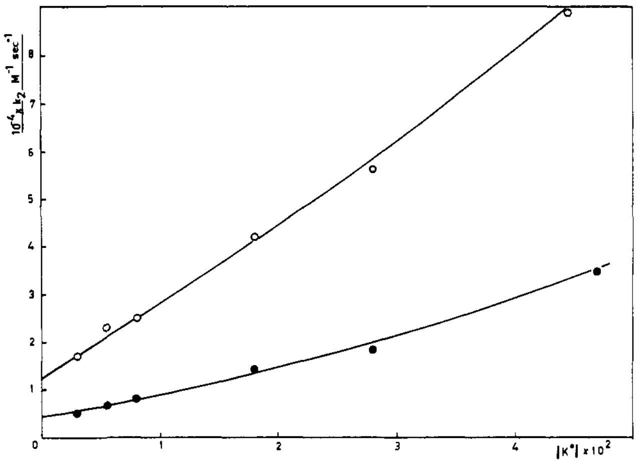


Figure 2. Dependence of k_{12} and k_{21} (filled circles) on the potassium ion concentration at pH ~7 and 25°.

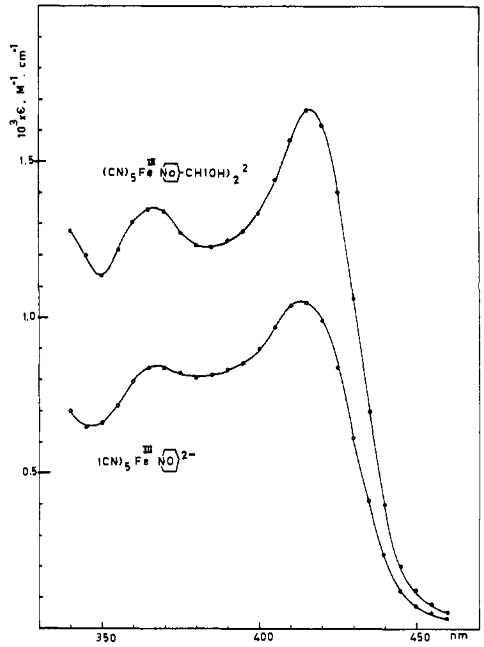


Figure 3. Near-uv absorption bands for the pentacyanoiron(III) complexes of pyridine and 4-formylpyridine in aqueous solution.

An interesting comparison can be made with the value "considerably greater than ten" obtained by Zanella and Taube for the ratio in the pentaammine(4-formylpyridine)ruthenium(II) complex. In the aqueous Ru(II) species the carbonyl/hydrate ratio is at least 14 times greater than in the free, unprotonated ligand. The ability of Ru(II) to stabilize the carbonyl form in spite of an adverse inductive effect is attributed to greater metal-to-ligand back-bonding interaction in the aldehydo form, relative to the hydrate.

On coordination of 4-formylpyridine to pentacyanoiron(II), the hydration equilibrium is not affected as strongly. The results given in Table I show that the carbonyl/hydrate ratio is 2.1 ± 0.1 at 37°, μ = 0.1 M, and pH 6.7. Relative to aqueous 4-formylpyridine, the ratio is changed by a factor of only 1.5. The result indicates that back-bonding to the heterocycle in the iron(II) complex is significantly less extensive than in the Ru(II) species. The enthalpy and entropy changes calculated for eq 1 are in the range usually found for the hydration of carbonyl complexes.[9,16,17]

While investigating the kinetics of dehydration subsequent to reduction of the pentacyano(4-formylpyridine)iron(II) complex by ferrocyanide ion, it was noted that the absorbance increase at 504 nm accompanying the hydration process is at least twice the initial change, which corresponds to the electron transfer reaction. Making the reasonable assumption that the carbonyl/hydrate ratio is unaltered during the reduction reaction and applying the appropriate value of K_{hyd} for the iron(II) product, we calculate that at least 80% of the 4-formylpyridine ligand exists in the hydrate form in the pentacyanoiron(III) complex. This is consistent with the inductive effect expected on coordination of 4-formylpyridine to a positive metal center.

Kinetics of Dehydration. The rate of dehydration of the carbonyl function in the pentacyano(4-formylpyridine)iron(II) complex was studied at pH 4.0–4.7. The range was somewhat limited because in more acidic solution protonation of the iron(II) complex occurs and at higher pH disproportionation of the iron(III) reactant takes place. The rate of dehydration varied only slightly in the range available, indicating that k_{obsd} corresponds to the pH-independent path for dehydration.

The observed rate constant is a sum of the specific rates of hydration and of dehydration, $k_{\mathrm{obsd}} = k_{\mathrm{hyd}} + k_{\mathrm{dehyd}}$. At 25°, k_{hyd} is 0.024 sec^{-1}, calculated from $k_{\mathrm{obsd}} = (6.5 \pm 0.3) \times 10^{-2}\ \mathrm{sec}^{-1}$ and $K_{\mathrm{hyd}} = 0.6$ (Table I). Agreement with known values of k_{hyd} for the aqueous free ligand (0.036 sec^{-1}, 25°)[12] is relatively close. We note that the pentacyanoiron(II) substituent does not catalyze dehydration of aqueous 4-formylpyridine as do some metal ions.[18]

Electron Transfer in the Hexacyanoiron(III)/-(II)-Pentacyano(pyridine)iron(II)/-(III) Reactions. Since both the products and the reactants in eq 4 are inert to substitution, the reaction is assigned to the outer-sphere class. Use of the Marcus equation[19]

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}$$

where

$$\ln f = (\ln K_{12})^2/4 \ln (k_{11}k_{22}/Z^2)$$

allows calculation of several interesting parameters, given in Table V. In the calculation, k_{11} and k_{22} are the self-exchange rate constants measured for the ferri–ferrocyanide couple[14] and calculated for the pentacyano(pyridine)iron(II) and -(III) system. K_{12} and k_{12} are equilibrium and specific rate constants referring to eq 4. Z is a frequency factor $\approx 10^{11}$.

Table V. Kinetics of Some Electron Transfer Reactions at 25°

Reaction	k, $M^{-1}\ \mathrm{sec}^{-1}$	ΔH^*, kcal/mol	ΔS^*, cal mol^{-1} $°\mathrm{K}^{-1}$
$\mathrm{Fe(CN)_6}^{4-} + \mathrm{Fe(CN)_6}^{3-}$	5×10^{3} [a]	4.2	−32
	24 [b]	9.1	−24
$\mathrm{Fe(CN)_6}^{3-} + \mathrm{Fe(CN)_5py}^{3-}$	3.4×10^{4} [c]	5.4	−20
	1.2×10^{4} [d]		
$\mathrm{Fe(CN)_6}^{4-} + \mathrm{Fe(CN)_5py}^{2-}$	8.7×10^{4} [c]	4.7	−20
	0.5×10^{4} [d]		
$\mathrm{Fe(CN)_5py}^{2-} + \mathrm{Fe(CN)_5py}^{3-}$	7×10^{5} [c,e]		
	2.5×10^{6} [d,e]		

[a] k at $[\mathrm{K}^+] = 0.05\ M$ found by extrapolation of data in ref 14. [b] k at $\mu \to 0$ calculated from ref 14. [c] $[\mathrm{KNO_3}] = 0.05\ M$. [d] $[\mathrm{KNO_3}] \to 0\ M$. [e] Calculated using the Marcus relationship.

The calculated value given in Table V for the specific rate of self-exchange in the pentacyano(pyridine)iron(II)/-(III) system is $2.5 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$ at 25° and $\mu = 0$. On comparison with the rate constant for self-exchange in the ferri–ferrocyanide system at $\mu = 0$, we note that replacement of cyanide by pyridine as a ligand results in a large increase, by a factor of 10^5, in the specific rate of iron(II)–iron(III) self-exchange.

Part of the rate enhancement should stem from the lower charges of the reactants when pyridine is substituted for a cyanide ligand. One expects that the contribution to ΔG^* due to Coulombic repulsion should decrease if the charges of the reactants are decreased. An estimate of this factor can be made using the equation[19]

$$\Delta G^* = \left[\frac{e_1e_2}{D_{\mathrm{s}}} + \frac{(\Delta e)^2}{4}\left(\frac{1}{\eta^2} - \frac{1}{D_{\mathrm{s}}}\right)\right]\frac{1}{2r}$$

In this expression e_1 and e_2 are the charges of the reactants, $2r$ is the distance between iron centers (assumed to be 8.8 Å), Δe is the number of electrons to be transferred, and η and D_{s} are respectively the refractive index and static dielectric constant of water. For the pentacyano(pyridine)iron(II)/-(III) electron exchange process, ΔG^* is estimated as 8.1 kcal/mol. In the case of electron exchange between ferri- and ferrocyanide, ΔG^* is calculated to be 11 kcal/mol. The difference between these values, approximately 3 kcal/mol, corresponds to a factor of $\sim 10^2$ in k.

After accounting in this way for the effect of charge, we note that the two rates still differ by three orders of magnitude. Part of this difference may be due to inaccuracies, discussed by Wahl and coworkers,[14] in the model upon which the calculation of electrostatic effects is based. However, it is also likely that a significant part of the rate enhancement results from the ability of the pyridine ligand to conduct electrons through the first coordination sphere of iron. This type of effect has been observed both by Wahl and coworkers[20] and by Taube, *et al.*[21] It seems to be particularly important for complexes in which the highest occupied metal–ligand bonding orbital allows delocalization of the exchanged electron into a ligand π system.

Conclusion

The two studies presented here provide an interesting comparison. In the case of the influence of the $\mathrm{Fe(CN)_5}^{3-}$ substituent on the hydration equilibrium of 4-formylpyridine, we find a small effect, indicating that back-bonding interaction between iron(II) and the heterocycle is rather less extensive than in a corresponding pentaammineruthenium(II) complex. Nevertheless, we note that the specific rate of the electron self-exchange process increases substantially on replacing cyanide in hexacyanoiron(II)/-(III) with a pyridine ligand. The two results demonstrate, at least qualitatively, that even a small degree of electron delocalization into a conducting system of appropriate symmetry may significantly increase the reactivity of a metal complex *vis-à-vis* electron exchange.

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Coordination Isomers of Biological Iron Transport Compounds. IV.[1-3] Geometrical Isomers of Chromic Desferriferrioxamine B

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Abstract: A number of microbial iron sequestering and transport agents (the siderochromes) are polyhydroxamic acids. In several of these agents, ferric ion has been replaced by chromic ion to induce kinetic inertness and thereby allow the possibility of isomer separation. The preparation and characterization of the chromic complex of desferriferrioxamine B are reported. Five enantiomeric pairs of geometrical coordination isomers are possible: one cis and four trans. The separation of the cis geometrical isomer from one or more trans isomers and their characterization are described. This is the first preparation and characterization of coordination isomers for metal complexes of ligands involved in microbial iron transport. The cis isomer has visible absorption maxima at 419 (68) and 583 (71) nm (ε), while the trans isomers have the same bands at 411 (51) and 589 (72) nm. Both the cis and trans isomers of chromic desferriferrioxamine B isomerize with half-lives of several days in solution at room temperature. The structurally similar chromic complex of desferriferrioxamine D_1 also has been prepared and characterized. The corresponding cobaltic complexes appear to be unstable because of gradual oxidation of the ligands by cobaltic ion.

The linear ferrioxamines (Figure 1), an important class of microbial iron transport agents,[4] are produced by several species of *Streptomyces* and *Nocardia*.[5-11] A characteristic structural feature of the ferrioxamines is repeating units of 1-amino-5-hydroxyaminopentane and succinic acid, such that a stable octahedral ferric complex is formed from three hydroxamate groups. The pathogenicity of certain infections apparently is associated with microbial iron transport, and several ferrioxamines are potent and broad spectrum antibiotics, while others are growth factors.[4,10-13] For example, ferrioxamine B is a growth factor for *Microbacterium lacticum*[10,14] and is capable of reversing ferrimycin antibiotic activity[10,13,15-19] against Gram-positive organisms such as *Bacillus subtilis*.[12,16,20] Ferrimycin A_1 is a derivative of ferrioxamine B in which the free amino group of the latter is substituted.[10,19] The substituent thus converts a growth factor, ferrioxamine B, into a powerful antibiotic.

The sequestering agent desferriferrioxamine B (Desferal) is used in the treatment of acute, accidental iron poisoning.[13,21,22] Schwarzenbach and coworkers demonstrated that desferriferrioxamine B exhibits remarkable affinity for ferric ion, little affinity for other ions which differ in charge or size, and, in particular, little or no affinity for ferrous ion.[23] Emery concluded from proton exchange rates that desferriferrioxamine B undergoes a dramatic conformational change upon complexation with ferric ion,[24] and Bock and Lang interpreted the Mössbauer spectrum of ferrioxamine B.[25] Ferrioxamine E, a cyclic ferrioxamine, crystallizes as a racemic mixture of Λ-cis and Δ-cis isomers.[26,27] All of these considerations raise the question of the possible role specific coordination isomers of siderochromes might play in microbial iron transport.

Many of the questions regarding the structure–function relationships of the siderochromes cannot be answered because of the kinetic lability of these high-spin ferric complexes. The coordination chemistry of hydroxamic acids with metal ions other than ferric is largely unknown.[28] In a previous paper[1] we described the preparation of a simple model diastereoisomeric chromic complex, tris(*N*-methyl-*l*-menthoxyacethydroxamato)chromium(III), and the resolution and characterization of its four geometrical and optical isomers: Λ-cis, Δ-cis, Λ-trans, and Δ-trans.[27] We also prepared and characterized the Λ-cis coordination isomer of two metal-substituted desferrisiderochrome complexes, chromic desferriferrichrome and chromic desferriferrichrysin,[2] and found that Λ-cis chromic desferriferrichrome transports at comparable rates to the native ferric complex in *Ustilago sphaerogena*.[3]

Five enantiomeric pairs of geometrical isomers of ferrioxamine B are possible from an examination of molecular models: one cis and four trans[5] (Figure 2). These five geometrical isomers are named as follows.[27] (i) The absolute configuration about the metal ion defines a rotation direc-