Contribution from the Department of Chemistry,
University of Missouri, Columbia, Missouri 65201

Electron Transfer and Ligand Substitution Reactions of the Ion Pentacyano(4-aminopyridine)ferrate(II)

NICOLAS V. HREPIC and JOHN M. MALIN*

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The ion pentacyano(4-aminopyridine)ferrate(II) has been characterized in aqueous solution. The complex exhibits a strong metal-to-ligand charge-transfer absorption (ϵ_{max} 4.4 × 10^3 M^{-1} cm^{-1}) at 320 nm. In the presence of excess heterocycle, the rate law for formation of the complex from pentacyanoaquaferrate(II) is $d[Fe(CN)_5L^{3-}]/dt = k_f[Fe(CN)_5OH_2^{3-}][L]$ with $k_f = 432 \pm 10$ M^{-1} s^{-1}, $\Delta H_f^\ddagger = 15.0 \pm 0.6$ kcal/mol, and $\Delta S_f^\ddagger = 4 \pm 2$ cal deg^{-1} mol^{-1} (25 °C, $\mu = 0.1$ M, pH ~7). Ligand-exchange studies yield a value for the specific rate of dissociation of 4-NH_2py: $k_d = (2.5 \pm 0.1) \times 10^{-3}$ s^{-1}, with $\Delta H_d^\ddagger = 21.4 \pm 0.2$ kcal/mol and $\Delta S_d^\ddagger = 1.2 \pm 1.6$ cal mol^{-1} deg^{-1}. One-electron oxidation of the complex by cyclic voltammetry is reversible, with $E° = -0.35 \pm 0.03$ V (0.1 M $LiClO_4$, 23 °C). The oxidation product is the violet pentacyano(4-aminopyridine)ferrate(III) ion (λ_{max} 560 nm, ϵ 2.7 × 10^3 M^{-1} cm^{-1}). A study of the kinetics of oxidation of the iron(II) complex by ferricyanide yielded the rate law $d[Fe(CN)_5L^{2-}]/dt = k_{et}[Fe(CN)_5L^{3-}][Fe(CN)_6^{3-}]$ where $k_{et} = (4.3 \pm 0.2) \times 10^5$ M^{-1} s^{-1}, $\Delta H_{et}^\ddagger = 2.0 \pm 0.5$ kcal/mol, and $\Delta S_{et}^\ddagger = -26 \pm 2$ cal mol^{-1} deg^{-1} (25 °C, $\mu = 0.05$ M ($LiClO_4$), pH 9.0).

Introduction

Complexes of aromatic N heterocycles with the pentacyanoferrate(II) moiety exhibit well-defined metal-to-ligand charge-transfer (MLCT) absorption spectra, due to electron transfer from the d orbitals of iron(II) to π^* orbitals of the heterocycle.[1,2] For a series of these complexes a well-established ordering of oxidation potentials,[1,3] Mössbauer isomer shifts,[4] NMR chemical shifts,[5] rates of substitution,[1] and stability constants[6] indicates that increasing $d\pi-p\pi$ back-bonding interaction accompanies increasing λ_{max}(MLCT).

We have recently identified a new complex of this type. The ion pentacyano(4-aminopyridine)ferrate(II) presents an MLCT band at 320 nm, the shortest wavelength yet observed in the pyridine series. Compared with other members of this group, the complex is particularly susceptible to oxidation and to displacement of the heterocycle by other ligands. The electron-rich character of 4-aminopyridine (4-NH_2py) is consistent with the observation that one-electron oxidation of the complex yields a violet species with a strong ligand-to-metal charge-transfer (LMCT) transition at a relatively great wavelength (560 nm). Our experiments involving the characterization of the iron(II) complex and its reactivity toward ligand substitution and electron transfer form the subject of this article.

Experimental Section

Materials. Previously published methods were employed to prepare sodium pentacyanoammineferrate(II) dihydrate[7] and also the lithium perchlorate solutions,[8] added to maintain ionic strength. Reagent grade potassium ferricyanide was used directly as supplied (Fisher Scientific Co.). 4-Aminopyridine (Aldrich Chemical Co.) was recrystallized several times from aqueous solution. 2-Methylpyrazine (J. T. Baker, reagent grade) was redistilled before use. Water was purified by deionization and redistillation. Phosphate buffer solution was used when pH 7.0 was required.[9] The pH 9.0 buffer was prepared using tris(hydroxymethyl)aminomethane (Fisher).

Apparatus. Kinetics data and spectra were obtained employing Cary Models 14 and 15 spectrophotometers or a Durrum Model D-150 stopped-flow instrument. Cell compartments in these instruments were thermostated within ±0.5 °C. An Orion 801 pH meter was used for the pH measurements. Cyclic voltammetry was performed using a Princeton Applied Research Model 173 potentiostat, controlled by a PAR Model 175 Universal Programmer and connected to a Houston Instruments Model 200 X-Y recorder. Platinum wire working and auxiliary electrodes and a silver/silver chloride reference electrode were employed. NMR spectra were obtained using a Varian A-60 instrument.

Treatment of Kinetics Data. Rate constants were computed from absorbance vs. time data by methods described previously.[10] Reaction conditions were adjusted to yield pseudo-first-order rate processes. In the kinetics of complexation of $Fe(CN)_5OH_2^{3-}$(aq), slow, secondary absorbance increases due to the presence of polynuclear iron(II) cyanides[11] were observed. These could be easily separated from the considerably more rapid reactions of the mononuclear species. In all reactions studied, agreement between computer-generated, first-order kinetics curves and those obtained by experiment was excellent over at least 3 half-lives.

Table I. Maxima for the Absorption Bands of Pentacyanoferrate(II) and -(III) Complexes of Aromatic N Heterocycles

	Fe(II)		Fe(III)	
ligand	λ_{max}, nm	log ϵ_{max}	λ_{max}, nm	log ϵ_{max}
4-aminopyridine	320[a]	3.64	560	3.44
4-methylpyridine	356[b]	3.55	418[c]	3.14
pyridine	362[b]	3.57	414[c]	3.04
			368	2.90
4-chloropyridine	383[b]	3.61		
isonicotinamide	435[b]	3.66	418[c]	3.00
			364	2.95
pyrazine	452[b]	3.70		
N-methylpyrazinium	655[b]	4.08	422[c]	3.45

[a] This work. [b] Reference 1. [c] Reference 14.

Results

Characterization of $[Fe(CN)_5(4\text{-}NH_2py)^{3-}]$. The pentacyano(4-aminopyridine)ferrate(II) complex is generated by adding solid sodium pentacyanoammineferrate(II) hydrate to aqueous solutions of the free ligand. A strong absorption band (λ_{max} 320 nm, ϵ_{max} 4.4 × 10^{-3} M^{-1} cm^{-1}) develops. This band can be assigned to metal-to-ligand charge-transfer (MLCT) excitation, by analogy with results obtained for similar complexes.[1,2] These are given in Table I.

The complex normally was studied in the presence of a 50-fold excess of 4-NH_2py. The spectrophotometric and kinetics experiments indicated that the complex contains one iron per 4-NH_2py ligand. Furthermore, the cyclic voltammetry measurements showed that the Fe(II) complex is a one-electron reducing agent, eliminating the possibility of a binuclear species. Thus, because the amine ligand initially present in $[Fe(CN)_5NH_3]^{3-}$ is rapidly aquated,[12] we conclude that the complexation reaction is represented by eq 1.

$$(NC)_5FeOH_2^{3-}(aq) + 4\text{-}NH_2py(aq) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (NC)_5Fe\text{-}4\text{-}NH_2py^{3-}(aq) \quad (1)$$

Although the spectrum of the complex and the kinetics of dissociation (vide infra) were consistent with bonding of 4-NH_2py via the pyridine nitrogen, additional evidence was sought by NMR spectroscopy. The spectrum of 4-NH_2py in D_2O features multiplets at 6.5 and 8.03 ppm which correspond, respectively, to the protons at the β and α positions relative

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Table II. Kinetics of Formation[a]

run	$10^2 \times$ [4-NH_2py], M	t, °C	k_{obsd}, s^{-1}	$10^{-2}k_f$, M^{-1} s^{-1}
1	0.50	25.0	2.22	4.4
2	1.00	25.0	4.32	4.3
3	2.00	25.0	8.68	4.3
4	1.00	18.3	2.32	2.3
5	1.00	30.8	7.02	7.0

[a] [$Fe(CN)_5OH_2^{3-}$] = 2.0×10^{-5} M initially, pH 7 (unbuffered), $\mu = 0.10$ M ($LiClO_4$), λ 320 nm. Estimated error in k_{obsd} is ±8%.

Table III. Kinetics of Ligand Exchange[a]

run	t, °C	[L], M	10^3k_{obsd}, s^{-1}
1	25.3	0.0025	1.5
2	25.3	0.0050	1.6
3	25.3	0.0125	1.9
4	25.3	0.0250	2.0
5	25.3	0.050	2.1
6	25.3	0.125	2.3
7	25.3	0.250	2.6
8	25.3	0.50	2.5
9	13.0	0.50	0.50
10	21.0	0.50	1.4
11	29.6	0.50	4.0
12	37.9	0.50	11.0

[a] $\mu = 0.10$ M ($LiClO_4$), pH 9 (unbuffered), [Fe(II)] = 8.15×10^{-5} M, [4-NH_2py] = 5.29×10^{-3} M. Estimated error in k_{obsd} is ±7%.

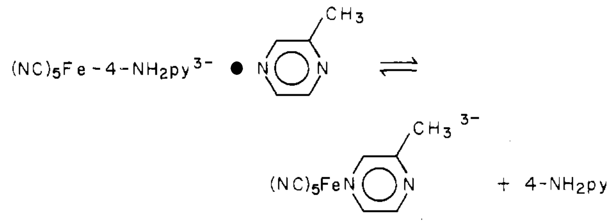
to the pyridine nitrogen.[13] When the pentacyanoferrate(II) ion was introduced into the solution, new bands arose at 6.0 and 8.6 ppm, attributable to the β and α protons, respectively. The influence of the $Fe(CN)_5^{3-}$ substituent upon the chemical shifts of coordinated N heterocycles is known to be downfield at the α position and upfield at the β position.[5] Therefore, the only isomer detectable by NMR technique was the one bonded through pyridine.

Kinetics of Formation. The rate of formation of the 4-NH_2py complex was measured spectrophotometrically by the stopped-flow technique at 320 nm. The concentration of iron(II) reagent was 2.0×10^{-5} M. Concentration of 4-NH_2py varied in the range 0.005–0.020 M, ensuring a substantial excess of the ligand. Representative kinetics data are given in Table II. A plot of k_{obsd} vs. [4-NH_2py] gave a straight line which passed through the origin. The rate law is

$$d[Fe(CN)_5\text{4-}NH_2py^{3-}]/dt = k_f[Fe(CN)_5OH_2^{3-}][\text{4-}NH_2py]$$

From the variation of k_f with temperature the activation parameters were computed. $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger}$ are, respectively, 15.0 ± 0.7 kcal/mol and 3.8 ± 2.0 cal deg^{-1} mol^{-1}; at pH 7, $\mu = 0.10$ M; at 25 °C, k_f is 432 ± 20 M^{-1} s^{-1}.

Kinetics of Ligand Exchange. The ligand exchange reaction given in eq 2 was studied in order to determine the specific rate of dissociation of the 4-NH_2py complex. The rates of ligand exchange were measured as a function of [L], the concentration of 2-methylpyrazine. The concentration of this species was allowed to vary in the range 0.0025–0.50 M. Reactions were monitored by following the appearance of the product MLCT band at 452 nm. The process of ligand exchange obeyed apparent first-order kinetics at all concentrations of the attacking ligand. Values of k_{obsd} under various conditions are given in Table III.



(2)

Toma and Malin[1] have suggested the following mechanism for ligand exchange in pentacyanoferrate(II) complexes:

$$Fe(CN)_5L'^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(CN)_5OH_2^{3-} + L'$$

$$L + Fe(CN)_5OH_2^{3-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe(CN)_5L^{3-}$$

In the mechanism, L′ refers to the 4-NH_2py ligand and L is 2-methylpyrazine. If the steady-state approximation is applied to the concentration of the pentacyanoaquaferrate(II) ion, one obtains eq 3. Values of k_{obsd} are plotted vs. [L] in Figure 1.

$$k_{obsd} = \frac{k_1k_2[L] + k_{-1}k_{-2}[L']}{k_2[L] + k_{-1}[L']} \tag{3}$$

At high [L], k_{obsd} is found to be independent of [L], in agreement with eq 3. The solid curve in Figure 1 was computed using values of k_{-1}, k_1, k_2, and k_{-2} equal to 2.53×10^{-3} s^{-1}, 432 M^{-1} s^{-1}, 448 M^{-1} s^{-1}, and 8.85×10^{-4} s^{-1}, respectively.[15] Agreement is good within experimental error.

From the temperature dependence of k_{obsd} at rate saturation (runs 8–12), values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, referring to k_1, were calculated. These are 21.4 ± 0.5 kcal/mol and 1.2 ± 1.6 cal mol^{-1} deg^{-1}, respectively.

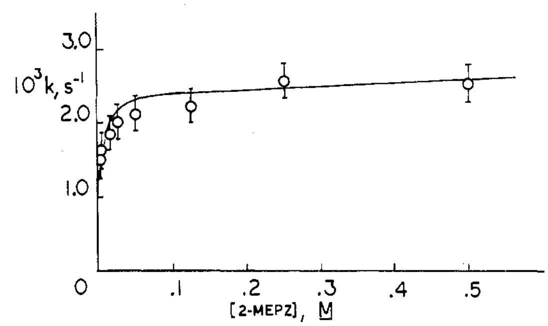


Figure 1. k_{obsd} for ligand exchange vs. the concentration of attacking ligand, 2-methylpyrazine.

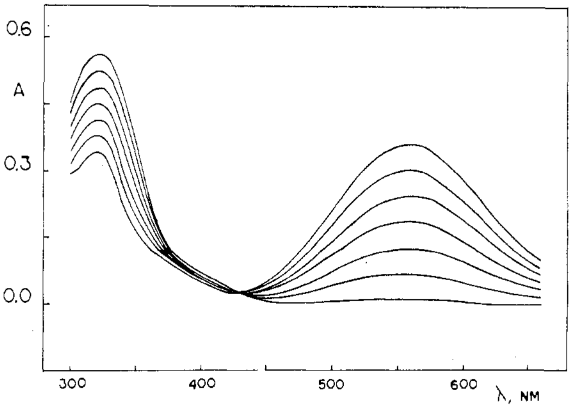


Figure 2. Spectrophotometric titration of $Fe(CN)_5$-4-NH_2py^{3-}(aq) with I_3^-(aq).

Oxidation of $Fe(CN)_5$-4-NH_2py^{3-}. It normally is observed that pentacyanoferrate(II) complexes of aromatic N heterocycles are resistant to oxidation by air. However, when aqueous solutions of pentacyano(4-aminopyridine)ferrate(II) are allowed to remain in contact with the atmosphere for ca. 12 h, their color changes from yellow to purplish, and a strong absorption band appears (λ_{max} 560 nm). The same band develops immediately when oxidants Ce(IV), H_2O_2, or $Fe(CN)_6^{3-}$ are used. A series of spectra taken in the course of oxidation by aqueous triiodide ion are given in Figure 2. As

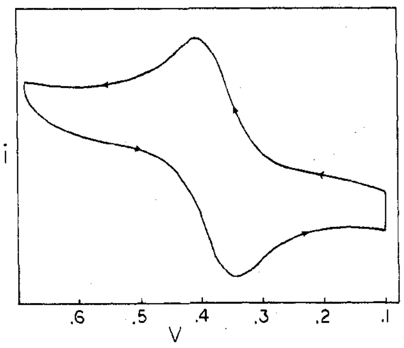


Figure 3. Cyclic voltammogram of $Fe(CN)_5$-4-NH_2py^{3-}(aq) (10^{-3} M, pH 8, 1 M $NaNO_3$, 23 °C) at a platinum wire electrode. Anodic current is toward top of figure. SHE is 0.0 V.

Table IV. Kinetics of Oxidation of $(NC)_5Fe$-4-NH_2py^{3-} by $Fe(CN)_6^{3-}$ [a]

run	t, °C	$10^5 \times$ $[Fe^{II}]$, M	$10^4 \times$ [4-NH_2-py], M	$10^5 \times$ $[Fe^{III}]$, M	k_{obsd}, s^{-1}	$10^{-5}k_{et}$, M^{-1} s^{-1}
1	25.3	5.0	5.0	25.0	109	4.4
2	25.3	5.0	5.0	50.0	214	4.3
3	24.6	1.0	1.0	5.0	20.9	4.2
4	24.6	1.0	1.0	10.0	43.9	4.4
5	15.5	1.0	1.0	5.0	17.6	3.5
6	15.5	1.0	1.0	10.0	37.9	3.8
7	34.0	1.0	1.0	10.0	49.7	5.0

[a] pH 9, $\mu = 0.05$ M ($LiClO_4$), λ 560 nm. Estimated error in k_{et} is ±10%.

I_3^- was added, the 320-nm band of the iron(II) form decreased in proportion to the growth of the new band. An isosbestic point is seen at 432 nm. ϵ_{max} at 560 nm is 2.8×10^3 M^{-1} cm^{-1}.

Cyclic voltammetric measurements at a platinum wire electrode (vs. Ag/AgCl) yielded the voltammogram shown in Figure 3. Separation between the anodic and cathodic peaks was near 60 mV, denoting a reversible, one-electron oxidation process.[16] Taken together, the observations indicate that the 560-nm band results from one-electron oxidation of the iron(II) complex to an iron(III) form, according to eq 4. Under the

$$(NC)_5Fe\text{-}4\text{-}NH_2py^{3-}(aq) = (NC)_5Fe\text{-}4\text{-}NH_2py^{2-}(aq) + e^- \quad (4)$$

experimental conditions, 0.10 M $LiClO_4$, 23 °C, $E°$ for eq 4 is -0.35 ± 0.04 V. In 1.0 M $NaNO_3$, 23 °C, at pH 9, $E°$ (vs. SHE) is -0.38 ± 0.04 V.

Electron-Transfer Kinetics. The kinetics of the reaction

$$(NC)_5Fe\text{-}4\text{-}NH_2py^{3-} + Fe(CN)_6^{3-} \rightarrow (CN)_5Fe\text{-}4\text{-}NH_2py^{2-} + Fe(CN)_6^{4-} \quad (5)$$

were examined in aqueous solution by stopped-flow techniques at 560 nm. As seen in Table IV, the reaction was studied under conditions of excess ferricyanide ion. Although only a fivefold excess was used in some of the experiments, kinetics plots showed clear pseudo-first-order behavior. The rate law is

$$d[(NC)_5Fe\text{-}4\text{-}NH_2py^{2-}]/dt = k_{et}[(NC)_5Fe\text{-}4\text{-}NH_2py^{3-}][Fe(CN)_6^{3-}] \quad (6)$$

At 25 °C, $\mu = 0.05$ M ($LiClO_4$), and pH 9.0, k_{et} is $(4.3 \pm 0.3) \times 10^5$ M^{-1} s^{-1}. The calculated values of $\Delta H^‡$ and $\Delta S^‡$ were respectively 2 ± 1 kcal/mol and -26 ± 5 cal deg^{-1} mol.

Discussion

Charge-Transfer Spectra. It was noted in Table I that the electron-transfer band in pentacyano(4-aminopyridine)ferrate(II) is found at high energy compared with the case of other pyridine complexes of $Fe(CN)_5^{3-}$. This is consistent with the MLCT assignment of the band. The electron-rich character conferred by the 4-NH_2 substituent upon the pyridine ring raises E_{MLCT} by lowering the electron affinity, A_L, of 4-NH_2py.

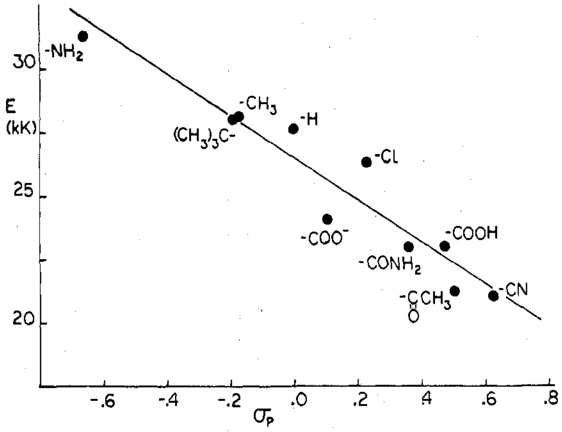


Figure 4. E(MLCT) for γ-substituted pyridines in $Fe(CN)_5L^{3-}$(aq) vs. Hammett's σ_p.

For a series of closely related $Fe(CN)_5L^{3-}$ complexes, one expects a nearly linear, inverse relationship between E_{MLCT} and A_L. Because A_L values are not available, we have constructed a plot of E_{MLCT} vs. the Hammett σ_p values for a series of γ substituents.[17] This is shown in Figure 4. A decrease in E_{MLCT} is observed as σ_p, which is a measure of the relative electron withdrawing power of the γ substituent, increases.

The violet color (560 nm, log $\epsilon \approx 3.44$) produced by one-electron oxidation of $Fe(CN)_5(4\text{-}NH_2py)^{3-}$ is relatively intense. Therefore it is assigned to a charge-transfer transition. Arguments based upon the energy of the MLCT band in the pentacyanoferrate(II) complex, and the ionization potential expected of Fe(III) relative to Fe(II), eliminate the possibility that the new band is an MLCT transition. However, good precedents exist in low-spin, d^5 iron(III) complexes, e.g., $Fe(CN)_5NCS$,$^{3-}$ [18] for ligand-to-metal charge-transfer (LMCT) processes. LMCT bands have been observed near 400 nm in pentacyanoferrate(III) complexes of substituted pyridines and pyrazine.[14] Since these bands are relatively independent of the identity of the heterocycle and because they resemble the spectrum of the ion $Fe(CN)_5OH_2^{2-}$(aq), it seems likely that charge in these complexes is transferred from cyanide to iron(III). In comparison, the LMCT band in pentacyano(4-aminopyridine)ferrate(III) occurs at relatively high wavelength, implicating the ligand 4-NH_2py as the electron donor. We postulate that LMCT excitation is facilitated by conjugation of the $-NH_2$ lone pair with the pyridine π^* orbitals, which are of appropriate symmetry to interact with the half-vacant iron(III) acceptor orbital (d_{xz} or d_{yz}).

Kinetics of Formation and Ligand Exchange. Little variation has been found among the kinetics parameters for complexation of pentacyanoaquaferrate(II) by uncharged ligands of diverse basicities, although there is a notable correlation of the formation rates with the charge type of the attacking ligand.[6,10,19-23] In the present work the specific rate of formation, k_f, for 4-NH_2py is observed to be similar to those for 4-picoline and pyridine.[6] The activation parameters, $\Delta H^‡$ and $\Delta S^‡$, are comparable for all three systems, indicating a common mechanism. The observations indicate a dissociative type of mechanism in which the rate-determining step is probably the loss of the water ligand from pentacyanoaquaferrate(II). However, the evidence presently available does not permit the unambiguous assignment of the complexation reactions of $Fe(CN)_5OH_2^{3-}$(aq) either to the D (dissociative, limiting) or to the I_d (dissociative interchange) subclass.

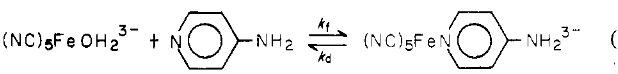
Table V. Formal Potentials and Association Constants for Pentacyanoferrate(II) and -(III) Complexes at 25 °C

L in $Fe(CN)_5L^{3-}$	$E°_{III/II}$,[a] V	K_{II},[b] M^{-1}	K_{III}, M^{-1}	pK_a[d]
H_2O	0.39 (POT)	1	1	
4-aminopyridine[e]	0.35 (CV)	1.7×10^5	6.8×10^5	9.17
γ-picoline	0.45 (POT)	3.1×10^5	2.9×10^4 [c]	6.11
pyridine	0.48 (CV)	3.3×10^5	9.4×10^3 [c]	5.23
isonicotinamide	0.50 (POT)	4.0×10^5	5.2×10^3 [c]	3.61
pyrazine	0.55 (POT)	9.0×10^5	1.7×10^3 [c]	0.65
N-methylpyrazinium	0.79 (CV)	2.0×10^6	4.7×10^{-1} [c]	-5.8[c]

[a] CV = cyclic voltammetry; POT = potentiometry. Except for $4\text{-}NH_2py$, the values are listed in ref 3. [b] $\mu = 0.5$ M (LiCl) unless stated otherwise. From ref 3 and 6c. [c] Reference 3. [d] Reference 26. [e] 0.10 M $LiClO_4$.

In comparison with studies of other aromatic N heterocycles as leaving groups,[6] the ligand exchange experiments show that the $4\text{-}NH_2py$ complex is relatively labile. This species dissociates 2.3 times more rapidly at 25 °C than does the pyridine complex and 6 times more rapidly than that of pyrazine. As mentioned in the Introduction, the higher value of E_{MLCT} for the $4\text{-}NH_2py$ complex would lead us to predict that this ion is less stable than the pyridine complex, if dπ–pπ back-bonding effects are important.

One may employ the kinetics results to compute the overall stability constant for the $4\text{-}NH_2py$ complex, eq 7. Here, K_{II}



(7)

$= k_f/k_d = 1.7 \times 10^5\ M^{-1}$ when k_1 from eq 3 is taken as k_d. K_{II} is less than half the value of the pyridine analogue. In comparison with species having λ_{max} at greater wavelengths, e.g., the complexes of isonicotinamide and pyrazine, the $4\text{-}NH_2py$ complex is less stable, respectively, by factors of ca. 4 and 9.[6a]

The results of the ligand exchange studies support the conclusion based on the NMR spectra that $4\text{-}NH_2py$ in the complex is bonded via the pyridine nitrogen. This is because the saturation-limited rate constant and activation parameters for dissociation are consistent with the pattern of reactivity found for $Fe(CN)_5L^{3-}$ complexes of substituted pyridines.[6] On the other hand, the NH_2-bonded isomer is expected to dissociate at a specific rate similar to that of the aniline complex. Katz and co-workers[24] have estimated k_d for this complex to be ca. 0.1 s^{-1}. Making the reasonable assumption that k_f is similar for both the pyridine and NH_2-bonded forms, K_{II} for the latter isomer is calculated to be ca. $4.5 \times 10^3\ M^{-1}$. Thus, the NH_2-bonded linkage isomer is estimated to be unstable with respect to the pyridine-bonded form by a factor of approximately 40.

Reduction Potential. In Table V the reduction potential of $Fe(CN)_5\text{-}4\text{-}NH_2py^{2-}$ is listed along with values which have been obtained for other pentacyanoferrate(II) complexes. One notes that the $4\text{-}NH_2py$ complex is among the most easily oxidized to the iron(III) form. This is consistent with the diminished capacity of this ligand to act as a π acceptor. From the value of K_{II} and the oxidation potential of the $4\text{-}NH_2py$ complex along with that of $Fe(CN)_5OH_2^{3-}$, it is possible to estimate K_{III}, the stability constant for formation of the iron(III) complex. This is done using the cycle shown in Scheme I.

When the appropriate values are substituted into eq 8, one

$$E°(Fe(CN)_5L^{3-/2-}) = E°(Fe(CN)_5OH_2^{3-/2-}) + \frac{RT}{F}\ln\frac{K_{III}}{K_{II}} \qquad (8)$$

finds K_{III} equal to $6.8 \times 10^5\ M^{-1}$. This value is consistent with results of Toma and Creutz[3] who found relatively high values of K_{III} for comparatively strong pyridine bases.

The values of K_{II} and K_{III} vary according to the identity of L. The K_{III} values increase with increasing basicity of L. In contrast, the values of K_{II} correlate inversely with ligand basicity. The source of this inverse correlation lies in the fact that many unsaturated ligands which are weak σ donors are good π acceptors. A number of studies[1,4-6,12] have shown that the relative stabilities of substituted pentacyanoferrate(II) complexes apparently are affected by the degree of dπ–pπ back-bonding stabilization. In the pentacyanoferrate(III) complexes the comparatively large electron affinity of the metal center precludes metal-to-ligand back-donation. The relative importance in bonding of the ligands' σ-donor properties therefore is increased. This manifests itself as an enhanced sensitivity of K_{III}, compared with K_{II}, to variations in ligand basicity.

Scheme I

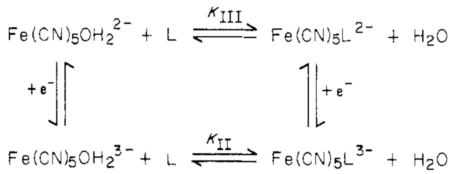


Table VI. Kinetics of Some Electron-Transfer Reactions at 25 °C and $\mu = 0.05$ M

reaction	k, $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}
$Fe(CN)_6^{3-} + Fe(CN)_6^{4-}$	5×10^3 [a]	4.2	-32
$Fe(CN)_6^{3-} + Fe(CN)_5py^{3-}$	3.4×10^4 [b]	5.4 ± 0.9	-19 ± 3
$Fe(CN)_6^{3-} + Fe(CN)_5\text{-}4\text{-}NH_2py^{3-}$	4.3×10^5 [c]	2 ± 1	-26 ± 5
$Fe(CN)_5py^{2-/3-}$	7×10^5 [d]		
$Fe(CN)_5\text{-}4\text{-}NH_2py^{2-/3-}$	7×10^5 [e]		

[a] k at $[K^+] = 0.05$ M, found by extrapolation of data in ref 18. [b] $[KNO_3] = 0.05$ M. [c] $[LiClO_4] = 0.05$ M. [d] Calculated in ref 12. [e] Calculated using the Marcus relationship.

Electron Transfer in the Hexacyanoferrate(III/II)–Pentacyano(4-aminopyridine)ferrate(II/III) Reaction. Because both the products and reactants in eq 5 are inert to substitution, the reaction can be assigned to the outer-sphere class. Use of the Marcus equations[26]

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

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

allows several comparisons which can be drawn from the values in Table VI. In the calculations, k_{11} is the self-exchange rate constant measured by Wahl and co-workers[27] for the ferricyanide–ferrocyanide reaction. k_{22} is calculated for the pentacyano(4-aminopyridine)ferrate(II/III) using Marcus' equations.[28] K_{12} and k_{12} are the equilibrium and specific rate constants referring to eq 5. Z is a frequency factor $\approx 10^{11}$.

The value in Table VI for the specific rate of self-exchange in the pentacyano(4-aminopyridine)ferrate(II/III) reaction is $7 \times 10^5\ M^{-1}\ s^{-1}$ at 25 °C, $\mu = 0.05$ M. This agrees exactly with the value which was computed by Toma and Malin[14] for self-exchange in pentacyano(pyridine)ferrate(II/III). The reactions are ca. 200 times faster than ferricyanide/ferrocyanide self-exchange under similar experimental conditions. The agreement for the pentacyanoferrates probably is fortuitous, since different electrolytes ($LiClO_4$, KNO_3) were used in the two studies. Nevertheless, it is indicated that the pentacyanoferrate(II) self-exchange reactions have a common feature. This is that pyridine and 4-aminopyridine both facilitate electron transfer in complexes by conducting electrons through the first coordination sphere of iron(II). The close correspondence in the two computed rates of self-exchange is intriguing in view of the evidence presented in this work that the degree of delocalization of iron(II) electrons into the heterocycle's π system is somewhat greater for pyridine than for 4-NH_2py. In agreement with a previous result,[14] this would indicate that a rather small degree of delocalization may suffice to affect the electron transfer process.

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Registry No. $Fe(CN)_5(4\text{-}NH_2py)^{3-}$, 68378-75-6; $Fe(CN)_5OH_2^{3-}$, 18497-51-3; 4-NH_2py, 504-24-5; $Fe(CN)_6^{3-}$, 13408-62-3; $Fe(CN)_5py^{3-}$, 37475-75-5; I_3^-, 14900-04-0; 2-methylpyrazine, 109-08-0.

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Contribution from the Chemistry Department,
Purdue University, West Lafayette, Indiana 47907

Heavy-Metal–Nucleoside Interactions. 13. Synthesis and Spectroscopic Study of Organomercury Derivatives of Guanosine and Thymidine[1,2]

ALLAN J. CANTY*[3] and R. STUART TOBIAS*

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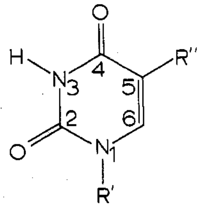
Complexes of the stoichiometry $RHg(GuoH_{-1})$, $[RHg(Guo)]NO_3$, and $[(RHg)_2GuoH_{-1}]NO_3$ have been synthesized by reaction of the nucleoside guanosine (Guo) and RHg^{II} in water (R = Me) or aqueous ethanol (R = Ph). Comparison of infrared spectra of the solid complexes and ^1H nuclear magnetic resonance spectra of the complexes in dimethyl-d_6 sulfoxide with spectra of Guo, $[GuoH]NO_3$, and $Na[GuoH_{-1}]\cdot H_2O$ allows assignment of structures for these ambidentate ligand complexes. Deprotonation of N_1 of Guo leads to coordination of RHg^{II} at N_1 in $RHg(GuoH_{-1})$ and to both N_1 and N_7 in $[(RHg)_2GuoH_{-1}]NO_3$. The complexes $[RHg(Guo)]NO_3$ have RHg^{II} bonded at N_7 of the guanine base. Phenylmercuric hydroxide reacts with thymidine (dThd) in aqueous ethanol to form $PhHg(dThdH_{-1})\cdot H_2O$ with $PhHg^{II}$ bonded to N_3 after deprotonation of dThd. Structures deduced for these solid complexes are in agreement with those suggested in earlier ultraviolet and Raman studies of the interaction of nucleosides and nucleotides with $MeHg^{II}$ in aqueous solution. The uses and limitations of vibrational spectra in assigning structures to such metal nucleoside complexes are outlined.

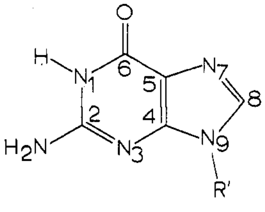
The $MeHg^{II}$ cation has been used for separations of polynucleotides with different base composition[4] and also as a simple unifunctional electrophile[5] to determine how spectroscopic properties of nucleotides alter with electrophilic attack at specific sites.[6-9] The spectroscopic perturbations are typical for heavy-metal binding and can be used to interpret data for other metal electrophiles.[2,10,11]

It has been observed that at low *r* values (total metal:total base), the first site of reaction with DNA's is N_3 of thymine and the second site N_1 of guanine bases.[9,12] The interaction with dThd[13] (I, R″ = Me, R‴ = H) and Urd (I, R″ = H, R‴ = OH) is well understood with both UV[14] and Raman[6a] spectral studies indicating binding to N_3 after deprotonation.

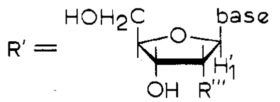
Guanosine (II, R‴ = OH) of the nucleosides exhibits the most complex reactions with $MeHg^{II}$. UV[14] and Raman studies[6b] on aqueous solutions of guanosine and GMP have indicated the formation of $MeHg(GuoH_{-1})$, $[MeHgGuo]^+$ and $[(MeHg)_2GuoH_{-1}]^+$ with binding at N_1, N_7, and both N_1 and N_7, respectively. Despite the extensive work with solutions, no solid complexes of $MeHg^{II}$ have been isolated. In view of the importance of guanosine in the interaction of heavy metals with nucleotides, a series of $MeHg^{II}$ and $PhHg^{II}$ derivatives have been synthesized and characterized, together with a $PhHg^{II}$ derivative of thymidine.



I



II



Experimental Section

Guanosine (Aldrich), thymidine (Sigma), and phenylmercuric hydroxide (Alfa) are commercially available and were used as received.

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