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Kinetics of Formation and Dissociation of Complexes of Pentacyanoferrate(II) with Benzonitrile, Dicyanobenzenes and Cyanopyridines[1a]

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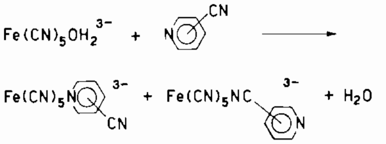
A series of organonitrile complexes of pentacyanoferrate(II) have been prepared in aqueous solution by the reaction of $Fe(CN)_5OH_2^{3-}$ with the appropriate nitrile. The complexes exhibit a metal to ligand charge transfer absorption at 341 (benzonitrile), 413 (1,2-dicyanobenzene), 381 (1,3-dicyanobenzene) and 419 nm (1,4-dicyanobenzene). The rate constants for the formation of these complexes at 25° and ionic strength 0.10 M *(lithium perchlorate) are (same order as above): 270, 453, 638 and 410* M^{-1} *sec*$^{-1}$*. The rate constants for the dissociation under the same conditions are: 0.115, 0.0812, 0.0786 and 0.0663 sec*$^{-1}$*. The reactions of $Fe(CN)_5OH_2^{3-}$ with 2-, 3-, and 4-cyanopyridine proceed in two stages. The first corresponds to the formation of a mixture of pyridine-bound and nitrile-bound linkage isomers, and the second to the linkage isomerization of the unstable isomer. For 3- and 4-cyanopyridine, the unstable isomers are nitrile-bound, but for 2-cyanopyridine, because of the steric hindrance between the nitrile group in the 2-position and the* cis *cyanide groups attached to the iron, the unstable isomer is pyridine-bound. The metal to ligand charge transfer bands of the nitrile-bound isomers are at 387, 370 and 405 nm for 2-, 3-, and 4-cyanopyridine, respectively. The bands for the pyridine bound isomers are at 470, 414 and 477 nm. The rate constants for the formation and the dissociation of the nitrile bound isomers are: 365–441* M^{-1} *sec*$^{-1}$ *and* 9.3×10^{-2} *sec*$^{-1}$ *(2-cyanopyridine); 223* M^{-1} *sec*$^{-1}$ *and 0.117 sec*$^{-1}$ *(3-cyanopyridine); 235* M^{-1} *sec*$^{-1}$ *and* 9.7×10^{-2} *sec*$^{-1}$ *(4-cyanopyridine). The rate constants for the pyridine bound isomers are, in the same order: 155–231* M^{-1} *sec*$^{-1}$ *and 1.18 sec*$^{-1}$*; 413* M^{-1} *sec*$^{-1}$ *and* 2.80×10^{-3} *sec*$^{-1}$*; 383* M^{-1} sec^{-1} *and* 1.02×10^{-3} *sec*$^{-1}$*. The rate and equilibrium data for the dissociation of these complexes exhibit a linear free energy relationship of slope 0.98, indicating a dissociative mechanism. An intramolecular pathway for linkage isomerization is absent in the 3- and 4-cyanopyridine systems and makes, at most, an 18% contribution in the 2-cyanopyridine system.*

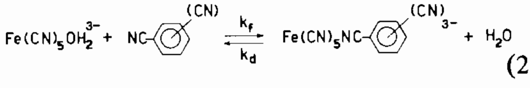
Introduction

In extending our studies of intramolecular electron transfer from iron(II) to cobalt(III) mediated by nitrogen heterocycles [2, 3], we became interested in using cyanopyridines as bridging ligands [4]. As done previously [2, 3], comparisons between the reactions of aquopentacyanoferrate(II) with the ligands and with the corresponding pentaamminecobalt(III) complexes were carried out, and the identities of the iron(III) products were investigated. Two unusual features emerged from these studies. First, the observed product of the $Fe(CN)_5OH_2^{3-}$–$Co(NH_3)_5N$⌬$\text{-}CN^{3+}$ reaction was $Fe(CN)_5OH_2^{2-}$ rather than the $Fe(CN)_5NC\text{-}$⌬N^{2-} complex anticipated on the basis of an inner-sphere mechanism with ligand transfer. Second, in the $Fe(CN)_5OH_2^{3-}$ –N⌬$\text{-}CN$ reaction, the kinetically controlled products were identified as mixtures of the linkage isomers $Fe(CN)_5N$⌬$\text{-}CN^{3-}$ and $Fe(CN)_5NC\text{-}$⌬N^{3-}, whereas the thermodynamically controlled product is exclusively the pyridine bound isomer. On the basis of these observations and of the current interest in reactions of $Fe(CN)_5OH_2^{3-}$ [5–9], we carried out a complete mechanistic investigation of the reactions of $Fe(CN)_5OH_2^{3-}$ with the three isomeric cyanopyridines (eq. 1). For comparison



(1)

purposes, we also studied the corresponding reactions of benzonitrile and the three isomeric dicyanobenzenes (eq. 2). Finally, we studied the aquation



(2)

reactions of the nitrile-bound cyanopyridinepentacyanoferrate(III) complexes (eq. 3).

(3)

Reactions 1 and 2 are of additional interest because of useful comparisons with the well-studied reactions of aquopentaammineruthenium(II) with cyanopyridines and dicyanobenzenes [10–13].

Experimental

Materials

House distilled water was passed through a Barnstead ion exchange demineralizer, and then distilled in a modified, all-glass Corning AG-1b distilling apparatus. The nitriles, cyanopyridines and lithium perchlorate were purified using standard procedures. All other chemicals, except sodium perchlorate, which was purified grade, were reagent grade. All the manipulations of iron(II) solutions were performed under an atmosphere of argon.

Preparation of Complexes

Sodium amminepentacyanoferrate(II) trihydrate was prepared by the standard method [14]. Purification was accomplished by recrystallization from room temperature 28% aqueous ammonia by addition of 95% ethanol until the first permanent sign of turbidity, followed by cooling to 0 °C. The small, yellow needles formed were collected, washed with ethanol and ether, and then dried over drierite for 24 hours. The product was stored in a number of tightly stoppered bottles, and kept at –10 °C until used. *Anal.* Calcd. for $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$: Fe, 17.13. Found: Fe, 17.19%.

Sodium 3-cyanopyridinepentacyanoferrate(II) monohydrate was prepared by mixing 0.31 g of 3-cyanopyridine and 0.33 g of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ in 10 ml of water. The resulting solution was allowed to stand in the dark for 30 min, and then a tenfold excess of 95% ethanol at –15 °C was added. After 1 hour, the product was collected by filtration and then washed with cold ethanol and ether. The product was purified by dissolution in water followed by precipitation with excess ethanol. Yield: 0.24 g of yellow powder (64%). *Anal.* Calcd. for $Na_3[Fe(CN)_5(C_6H_5N_2)]\cdot H_2O$: Fe, 14.81. Found: Fe, 14.65%. Sodium 4-cyanopyridinepentacyanoferrate(II) monohydrate was prepared using the same procedure as that for the 3-cyanopyridine analog. Yield: 0.28 g of dark orange powder (74%). *Anal.* calcd for $Na_3[Fe(CN)_5(C_6H_5N_2]\cdot H_2O$: Fe, 14.81. Found: Fe, 14.65%. Attempts to prepare the 2-cyanopyridine analog resulted in the formation of intractable oils.

Analytical Methods

Following decomposition of the iron complex by repeated fuming with sulfuric, nitric and hydrochloric acids, iron was analyzed by a standard [15] method. Infrared spectra of the solid complexes, as KBr pellets, were measured with a 467 or 567 Perkin–Elmer spectrophotometer.

Electronic Spectra

The thermodynamically stable complexes were prepared in solution by reaction of $Fe(CN)_5NH_3^{3-}$ or $Fe(CN)_5OH_2^{3-}$ (prepared by aquation [16] of $Fe(CN)_5NH_3^{3-}$ at pH 5) with an excess of the desired ligand. The visible and ultraviolet spectra of the resulting solutions were measured with a Cary 118 or a Cary 17 recording spectrophotometer. All the reported molar absorbances are referenced to the well-characterized complex $Fe(CN)_5N\bigcirc^{3-}$ for which $\log \epsilon = 3.57$ at 362 nm [17].

The visible spectra of the unstable, nitrile-bonded isomers of 3- and 4-cyanopyridinepentacyanoferrate(II) were obtained using the following procedure. Solutions of $Fe(CN)_5OH_2^{3-}$ and of 3- or 4-cyanopyridine at 5 °C were mixed and transferred to a cell which was rapidly placed in the thermostatted (5 °C) cell compartment of the Cary 17 spectrophotometer. The absorption spectra were scanned repeatedly. Extrapolation of absorbance vs time curves for each wavelength to the mixing time and subtraction of the absorbance contributions of the pyridine-bound isomers formed immediately after mixing yielded the desired absorption spectra.

The visible spectrum of the unstable, pyridine-bound isomer of 2-cyanopyridinepentacyanoferrate(II) was measured point by point using a Durrum stopped-flow spectrophotometer. When solutions of $Fe(CN)_5OH_2^{3-}$ and 2-cyanopyridine are mixed, the absorbance in the 450–500 nm region first increases, then goes through a maximum and finally decreases. Molar absorbances were calculated from the measured values of A_{max}, A_∞ and t_{max} by means of eq. 17 of the appendix. A_{max} is the maximum absorbance reached during the course of the reaction, A_∞ is the absorbance at the completion of the reaction and t_{max} is the time at which the absorbance is at its maximum.

Kinetic Measurements

Formation rates were measured using a Durrum 110 stopped-flow spectrophotometer interfaced to an 1800 IBM computer [3]. Solutions of $Fe(CN)_5OH_2^{3-}$ were obtained by aquation of $Fe(CN)_5NH_3^{3-}$ in a pH 5 buffer at a temperature equal to that for the kinetic measurement. At 25 °C the time allowed for aquation was 4–5 minutes, and measurements were obtained within 10 minutes from dissolution of the $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ by mixing the $Fe(CN)_5OH_2^{3-}$ solution with a solution of the ligand containing the desired amounts of buffer and lithium perchlorate. Using this procedure plots of $\ln(A_t - A_\infty)$ *vs.* time were reasonably linear, except for the reactions of the dicyanobenzenes. For benzonitrile and the dicyanobenzenes, wavelengths of observation were at the absorption maximum of the respective products. For the reactions of the cyanopyridines, wavelengths were the isosbestic points between the pyridine- and nitrile-bound isomers. In this manner, the formation rates were obtained without interference by the subsequent linkage isomerization.

Dissociation rates of the stable nitrile-bound complexes were measured in the stopped-flow apparatus by mixing solutions of the desired pentacyanoferrate(II) complex with solutions of pyridine at the appropriate ionic strength. Dissociation rates of the stable pyridine-bound complexes were measured in a Cary 118 spectrophotometer by adding an excess of pyridine to the solution of the desired complex. In all cases, the pyridine and free ligand concentrations were adjusted to yield at least a 500-fold faster rate of reaction of $Fe(CN)_5OH_2^{3-}$ with pyridine as compared to the ligand. Measurements were carried out by following the disappearance of the complex at its absorption maximum.

Rates of isomerization of the unstable isomers formed in the reactions of $Fe(CN)_5OH_2^{3-}$ with the cyanopyridines were measured in the stopped-flow apparatus (using a Hewlett–Packard 7101B strip chart recorder) by following the slow reaction subsequent to the fast formation reaction. Measurements were made of the absorbance increase at the absorption maximum of the stable isomers and of the absorption decrease near the absorption maximum of the unstable isomers.

Rates of aquation of the nitrile-bound isomers of 3- and 4-cyanopyridinepentacyanoferrate(III) were obtained as follows. A solution of $Fe(CN)_5OH_2^{3-}$ was added *en masse* to a rapidly stirred 0.20 *M* ligand solution. One second was allowed for the formation reaction to proceed to completion, and then the iron(II) products were oxidized to iron(III) by adding a two-fold excess of cerium(IV). In order to remove the cerium, the resulting solution was passed, with suction, through a thermostatted column of Dowex 50W X-12 cation exchange resin (rinsed previously with 0.10 *M* $LiClO_4$). The column was then rinsed with 0.10 *M* $LiClO_4$, and the effluent was transferred to a spectrophotometric cell. The absorbance decrease at 420 nm was followed as a function of time. At the end of the experiment, the pH of the solution was measured with an Orion model 801 or a Radiometer model 26 pH meter.

All kinetic measurements were carried out under first-order or pseudo-first order conditions and observed rate constants, k_{obs}, were obtained by least squares treatment of the appropriate function of absorbance *vs.* time data.

Stoichiometric Measurements

The amounts of pyridine- and nitrile-bound isomers formed in the reactions of $Fe(CN)_5OH_2^{3-}$ with the three cyanopyridines were determined using two different methods. In the first, applicable to 3- and 4-cyanopyridine, a solution of $Fe(CN)_5OH_2^{3-}$ was added *en masse* to an equal volume of rapidly stirred 0.20 *M* solution of the desired ligand. The formation reaction was allowed to proceed for one second. A five-fold excess of cerium(IV) was then added in order to oxidize iron(II) to iron(III) and, thus, quench the isomerization reaction. The solution was added to a column of Bio Rex 9 anion exchange resin in the sulfate form. Following rising with water, the iron(III) complexes were eluted with 1.0 *M* sodium perchlorate. The resulting solution was mixed with a solution of pyridine and ascorbic acid at 15 °C. At this point, the solution contains $Fe(CN)_5N$⌬$^{3-}$ and $Fe(CN)_5N$⌬$^{(CN)\ 3-}$ and the slow conversion of the latter to the former takes place. Therefore, the absorbance was measured for a period of time (~40 sec) and extrapolated linearly to the mixing time. The fraction of pyridine-bound isomer produced in the $Fe(CN)_5OH_2^{3-}$–3- or 4-cyanopyridine reaction was calculated from eq. 4, where A_{extrap} is the value of the

$$\text{Fraction of pyridine-bound isomer} = \frac{A_{extrap} - A_\infty}{A_{tot} - A_\infty} \qquad (4)$$

absorbance at the mixing time and A_∞ and A_{tot} are the absorbances of $Fe(CN)_5N$⌬$^{3-}$ and of $Fe(CN)_5$-N⌬$^{CN\ 3-}$, respectively, at a concentration equal to the total concentration of iron in the isomeric mixture solution.

In the second method, applicable to all the cyanopyridine isomers, the procedure is entirely similar except that the quenching of the isomerization subsequent to the formation was accomplished by adding a large excess of pyridine. Absorbance measurements were initiated after the unstable isomer had disappeared, and the extrapolation to the mixing time was done by plotting $\ln(A_t - A_\infty)$ *vs.* time. For the 2-cyanopyridine case, the stable isomer is nitrile-bound and, thus, application of eq. 4 yields the fraction of nitrile-bound isomer formed.

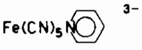
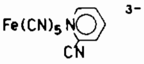
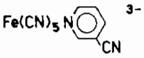
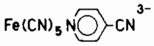
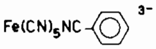
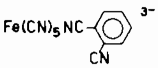
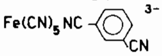
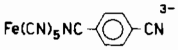
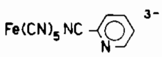
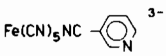
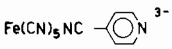
Wavelengths of observation for the stoichiometry measurements were the absorption maximum of the pyridine-bound isomer in the case of 4-cyanopyridine, and the isosbestic point between pyridine-bound and nitrile-bound isomers in the case of 2- and 3-cyanopyridine.

Results

Absorption Spectra

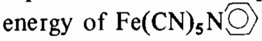
The absorption maxima in the visible or near ultraviolet region and corresponding molar absorbances for the complexes of pentacyanoferrate(II) with nitriles and cyanopyridines are listed in Table I. In the case of the cyanopyridines there are two entries for each compound, one for the pyridine-bound isomer and the other for the nitrile-bound isomer. As is the case for pyridine complexes of pentacyanoferrate(II) [17, 18] and pentaammineruthenium(II) [19] and for nitrile complexes of pentaammine-

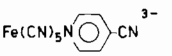
TABLE I. Absorption Maxima and Molar Absorbances of Pentacyanoferrate(II) Complexes with Nitriles and Cyanopyridines^a.

Complex	λ, nm^b	A, M^{-1} cm^{-1} ^{c}
	362^d	3.7×10^3
	470^e	4.4×10^3 ^{f}
	414	3.2×10^3
	477	5.7×10^3
	341	5.1×10^3 ^{g}
	413	5.2×10^3 ^{g}
	381	5.5×10^3 ^{g}
	419	8.0×10^3 ^{g}
	387	5.5×10^3
	370^e	6.0×10^3 ^{f}
	405^e	7.4×10^3 ^{f}

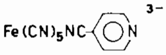
^{a}Measured in aqueous solution with [Fe(II)] = (2–5) × 10^{-5} M and ligand concentrations ≥ 10^{-3} M. ^{b}Uncertainty ±2 nm, unless stated otherwise. ^{c}Uncertainty 5%, unless stated otherwise. ^{d}From reference 17. ^{e}Uncertainty ±10 nm. ^{f}Uncertainty 15%. ^{g}Observed absorbance corrected for incomplete formation of complex.

ruthenium(II) [10, 11], the observed bands in the visible and near ultraviolet are assigned to metal to ligand charge transfer (MTLCT) and show the expected substituent effects. Thus, a considerable increase in wavelength is observed in going from the benzonitrile complex to the 1,2- and 1,4-dicyanobenzene complexes, consistent with the electron-withdrawing effect of cyanide. Moreover, it will be seen that the effect of cyanide in the 3 position is smaller than in the 2 or 4 positions.

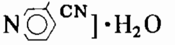
Two linkage isomers have been identified for each cyanopyridine ligand, one a stable isomer and the other a transient intermediate detected in the reaction of Fe(CN)$_5$OH$_2^{3-}$ with the appropriate cyanopyridine (*vide infra*). In the case of 3- and 4-cyanopyridine, the stable isomers, which were also isolated as solids, exhibit the MTLCT bands at longer wavelengths than do the transients. For the 2-cyanopyridine system, the stable isomer absorbs at shorter wavelengths. In all cases, however, the pyridine-bound structure is assigned to the isomer that absorbs at the longer wavelength. This assignment, consistent with the one previously proposed [11] for the analogous 4-cyanopyridinepentaammineruthenium(II) system, is based on the anticipated substituent effects. Thus the electron-withdrawing, π-acceptor CN group in the 4 position would be expected to lower the transition energy of  more than, for example, a p-carboxamido group. Since the latter group leads to a transition at 435 nm [17], the observed maximum at 477 nm for 4-cyanopyridinepentacyanoferrate(II) is consistent with structure **I**, and, therefore, the transient that absorbs at 405 nm is assigned the nitrile-bound structure **II**. Similarly, isomeric assignments have been made for the complexes derived from 2- and 3-cyanopyridine.



I



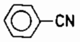
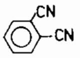
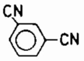
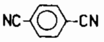
II

Additional evidence for the proposed assignment comes from the infrared spectra of the stable isomers, isolated as solids, in the 3- and 4-cyanopyridine systems. The nitrile cyanide stretching frequencies in  and Na$_3$[Fe(CN)$_5$-  occur at 2250 cm^{-1}, to be compared with 2240 and 2250 cm^{-1} for the corresponding free ligands. The fact that the nitrile stretching frequency is essentially unaffected by coordination suggests attachment at the pyridine nitrogen. Nitrile coordination to a moiety capable of back-bonding into appropriate π^* ligand orbitals, such as Fe(CN)$_5^{3-}$ [17], would have been expected to decrease considerably [11, 12] the nitrile stretching frequency.

Rates of Formation and Dissociation of Complexes of Pentacyanoferrate(II) with Benzonitrile and with Dicyanobenzenes

The affinity of pentacyanoferrate(II) for organic nitriles is considerably less than that for pyridines and the solubilities of the organic nitriles in water are very limited. Therefore, the reactions represented by eq. 2 do not go to completion and plots of log ($A_\infty - A_t$) *vs.* time [20] yield values of $k_{obs} = k_f[L] + k_d$ where k_f and k_d are defined by eq. 2 and [L] is the concentration of the ligand. Values of k_{obs} for benzonitrile and for the three isomeric dicyanobenzenes are listed in Table II. Values of k_d, also listed in Table II, were obtained independently by preparing the desired complex in solution and then adding an excess of pyridine. Under these conditions the net reaction is the substitution of the organic nitrile by pyridine, but the rate-determining step is the dissociation of the nitrile [17]. Least-squares treatment of the k_{obs} *vs.* [L] data yielded values of k_f for each organic nitrile. For the benzonitrile system, additional measurements were carried out in triplicate at 15, 20 and 30 °C. The following activation parameters are

TABLE II. Rate Constants for Reactions of $Fe(CN)_5OH_2^{3-}$ with Benzonitrile and with 1,2-, 1,3- and 1,4-Dicyanobenzene[a].

Ligand	Concentration, $M \times 10^4$	k_{obs}, sec^{-1} [b]
	5.05	0.250 ± 0.010
	5.24	0.237 ± 0.011
	10.2	0.385 ± 0.010
	10.6	0.407 ± 0.003[c]
	9.7	0.117 ± 0.001[d]
	20.8	0.113 ± 0.002[d]
	5.43	0.332 ± 0.005
	9.63	0.517 ± 0.015
	2.02	0.0812 ± 0.0025[d]
	5.02	0.374 ± 0.006
	10.4	0.740 ± 0.010
	1.96	0.0786 ± 0.0033[d]
	5.19	0.279 ± 0.009
	1.99	0.0663 ± 0.0019[d]

[a] At 25 °C, ionic strength 0.100 *M* ($LiClO_4$), pH 8 (tris buffer), $[Fe(CN)_5OH_2^{3-}] = (1.93–3.16) \times 10^{-5}$ *M*. Measurements at the absorption maximum of the nitrile complex. [b] Average and standard deviation of 3–4 replicate measurements. [c] Duplicate measurements. [d] Rate constant for dissociation measured in the presence of 0.0993 *M* pyridine.

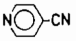
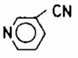
calculated: for k_f, $\Delta H^{\ddagger} = 14.1 \pm 0.2$ kcal/mol, $\Delta S^{\ddagger} = -0.17 \pm 0.20$ eu; for k_d, $\Delta H^{\ddagger} = 22.8 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = 13.6 \pm 0.4$ eu.

Rates of Formation of Complexes of Cyanopyridines with Pentacyanoferrate(II)

When solutions of $Fe(CN)_5OH_2^{3-}$ are mixed with any of the cyanopyridines, a two-stage reaction is observed. The rate of the first stage is dependent on the ligand concentration, whereas that of the second stage shows no such dependence. These observations are interpreted in terms of the formation of mixtures of pyridine-bound and nitrile-bound isomers in the first stage, followed by isomerization of the unstable isomer (nitrile-bound for the 3- and 4-cyanopyridine systems, pyridine-bound for the 2-cyanopyridine system) in the second stage.

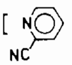
In order to simplify the handling of the kinetic data, the first stages of the reactions were studied at the isosbestic points between the two isomers and, thus, any subsequent isomerization did not interfere with the initial formation reaction. The reactions of the 3- and 4-cyanopyridine ligands with $Fe(CN)_5OH_2^{3-}$ proceed to completion under the conditions studied and therefore values of k_{obs} are $(k_f^N + k_f^{NC})$ [L], where k_f^N and k_f^{NC} are defined in Scheme I, and [L] is the ligand concentration. The results obtained are presented in Table III. In the case of 4-cyanopyridine, where the rate of the second reaction is at least 200 times slower than that of the first reaction, measurements were also made at wavelengths near the maxima for the pyridine-bound or the nitrile-bound isomers. It will be seen that the formation reactions are first-order in ligand and independent of wavelength. Included in Table III are the rate constants for the dissociation of the pyridine-bound isomers, measured by the pyridine scavenger technique.

TABLE III. Rate Constants for the Formation and Dissociation of 4- and 3-Cyanopyridinepentacyanoferrate(II) Complexes[a].

Ligand	Concentration, $M \times 10^2$	k_{obs}[b], sec^{-1}	$k_f^N + k_f^{NC}$, M^{-1} sec^{-1}
	1.91	13.0 ± 0.1[c]	682
	1.91	11.4 ± 0.2[d]	598
	2.15	13.4 ± 0.1	623
	2.15	13.1[e]	609
	9.54	62.2 ± 0.2[c,f]	652
	9.54	55 ± 6[d]	577
	9.94	58 ± 2	584
	0.0096	$(1.02 \pm 0.05) \times 10^{-3}$ [g]	–
 [h]	0.982	6.27 ± 0.03	635
	4.98	31.6 ± 0.2	638
	0.0092	$(2.80 \pm 0.06) \times 10^{-3}$ [g]	–

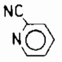
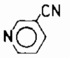
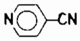
[a] At 25 °C, ionic strength 0.100 *M* ($LiClO_4$), pH 8 (tris buffer), $[Fe(CN)_5OH_2^{3-}] = (1.93–3.31) \times 10^{-5}$ *M*. Measurements at 412 and 439 nm for 3- and 4-cyanopyridine, respectively. [b] Average and standard deviation of 3–4 replicate measurements. [c] Measured at 390 nm. [d] Measured at 477 nm. [e] Single measurement. [f] Duplicate measurements. [g] Rate constant for dissociation of pyridine-bound isomer, measured in the presence of 0.0996 *M* pyridine. [h] Previous measurements of rate constants for formation and dissociation are 730 M^{-1} sec^{-1} at 25.2 °C and unspecified ionic strength and 2.5×10^{-3} sec^{-1} at 25.4 °C and ionic strength 0.20 *M*. See ref. 6 and M. J. Blandamer, J. Burgess and R. I. Haines, *J. Chem. Soc. Dalton,* 1293 (1976).

TABLE IV. Rate Constants for the Formation and Dissociation of 2-Cyanopyridinepentacyanoferrate(II)[a].

[] $M \times 10^2$	k_{obs}[b] sec^{-1}	P_1^{extra} [c]	t[c] m sec	θ_1[c] sec^{-1}	$k_{12} + k_{13}$ [c] sec^{-1}	$k_f^N + k_f^{NC}$ M^{-1} sec^{-1}
2.43	14.9 ± 0.1	0.014	90	15.6	15.2	626
4.91	28.0 ± 0.4[d]	0.005	45	28.7	28.3	578
4.99	29.6 ± 0.4	0.004	45	30.3	29.9	601
7.58	43.6 ± 0.6	0.001	30	44.4	44.0	580
9.72	57.4 ± 1.7	–0.001	25	58.2	57.8	595
0.20	0.0093 ± 0.002[e]	–	–	–	–	–

[a] At 25 °C, ionic strength 0.100 M ($LiClO_4$), pH 8 (tris buffer), $[Fe(CN)_5OH_2^{3-}]$ = (2.26–3.30) × 10^{-5} M. Measurements at 436 nm. [b] Average and standard deviation of 3–4 replicate measurements. [c] Defined in the appendix. [d] Duplicate measurements. [e] Rate constant for dissociation of nitrile-bound isomer, measured in the presence of 0.0996 M pyridine.

TABLE V. Rate Constants for Isomerization of Pyridine-Bound 2-Cyanopyridinepentacyanoferrate(II) and Nitrile-Bound 3- and 4-Cyanopyridinepentacyanoferrate(II)[a].

Ligand	Concentration, $M \times 10^2$	10^2 k_{iso}, sec^{-1} [b]
 [c]	1.10	85 ± 1
	4.90	91 ± 1
 [d]	0.98	7.8 ± 0.2
	4.98	7.3 ± 0.4
 [e]	1.91	5.2 ± 0.5
	1.91	6.0 ± 0.4
	9.54	6.2 ± 0.5
	9.54	6.2 ± 1.1

[a] At 25 °C, ionic strength 0.100 M ($LiClO_4$), pH 8 (tris buffer), $[Fe(CN)_5OH_2^{3-}]$ = (2.22–3.26) × 10^{-5} M. [b] Average and standard deviations of 3–4 replicate experiments. [c] Measured at 480 nm. [d] Measured at 375 nm. [e] First and third experiment with this ligand measured at 390 nm; second and fourth experiment measured at 477 nm.

The reaction of 2-cyanopyridine with $Fe(CN)_5OH_2^{3-}$ does not proceed to completion and, therefore, in order to obtain $k_f^N + k_f^{NC}$, the observed rate constants were first corrected as described in the appendix. The results obtained, presented in Table IV, show that the formation reaction is first-order in ligand. Included in Table IV is the rate constant for the dissociation of the nitrile-bound isomer.

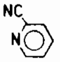
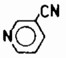
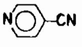
Rate Constants for Isomerization of Unstable Linkage Isomers, of 2-, 3- and 4-Cyanopyridinepentacyanoferrate(II)

At sufficiently high ligand concentrations (≥0.01 M), the formation reactions are sufficiently rapid ($t_{1/2} \leq 120$ msec) compared to the isomerization reactions ($t_{1/2} \sim 1$ sec for 2-cyanopyridine and ~10 sec for 3- and 4-cyanopyridine) that the latter can be followed without much interference from the former. The spectroscopic studies (*vide supra*) suggest that the transient, unstable linkage isomers produced in the reactions of $Fe(CN)_5OH_2^{3-}$ with 3- and 4-cyanopyridine are nitrile-bound, whereas the unstable isomer produced in the reaction with 2-cyanopyridine is pyridine-bound. The rate constants for isomerization of the three unstable isomers are presented in Table V.

Stoichiometries of the Reactions of $Fe(CN)_5OH_2^{3-}$ with 2-, 3- and 4- Cyanopyridine

The reactions of $Fe(CN)_5OH_2^{3-}$ with 0.10 M ligand were allowed to proceed for 1 sec. At 25 °C, the calculated half-life for the formation reactions are ~10 msec, and therefore the formation reactions were complete during the allotted period. The quenching of the isomerization reactions for the 3- and 4-cyanopyridine systems was accomplished by oxidation with Ce(IV), followed by absorption of the resulting iron(III) complexes onto an anion exchange resin. The complexes were eluted, and at this point the solutions contained mixtures of the pyridine-bound isomer and $Fe(CN)_5OH_2^{2-}$. As shown below, the aquation of nitrile-bound pentacyanoferrate(III) complexes is fairly rapid, and, therefore, during the time necessary for the ion exchange procedure, all the nitrile-bound iron(III) complexes aquate. The analysis of the mixture of pyridine-bound complex and $Fe(CN)_5OH_2^{2-}$ was accomplished by mixing with ascorbic acid in the presence of excess pyridine. Reduction of iron(III) to iron(II) is very rapid [21], and the resulting $Fe(CN)_5OH_2^{3-}$ reacts very rapidly with pyridine to produce $Fe(CN)_5py^{3-}$. The mixture of $Fe(CN)_5py^{3-}$ and the pyridine-bound isomer of the cyanopyridine complex was then analyzed spectrophotometrically as described in the experimental section (extrapolation required). The results of these measurements are presented in Table VI and it will be seen that, although the pyridine bound iso-

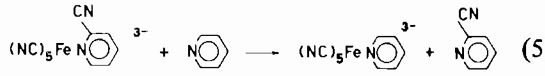
TABLE VI. Stoichiometries of the Reactions of Fe(CN)$_5$OH$_2^{3-}$ with 2-, 3- and 4-Cyanopyridine[a].

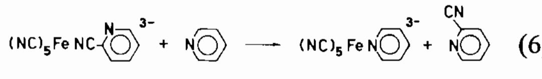
Ligand	Method	t, °C	% Nitrile-Bound Isomer[b]
	c	10.0	74 ± 4[d]
	c	25.0	35 ± 2
	e	25.0	35 ± 2
	e	5.0	37 ± 2
	c	25.0	34 ± 6
	e	25.0	41 ± 2
	e	5.0	41 ± 4

[a] Ligand concentration 0.10 *M*; [Fe(CN)$_5$OH$_2^{3-}$] = 5.0 × 10^{-5} *M*. [b] Duplicate measurements, estimated uncertainty. [c] Pyridine method. [d] Triplicate measurements. [e] Cerium(IV) quenching method.

mers are the more stable ones, substantial amounts of the nitrile-bound isomers are also produced.

The method used for 3- and 4-cyanopyridine cannot be used for the 2-cyanopyridine system because both linkage isomers of the iron(III) complex undergo aquation during ion exchange. Therefore, another method (which in fact yields additional information, *vide infra*) was utilized. Following the formation reaction, pyridine was added. Under the conditions used, both isomers produce the pyridine complex (eq. 5 and 6, except for a possible intramolecular isomerization pathway, *vide infra*) but reaction 5 is faster, and after a certain time,


(5)

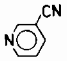
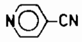

(6)

only the nitrile-bound isomer remains and is undergoing reaction 6. Extrapolation of this phase of the reaction to time zero yields the amount of nitrile-bound isomer produced in the formation reaction. The results are presented in Table VI and it will be seen that the thermodynamically stable isomer is again the one produced in higher abundance. The pyridine method was also applied to the 3- and 4-cyanopyridine systems, and the results, presented in Table VI, are the same as those obtained using the cerium(IV) quenching method. The significance of this observation will be discussed below.

Rate Constants for Dissociation of Nitrile-Bound-3- and 4-Cyanopyridinepentacyanoferrate(III) Complexes

The results are presented in Table VII, and it will be seen that the rates of aquation are independent of ligand concentration, of pH in the range 3–5, and of added Fe(CN)$_5$OH$_2^{3-}$ (which immediately yields the appropriate iron(II) complex). At pH 8, the nitrile-bound complexes undergo reactions which lead to unidentified pink products. The 2-cyanopyridine system was not investigated thoroughly, but preliminary kinetic experiments indicated biphasic behavior, consistent with aquation of both linkage isomers at somewhat different rates. It is noteworthy that these dissociation reactions are *not* catalyzed by iron(II) [7].

TABLE VII. Rate Constants for Aquation of Nitrile-Bound 3- and 4-Cyanopyridinepentacyanoferrate(III)[a].

Ligand	Concentration, $M \times 10^2$	pH	10^3 k$_{obs}$, sec^{-1}
	4.34	4.78	3.25
	4.37	4.77	2.86
	7.65	3.37	2.77[b]
	7.82	3.41	2.80[c]
	8.02	3.54	3.15
	8.13	3.44	2.95
	3.92	4.78	4.47
	3.98	4.80	4.78
	7.65	3.74	4.86[d]
	7.68	3.88	4.51
	7.80	3.53	4.85[e]
	7.88	3.86	4.74

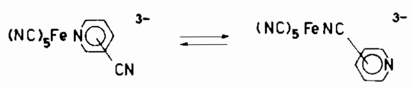
[a] At 25 °C, ionic strength 0.100 *M* (LiClO$_4$). Measurements at 420 nm. [Fe(III)] = (2.1–4.6) × 10^{-5} *M*. [b] 2.68 × 10^{-6} *M* Fe(CN)$_5$OH$_2^{3-}$ added. [c] 2.88 × 10^{-6} *M* Fe(CN)$_5$OH$_2^{3-}$ added. [d] 2.48 × 10^{-6} *M* Fe(CN)$_5$OH$_2^{3-}$ added. [e] 2.82 × 10^{-6} *M* Fe(CN)$_5$OH$_2^{3-}$ added.

Discussion

Toma and Malin [17, 18] have demonstrated the parallelism that exists between pyridine complexes of Ru(NH$_3$)$_5^{2+}$ [19] and of Fe(CN)$_5^{3-}$. These complexes are characterized by high stability constants (10^6 – 10^7) and intense, metal to ligand charge transfer bands in the visible or near ultraviolet. Clarke and Ford [10, 11] reported that the rich chemistry of pentaammineruthenium(II)–pyridine complexes was also featured in the analogous nitrile complexes. In the present work, we have prepared, in solution, a number of nitrile complexes of pentacyanoferrate(II), and again the similarity with the corresponding pentaammineruthenium(II) complexes is notable. Thus, a plot of the energy of the MTLCT transition of a Ru(NH$_3$)$_5^{2-}$ –nitrile complex *vs.* the energy of the corresponding Fe(CN)$_5^{3-}$ complex is linear with a slope of 0.7. The analogous plot for the corresponding pyridine complexes [17] is also linear and has a slope of 0:8.

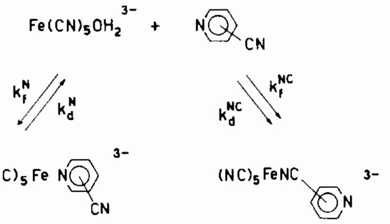
For the cyanopyridine complexes of Fe(CN)$_5^{3-}$, we have prepared and characterized, in solution (and in part in the solid state), three pairs of linkage isomers. The positions of the charge transfer bands in the visible and ultraviolet region, and of the nitrile stretching bands in the infrared spectra serve to assign structures to the isomers (see results section). In the case of 3- and 4-cyanopyridine, the pyridine-bound isomers are the more stable ones, whereas the opposite holds true for 2-cyanopyridine. The reversal in the relative stabilities of the isomers is readily understood on the basis of steric effects. The affinity of a pyridine nitrogen for Fe(CN)$_5^{3-}$ is about 10^2 higher than that of a nitrile nitrogen and, thus, in the case of 3- and 4-cyanopyridine where the nitrile does not interfere sterically with the coordination sphere of the iron(II) center, the predominant isomer at equilibrium is pyridine-bound. However, in the case of 2-cyanopyridine, molecular models of the pyridine-bound isomer show a strong steric interaction between the nitrile group in the 2 position and the cyanide groups *cis* to the pyridine nitrogen. In fact, the steric hindrance is so pronounced that the pyridine ring cannot be coplanar with the *cis* ligands. In this confirmation, back-bonding from the iron to the pyridine cannot obtain and this, together with the steric problem, decreases substantially the stability of the pyridine-bound isomer. As will be seen below, the decrease in stability is associated with both a decrease in the rate of formation and an increase in the rate of dissociation of the complex. In fact, the stability decrease is so pronounced, that the nitrile-bound isomer becomes the more stable one.

Although equilibrated solutions of Fe(CN)$_5$OH$_2^{3-}$ and the appropriate cyanopyridine contain predominantly one linkage isomer, a close examination of the spectra showed that, in the case of 3-cyanopyridine, a detectable amount of the unstable nitrile-bound isomer could be present at equilibrium. Thus, the half-widths for the pyridine-bound 4-cyanopyridine complex and for the nitrile complexes are near 100 nm, whereas the half-width for the 3-cyanopyridine complex is 120 nm. Therefore, for this compound an attempt was made to determine the ratio of isomers present at equilibrium. The cerium(IV) method was applied to equilibrium mixtures of 5 × 10^{-5} *M* Fe(CN)$_5$OH$_2^{3-}$ and 0.10 *M* 3-cyanopyridine. The average value (6 experiments in the range 5–40 °C) of the equilibrium constant


(7)

for reaction 7 was 0.04 ± 0.01. This value is in acceptable agreement with the 0.02 value calculated from the kinetic parameters (*vide infra*). Assuming that 5% of the unstable isomer would have been spectroscopically detectable in the 2- and 4-cyano pyridine complexes, we estimate that the equilibrium constants for reaction 7 in these systems are >20 and <0.05, respectively. This upper limit is consistent with the 0.01 value from the kinetic parameters for the 4-cyanopyridine system. For the 2-cyanopyridine system, as shown below, the value of 20 as lower limit for the equilibrium constant for reaction 7 will be used to place limits on the rate constants.

The unstable isomers are transient intermediates produced, in a kinetically controlled manner, by the reaction of Fe(CN)$_5$OH$_2^{3-}$ with the cyanopyridines. The proposed mechanism is presented in Scheme I.

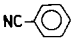
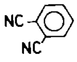
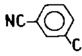
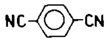
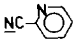
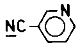
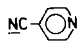
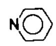
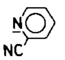
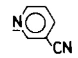
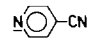


Scheme I.

In this scheme, the quantities $k_f^N + k_f^{NC}$, the rate constants for the formation of the two isomers, and k_d^N (for the 3- and 4-cyanopyridine complexes) or k_d^{NC} (for the 2-cyanopyridine complex), the rate constants for the dissociation of the stable linkage isomers, have been measured as described in the results section. Three related questions remain. How are the values of $k_f^N + k_f^{NC}$ to be divided into the individual contributions for the formation of each isomer? How are the rate constants for isomerization related to the rate constants in Scheme I? Finally, since Scheme I implies an *inter*molecular mechanism for isomerization, it is also pertinent to inquire whether an *intra*molecular mechanism is also operative. Since the first two questions are dependent on the third, let us first consider the latter.

For the 3- and 4-cyanopyridine complexes, the intramolecular pathways for isomerization of the nitrile-bound isomers can be ruled out on the basis of the two sets of stoichiometric measurements. The cerium(IV) method yields the amounts of nitrile- and pyridine bound isomers produced in the kinetically-controlled formation step [22], and, therefore, the fraction of pyridine-bound isomer produced is simply $k_f^N/(k_f^N + k_f^{NC})$. The pyridine method yields the amount of pyridine-bound isomer produced in the formation step plus any amount produced *via* an intramolecular isomerization pathway during the subsequent period while the nitrile-bound isomer is disappearing. It can be shown (see *Appendix*) that the fraction of pyridine-bound isomer measured by the pyridine method is given by eq. 8, where k_{intra} is the rate constant for isomerization of nitrile-bound to

TABLE VIII. Rate Constants for Formation and Dissociation of Complexes of $Fe(CN)_5^{3-}$ with Nitriles and Cyanopyridines[a].

Ligand[b]	$10^{-2}\ k_f, M^{-1}\ sec^{-1}$	$10^3\ k_d, sec^{-1}$	$K \times 10^{-3}$
	2.70	117	2.35
	4.53	81.2	5.58
	6.38	78.6	8.12
	4.10	66.3	6.18
	3.65–4.41[c]	93	3.92–4.74[c]
	2.23	117	1.90
	2.35	97	2.42
	3.65	1.10	331
 [d]	2.31–1.55[c]	1,180–1,190[c]	0.196–0.130[c]
	4.13	2.80	148
	3.83	1.02	375

[a] At 25 °C and ionic strength 0.10 *M* ($LiClO_4$). [b] Underlined atom represents the binding site. [c] See text for explanation of limits. [d] From ref. 17, ionic strength 1.0 *M*.

$$f_N = \frac{k_f^N}{k_f^{NC} + k_f^N} + \frac{k_{intra}}{k_{intra} + k_d^{NC} - k_d^N} \qquad (8)$$

pyridine-bound isomer *via* an intramolecular mechanism. Since the values of f_N measured by the two methods are not significantly different from each other (*cf.* Table VI), we conclude that isomerization *via* an intramolecular pathway does not obtain for the 3- and 4-cyanopyridine complexes. Therefore, from the measured values of $k_f^N + k_f^{NC}$ and f_N, individual values of k_f^N and k_f^{NC} were calculated.

Moreover, in the absence of intramolecular isomerization, it can be shown that $k_{iso} = k_d^{NC}\ k_f^N/(k_f^N + k_f^{NC})$, and therefore, from measured values of k_{iso} and f_{NC}, values of k_d^{NC} were calculated. The resulting rate constants from all these calculations are presented in Table VIII, together with the equilibrium constants obtained from the relation $K = k_f/k_d$. Included in Table VIII are the kinetic and equilibrium parameters for benzonitrile and the dicyanobenzenes.

The entries for 2-cyanopyridine included in Table VIII call for special comment. Since for this compound, the cerium(IV) method could not be used (*vide supra*) and the fraction of pyridine-bound isomer measured by the pyridine method gives an *upper* limit for $k_f^N/(k_f^N + k_f^{NC})$, individual values of the rate constants cannot be obtained unless some assumption is made about the extent of intramolecular isomerization. If it is assumed, as in the case for the 3- and 4-cyanopyridine systems, that intramolecular isomerization does not obtain, then upper limits are obtained for k_f^{NC} and k_d^N and a lower limit is obtained for k_f^N. Lower limits for k_f^{NC} and k_d^N and an upper limit for k_f^N can be estimated if it is assumed that some intramolecular isomerization obtains. Under these circumstances, the fraction of nitrile-bound isomer measured by the pyridine method and the rate constant for isomerization are given by eq. 9 and 10, respectively, where k'_{intra} is the rate constant for isomerization of the pyridine-bound to the nitrile-bound isomer *via* the intramolecular pathway. Using the measured values of k_{iso}, f_{NC},

$$f_{NC} = \frac{k_f^{NC}}{k_f^N + k_f^{NC}} + \frac{k'_{intra}}{k'_{intra} + k_d^N - k_d^{NC}} \qquad (9)$$

$$k_{iso} = k_d^N\ \frac{k_f^{NC}}{k_f^N + k_d^{NC}} + k'_{intra} \qquad (10)$$

$k_f^N + k_f^{NC}$, k_d^{NC} and the upper limit of 0.05 for $k_f^N \cdot k_d^{NC}/(k_d^N k_f^{NC})$, values of k'_{intra}, k_f^{NC}, k_f^N and k_d^N can be calculated. The value of k'_{intra} is 0.16 sec^{-1} and the other values are presented in Table VIII. The value 0.16 sec^{-1} is an upper limit for k'_{intra}, and therefore less than 18% of the isomerization proceeds *via* an intramolecular pathway. Since 0.16 sec^{-1} is a generous upper limit, it is apparent that the intramolecular mechanism is not important for the 2-cyanopyridine system, as was the case for the analogous 3- and 4-cyanopyridine systems.

It will be seen that the rate constants for the formation of pentacyanoferrate(II) complexes of nitriles and pyridines fall in the narrow range of (2.0–4.5) X 10^2 M^{-1} sec^{-1} per ligand binding site. The lack of sensitivity of the rate to the nature of the entering ligand (for a series of ligands of the same charge) can be taken to indicate the operation of a dissociative mechanism [18]. The similarity in rates for pyridines and nitriles is to be contrasted with the 2–3 fold preference for nitriles in the analogous substitution [12, 13] reactions of $Ru(NH_3)_5OH_2^{2+}$. This was explained [12, 13] on the basis of steric hindrance between ortho hydrogens and ammine hydrogens. Steric effects are much less pronounced for the $Fe(CN)_5^{3-}$ moiety, and, thus, there is little discrimination between nitriles and pyridines. However, the steric effect is important for the pyridine-bound 2-cyanopyridine complex which has a value of k_f^N *ca.* half that of pyridines without substituents in the 2 position.

In contrast to the rate constants for formation reactions, the rate constants for dissociation depend on the nature of the ligand. The reactions of the nitrile complexes are *ca.* 2 orders of magnitude faster than those of the pyridine complexes. As seen by comparing the activation parameters of benzonitrile ($\Delta H^{\ddagger}$ = 22.8 kcal/mol, $\Delta S^{\ddagger}$ = 13.6 eu) with those for pyridine [17] ($\Delta H^{\ddagger}$ = 24.8 kcal/mol, $\Delta S^{\ddagger}$ = 11 eu), the relative reactivities are associated with a weaker bond for nitriles as compared to pyridines, presumably because of the weaker basicity of nitriles. The rate constant for dissociation of the pyridine-bound 2-cyanopyridine complex is *ca.* 10^3 faster than rate constants for pyridines without ortho substituents, an obvious consequence of the steric hindrance of the cyanide group in the 2-position. In fact, it is somewhat remarkable that the pyridine-bound isomer is formed at all. Perhaps a limiting S_N1 mechanism is operative in this sytem, and the highly reactive pentacoordinate intermediate reacts indiscriminately with any binding site of the incoming ligand.

Additional evidence for a highly dissociative mechanism comes from a comparison of equilibrium constants with rate constants for dissociation. It was noted previously [23] that a plot of log k_d *vs.* log K was linear with a slope of 1.0 ± 0.05. The plot, shown in Fig. 1, includes data published since then as well as the data obtained in the present work. The points obey a linear correlation with slope 0.98 ± 0.03, and as shown previously [24, 25], the correlation strongly supports a dissociative mechanism for all these reactions.

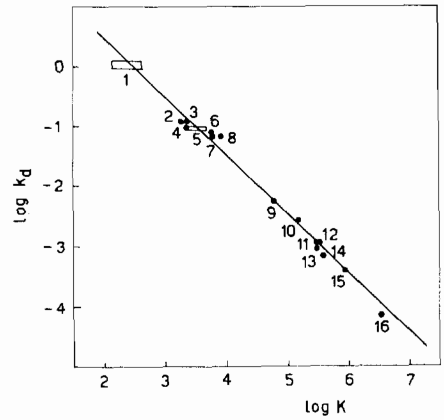
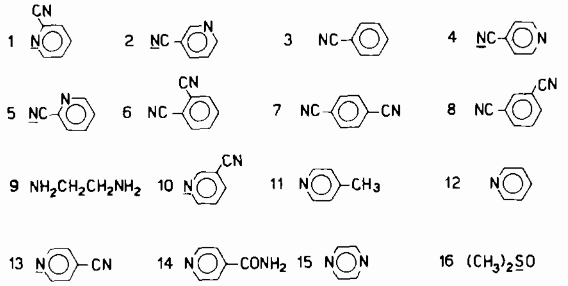


Figure 1. Plot of logk_d *vs.* logK for pentacyanoferrate(II) complexes of neutral ligands. The line is the least-squares equation log k_d = 2.45 – 0.98 logK_{eq}.

Key to Figure 1:



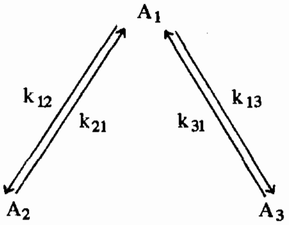
A comparison between the stability constants of the pyridine-bound 2- and 4-cyanopyridine complexes [26] allows an estimate to be made of the contribution of π-bonding to the stability of these complexes. Because of steric hindrance, in the 2-cyanopyridine complex, the aromatic ring cannot be coplanar with the *cis* cyanide groups, and, consequently, a π-bonding contribution to the stability of the complex seems unlikely. The difference in stabilities between 2- and 4-cyanopyridine complexes, converted into a free energy quantity, is ~4 kcal/mol, and this value can be used as a measure of the π-bonding contribution to the stability of the 4-cyanopyridine complex. The value of 4 kcal/mol appears to be reasonable when it is compared with previous estimates of the extra stability gained from back-bonding contributions in $Ru(NH_3)_5N\bigcirc^{2+}$ (~5 kcal/mol [13]) and in $Fe(CN)_5N\bigcirc^{3-}$ (<4.6 kcal/mol [16]).

The importance of π-bonding in the iron(II) complexes can also be seen by comparing the equilibrium constants for the formation of benzonitrile complexes of iron(II) and iron(III) complexes. The values are 2.33 X 10^3 and 0.30 [27], respectively. Since iron(III) is a stronger σ acid than iron(II), the increase in stability going from iron(III) to iron(II) reflects the increase in π basicity of iron(II) as compared to iron(III).

Appendix

Kinetics of Reaction of $Fe(CN)_5OH_2^{3-}$ with 2-Cyanopyridine

Consider the kinetic scheme



where

$A_1 = \mathrm{Fe(CN)_5OH_2^{3-}}$,

$A_2 = \mathrm{Fe(CN)_5N}\underset{\mathrm{CN}}{\bigcirc}^{3-}$ and

$A_3 = \mathrm{Fe(CN)_5NC}\overset{\mathrm{N}}{\bigcirc}^{3-}$.

This scheme, including interconversion between A_2 and A_3, has been treated fully [28]. The integrated equation for A_1 when $A_1 = A_1^\circ$ and $A_2 = A_3 = 0$ at t = 0 is:

$$\frac{A_1}{A_1^\circ} = P_1 + P_2\,e^{-\theta_1 t} + P_3\,e^{-\theta_2 t} \tag{11}$$

where

$$P_1 = 1 + \frac{k_{12}(k_{21} - k_{31}) - k_{21}(k_{12} + k_{13})}{\theta_1\theta_2}$$

$$P_2 = \frac{k_{12}k_{31} + k_{13}k_{21} - \theta_1(k_{12} + k_{13})}{(\theta_2 - \theta_1)\theta_1}$$

$$P_3 = \frac{\theta_2(k_{12} + k_{13}) - k_{12}k_{31} - k_{21}k_{13}}{(\theta_2 - \theta_1)\theta_2}$$

$$\theta_{1(2)} = \frac{k_{12} + k_{13} + k_{31} + k_{21}}{2} + (-)\sqrt{\frac{(k_{12} + k_{13} + k_{31} - k_{21})^2}{4} + k_{12}(k_{21} - k_{31})} \tag{12}$$

According to eq. 11, a plot of $\ln(A_1/A_1^\circ)$ (or $\ln(A_t - A_\infty)$ where A_t and A_∞ are the absorbances at time t and at ∞ at the isosbestic point between A_2 and A_3) *vs.* time is not linear. However, the observed plots were linear within experimental error and, therefore,

$$A_1/A_1^\circ = e^{-k_{obs}t} = P_1 + P_2e^{-\theta_1 t} + P_3e^{-\theta_2 t} \tag{13}$$

Data for A_1/A_1° *vs.* t were generated using $k_{13} = 3\,k_{12}$, $15 \leq k_{12} + k_{13} \leq 60$, $k_{21} = 1.0$ and $k_{31} = 0.1$. The data generated obeyed the linear dependence and it was found that $P_3e^{-\theta_2 t} = 0.007$ for 3–4 lives and P_1 falls in the range −0.001 to 0.015. Therefore, eq. 13 can be rearranged to give

$$(1/t)\ln\left[(0.007 + P_1) + (0.993 - P_1)e^{-\theta_1 t}\right] = -k_{obs} \tag{14}$$

In order to obtain θ_1 from the observed rate constant, the following procedure was used. t was taken to be equal to the observed half-life. P_1 was estimated from the data generated using the parameters given above. An initial estimate of θ_1 was made (k_{obs} + 0.7), the left-hand side of eq. 14 was calculated and compared to k_{obs}. The value of θ_1 was changed until the calculated value of the left-hand side of eq. 14 matched the observed value of k_{obs}. Using the value of θ_1 obtained in this manner, the known value of k_{31} and the values of k_{21} and k_{12} estimated assuming no intramolecular linkage isomerization pathway, values of $k_{12} + k_{13}$ were obtained from eq. 12.

Determination of the Molar Absorbance of Pyridine-Bound 2-Cyanopyridinepentacyanoferrate(II)

Using the above kinetic scheme, the integrated equation for A_2 is

$$\frac{A_2}{A_1^\circ} = P_4 + P_5\,e^{-\theta_1 t} + P_6\,e^{-\theta_2 t} \tag{15}$$

where

$$P_4 = \frac{(\theta_2 - \theta_1)(k_{21} - \theta_1)(k_{21} - \theta_2)(k_{12} + k_{13}) + k_{12}(k_{21} - k_{31})[\theta_1(k_{21} - \theta_1) - \theta_2(k_{21} - \theta_2)]}{(k_{21} - k_{31})(\theta_2 - \theta_1)\theta_1\theta_2}$$

$$P_5 = \frac{(k_{21} - \theta_2)[\theta_1(k_{12} + k_{13}) - k_{21}k_{13} - k_{31}k_{12}]}{(k_{21} - k_{31})(\theta_2 - \theta_1)\theta_1}$$

$$P_6 = \frac{(k_{21} - \theta_1)[k_{21}k_{13} + k_{31}k_{12} - \theta_2(k_{12} + k_{13})]}{(k_{21} - k_{31})(\theta_2 - \theta_1)\theta_2}$$

The absorbance of the solution per cm, Abs, is given by:

$$\mathrm{Abs} = \epsilon_1A_1 + \epsilon_2A_2 + \epsilon_3(A_1^\circ - A_1 - A_2) \tag{16}$$

where ϵ_1, ϵ_2 and ϵ_3 are the molar absorbances of $\mathrm{Fe(CN)_5OH_2^{3-}}$, $\mathrm{Fe(CN)_5N}\underset{\mathrm{CN}}{\bigcirc}^{3-}$ and $\mathrm{Fe(CN)_5\text{-}NC}\overset{\mathrm{N}}{\bigcirc}^{3-}$, respectively.

Introducing eq. 11 and 15 into 16 and subtracting A_∞, the absorbance per cm at long times, we get eq. 17, the desired relation

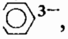
$$\mathrm{Abs_{max}} - A_\infty = (\epsilon_1 - \epsilon_3)(P_2e^{-\theta_1 t_{max}} + P_3e^{-\theta_2 t_{max}}) + (\epsilon_2 - \epsilon_3)(P_5\,e^{-\theta_1 t_{max}} + P_6e^{-\theta_2 t_{max}}) \tag{17}$$

Abs_{max} and t_{max} are the maximum absorbance of the solution and the time at which that absorbance occurs, respectively.

Analysis of Isomeric Mixtures by the Pyridine Method

Consider the kinetic scheme

$$\begin{tikzcd}
A_1 \arrow[rr, "k_{12}"] \arrow[dr, "k_{13}"'] & & A_2 \arrow[dl, "k_{23}"] \\
& A_3 &
\end{tikzcd}$$

where A_1, A_2 and A_3 are the unstable isomer of any cyanopyrinepentacyanoferrate(II) complex, the corresponding stable isomer and $Fe(CN)_5N$$^{3-}$, respectively. With $A_1 = A_1^\circ$, $A_2 = A_2^\circ$ and $A_3 = 0$ at time 0, the concentration of A_2 as a function of time is given by eq. 18.

$$\frac{A_2}{A_1^\circ + A_2^\circ} = \frac{k_{12}}{k_{23} - (k_{12} + k_{13})}$$

$$[e^{-(k_{12}+k_{13})t} - e^{-k_{23}t}] + \frac{A_2^\circ}{A_1^\circ + A_2^\circ} e^{-k_{23}t} \quad (18)$$

At long times exp $-(k_{12} + k_{13})t$ becomes negligible compared to exp $(-k_{23}t)$, and eq. 15 reduces to eq. 19:

$$\frac{A_2}{A_1^\circ + A_2^\circ} = \left(\frac{k_{12}}{k_{12} + k_{13} - k_{23}} + \frac{A_2^\circ}{A_1^\circ + A_2^\circ}\right) e^{-k_{23}t} \quad (19)$$

Extrapolation of eq. 19 to t = 0 yields the desired equation

$$\frac{A_2^{extra}}{A_1^\circ + A_2^\circ} = \frac{k_{12}}{k_{12} + k_{13} - k_{23}} + \frac{A_2^\circ}{A_1^\circ + A_2^\circ}$$

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1 (a) This work was supported by Grant CHE 76-10449 from the National Science Foundation. (b) Abstracted in part from the B.S. thesis of S. M., May (1975).

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20 In our earlier [3] work, $Fe(CN)_5OH_2^{3-}$ was prepared by aquation of $Fe(CN)_5NH_3^{3-}$ at 10 °C for 30 min, and ln $|A_t - A_\infty|$ *vs.* t plots for formation reactions were non-linear. In the present work, $Fe(CN)_5OH_2^{3}$ was prepared by aquation of $Fe(CN)_5NH_3^{3-}$ at 25 °C for 5 min, and ln $|A_t - A_\infty|$ *vs.* t plots were linear for all compounds studied except the dicyanobenzenes. We have no explanation for this observation. For non-linear plots, rate constants were evaluated from initial slopes.

21 For example, the rate constant for the $Fe(CN)_5OH_2^{2-}$–ascorbic acid reaction at pH 8 is $\sim 10^4$ M^{-1} sec^{-1} (unpublished studies).

22 It is assumed that the nitrile-bound iron(III) complexes undergo exclusively aquation.

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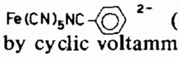
26 The 4-cyanopyridine is used for the comparison because of the similarity of substituent effects in the 2- and 4-positions.

27 This value is calculated from the reduction potentials of  $Fe(CN)_5NC$–$^{2-}$ (0.62v, measured, in the present work by cyclic voltammetry), and $Fe(CN)_5OH_2^{2-}$ (0.39v, H. E. Toma and C. Creutz, *Inorg. Chem., 16,* 545 (1977)) and the formation constant of the iron(II) complex.

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