noanions are better competitors than $SO_4^{2-}$[31] (Table V). The $[(NH_3)_5CoF]^{2+}$ ion appears to behave anomalously both in its competition properties with anions[32] and with the isotopes of water[6] and is the sole exception to this generalization. Furthermore, NCS⁻ can be captured either through nitrogen or through sulfur; S capture increases with increasing charge on the reactant while N capture appears to remain essentially constant (Table V). Finally, $[(NH_3)_5CoOSO_3]^+$ produces the amido precursor complex $[(NH_3)_4NH_2CoOSO_3]$ of zero charge, yet anion competition in 1 M NaN₃ occurs to an appreciable extent (Table VI). These observations are difficult to reconcile with an ion pair mechanism.

There is still, therefore, a considerable degree of consistency in the evidence in favor of an $S_N1cB$ mechanism which generates a reactive five-coordinate intermediate on a time scale comparable with, or shorter than, that for the relaxation of its precursor's ionic atmosphere. The atmosphere appears to be at least partly controlled by the overall charge and largely independent of the leaving group. There is no correlation with the size, geometry, or electronic properties of the leaving group. Nor is there a general correlation with the ion-pairing ability of competitors. Moreover, it appears that ion-paired species do not always capture the paired ion effectively and that ion pairing may even inhibit the competition properties of the generated intermediate at least toward anions.

The evidence for discrete intermediates is compelling not only in this instance but also in related systems. Notable examples are the base hydrolyses of the (*R*)- and (*S*)-α,β-[(nitrato)(tetraethylenepentamine)cobalt(III)](2+) and $\beta_2$-(*RR*,*SS*)-[Co(trien)((gly)OR)Cl]²⁺ (R = H, C₂H₅) ions, which require intermediates to account for rearrangement after loss of the leaving group and before the entering group is captured.[43,44]

Although, for the pentaamminecobalt(III) complexes, the intermediate $[(NH_3)_4CoNH_2]^{2+}$ appears to be common to all of the systems, the data require it to be generated in different environments. The evidence indicates that it is a short-lived species which does not equilibrate with the total system. Yet it lives long enough to undergo rearrangements.[8]

There is still a need for more competition data, especially for low-charged, zero-charged, and anionic complexes, and we are currently exploring these aspects. The situation is akin to that of the "hot" carbonium ion in organic chemistry, and we can presume a variety of "solvent cage" phenomena will be observed in systems where the lifetimes of the intermediates are too short to allow their equilibration with the whole medium.

**Supplementary Material Available:** Two tables of kinetic data (Tables II and IV) (3 pages). Ordering information is given on any current masthead page.

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# Electron-Transfer Reactions of Ion Pairs: Reductions of Various Substituted (Pyridine)pentaamminecobalt(III) Complexes by Hexacyanoferrate(II)[1]

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The reductions of a series of substituted (pyridine)pentaamminecobalt(III) complexes by hexacyanoferrate(II) proceed via formation of an ion pair $Co(NH_3)_5L^{n+} + Fe(CN)_6^{4-} \rightleftharpoons Co(NH_3)_5L^{n+}|Fe(CN)_6^{4-}$, $Q_{IP}$, followed by internal electron transfer within the ion pair $Co(NH_3)_5L^{n+}[Fe(CN)_6^{4-} \rightarrow Co(NH_3)_5L^{(n-1)+}|Fe(CN)_6^{3-}$, $k_{et}$. Values of $Q_{IP}$ (in M⁻¹) and $k_{et}$ (in s⁻¹) at 25.0 °C, ionic strength 0.10 M, and pH 5.0 are as follows: nicotinamide, $(2.5 \pm 0.4) \times 10^3$, $(5.04 \pm 0.18) \times 10^{-2}$; isonicotinamide, $(5.3 \pm 2.3) \times 10^3$, $(3.58 \pm 0.25) \times 10^{-2}$; 4,4'-bipyridine (bpy), $(2.3 \pm 0.2) \times 10^3$, $(2.40 \pm 0.05) \times 10^{-2}$; 1,2-bis(4-pyridyl)ethane, $(2.8 \pm 0.4) \times 10^3$, $(1.01 \pm 0.03) \times 10^{-2}$; *N*-methyl-4,4'-bipyridinium (*N*-Mebpy), $(3.2 \pm 0.4) \times 10^3$, $(4.74 \pm 0.17) \times 10^{-2}$; pyridine-bonded 3-cyanopyridine, $(1.3 \pm 0.2) \times 10^3$, $(34.6 ● 2.4) \times 10^{-2}$; pyridine-bonded 4-cyanopyridine, $(2.5 \pm 0.2) \times 10^3$, $(15.1 \pm 0.3) \times 10^{-2}$; nitrile-bonded 3-cyanopyridine, $(1.5 \pm 0.2) \times 10^3$, $(76 \pm 4) \times 10^{-2}$. The ion pairs $Co(NH_3)_5py^{3+}|Fe(CN)_6^{4-}$ and $Co(NH_3)_5(N\text{-}Mebpy)^{4+}|Fe(CN)_6^{4-}$ exhibit charge-transfer bands at 445 (molar absorbance 160 M⁻¹ cm⁻¹) and 470 nm (molar absorbance 240 M⁻¹ cm⁻¹). It is postulated that the ion pairs feature approach of $Fe(CN)_6^{4-}$ on the ammonia side of the cobalt(III) complexes. The electron-transfer process is assumed to be adiabatic and the variations in rate are associated with changes in the reduction potentials and/or rate constants for self-exchange of the cobalt(III) complexes.
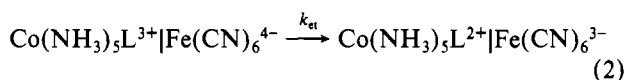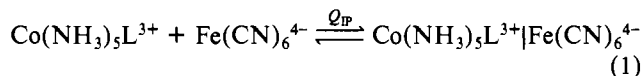
## Introduction

The importance of measuring rates of electron-transfer reactions in the intramolecular mode has been emphasized repeatedly.[2] In previous publications, we have reported rate constants for intramolecular electron transfer in binuclear

complexes containing iron(II) and cobalt(III) bridged by various pyridines.[3-6] For inner-sphere reactions, the geometries of the binuclear complexes are well established, and, therefore, structure-reactivity relationships can be studied. For

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example, we were able to find an inverse linear correlation between the free energy of activation and the distance between the metal centers.[6] In contrast, for outer-sphere reactions, because of the lability of the ion pairs, the relative orientation of the two metal complexes, when at least one of them is not symmetrical, is unknown.[7] Under these circumstances, indirect criteria must be invoked[7] to obtain information about the details of the pathway for the electron transfer, and it becomes important to accumulate kinetic data for outer-sphere reactions of a variety of complexes for which the inner-sphere reactivity is known. In the present paper, we report measurements of intramolecular electron transfer within ion pairs formed by hexacyanoferrate(II) and substituted (pyridine)-pentaamminecobalt(III) complexes (eq 1 and 2). The inner-sphere reactivity of these complexes toward pentacyanoferrate(II) has been studied extensively.[3-6,8]

$$Co(NH_3)_5L^{3+} + Fe(CN)_6^{4-} \underset{Q_{IP}}{\rightleftharpoons} Co(NH_3)_5L^{3+}|Fe(CN)_6^{4-}$$
(1)

$$Co(NH_3)_5L^{3+}|Fe(CN)_6^{4-} \xrightarrow{k_{et}} Co(NH_3)_5L^{2+}|Fe(CN)_6^{3-}$$
(2)

## Experimental Section

**Materials.** The purifications of the distilled water, the sodium and lithium perchlorates, the argon, and the sodium hexacyanoferrate(II) were described previously.[6,7] All other materials were reagent grade and used as received.

**Preparation of Complexes.** The perchlorate salts of the pentaamine complexes of nicotinamide,[9] isonicotinamide,[9] 4,4'-bipyridine,[10] N-methyl-4,4'-bipyridinium,[10] 1,2-bis(4-pyridyl)ethane,[5] 3-cyanopyridine (both linkage isomers),[8] and 4-cyanopyridine[8] (pyridine-bonded isomer) were prepared according to the references cited.

**Kinetic Measurements.** The slower (half-lives longer than ~15 s) reactions were measured spectrophotometrically with a Cary 14 spectrophotometer according to the method described previously for $Co(NH_3)_5py^{3+}$.[7] The faster reactions (half-lives shorter than ~10 s) were measured with a Durrum 110 stopped-flow apparatus. Rate constants were obtained by nonlinear least-squares fitting of absorbance vs. time measurements to the equation $A_t = A_\infty + (A_0 - A_\infty)$ exp-$(-k_{obsd}t)$. $A_0$ and $k_{obsd}$ were taken as floating parameters, and excellent agreement between experimental and calculated $A_t$ values was obtained for about 4 half-lives.

**Spectra of Ion Pairs.** The spectra of the ion pairs

$$Co(NH_3)_5N\langle\bigcirc\rangle^{3+}|Fe(CN)_6^{4-}$$

$$Co(NH_3)_5N\langle\bigcirc\rangle\langle\bigcirc\rangle NCH_3^{4+}|Fe(CN)_6^{4-}$$
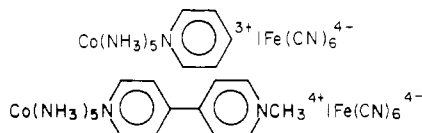
were obtained by mixing rapidly at 5 °C a solution of the appropriate cobalt(III) complex with a large excess of $Fe(CN)_6^{4-}$, followed by repetitive scanning of the resulting solution. Extrapolation to the time of mixing gave the spectra of the ion pairs.

## Results and Discussion

All measurements were carried out in the presence of $EDTA^{2-}$ to prevent precipitation of cobalt(II) hexacyanoferrate(II) and/or -(III).[11] Under these conditions, mixing of the yellow-orange pyridine complex of pentaamminecobalt(III) with the colorless hexacyanoferrate ion results in a sequence of three color changes. The first is the instantaneous formation of an orange color. This is followed by a change, over a period of seconds, to a yellow color. Finally, a reddish purple color is produced over a period of hours. The interpretation of the color changes is straightforward. The
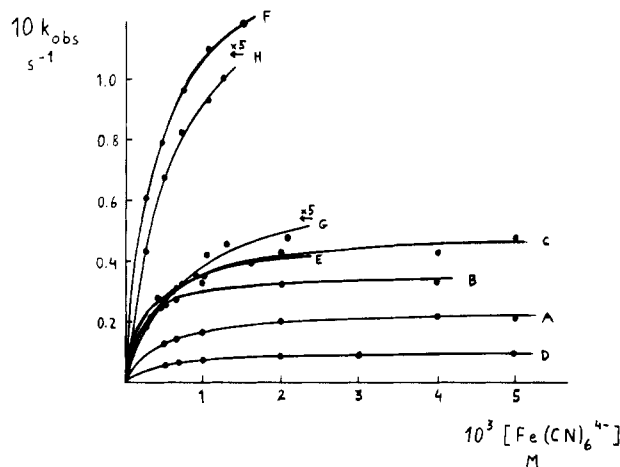
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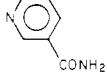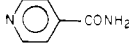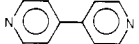(9) Nordmeyer, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1162.
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**Figure 1.** Pseudo-first-order rate constants ($k_{obsd}$) for reduction of various pyridine complexes of pentaamminecobalt(III) by hexacyanoferrate(II) at 25 °C, $\mu$ 0.10 M, pH 5.0, $[EDTA^{2-}] = (1.5-2.0) \times 10^{-4}$, $[Co(III)] = (2.0-5.0) \times 10^{-5}$ M. Each point is the average of 2-4 replicate measurements. Complexes: A, IV; B, III; C, II; D, V; E, VI; F, VIII; G, VII (bound at pyridine N); H, IX (bound at cyano N).

first change corresponds to the diffusion-controlled formation of the ion pairs (eq 1). The second change is the internal electron transfer which produces yellow $Fe(CN)_6^{3-}$ and, in the presence of $EDTA^{2-}$, $CoEDTA^{2-}$ (eq 2 and 3). Finally, the

$$Co(NH_3)_5L^{2+}|Fe(CN)_6^{3-} + EDTA^{2-} \rightarrow$$
$$CoEDTA^{2-} + Fe(CN)_6^{3-} + 5NH_3 \quad (3)$$
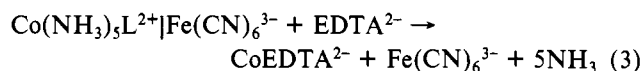
$CoEDTA^{2-}$ and $Fe(CN)_6^{3-}$ produced in eq 3 undergo an electron-transfer reaction[12] (eq 4) that produces purple $CoEDTA^-$. This reaction is very slow and does not interfere with the reaction of interest, eq 2.

$$CoEDTA^{2-} + Fe(CN)_6^{3-} \rightarrow CoEDTA^- + Fe(CN)_6^{4-} \quad (4)$$
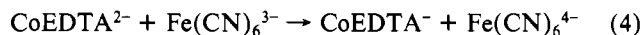
Values of $k_{obsd}$ for all the complexes studied are plotted vs. $[Fe(CN)_6^{4-}]$ in Figure 1. It will be seen that the reactions become less than first-order in $Fe(CN)_6^{4-}$ as its concentration increases. The ion pair mechanism represented by eq 1 and 2 predicts a value of $k_{obsd}$ given by eq 5. The measured values

$$k_{obsd} = \frac{k_{et}Q_{IP}[Fe(CN)_6^{4-}]}{1 + Q_{IP}[Fe(CN)_6^{4-}]} \quad (5)$$

of $k_{obsd}$ were fitted to eq 5 by means of a nonlinear least-squares calculation, and the resulting values of $k_{et}$ and $Q_{IP}$ are listed in Table I. The solid lines in Figure 1 are calculated from the parameters in Table I, and it will be seen that the parameters reproduce the experimental results reasonable well.

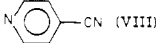The values of $Q_{IP}$, $(1.3-6.3) \times 10^3$ $M^{-1}$, are as expected for 4-/3+ ion pairs. By utilization of $4.5 \times 10^{-8}$[7] and $3.6 \times 10^{-8}$[13] for the radii of $Fe(CN)_6^{4-}$ and of the cobalt complex (if the approach by the iron complex is on the side of ammonia), respectively, the equilibrium constant calculated from eq 6 and 7 is $4.2 \times 10^2$ $M^{-1}$. If the approach of the iron complex is on

$$K_0 = \frac{4\pi Na^3}{3000} \exp(-U(a)/RT) \quad (6)$$

$$U(a) = Z_1Z_2e^2/Da(1 + \kappa a) \quad (7)$$

the side of the heterocyclic ligand, then the calculated equilibrium constants, with radii in the range $(6.0-12.0) \times 10^{-8}$ cm, are in the range 77-144 $M^{-1}$. The agreement with the
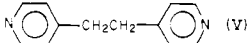
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Table I. Ion Pair Formation Constants and Internal Electron-Transfer Rate Constants for Reactions of $Fe(CN)_6^{4-}$ with $Co(NH_3)_5L^{3+}$ [a]

| L | $10^3 Q_{IP}$, $M^{-1}$ | $10^2 k_{et}$, $s^{-1}$ |
|---|---|---|
| (I) | $2.4 \pm 0.2$ | $1.51 \pm 0.08$ |
| (II) | $2.5 \pm 0.4$ | $5.04 \pm 0.18$ |
| (III) | $5.3 \pm 2.3$ | $3.58 \pm 0.25$ |
| (IV) | $2.3 \pm 0.2$ | $2.40 \pm 0.05$ |
| (V) | $2.8 \pm 0.4$ | $1.01 \pm 0.03$ |
| (VI) | $3.2 \pm 0.4$ | $4.74 \pm 0.07$ |
| (VII) | $1.3 \pm 0.2$ | $34.6 \pm 2.4$ |
| (VIII) | $2.5 \pm 0.2$ | $15.1 \pm 0.3$ |
| (IX) | $1.5 \pm 0.2$ | $76 \pm 4$ |

[a] At 25 °C, ionic strength 0.10 M, pH 5.0, $[EDTA^{2-}] = (1.5-2.0) \times 10^{-4}$ M.

experimental value of $Q_{IP}$ is considerably better for the calculation with $a = 8.1 \times 10^{-8}$ cm, and, therefore, we suggest that the structure of the ion pair involves closest approach between the iron and cobalt complexes on the side of the ammonia ligands. However, even with the smaller value of $a$, the calculated equilibrium constants are smaller than the experimental values. Perhaps, as suggested previously,[6] hydrogen bonding adds stability to the already favorable electrostatic interaction. The orientation assigned to the ion pairs is compatible with the spectroscopic information. The ion pairs $Co(NH_3)_5py^{3+}|Fe(CN)_6^{4-}$ and $Co(NH_3)_5(N\text{-Mebpy})^{4+}|Fe(CN)_6^{4-}$exhibit maxima at $445 \pm 10$ (molar absorbance $160 \pm 15$ $M^{-1}$ $cm^{-1}$) and $470 \pm 15$ nm (molar absorbance $240 \pm 25$ $M^{-1}$ $cm^{-1}$), respectively. Had the iron approached the cobalt complex on the side of the heterocyclic ligand, we would have expected the absorption maxima to be near those of the ligand-$Fe[CN]_6^{4-}$ charge-transfer complexes. No value is available for pyridine, but the $Fe(CN)_6^{4-}|N,N'\text{-Me}_2bpy^{2+}$ charge-transfer complex exhibits an absorption maximum at 530 nm.[14] The large difference between the wavelengths for the maxima of $Co(NH_3)_5(N\text{-Mebpy})^{4+}|Fe(CN)_6^{4-}$ and of $N,N'\text{-Me}_2bpy^{2+}|Fe(CN)_6^{4-}$ as well as the similarity between the former and the ion pair $(Co(NH_3)_5py^{3+}|Fe(CN)_6^{4-}$ leads us to suggest that the orange color of the ion pairs is associated

with a metal (Fe) to metal (Co) charge-transfer band.

Intramolecular electron transfer within the binuclear complexes $(NH_3)_5Co^{III}LFe^{II}$ $(CN)_5$ where

L = (IV), (IV), (V), (V),
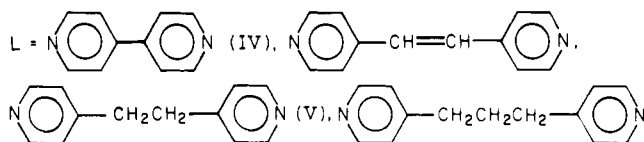
was found previously[5] to proceed with rate constants $2.6 \times 10^{-3}$, $1.4 \times 10^{-3}$, $2.0 \times 10^{-3}$, and $4.8 \times 10^{-3}$ $s^{-1}$, respectively. For the first two ligands, which are rigid and keep the two metal ions away from each other, electron transfer presumably occurs through the ligand. In contrast, for the last two ligands electron transfer is probably "outer sphere", the flexibility of the hydrocarbon chain that connects the two pyridine rings allowing for close approach between the cobalt and iron centers. The similarity in rate between the "inner sphere" and the "outer sphere" rates can be interpreted on the basis of adiabatic electron transfer, the coupling between the metal orbitals, whether through the aromatic ligand or through the ammonia and cyanide coordination shells, being sufficient to result in unit probability of electron transfer once the appropriate nuclear configuration has been achieved. With recognition of the insensitivity of these rates to the detailed pathway of electron transfer, it is noteworthy that the range of rates (from $1.5 \times 10^{-2}$ to $34.6 \times 10^{-2}$ $s^{-1}$) for internal, outer-sphere electron transfer within the ion pairs containing a pyridine bound to cobalt is somewhat wider than the range of rates for intramolecular electron transfer in the binuclear complexes. Presumably, the internal electron-transfer processes within the ion pairs are also adiabatic, whether through the aromatic ligand or the ammonia coordination shell, the variation in rates reflecting differences in the reduction potentials and/or the rate constants for self-exchange in the cobalt(III) complexes. Interestingly, the rate constants for intramolecular molecular electron transfer in the ion pairs $Co(NH_3)_5OS(CH_3)_2^{3+}|Fe(CN)_5L^{3-}$ (L = imidazole, ammonia, pyridine, pyrazine, isonicotinamide, pyrazine-2-carboxamide) after correction for the differences in the thermodynamic driving forces show little or no variation.[15] The implication is that electron transfer is adiabatic and that the rate constants for the self-exchange reaction of the iron complexes do not vary much.

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