# Kinetics and Mechanism of the Reactions between the Oxygen-Bonded Complexes 4-, 3-, and 2-Pyridinecarboxylatopentaamminecobalt(III) and Aquopentacyanoferrate(II)[1]

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**Abstract:** The reactions of 3- and 4-pyridinecarboxylatopentaamminecobalt(III) with aquopentacyanoferrate(II) produce binuclear complexes with the iron attached to the pyridine nitrogen. The rate constants for the formation ($k_f$) and dissociation ($k_d$) of the binuclear complexes have been measured at 25 °C, $\mu = 0.10$ M ($LiClO_4$) and pH 8.0. For the 4- and 3-pyridinecarboxylate complexes the values are: $k_f = (1.5 \pm 0.2) \times 10^3$ and $(1.9 \pm 0.1) \times 10^3$ $M^{-1}$ $s^{-1}$; $k_d = (2.54 \pm 0.05) \times 10^{-3}$ and $(1.73 \pm 0.01) \times 10^{-3}$ $s^{-1}$. The metal to ligand charge-transfer band characteristic of the $Fe(CN)_5{}^{3-}$-nitrogen heterocyclic complex is shifted to longer wavelength when the $Co(NH_3)_5{}^{3+}$ moiety is attached to the carboxylate in the 4 position, but to shorter wavelength when the carboxylate is in the 3 position. Because of steric problems, no binuclear complex is produced when 2-pyridinecarboxylatopentaamminecobalt(III) is added to $Fe(CN)_5OH_2{}^{3-}$. The binuclear complex $(NH_3)_5CoO_2C$(4-py*N*)$Fe(CN)_5{}^{-}$ undergoes intramolecular electron transfer with a rate constant $(1.75 \pm 0.31) \times 10^{-4}$ $s^{-1}$. For the corresponding 3-carboxylate isomer, intramolecular electron transfer is not detected, and the upper limit for the rate constant is $3 \times 10^{-5}$ $s^{-1}$.

It is widely recognized[2] that inner sphere oxidation reduction reactions proceed by a sequence of elementary steps, namely, formation of a precursor binuclear complex, intramolecular electron transfer within the binuclear unit, and dissociation of the successor complex. For most redox systems investigated so far, the first step is an unfavorable, extremely rapid equilibrium ($Q$), and electron transfer is rate-determining ($k_{et}$). Under these circumstances, the measured second-order rate constants are composite quantities ($Qk_{et}$). It is important to obtain rates for each of the elementary steps, and although a great deal of effort has been devoted toward attaining this goal, only in a few cases has success been achieved.[3,4] In this context, mention must be made of an ingenious approach, based on the "artificial" production of precursor complexes, to the successful measurement of intramolecular electron transfer rates.[5]

We previously reported[6] the direct detection and characterization of the precursor complex formed by the reaction between 4,4′-bipyridinepentaamminecobalt(III) and aquopentacyanoferrate(II), as well as the rate constant for intramolecular electron transfer from Fe(II) to Co(III), mediated by the 4,4′-bipyridine bridging ligand. The success in measuring two of the elementary steps in that system was associated with the lability[7] of the water in $Fe(CN)_5OH_2{}^{3-}$ and the high affinity[8] of the $Fe(CN)_5{}^{3-}$ moiety for unsaturated nitrogen heterocycles. In view of the importance of measuring (and trying to understand) rates of intramolecular electron transfer, we are beginning a systematic investigation of the $Fe(CN)_5OH_2{}^{3-}$ reduction of cobalt(III) complexes of the pentaammine class with the sixth ligand being one that contains an exposed nitrogen in an unsaturated heterocyclic ring. In the present paper we report the results obtained with the oxygen-bonded 4-, 3-, and 2-pyridinecarboxylatocobalt(III) complexes.

## Experimental Section

**Materials.** Picolinic acid (2-pyridinecarboxylic acid), nicotinic acid (3-pyridinecarboxylic acid), isonicotinic acid (4-pyridinecarboxylic acid), and pyrazine were Aldrich analyzed reagents and were used as received. Pyridine was the A.C.S. certified Fisher Scientific Company product. All other chemicals were reagent grade. Distilled water was passed through a Barnstead ion-exchange demineralizer and then was distilled in a Corning Model AG-lb apparatus. Lithium perchlorate was made by reaction of lithium carbonate with perchloric acid and purified by recrystallization.

**Preparation of Complexes.** Aquopentaamminecobalt(III) perchlorate was prepared by reaction of carbonatopentaamminecobalt(III) nitrate[9] with excess perchloric acid, and recrystallization from water-perchloric acid mixtures.

The three isomeric pyridinecarboxylatopentaamminecobalt(III) perchlorates were prepared by a slight modification of the literature[10] procedure. Following the formation of the desired complex in solution by reaction of $[Co(NH_3)_5OH_2](ClO_4)_3$ with the appropriate ligand, the product solution was allowed to cool to room temperature and the resulting solid was filtered out. In the case of the 3- and 4-pyridinecarboxylate reactions, the solid was unreacted ligand. The solid was washed with a minimum amount of water, and the washings were combined with the filtrate containing the cobalt(III) complex. In the case of the 2-pyridinecarboxylate reaction, the solid was mostly the desired complex, and it was dissolved in water (30 ml/g of $[Co(NH_3)_5OH_2](ClO_4)_3$). At this point, the precipitation of the desired salts and recrystallizations were carried out as described.[10]

Anal. Calcd for $[Co(NH_3)_5C_6H_5NO_2](ClO_4)_3$: C, 12.74; H, 3.56; N, 14.86; $ClO_4$, 52.75. Found: (for $C_6H_5NO_2$ = 4-pyridinecarboxylic acid) C, 12.70, 12.71; H, 3.44, 3.58; N, 14.70, 14.85; $ClO_4$, 52.83. Found: (for $C_6H_5NO_2$ = 3-pyridinecarboxylic acid) C, 12.87, 12.77; H, 3.48, 3.55; N, 14.56, 14.61; $ClO_4$, 52.38. Found: (for $C_6H_5NO_2$ = 2-pyridinecarboxylic acid) C, 12.27, 12.10; H, 3.71, 3.79; N, 14.74, 14.95; $ClO_4$, 52.20.

Sodium pentacyanoammineferrate(II) trihydrate was prepared by the literature method.[11] The product was purified by dissolution in the minimum amount of 28% ammonia at room temperature, followed by addition of 90% ethanol until a permanent turbidity was observed. Upon cooling to 0 °C, fine, bright yellow needles crystallized. The crystals were filtered out, washed with ethanol and ether, and then kept in a desiccator over drierite for 24 h. The crystals were then stored in a tightly stoppered vessel at −10 °C.

**Analytical Methods.** Perchlorate analyses were carried out gravimetrically using tetraphenylarsonium chloride as the precipitating agent.[12] pH measurements were carried out with an Orion Model 801 pH meter. Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories, Inc.

**Kinetic Measurements.** Rates of formation of the binuclear complexes $(NH_3)_5CoLFe(CN)_5{}^{-}$ (L = 3- or 4-pyridinecarboxylate) were measured spectrophotometrically in a Durrum Model D-110 stopped flow apparatus. Solutions of $Fe(CN)_5OH_2{}^{3-}$ were obtained by aquation (absence of light) of $Fe(CN)_5NH_3{}^{3-}$ at 10 °C,[13] and then, after dilution to about $10^{-5}$ M, they were kept in the thermostated (25 °C) compartment of the stopped flow apparatus for no more than 15 min prior to the measurements.[7] Absorbance vs. time data were collected by means of an 1800 IBM computer, and pseudo-first-order rate constants were obtained from the slopes of the computer drawn ln $(A_t - A_\infty)$ vs. time plots.

Rates of dissociation of the binuclear complexes $(NH_3)_5CoLFe(CN)_5^-$ and of $Fe(CN)_5L^{4-}$ (L = 3- or 4-pyridinecarboxylate) were measured spectrophotometrically using a Cary 118 or a Cary 17 recording spectrophotometer equipped with a thermostated cell compartment and a modified thermostated cell holder. The cell holder ends were sealed with Suprasil windows (Amersil Inc., Hillside, N.J.), and the holder was filled with water. Solutions of the desired Fe(II) complexes were prepared by allowing $Fe(CN)_5OH_2^{3-}$ to react with the appropriate ligand, and then an excess of pyridine or pyrazine was added in the presence of ethylenediaminetetraacetate and ascorbic acid.[6] The first absorbance reading was taken 1 min after the addition of the pyridine or pyrazine. For $Fe(CN)_5L^{4-}$ and for $(NH_3)_5CoLFe(CN)_5^-$ with L = 3-pyridinecarboxylate, plots of ln $(A_t - A_\infty)$ vs. time were linear, and therefore first-order rate constants $k$ were obtained from a nonlinear least-squares fitting of $A_t$ to the equation $A_t = A_\infty + (A_0 - A_\infty)\exp(-kt)$, where $A_t$, $A_0$, and $A_\infty$ are the absorbances at time $t$, 0, and $\infty$, respectively. $A_\infty$ and $k$ were taken as adjustable parameters. For $(NH_3)_5CoLFe(CN)_5^-$ with L = 4-pyridinecarboxylate, plots of ln $(A_t - A_\infty)$ vs. time suggested the presence of two exponentials, and therefore rate constants $(k_d + k_{et})$ and $k_{-L}$ were obtained by nonlinear least-squares fitting of $A_t$ to the equation $A_t = A_\infty + f\exp[-(k_d + k_{et})] + g\exp(-k_{-L}t)$, where $f$, $g$, $k_d + k_{et}$, and $k_{-L}$ (defined below) were taken as adjustable parameters.

## Results

**Absorption Spectra.** Solutions of $Co(NH_3)_5L^{2+}$ with L = 2-, 3-, or 4-pyridinecarboxylate exhibit the characteristic absorption maximum of carboxylatopentaamminecobalt(III) complexes at 502 nm with extinction coefficients 74.4, 79.3, and 74.9 $M^{-1}$ $cm^{-1}$, respectively. On mixing $\sim 2 \times 10^{-4}$ M solutions of $Co(NH_3)_5L^{2+}$ (L = 3- or 4-pyridinecarboxylate) with $\sim 1 \times 10^{-5}$ M $Fe(CN)_5OH_2^{3-}$, the characteristic[8] metal to ligand charge transfer bands of complexes of pentacyanoferrate(II) with nitrogen heterocycles are produced, and it is inferred that the interaction of the cobalt(III) and iron(II) complexes produces a precursor binuclear complex.

$$Co^{III}(NH_3)_5L^{2+} + Fe^{II}(CN)_5OH_2^{3-} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} (NH_3)_5Co^{III}LFe^{II}(CN)_5^- + H_2O \quad (1)$$

In the case of the 2-pyridinecarboxylatopentaamminecobalt(III) complex, no charge transfer band can be detected on addition of $Fe(CN)_5OH_2^{3-}$ (the resulting spectrum was the sum of the components) and it is concluded that for this compound the binuclear complex is not formed. Similarly, addition of $\sim 10^{-3}$ M 3- or 4-pyridinecarboxylate to $Fe(CN)_5OH_2^{3-}$ results in the formation of the corresponding complexes (eq 2), but no complex formation is detected in the case of the 2-pyridinecarboxylate ligand. The wavelengths and molar absorbances for the pertinent complexes are presented in Table I. It is seen that addition of electron withdrawing substituents in the 3- or 4-position of the pyridine ring in $Fe(CN)_5py^{3-}$ results in a bathochromic shift. Moreover, addition of $CH_3^+$ or $Co(NH_3)_5^{3+}$ to an oxygen in $Fe(CN)_5(N\text{py-}4)CO_2^{4-}$ and of $CH_3^+$ to $Fe(CN)_5(N\text{py-}3)CO_2^{4-}$ also results in a bathochromic shift, but a hypsochromic shift is observed for addition of $Co(NH_3)_5^{3+}$ to an oxygen in $Fe(CN)_5(N\text{py-}3)CO_2^{4-}$.

$$Fe(CN)_5OH_2^{3-} + L^- \underset{k_{-L}}{\overset{k_L}{\rightleftharpoons}} Fe(CN)_5L^{4-} + H_2O \quad (2)$$

**Kinetics of Formation of Binuclear Complexes.** In our hands, measurements of rates of substitution of water in $Fe(CN)_5OH_2^{3-}$ by various ligands presented serious difficulties.[14] In the presence of oxygen, absorbance changes for successive runs (perhaps at 1-min intervals) rapidly decreased in magnitude, and within a few minutes the traces obtained were unusable. However, removing the oxygen[15] either by flushing all solutions with argon or by addition of ascorbic acid resulted in fairly reproducible successive traces. At pH 8, the absorbance changes for the reactions with $Co(NH_3)_5L^{2+}$ (L = 3- or 4-pyridinecarboxylate) and with 4,4′-bipyridine showed nonexponential behavior. Under the conditions used, a fast and slow absorbance change were detected, differing in rate by as much as a factor of two. The fast absorbance change was dependent on the ligand concentration, whereas the slow change appeared to be independent of ligand concentration. Since aquopentacyanoferrate(II) solutions are known to undergo dimerization,[16] it appears reasonable to assign the fast and slow rates to reaction of the monomer with ligand and to dissociation of the dimer, respectively. Based on the above considerations, pseudo-first-order rate constants $k_{obsd}$ were obtained from initial slopes of ln $(A_\infty - A_t)$ vs. time plots, and second-order rate constants $k_f$ (see eq 1) were calculated as $k_{obsd}/[Co(III)]$. The reactions of the 4- and 3-pyridinecarboxylate complexes were followed at 434 and 370 nm, respectively, with [Co(III)] = $(0.2\text{–}1.0) \times 10^{-3}$ M, [Fe(II)] = $1.0 \times 10^{-5}$ M, $\mu$ = 0.10 M (adjusted with $LiClO_4$), $[Na_2H_2EDTA] = 2.0 \times 10^{-4}$ M, [ascorbic acid] = $2.0 \times 10^{-4}$ M, and pH 8.0 (Tris buffer). The values of $k_f$ at 25 °C are $(1.5 \pm 0.2) \times 10^3$ and $(1.9 \pm 0.1) \times 10^3$ $M^{-1}$ $s^{-1}$ for the 4- and 3-pyridinecarboxylate complexes, respectively.

Table I. Electronic Spectra of $Fe(CN)_5L^{n-}$ Complexes[a]

| Complex | λ, nm[b] | $A$, $M^{-1}$ $cm^{-1}$ [c] |
|---|---|---|
| $Fe(CN)_5OH_2^{3-}$ | 440 | $7.0 \times 10^2$ [d] |
| $Fe(CN)_5NH_3^{3-}$ | 405 | $4.5 \times 10^2$ [d,e] |
| $Fe(CN)_5py^{3-}$ | 362 | $3.7 \times 10^3$ [f] |
| $Fe(CN)_5(N\text{py-}4)CO_2^{4-}$ | 413 | $4.4 \times 10^3$ |
| $Fe(CN)_5(N\text{py-}4)CONH_2^{3-}$ | 437 | $4.6 \times 10^3$ |
| $Fe(CN)_5(N\text{py-}4)COOCH_3^{3-}$ | 465 | $5.0 \times 10^3$ |
| $Fe(CN)_5(N\text{py-}4)COOCo(NH_3)_5^-$ | 434 | $4.5 \times 10^3$ |
| $Fe(CN)_5(N\text{py-}3)CO_2^{4-}$ | 382 | $3.2 \times 10^3$ |
| $Fe(CN)_5(N\text{py-}3)CONH_2^{3-}$ | 392 | $3.3 \times 10^3$ |
| $Fe(CN)_5(N\text{py-}3)COOCH_3^{3-}$ | 388 | $3.0 \times 10^3$ |
| $Fe(CN)_5(N\text{py-}3)COOCo(NH_3)_5^-$ | 370 | $3.1 \times 10^3$ |

[a] Measured in aqueous solution with [Fe] = $2 \times 10^{-5}$ M and [L]/[Fe] ≥ 10. [b] Wavelength for absorption maximum. [c] Molar absorbance at maximum. [d] Reference 15. [e] E. J. Baran and A. Muller, *Z. Anorg. Allg. Chem.*, 368, 144 (1969). [f] Reference 8.

**Kinetics of Dissociation and of Internal Electron Transfer of Binuclear Complexes.** Once the binuclear complexes $(NH_3)_5Co^{III}LFe^{II}(CN)_5^-$ are formed, they can undergo two reactions: dissociation into mononuclear reactants (reverse of eq 1) or internal electron transfer (eq 3).

$$(NH_3)_5Co^{III}LFe^{II}(CN)_5^- \xrightarrow{k_{et}} (NH_3)_5Co^{II}LFe^{III}(CN)_5^- \quad (3)$$

In the presence of excess cobalt(III) complex, dissociation is unproductive since it leads back to the precursor complex. Internal electron transfer followed by rapid dissociation of the successor complex produces $Fe(CN)_5L^{3-}$. We had found previously[6] that the Fe(III) product reacts rapidly with the precursor complex, a reaction which results in serious kinetic complications. These were circumvented by addition of ascorbic acid[6] which reacts rapidly with $Fe(CN)_5L^{3-}$ to produce $Fe(CN)_5L^{4-}$, but a new complication is now introduced. Aquation of $Fe(CN)_5L^{4-}$ by the reverse of eq 2 produces $Fe(CN)_5OH_2^{3-}$ which reacts with the excess Co(III) complex to produce more binuclear precursor.[17] This complication was circumvented[6] by addition

Table II. Kinetics of Dissociation and of Internal Electron Transfer of $(NH_3)_5CoO_2C(4\text{-py}N)Fe(CN)_5^-$ [a]

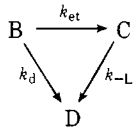
| $10^5\ [Fe(CN)_5OH_2^{3-}]$, [b] M | $10^4\ [(NH_3)_5CoO_2C(4\text{-py}N)^{2+}]$, M | $10^3\ (k_d + k_{et})$, $s^{-1}$ | $10^4\ k_{-L}$, $s^{-1}$ | $10^4\ k_{et}$, $s^{-1}$ | $10^3\ k_d$, $s^{-1}$ |
|---|---|---|---|---|---|
| 1.0 [c] | 1.0 | 2.79 | 3.16 | — | — |
| 1.0 | 1.0 | 2.81 | 3.38 | 2.08 | 2.60 |
| 1.0 [d] | 1.0 | 2.76 | 3.16 | 2.33 | 2.53 |
| 4.0 | 1.0 | 2.72 | 2.91 | 1.76 | 2.54 |
| 1.0 | 2.0 | 2.78 | 3.55 | 1.70 | 2.61 |
| 1.0 [e] | 1.0 | 2.73 | 3.55 | 1.73 | 2.56 |
| 2.0 | 2.0 | 2.59 | 2.96 | 1.44 | 2.45 |
| 2.0 | 2.0 | 2.71 | 2.83 | 1.42 | 2.57 |
| 2.0 | 2.0 | 2.67 | 3.13 | 1.37 | 2.53 |
| 4.0 | 4.0 | 2.65 | 3.48 | 1.73 | 2.48 |
| 4.0 | 4.0 | 2.68 | 3.56 | 1.95 | 2.48 |
| 1.0 [f,g] | — | — | 3.63 | — | — |
| 1.0 [c,f,h] | — | — | 3.79 | — | — |
| 1.0 [f] | — | — | 3.77 | — | — |
| 1.0 [f,i] | — | — | 3.78 | — | — |

[a] At 25 °C, pH 8.0 (Tris buffer), $[Na_2H_2EDTA] = 1.67 \times 10^{-4}$ M, [pyridine] = 0.10 M, [ascorbic acid] = $4.0 \times 10^{-4}$ M, $\mu = 0.10$ M (adjusted with $LiClO_4$), 434 nm. [b] Based on the concentration of $Fe(CN)_5NH_3^{3-}$. This is also the concentration of $(NH_3)_5CoOCO(4\text{-py}N)Fe(CN)_5^-$. [c] [ascorbic acid] = $2.0 \times 10^{-4}$ M. [d] [ascorbic acid] = $1.0 \times 10^{-3}$ M. [e] [pyridine] = 0.010 M. [f] This is the concentration of $Fe(CN)_5(N\text{py-4})CO_2^{4-}$; $[(N\text{py-4})CO_2^-] = 1.0 \times 10^{-4}$ M. [g] No ascorbic acid. [h] Measurements at 413 nm. [i] Measurements at 440 nm.

of pyridine which reacts rapidly[7] with $Fe(CN)_5OH_2^{3-}$. The mechanism represented by the reverse of eq 1, eq 3, the reverse of eq 2 and eq 4

$$Fe(CN)_5OH_2^{3-} + py \rightarrow Fe(CN)_5py^{3-}\ \text{fast} \qquad (4)$$

becomes Van der Borg's scheme,[18] and the absorbance depends on time according to



$B = (NH_3)_5Co^{III}LFe^{II}(CN)_5^-$
$C = Fe^{II}(CN)_5L^{4-}$
$D = Fe^{II}(CN)_5py^{3-}$

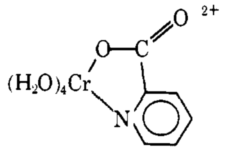
$$A_t = A_\infty + f\exp[-(k_d + k_{et})t] + g\exp(-k_{-L}t)$$

where $g = (A_C - A_D)k_{et}/(k_d + k_{et} - k_{-L})$, $f = (A_0 - A_\infty) - g$. $A_0$ and $A_\infty$ are the initial and final absorbances, respectively, and $A_C$ and $A_D$ are the absorbances of C and D, respectively, at a concentration equal to the initial concentration of B. A nonlinear least-squares treatment of the $A_t$ vs. $t$ data (usually 60-70 points) yielded values of $k_d + k_{et}$, $k_{-L}$, $f$, and $g$. Excellent fits were obtained as seen by the fact that the average deviation between calculated and experimental $A_t$ values was less than 0.001 unit for a total change in $A_t$ of about 0.7. A summary of the kinetic measurements for 4-pyridinecarboxylato complex is presented in Table II. Values of $k_{et}$ were calculated from the values of $g$, $k_d + k_{et}$, and $k_{-L}$ obtained from the least-squares treatment and the experimentally determined values of $A_C$ and $A_D$. We were concerned about the possibility that the $Fe(CN)_4L^{4-}$ product was formed by direct reduction of the binuclear precursor by ascorbic acid. However, this interpretation can be ruled out since (cf. the first three experiments of Table I) the overall rate constant $(k_d + k_{et})$ for the disappearance of the precursor complex is independent of ascorbic acid concentration in the range $2.0 \times 10^{-4}$ to $1.0 \times 10^{-3}$. Strong confirmation for the proposed scheme comes from the excellent[19] agreement between the values of $k_{-L}$ obtained by this procedure (average $(3.25 \pm 0.29) \times 10^{-4}\ s^{-1}$) with the values obtained independently by a direct measurement of the aquation of $Fe(CN)_5L^{4-}$ (last four entries of Table II, average $(3.74 \pm 0.08) \times 10^{-4}\ s^{-1}$). The average values of $k_d$ and $k_{et}$ are $(2.54 \pm 0.05) \times 10^{-3}$ and $(1.75 \pm 0.31) \times 10^{-4}\ s^{-1}$, respectively. The equilibrium constant for reaction 1 calculated from $k_f/k_d$ is $(5.9 \pm 0.6) \times 10^5\ M^{-1}$ at 25 °C.

The results for the 3-pyridinecarboxylate complex are summarized in Table III. Pyrazine was used to trap the $Fe(CN)_5OH_2^{3-}$ produced because absorbance changes using pyridine were too small. In this system, the $A_t$ vs. $t$ data points conform to a single exponential and only values of $k_d$ could be obtained. Assuming that less than 2% of the binuclear complex reacts via intramolecular electron transfer, we estimate that $k_{et} < 3 \times 10^{-5}\ s^{-1}$. The equilibrium constant for reaction 1 is $k_f/k_d = (1.1 \pm 0.1) \times 10^6\ M^{-1}$.

## Discussion

The most significant result of the present investigation relates to the dramatic difference in the behavior of the three isomeric pyridinecarboxylatopentaamminecobalt(III) complexes toward aquopentacyanoferrate(II). The 4-pyridinecarboxylate complex reacts with the iron(II) to form a precursor binuclear complex which undergoes internal electron transfer. The 3-pyridinecarboxylate complex forms a binuclear complex, but electron transfer is not detectable. Finally, the 2-pyridinecarboxylate complex does not form a binuclear complex. These findings contrast, in part, with those for the corresponding reactions with chromium(II),[20,21] but conform nicely to the trends in intramolecular electron transfer rates[5] for the Co(III)-Ru(II) binuclear complexes bridged by the pyridine carboxylate ligands. The results for the three reducing agents are summarized in Table IV. With Cr(II) as the reductant, the 2-pyridinecarboxylate complex is the most reactive, whereas with Fe(II) and Ru(II) inner sphere reduction via attack at N has not been observed. Since the chromium(III) product is the chelated complex



and the redox reaction is quite rapid, it was inferred[21] that chelation obtains in the transition state. Using this conclusion, it is easy to account for the difference in behavior between Cr(II) on one hand and Ru(II) and Fe(II) on the other. Two labile cis positions are available in the coordination sphere of Cr(II), and, therefore, the precursor complex with Cr(II) chelated to the bridging ligand is accessible. In contrast, only one labile position is available in the coordination sphere of Fe(II) and the two labile positions in the Ru(II) bear a trans relation. Molecular models show a

Table III. Kinetics of Dissociation of $(NH_3)_5CoO_2C(3\text{-py}N)Fe(CN)_5^{-a}$

| $10^5$ [$Fe(CN)_5$-$OH_2^{3-}$],$^b$ M | $10^4$ [$(NH_3)_5$-$CoO_2C$(3-py-$N)^{2+}$], M | $10^3 k_d$, $s^{-1}$ | $10^4 k_{-L}$, $s^{-1}$ |
|---|---|---|---|
| 1.0 | 1.0 | 1.72 | |
| 4.0 | 1.0 | 1.73 | |
| 1.0 | 2.0 | 1.74 | |
| 1.0 | 1.0$^c$ | | 8.32 |
| 1.0 | 1.0$^c$ | | 8.37 |
| 1.0 | 1.0$^c$ | | 8.44 |

[a] At 25 °C, pH 8.0 (Tris buffer), [$Na_2H_2EDTA$] = $1.67 \times 10^{-4}$ M, [ascorbic acid] = $2.0 \times 10^{-4}$ M, [pyrazine] = 0.010 M, $\mu = 0.10$ M (adjusted with $LiClO_4$), 370 nm. [b] Based on the concentration of $Fe(CN)_5NH_3^{3-}$. This is also the concentration of $(NH_3)_5CoO_2C(3\text{-py}N)Fe(CN)_5^{-3}$ and $Fe(CN)_5(N\text{py-3})CO_2^{4-}$. [c] This is the concentration of $(N\text{py-3})CO_2^-$.

Table IV. Rate Constants at 25 °C for Reduction of 2-, 3-, and 4-Pyridinecarboxylatopentaamminecobalt(III) by Iron(II), Chromium(II), and Ruthenium(II)

| | Reductant | | |
|---|---|---|---|
| Oxidant | $Fe(CN)_5^{3-a}$ | $Cr(H_2O)_6^{2+b}$ | $Ru(NH_3)_4OH_2^{2+a}$ |
| $Co(NH_3)_5O_2C$-(4-py$N)^{2+}$ | $1.75 \times 10^{-4}$ | $1.1 + 0.01/[H^+]$ | $\sim 10^2$ |
| $Co(NH_3)_5O_2C$-(3-py$N)^{2+}$ | $<3 \times 10^{-5}$ | 0.10 | $\sim 2 \times 10^{-3}$ |
| $Co(NH_3)_5O_2C$-(2-py$N)^{2+}$ | — | $36/[H^+]$ | |

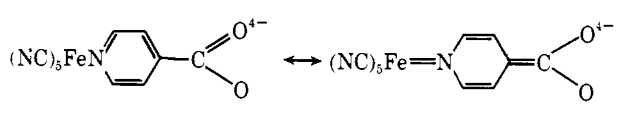
[a] First-order rate constant for intramolecular electron transfer. The metal ion reductant is bound to the ring nitrogen. The water in the Ru(II) is trans to the bridging ligand. [b] Rate law is based on the protonated pyridine complex being the dominant species in solution. Units of acid independent term are $M^{-1}$ $s^{-1}$. Units of inverse acid term are $s^{-1}$.

strong steric hindrance by the 2-carboxylate group to metal binding at the pyridine nitrogen. Moreover, we found no detectable complex formation between $Fe(CN)_5OH_2^{3-}$ and 2-pyridinecarboxylate, even at 0.01 M ligand concentration. Consequently, the formation of a binuclear complex between $Co(NH_3)_5O_2C(2\text{-py}N)^{2+}$ and $Fe(CN)_5OH_2^{3-}$ or *trans*-$Ru(NH_3)_4(OH_2)_2^{2+}$ with the Fe or Ru attached at the pyridine N is sterically precluded for these metal complexes with only one coordination position available.

The trends for the reactions of the 3- and 4-pyridinecarboxylatocobalt(III) complex isomers with the three reductants parallel each other quite nicely. Thus, the 4-pyridinecarboxylate complex reacts $10^5$ times faster than the corresponding 3-isomer when Ru(II) is the reductant.[5,20] With Fe(II) and Cr(II)[21,22] as the reductants, the inner sphere path for reduction via the N in the 3-pyridinecarboxylate isomer is not detected, and only a lower limit of about 10 can be placed on the reactivity ratio for the 4- to the 3-isomer. For all the reductants, the higher reactivity of the 4-isomer is probably associated with conjugation effects, the transmission of electronic interactions in aromatic rings being more efficient across para positions than across meta positions.

In this context, it is noteworthy that the shifts in the energies of the charge transfer bands of substituted pyridinepentacyanoferrate(II) complexes are much larger when the substituents are located in the 4 than the 3 position.[8] Thus, the 362-nm band of the pyridine complex shifts to 413 nm when the electron withdrawing carboxylate substituent is in the 4 position, and to 382 nm for substitution in the 3 position. Moreover, the replacement of one of the oxygen atoms in the carboxylate by an electron withdrawing group results in additional, substantial bathochromic shifts when the replacement is made in the 4 position (maxima at 413, 434, 437, and 465 nm for $CO_2^-$, $CO_2Co(NH_3)_5^{2+}$, $CONH_2$, and $CO_2CH_3$, respectively), whereas very modest shifts are observed when one of the oxygen atoms in the 3-carboxylate complex is replaced (maxima at 382, 388, 392, and 370 nm for $CO_2^-$, $CO_2CH_3$, $CONH_2$, and $CO_2$-$Co(NH_3)_5^{2+}$, respectively). With at least one exception, these trends can be understood, at least qualitatively, on the basis of the increased electronegativity of the ligand caused by addition of electron withdrawing substituents, and the accompanying decrease in the energy of the metal to ligand charge transfer band. The exception noted above corresponds to the *shorter* wavelength for $Fe(CN)_5(N\text{py-3})CO_2Co(NH_3)_5^-$ as compared to $Fe(CN)_5CO_2^{4-}$ (370 vs. 382 nm), and a possible rationalization of this unexpected result is presented.

Based on simple electrostatic charge arguments, addition of a positively charged substituent to an oxygen in 3- or 4-pyridinecarboxylatopentacyanoferrate(II) would be expected to lower the energies of all the ligand orbitals, the effect being more important the higher the charge of the substituent. In the absence of any other effect, the energy of the metal to ligand charge transfer band would be expected to decrease, and a bathochromic shift would obtain. At least two observations, however, demand that additional factors come into play: the larger shift for $CH_3^+$ as compared to $Co(NH_3)_5^{3+}$ when substitution is effected in the 4-carboxylate group (maxima at 465 and 437 nm, respectively), and the hypsochromic shift caused by addition of $Co(NH_3)_5^{3+}$ to the 3-carboxylate group. We suggest that the additional factors correspond to the influence of the substituent on the $\sigma$ basicity of the pyridine N and on the extent of back-bonding from one of the $t_{2g}$ orbitals of the metal to the appropriate ligand $\pi^*$ orbital. The addition of a positive group decreases the $\sigma$ basicity of the pyridine N and, through the synergistic bonding mechanism,[23] the back-bonding is also decreased. This effect, which opposes that of the increased electronegativity of the ligand, would be accompanied by a shift toward shorter wavelengths. However, counteracting this effect, in the case of the 4-carboxylate isomer, is the stabilization of the back-bonding by an increase in the contribution of the canonical form II upon addition of a positive substituent to an oxygen atom. The interplay of these opposing effects, the results indicate, is a shift to longer wavelengths for addition of $Co(NH_3)_5^{3+}$ and $CH_3^+$. In the case of the 3-carboxylate derivative, the resonance form with the iron-nitrogen double bond does not place the negative charge on the oxygen atoms and, consequently, addition of a positive group does not improve the back-bonding. Under these circumstances, a close balance between the increased electronegativity of the ligand and the decreased $\sigma$ basicity of the pyridine N (and the concomitant decrease in $\pi$ bonding) results in a small blue shift for addition of $Co(NH_3)_5^{3+}$ and a small red shift for addition of $CH_3^+$. Admittedly, this rationalization comes after the fact, but it is noteworthy that these trends are very closely reproduced in the pentaammineruthenium(II) complexes with substituted pyridines. Thus, the wavelengths for maximum absorption of $Ru(NH_3)_5(N\text{py-4})X^{2+}$ with X = H, $CONH_2$, and $CO_2CH_3$ are at 407, 478, and 495 nm, respectively.[24,25] For $Ru(NH_3)_5(N\text{py-3})X$ with X = $CONH_2$ and $CO_2CH_3$, the maxima are at 427 and 417 nm, respectively. Addition



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of $Cr(H_2O)_5^{3+}$ to the O of $CONH_2$ when in the 4-position results in a strong bathochromic shift to 523 nm,[25] but binding of the O in $Ru(NH_3)_5(N\text{py-3})CONH_2^{2+}$ by $Cr(H_2O)_5^{3+}$ results in a small hypsochromic shift to 420 nm.[24] Again, these trends can be rationalized by the interplay of the increased electronegativity of the ligand, the decreased $\sigma$ basicity of the N, and the increase in back-bonding caused by the addition of positive substituents. We have another example of a hypsochromic shift in the addition of $Co(NH_3)_5^{3+}$ to $Fe(CN)_5(N\text{py-3})CH{=}CHCO_2^{4-}$. The maximum shifts from 371 to 360 nm.

Finally, it is noteworthy that the rate constant for intramolecular electron transfer from $Fe(CN)_5^{3-}$ to $Co(NH_3)_5^{3+}$ mediated by 4-pyridinecarboxylate ($1.75 \times 10^{-4}$ $s^{-1}$) is of the same order of magnitude as that measured[6] for the corresponding reaction mediated by 4,4′-bipyridine ($2.6 \times 10^{-3}$ $s^{-1}$). It was suggested previously[6] that a resonance exchange mechanism is operative, and the low rates were ascribed to the mismatching of the symmetries of donor and carrier orbitals ($\pi$) on one hand and acceptor orbital ($\sigma$) on the other. This suggestion is still reasonable, but leaves unanswered the question as to why the corresponding intramolecular Co(III)-Ru(II) electron transfer mediated by 4-pyridinecarboxylate is so much faster ($\sim 10^2$ $s^{-1}$). Arguments based on orbital symmetry, overall free energy of reaction, or inner coordination shell rearrangements would lead us to predict similar rates for reduction of Co(III) by $Ru(NH_3)_5^{2+}$ or $Fe(CN)_5^{3-}$.

## References and Notes

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(14) Previous workers[7] reported difficulties with "$Fe(CN)_5OH_2^{3-}$" prepared by reaction of $Fe(CN)_5NO^{2-}$ with hydroxylamine, but were able to circumvent these difficulties by preparing $Fe(CN)_5OH_2^{3-}$ in situ through aquation of dilute ($\leqslant 10^{-5}$ M) solutions of $Fe(CN)_5NH_3^{3-}$. We used the precautions detailed by the previous workers,[7] but were unsuccessful in eliminating the problems.

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(20) In fact, the rates for the 4- and 3-pyridinecarboxylate complexes pertain to reduction by *trans*-$Ru(NH_3)_4SO_4$ and *trans*-$Ru(NH_3)_4OH_2^{2+}$, respectively. Isied and Taube[5] argue that replacement of sulfate by water is unlikely to result in a rate change larger than a factor of 10.

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