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The Outer-Sphere Reductions of Pyridinepentaamminecobalt(III) and Pyridinepentaammineruthenium(III) by Hexacyanoferrate(II)[1a,b]

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Abstract: The rate law for the $Co(NH_3)_5py^{3+}$–$Fe(CN)_6^{4-}$ reaction is $k_{et}^{Co}Q_p^{Co}[Fe(CN)_6^{4-}][Co(NH_3)_5py^{3+}]/(1 + Q_p^{Co}\cdot[Fe(CN)_6^{4-}])$. At 25 °C and ionic strength 0.10 M, $k_{et}^{Co} = (1.5 \pm 0.5) \times 10^{-2}\ s^{-1}$ and $Q_p^{Co} = (2.4 \pm 0.4) \times 10^3\ M^{-1}$. Q_p^{Co} is the equilibrium quotient for the formation of the outer-sphere complex $Co(NH_3)_5py^{3+}\cdot Fe(CN)_6^{4-}$ and k_{et}^{Co} is the rate constant for electron transfer within the ion pair. The equilibrium and rate constants (25 °C, ionic strength 0.10 M) for the $Ru(NH_3)_5py^{3+}$–$Fe(CN)_6^{4-}$ reaction are $(1.0 \pm 0.1) \times 10^{-2}$ and $(4.3 \pm 1.0) \times 10^6\ M^{-1}\ s^{-1}$, respectively. The rate constant at 25 °C and ionic strength 0.10 M for the $Ru(NH_3)_5py^{3+}$–$Ru(NH_3)_6^{2+}$ reaction is $(7.2 \pm 0.4) \times 10^5\ M^{-1}\ s^{-1}$. The mechanisms of these reactions are discussed in the context of Marcus' equation, electrostatic effects, and orbital symmetry considerations.

Electron transfer reactions between transition metal coordination compounds can proceed via inner-sphere or outer-sphere mechanisms. It is generally accepted that a sequence of three elementary steps brings about the overall reaction.[2] For outer-sphere reactions, the steps are formation of a reactant ion pair or outer-sphere precursor complex (eq 1), electron transfer (eq 2), and dissociation of the product ion pair or outer-sphere successor complex (eq 3).

$$\text{ox} + \text{red} \rightleftarrows \text{ox}\|\text{red} \qquad Q_p \qquad (1)$$

$$\text{ox}\|\text{red} \rightleftarrows \text{ox}^-\|\text{red}^+ \qquad k_{et} \qquad (2)$$

$$\text{ox}^-\|\text{red}^+ \rightleftarrows \text{ox}^- + \text{red}^+ \qquad 1/Q_s \qquad (3)$$

The first and third steps are diffusion-controlled reactions, and reaction 2 is often rate determining. If one of the reactants is in excess (say red) and the reaction proceeds to completion, this mechanism leads to the rate law given by eq 4.

$$\text{rate} = \frac{Q_p k_{et}[\text{red}][\text{ox}]}{1 + Q_p[\text{red}]} \qquad (4)$$

For most systems, $Q_p[\text{red}] \ll 1$ because the reactants have the same charge (and therefore Q_p is very small) and/or because the reactions are very fast (and therefore to obtain measurable rates, [red] is very small). Under these circumstances, measured second-order rate constants are equal to $Q_p k_{et}$.

It is important to obtain quantitative information about the individual elementary steps, and we previously[3] reported the results of our studies of the $Co(NH_3)_5OH_2^{3+}$–$Fe(CN)_6^{4-}$ reaction. The presence of a precursor outer-sphere complex was detected kinetically, and the first-order rate constant for intramolecular electron transfer within the ion pair was calculated. The success in obtaining values of Q_p and k_{et} for this system is associated, in part, with the choice of reactants of high and opposite charge. This results in the formation of substantial amounts of the precursor complex even at relatively low reactant concentrations.

On the basis of these results, a systematic study of outer-sphere electron transfer reactions between ions of high and opposite charge was undertaken. In the present paper we report our results on the reduction of the low-spin d^5 and d^6 ions $Ru(NH_3)_5py^{3+}$ and $Co(NH_3)_5py^{3+}$ by $Fe(CN)_6^{4-}$. For comparative purposes, we have also studied the reduction of $Ru(NH_3)_5py^{3+}$ by $Ru(NH_3)_6^{2+}$.

Experimental Section

Materials. House distilled water was passed through a Barnstead ion exchange demineralizer, and then distilled in a modified Corning AG-1b distilling apparatus. Sodium perchlorate, obtained by neutralization of sodium carbonate with perchloric acid, was recrystallized three times. Analytical grade sodium hexacyanoferrate(II) decahydrate was recrystallized twice. Argon was purified by passing it through BTS catalyst. All other chemicals were reagent grade and used as received.

Preparation of Complexes. Pyridinepentaamminecobalt(III) perchlorate prepared by the method of Nordmeyer and Taube[4] was found to be contaminated with hexaamminecobalt(III) perchlorate. Therefore, a concentrated aqueous solution of the impure product was treated with half its volume of alcohol, and the precipitate was discarded. Perchloric acid was added to the filtrate and the precipitate of $[Co(NH_3)_5py](ClO_4)_3$ that formed was collected, washed with alcohol and ether, and then dried in air.

Pyridinepentaammineruthenium(III) bromide dihydrate was prepared by bromine oxidation of $Ru(NH_3)_5py^{2+}$.[5] $[Ru(NH_3)_5Cl]Cl_2$[6] (0.30 g) in 20 ml of water was treated with 10-15 g of amalgamated zinc and 3 ml of pyridine. Argon was bubbled through the system for 30 min. The zinc was filtered out, and 7 ml of concentrated hydrobromic acid (48%) was added to the solution. Bromine vapor was added to the solution, and, as the bromine dissolved, the deep orange color of $Ru(NH_3)_5py^{2+}$ changed to the yellow color of $Ru(NH_3)_5py^{3+}$. Sodium bromide (20 g) was added, and upon cooling to 0 °C, the crude $[Ru(NH_3)_5py]Br_3$ precipitated. The solid was recovered and then treated with 12 ml of water. After filtering any insoluble residue, 5 g of sodium bromide was added to the solution. Upon cooling to 0 °C, fine, yellow, needle-like crystals were obtained. The crystals were filtered out, washed with alcohol and ether, and then air-dried. Yield: 0.10 g (19%). Anal. Calcd for $[Ru(NH_3)_5(NC_5H_5)]Br_3{\cdot}2H_2O$: C, 11.10; H, 4.47; N, 15.53. Found: C, 11.03, 11.03; H, 4.59, 4.70; N, 15.59, 15.60.

Hexaammineruthenium(III) chloride, purified according to the method of Meyer and Taube,[7] was the source of $Ru(NH_3)_6^{2+}$, reduction being accomplished by amalgamated zinc under an atmosphere of argon.

Equilibrium Measurements. The equilibrium constant Q for reaction 5 was measured by a spectrophotometric technique.

$$Ru(NH_3)_5py^{3+} + Fe(CN)_6^{4-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Ru(NH_3)_5py^{2+} + Fe(CN)_6^{3-} \tag{5}$$

A solution (25 ml) containing the desired concentrations of $Fe(CN)_6^{4-}$ and KNO_3 was placed in a 10-cm cell. The cell was covered with a rubber septum and placed in the thermostated cell holder of a Cary 17 spectrophotometer, and argon was bubbled through the solution for 30 min. A solution of the desired concentration of $Ru(NH_3)_5py^{3+}$, contained in a serum bottle fitted with a rubber septum, was placed in a bath at the same temperature as the cell. Argon was bubbled through the ruthenium solution for 30 min, 3.5 ml of the latter solution was added to the cell, and, after thorough mixing, the absorbance A at 407 nm was recorded immediately. The equilibrium constant for reaction 5 was calculated from eq 6, where a_0 and b_0 are the initial concentration of the ruthenium(III) and iron(II) complexes, respectively, and x is the equilibrium concentration of the ruthenium(II) or iron(III) complex, obtained from eq 7.

$$Q = \frac{x^2}{(a_0 - x)(b_0 - x)} \tag{6}$$

$$x = \left(\frac{A}{10} - \epsilon_1 a_0 - \epsilon_2 b_0\right) \Big/ (\epsilon_3 + \epsilon_4 - \epsilon_1 - \epsilon_2) \tag{7}$$

The molar absorbances at 407 nm of $Ru(NH_3)_5py^{3+}$, $Fe(CN)_6^{4-}$, $Ru(NH_3)_5py^{2+}$, and $Fe(CN)_6^{3-}$, measured in the present work, are ϵ_1 1.5 × 10^2, ϵ_2 5, ϵ_3 7.2 × 10^3, and ϵ_4 9.7 × 10^2, respectively.

Kinetic Measurements. The reaction of $Co(NH_3)_5py^{3+}$ with $Fe(CN)_6^{4-}$ is slow, and, therefore, the rate was measured spectrophotometrically using a Cary 14 spectrophotometer. A solution containing the desired concentrations of $Fe(CN)_6^{4-}$, sodium perchlorate, and disodium ethylenediaminetetraacetate in oxygen-free water was placed in a 10-cm cell which was then covered with a rubber septum. The cell holder of the spectrophotometer was modified[8] so that it could be filled with water. The cell was placed in the holder and, after temperature equilibration, the solution containing the cobalt(III) complex was added anaerobically (syringe technique). After mixing, the absorbance at 420 nm was recorded as a function of time. Plots of ln $(A_t - A_\infty)$ vs. time were linear for ca. four half-lives, and values of the pseudo-first-order rate constants k_{obsd} were obtained by fitting the measured absorbances A_t to the equation $(A_t - A_\infty) = (A_0 - A_\infty)\exp(-k_{obsd}t)$.

The very rapid $Ru(NH_3)_5py^{3+}$-$Fe(CN)_6^{4-}$ reaction was measured by the temperature-jump technique using a Durrum Model D-150 apparatus. Solutions of the desired concentrations of $Ru(NH_3)_5py^{3+}$ in 0.10 M potassium nitrate and of $Fe(CN)_6^{4-}$ in 0.10 M potassium nitrate were mixed, a 3 kV pulse, truncated after 50 μs, was applied, and the transmittance change at 407 nm was collected using a Biomation 802 transient recorder. The transmittance vs. time curves were displayed in a Tektronix 602 unit, and stored in an IBM 1800 computer.[9] Six replicate measurements were averaged and relaxation times τ were obtained from the plots of log $|(T - T_\infty)|$ vs. time.

The $Ru(NH_3)_5py^{3+}$-$Ru(NH_3)_6^{2+}$ reaction was studied in a Durrum D-110 stopped-flow apparatus. Solutions of the desired concentrations of the ruthenium complexes in 0.10 M potassium nitrate were mixed, and the absorbance change at 407 nm was collected directly in the IBM 1800 computer. Six replicate experiments were carried out with each pair of solutions, and values of k_{obsd}, the pseudo-first-order rate constant (excess $Ru(NH_3)_6^{2+}$), were obtained from the slopes of ln $(A_\infty - A_t)$ vs. time plots.

Results

The $Co(NH_3)_5py^{3+}$-$Fe(CN)_6^{4-}$ Reaction. When solutions of $Co(NH_3)_5py^{3+}$ and $Fe(CN)_6^{4-}$ are mixed at ~10^{-4} M concentrations, a precipitate (presumably cobalt(II) hexacyanoferrate(II) and/or cobalt(II) hexacyanoferrate(III)) forms within a few seconds. Therefore, homogeneous kinetic studies are precluded under these conditions. However, when disodium ethylenediaminetetraacetate (EDTA) is present in the solution to sequester the Co(II), no precipitate is formed, and therefore all the experiments were carried out in the presence of EDTA. The stoichiometry is given by eq 8.

$$Co(NH_3)_5py^{3+} + Fe(CN)_6^{4-} \xrightarrow{\text{EDTA}} CoEDTA^{2-} + Fe(CN)_6^{3-} \tag{8}$$

The quantitative formation of $Fe(CN)_6^{3-}$ was established by comparing the increase in absorbance at 420 nm with that calculated from the concentration of the limiting reagent and the molar absorbance (1023 M^{-1} cm^{-1}) of $Fe(CN)_6^{3-}$. Agreement between measured and calculated absorbance increase was better than 2%.

The results of the kinetic measurements are summarized in Table I. It will be seen that k_{obsd} is independent of EDTA concentration in the range (0.75-2.50) × 10^{-4} M. Furthermore, two experiments with sulfosalicylate added, instead of EDTA, yielded the same values of k_{obsd} as experiments with EDTA. Therefore, we conclude that EDTA is not involved in, or prior to, the rate-determining step. EDTA acts as a sequestering agent to remove cobalt(II) and prevent its precipitation as a hexacyanoferrate salt. It will also be seen that the dependence of k_{obsd} on $[Fe(CN)_6^{4-}]$ is less than first order and that saturation obtains at high values of $[Fe(CN)_6^{4-}]$. The functional dependence conforms to eq 9. The measured values of k_{obsd} were fitted to eq 9 by means of a nonlinear least-squares program and yielded values of $k_{et}^{Co}(s^{-1})$ and $Q_p^{Co}(M^{-1})$ of (15.0 ± 0.5) × 10^{-3} and (2.4 ± 0.4) × 10^3 at 25 °C, (8.3 ± 0.4) × 10^{-3} and (1.7 ± 0.3) × 10^3 at 20 °C, (3.32 ± 0.05) × 10^{-3} and (2.6 ± 0.2) × 10^3 at 15 °C, and (2.17 ± 0.08) × 10^{-3} and (1.6 ± 0.3) × 10^3 at 10 °C. The mechanistic significance of Q_p^{Co} and k_{et}^{Co} will be discussed below.

$$k_{obsd} = \frac{k_{et}^{Co} Q_p^{Co}[Fe(CN)_6^{4-}]}{1 + Q_p^{Co}[Fe(CN)_6^{4-}]} \tag{9}$$

The $Ru(NH_3)_5py^{3+}$-$Fe(CN)_6^{4-}$ Reaction. The results of the determination of the equilibrium quotient for reaction 5 are given in Table II. The average values at 25 and 15 °C in 0.10 M KNO_3 are (1.0 ± 0.1) × 10^{-2} and (0.38 ± 0.08) × 10^{-2}, respectively. The value at 25 °C is in excellent agreement with the value 1.14 × 10^{-2} calculated from the reduction potentials of the $Fe(CN)_6^{3-/4-}$ [10] and $Ru(NH_3)_5py^{3+/2+}$ [11,12] couples.

The results of the kinetic measurements are presented in Table III. The reaction is very fast and, even at the low concentrations used, approaches the limit measurable with the Durrum instrument.[13] Nevertheless, the changes in transmittance followed an exponential decay for at least three half-lives. The relaxation times τ are related to equilibrium concentrations by eq 10.[14] The average value of k_r is (4.3 ±

Table I. Kinetics of the $Co(NH_3)_5py^{3+}$–$Fe(CN)_6^{4-}$ Reaction[a]

$10^4[Fe(CN)_6^{4-}]$, M	10^3k_{obsd}, s^{-1} 25 °C	20 °C	15 °C	10 °C
5.00	7.99, 8.19	3.85, 4.13	1.87, 1.91	1.00, 1.04
6.67	8.52, 8.77	4.41, 4.51	2.05, 2.16	1.11, 1.13
10.0	10.5, 11.8	5.06, 5.16	2.38, 2.39	1.26, 1.44
20.0	12.5, 13.9	6.14, 6.72	2.72, 2.86	1.48, 1.66
40.0	12.9, 13.9	6.49, 6.66	3.07, 3.12	2.00, 2.05
50.0	13.0, 13.8	7.59, 8.52	2.95, 3.10	1.79, 1.93
5.00	8.00, 8.66[b]			
5.00	6.93, 7.12[c]			
5.00	8.01, 8.11[d]			
5.00	7.88, 8.41[e]			
50.0	13.5, 13.8[f]			

[a] Unless specified otherwise, $[Co(NH_3)_5py^{3+}] = 5.00 \times 10^{-5}$ M, $[EDTA] = 1.50 \times 10^{-4}$ M, $\mu = 0.100$ M ($NaClO_4$). [b] $[EDTA] = 7.5 \times 10^{-5}$ M. [c] $[EDTA] = 1.00 \times 10^{-4}$ M. [d] $[EDTA] = 2.00 \times 10^{-4}$ M. [e] $[EDTA] = 2.50 \times 10^{-4}$ M. [f] [sulfosalicylate] = 0.010 M.

Table II. Equilibrium Quotient for Reaction 5[a]

$10^5[Ru(NH_3)_5py^{3+}]_0$, M	$10^4[Fe(CN)_6^{4-}]_0$, M	$10^6[Ru(NH_3)_5py^{2+}]_{eq}$[b]	$10^2 \cdot Q_5$,[c]
0.99	3.88	4.29	0.86
0.99	1.94	3.49	1.00
0.99	0.97	2.74	1.11
0.99	0.39	1.74	1.00
1.52	3.90	5.90	0.98
1.52	1.95	4.72	1.12
1.52	0.98	3.47	1.10
1.52	0.39	2.11	0.92
0.90	3.96	2.67	0.29
0.90	1.98	2.22	0.37
0.90	0.99	1.73	0.42
0.90	0.40	0.96	0.30
2.43	1.23	3.50	0.49
1.21	1.23	2.39	0.48
0.61	1.23	1.46	0.38
0.24	1.24	0.78	0.30

[a] In 0.10 M KNO_3; runs 1–8 at 25 °C; runs 9–16 at 15 °C. [b] Calculated from eq 7. [c] Calculated from eq 6.

Table III. Kinetics of the $Ru(NH_3)_5py^{3+}$–$Fe(CN)_6^{4-}$ Reaction[a]

$10^5[Ru(NH_3)_5py^{3+}]_0$, M	$10^4[Fe(CN)_6^{4-}]_0$, M	$10^6\tau$, s	$10^{-8}k_r$, M^{-1} s^{-1}[b]
6.15	7.13	53	4.4
11.5	6.61	48	3.7
5.88	3.35	72	4.9

[a] At 25 °C, 0.10 M KNO_3. [b] Calculated using eq 10.

Table IV. Kinetics of the $Ru(NH_3)_5py^{3+}$–$Ru(NH_3)_6^{2+}$ Reaction[a]

$10^5[Ru(NH_3)_5py^{3+}]_0$, M	$10^4[Ru(NH_3)_6^{2+}]_0$	$10^{-2}k_{obsd}$, s^{-1}	$10^{-5}k_f$, M^{-1} s^{-1}[b]
0.77	0.78	0.51	6.9
1.47	1.56	1.11	7.5

[a] At 25 °C, 0.10 M KNO_3. [b] Calculated from $k_{obsd}/[Ru(NH_3)_6^{2+}]_{av}$.

0.6) × 10^8 M^{-1} s^{-1}, and from the relation $Q_5 = k_f/k_r$, k_f is (4.3 ± 1.0) × 10^6 M^{-1} s^{-1}.

$$\frac{1}{\tau} = k_r\{Q_5([Ru(NH_3)_5py^{3+}]_{eq} + [Fe(CN)_6^{3-}]_{eq}) + [Ru(NH_3)_5py^{2+}]_{eq} + [Fe(CN)_6^{3-}]_{eq}\} \quad (10)$$

The $Ru(NH_3)_5py^{3+}$–$Ru(NH_3)_6^{2+}$ Reaction. The equilibrium constant for reaction 11 was estimated to be 2.0 × 10^4 using the reduction potentials of the $Ru(NH_3)_5py^{3+/2+}$ and $Ru(NH_3)_6^{3+/2+}$ couples.[15] The concentrations used in the kinetic measurements were chosen to give quantitative conversion of $Ru(NH_3)_5py^{3+}$ to $Ru(NH_3)_5py^{2+}$. The average value of the rate constant for the forward reaction is (7.2 ± 0.4) × 10^5 M^{-1} s^{-1} (cf. Table IV).

$$Ru(NH_3)_5py^{3+} + Ru(NH_3)_6^{2+} \rightleftarrows Ru(NH_3)_5py^{2+} + Ru(NH_3)_6^{3+} \quad (11)$$

Discussion

The functional form of k_{obsd} for the $Co(NH_3)_5py^{3+}$–$Fe(CN)_6^{4-}$ reaction is consistent with the mechanism represented by eq 12 and 13. Equation 12 is the diffusion-controlled formation and dissociation of the precursor ion pair, and is followed by the rate-determining electron transfer within the ion pair. The values of Q_p^{Co} and k_{et}^{Co} at 25 °C and 0.10 M ionic strength are 2.4 × 10^3 M^{-1} and 1.5 × 10^{-2} s^{-1}, respectively.

$$Co(NH_3)_5py^{3+} + Fe(CN)_6^{4-} \rightleftarrows Co(NH_3)_5py^{3+} \cdot Fe(CN)_6^{4-} \quad Q_p^{Co} \quad (12)$$

$$Co(NH_3)_5py^{3+} \cdot Fe(CN)_6^{4-} \rightarrow \text{products} \quad k_{et}^{Co} \quad (13)$$

Additional, direct evidence for the postulated outer-sphere association, eq 12, comes from measurements of the absorption of mixtures of $Co(NH_3)_5py^{3+}$ and $Fe(CN)_6^{4-}$ before any redox reaction takes place. The measurements were carried out in the stopped-flow apparatus by mixing $Fe(CN)_6^{4-}$ and EDTA in 0.10 M $NaClO_4$ with $Co(NH_3)_5py^{3+}$ in 0.10 M $NaClO_4$. Absorbance values at time zero were compared with the sum of the values obtained by mixing each solution with 0.10 M $NaClO_4$. The measurements are very inaccurate because the changes in absorbance are very small. Thus, the sum of the absorbances per centimeter at 5 nm of 4.00 × 10^{-3} M $Fe(CN)_6^{4-}$ and of 1.00 × 10^{-3} M $Co(NH_3)_5py^{3+}$ was 0.0104, while the absorbance of the mixture was 0.026. The measurements were carried out in the concentration ranges (1–10) × 10^{-4} for $Co(NH_3)_5py^{3+}$ and (5–40) × 10^{-4} for $Fe(CN)_6^{4-}$ and at wavelengths 420–470 nm, and yielded values of Q_p^{Co} = (1.6 ± 1) × 10^3 M^{-1}. Within the very large uncertainty, these values are in good agreement with the kinetically derived value 2.4 × 10^3.

The large value of the equilibrium constant for eq 12 is expected on theoretical grounds. Equation 14 has been used successfully to estimate values of outer-sphere association constants.[16]

$$K_0 = \frac{4\pi Na^3}{3000}\exp(-U(a)/kT) \quad (14)$$

where

$$U(a) = \frac{z_1 z_2 e^2}{Da(1 + \kappa a)} \quad (15)$$

and

$$\kappa = \left(\frac{8\pi Ne^2\mu}{1000DkT}\right)^{1/2}$$

Definitions: N, Avogadro's number; a, distance of closest approach; k, Boltzmann's constant; T, absolute temperature; z_1 and z_2, charges on ions 1 and 2, respectively; e, electronic charge; D, bulk dielectric solvent; μ, ionic strength. Two values of Q_p^{Co} can be calculated, depending on whether the approach between $Fe(CN)_6^{4-}$ and $Co(NH_3)_5py^{3+}$ occurs at the ammonia coordination sites or at the pyridine ligand. In the former case, the appropriate radius for $Co(NH_3)_5py^{3+}$ is 2.5×10^{-8} cm;[17] in the latter case, the estimated radius is 6.2×10^{-8} cm. Using the 4.5×10^{-8} cm for the radius of $Fe(CN)_6^{4-}$,[14] the values of Q_p^{Co} are 1.1×10^3 and 1.4×10^2 M^{-1} for $a = 7.0 \times 10^{-8}$ and 10.7×10^{-8} cm, respectively. The agreement with the experimental value of Q_p^{Co} is considerably better for the calculation with $a = 7.0 \times 10^{-8}$ cm, and, therefore, we suggest that the structure of the ion pair involves closest approach between the cobalt and iron complexes on the side of the ammonia ligands.

Within the rather large uncertainty, Q_p^{Co} is temperature independent in the 10–25 °C range, with an average value of 2.1×10^3 M^{-1}. Therefore, $\Delta H_{12}°$ and $\Delta S_{12}°$, the thermodynamic parameters for reaction 12, are 0 and 15 eu, respectively. This result conforms to well-known patterns in the formation of ion pairs: favorable outer-sphere association is governed by the entropy increase associated with the release of water of solvation as the ions of opposite charge come together.

The temperature dependence of k_{et}^{Co} yields the activation parameters $\Delta H^{\ddagger} = 21.7 \pm 2.2$ kcal/mol and $\Delta S^{\ddagger} = 5.8 \pm 7$ eu. If the overall reaction is expressed as a second-order process, then $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for that process are calculated to be 21.7 kcal/mol and 21 eu, respectively. The latter positive value is to be contrasted with the ca. −30 eu values usually encountered in redox controlled reaction between ions of charge +2, +2.[18] The change in the sign of $\Delta S^{\ddagger}$ in going from the +2, +2 reactions to the present −4, +3 reaction is readily understood (qualitatively, to be sure) since for reactions of ions of like charge an increase in solvation occurs in going from reactants to transition state, whereas for reactions of ions of opposite charge, charge neutralization obtains, water of solvation is released, and $\Delta S^{\ddagger}$ is positive. It is noteworthy that most of the positive value of $\Delta S^{\ddagger}$ for the $Fe(CN)_6^{4-}$-$Co(NH_3)_5py^{3+}$ reaction expressed as a second-order process is contributed by the ion-pair formation stage. The small positive value of $\Delta S^{\ddagger}$ for the intramolecular electron transfer within the ion pair (eq 13) appears reasonable since in going from precursor ion pair to successor ion pair the −4, +3 charge diminishes to −3, +2. The charge redistribution should result in a decrease in solvation and, consequently, a positive entropy change. Therefore, in going from precursor outer-sphere complex to transition state for electron transfer, the observed small positive $\Delta S^{\ddagger}$ could be accommodated on the basis of the charge redistribution concept. If this argument is accepted, there would be little or no contribution to the entropy of activation from the act of electron transfer itself, a result which would imply that the electron transfer is adiabatic.

Some additional considerations regarding the detailed path for the electron transfer are in order. Although, as suggested above, the structure of the *predominant* ion pair may involve approach of the cobalt and iron complexes on the side of the ammonia ligands, it must be noted that in the *reactive* (toward electron transfer) precursor outer-sphere complex, the iron may approach the cobalt on the side of the pyridine ligand. This would be the case if electron transfer were favored with pyridine acting as a mediator. Unfortunately, additional details about the actual path of electron transfer cannot be obtained from the above information. However, the insensitivity of the rates of ferrocyanide reduction of substituted pyridinepentaamminecobalt(III) complexes to the nature of the substituent in the pyridine ring,[1b,19] could be taken to indicate that electron transfer does not make use of the pyridine ligand as a mediator and, therefore, that the reactive ion pair involves approach of the iron to the ammonia side of the cobalt(III) complex.

Table V. Comparison of Rate Constants for Reduction of $Ru(NH_3)_5py^{3+}$ and $Co(NH_3)_5py^{3+}$

Reductant	k_{Ru}[a], $M^{-1}\,s^{-1}$	k_{Co},[b] $M^{-1}\,s^{-1}$	k_{Ru}/k_{Co}
$Fe(CN)_6^{4-}$	4.3×10^6 [c]	3.6×10^1 [c]	0.12×10^6
$Ru(NH_3)_6^{2+}$	7.2×10^5 [c]	6.7×10^{-1} [d]	1.1×10^6
Cr^{2+}	3.4×10^3 [e]	4.0×10^{-3} [f]	0.9×10^6
V^{2+}	1.2×10^5 [e]	2.4×10^{-1} [g]	0.5×10^6

[a] Rate constant at 25 °C and ionic strength 0.10 M for the reduction of $Ru(NH_3)_5py^{3+}$. [b] Rate constant at 25 °C and ionic strength 0.10 M for the reduction of $Co(NH_3)_5py^{3+}$, value for $Fe(CN)_6^{4-}$ is $Q_p^{Co}k_{et}^{Co}$. [c] Present work. [d] At ionic strength 0.50 M, F. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2647 (1974). [e] At ionic strength 1.0 M, ref 5. [f] At ionic strength, 1.1 M, E. R. Dokcal and E. S. Gould, *J. Am. Chem. Soc.*, **94**, 6673 (1972). [g] At ionic strength 1.1 M, J. C. Chen and E. S. Gould, *J. Am. Chem. Soc.*, **95**, 5539 (1973).

At the low ruthenium and iron concentrations used in the kinetic measurements of reaction 5, ion pair formation is negligible. Nevertheless, the importance of electrostatic effects are apparent when the measured rate constant for the forward reaction 5 is compared with the value calculated using Marcus' equation $k_{12} = (k_{11}k_{22}K_{12})^{1/2}$. The rate constants for the exchange reactions between $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ and between $Ru(NH_3)_5py^{3+}$ and $Ru(NH_3)_5py^{2+}$ are 1.9×10^4 and 4×10^5 $M^{-1}\,s^{-1}$, respectively.[14,20] Therefore, $k_{12} = 8.8 \times 10^3$ $M^{-1}\,s^{-1}$, in very poor agreement with the measured value $k_f = 4.3 \times 10^6$ $M^{-1}\,s^{-1}$. However, before comparing exchange and cross reactions for ions of different sign and charge,[14] a correction for electrostatic effects must be done by means of

$$\Delta G_{12}^{*} = \Delta G_{12}^{**} + w_{12}$$

where

$$\Delta G_{12}^{**} = (\Delta G_{11}^{**} + \Delta G_{22}^{**} + \Delta G_R°)/2$$

$$\Delta G_{11}^{**} = \Delta G_{11}^{*} - w_{11}$$

$$\Delta G_{22}^{**} = \Delta G_{22}^{*} - w_{22}$$

$$\Delta G_R° = \Delta G_{12}° + w_{21} - w_{12}$$

Definitions: single and double asterisks are used for measured and corrected free energies of activation, respectively; subscripts 1 and 2 pertain to the ruthenium and iron couples, respectively; w are the coulombic terms $z_1z_2e^2/Da$, and are corrected to the desired ionic strength using the Debye–Hückel expression given by eq 15.[21] Two different values of the radius of the ruthenium complex can be used depending on whether electron transfer occurs through the pyridine or ammonia ligands, the values being 6.4×10^{-8} and 2.7×10^{-8} cm, respectively.[22] We calculate (all values in kcal/mol): $\Delta G_{11}^{*} = 11.62$, $\Delta G_{11}^{**} = 8.71$, $\Delta G_{22}^{*} = 9.82$, $\Delta G_{22}^{**} = 6.82$ (ammonia) or 8.97 (pyridine), $\Delta G_{12}° = 2.72$, $\Delta G_R° = 4.73$ (ammonia) or 3.81 (pyridine), $\Delta G_{12}^{**} = 10.13$ (ammonia) or 10.74 (pyridine), $\Delta G_{12}^{*} = 6.11$ (ammonia) or 8.56 (pyridine). Therefore, the rate constant for reaction 5 is 2.1×10^8 or 3.3×10^6 $M^{-1}\,s^{-1}$ depending on whether the iron complex approaches the ruthenium complex on the side of the ammonia or of the pyridine. Comparison of these values with the experimental value of 4.3×10^6 $M^{-1}\,s^{-1}$ suggests to us that the actual path of electron tansfer is through the pyridine ligand.

The different mechanisms suggested for the $Co(NH_3)_5py^{3+}$-$Fe(CN)_6^{4-}$ and $Ru(NH_3)_5py^{3+}$-$Fe(CN)_6^{4-}$ reactions and their widely different rates can be rationalized on the basis of orbital symmetry considerations.[23] If the path of electron transfer involves the pyridine ligand, then the symmetry of donor, carrier, and acceptor orbitals is π, π, and σ, respectively, for cobalt, and π, π, and π, respectively, for ruthenium. The symmetry mismatch in the case of cobalt may render the path via pyridine inoperative, and the reaction proceeds, at a relatively slow rate, with the reducing agent approaching the cobalt on the ammonia side. In contrast, the ruthenium π orbital that accepts the electron is largely delocalized over the ligand, and the rapid rate is associated with resonance transfer directly from the reductant to the final acceptor orbital.[5]

Finally, it is noteworthy that the rate pattern for the reductions of $Ru(NH_3)_5py^{3+}$ and $Co(NH_3)_5py^{3+}$ by $Fe(CN)_6^{4-}$ extends to other reducing agents. The pertinent data are presented in Table V. It will be seen that the reactions of $Ru(NH_3)_5py^{3+}$ are ca. 5×10^5 faster than the corresponding reactions of $Co(NH_3)_5py^{3+}$, the ratio k_{Ru}/k_{Co} being fairly insensitive to the nature of the reductant. This is the expected result if Marcus' relation is applicable to all of these reactions. Since $k_{12} = (k_{11}k_{22}K_{12})^{1/2}$, it follows that the ratio $k_{Ru}/k_{Co} = (k_{RuRu}/k_{CoCo})^{1/2}K_{RuCo}{}^{1/2}$ and therefore is independent of the nature of the reducing agent.

References and Notes

(1) (a) This work was supported by Grant GP-37057X and CHE7610449 from *the National Science Foundation*; (b) *abstracted from the Ph.D. Dissertation* of A.J.M., State University of New York, Stony Brook, N.Y., July 1974, and from the B.S. Thesis of R.E.A., State University of New York, Stony Brook, N.Y., May 1976; (c) holder of a fellowship from the Instituto Venezolano de Investigaciones Cientifcas, 1971–1974.
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Oxidative Addition of Nitrosonium Ion to Sulfur-Bridged Binuclear Iron(II) and Cobalt(II) Complexes

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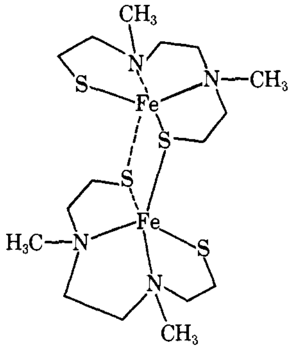
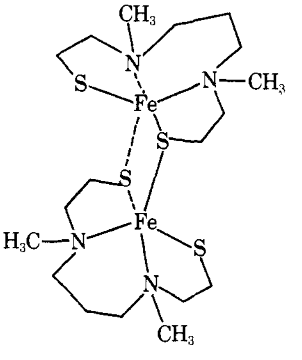
Abstract: The reactions of nitrosonium (NO^+) or nitronium ($NO_2{}^+$) salts with $(FeL)_2$, where L is the tetradentate N_2S_2 donor ligand derived from *N,N′*-dimethyl-*N,N′*-bis(2-mercaptoethyl)ethylenediamine (LH_2), afford $[(FeL)_2NO]^+$ in high yield. X-ray diffraction results show the product to consist of two distorted octahedra sharing a common face comprised of two bridging thiolate sulfur atoms and a symmetrically bridging nitrosyl ligand. An iron–iron single bond (2.468 (2) Å) enables each metal to have an 18-electron configuration. The analogous cobalt compound $(CoL)_2$, the synthesis of which is described, also reacts to form a binuclear adduct, $[(CoL)_2NO]^+$. An x-ray crystal structure analysis of the tetrafluoroborate salt of this cation shows it to have the same structure as the iron complex, but without a metal–metal bond (Co···Co = 2.770 (2) Å). The structural results, together with infrared (ν_{NO} ~1550 cm^{-1}) and Mössbauer studies (Fe complexes) of the adducts, are interpreted formally in terms of an oxidative addition of the nitrosonium ion to the bimetallic complexes, $(M^{II}L)_2 + NO^+ \rightarrow [(M^{III}L)_2(NO^-)]^+$, M = Fe or Co.

The synthesis,[1] structure,[2] and magnetic properties[3] of the iron(II) complexes $(FeL)_2$ and $(FeL')_2$ have been previously described. The five-membered ethylenediamine chelate ring in $(FeL)_2$ imposes a steric constraint[2] that is substantially relieved in $(FeL')_2$, which has a six-membered 1,3-propanediamine chelate ring. Since the complex $(FeL)_2$ contains high spin iron(II) atoms,[1,3] an alternative way of relieving the steric constraint in this molecule is to generate low spin iron, for example, by increasing the coordination number. A high to low spin conversion will shorten the Fe-N bond lengths with a concomitant increase in the N-Fe-N bond angle. The reactions of $(FeL)_2$ with carbon monoxide and alkyl isocyanides to form $FeL(CO)_2$ and $FeL(CNR)_2$ illustrate this point.[1]

It was also of interest to study the oxidation of the com-



$(FeL)_2$



$(FeL')_2$