Intramolecular Electron Transfer from Pentacyanoferrate(II) to Pentaamminecobalt(III) via an Imidazolate Bridge. The Role of Distance in Inner-Sphere Reactions[1a,b]

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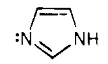
Abstract: The reaction of (imidazolato)pentaamminecobalt(III) with aquopentacyanoferrate(II) proceeds in two stages. The first corresponds to the formation of the imidazolato-bridged precursor complex I, $(NC)_5Fe^{II}NC_3H_3NCo^{III}(NH_3)_5^-$, and the second to the intramolecular electron transfer from Fe(II) to Co(III) in I. The rate of the first reaction was measured by using *N*-methylpyrazinium as a competitive indicator. At 25 °C and 0.10 M ionic strength, $Co(NH_3)_5NC_3H_3N^{2+}$ and $Fe(CN)_5OH_2^{3-}$ form an ion pair with a formation constant of 670 ± 390 M^{-1}. Inner-sphere substitution within the ion pair produces I with a rate constant equal to 4.9 ± 1.6 s^{-1}. The kinetic parameters for the internal electron transfer of I are $k = 0.165 \pm 0.015$ s^{-1}, $\Delta H^\ddagger = 19.2 \pm 0.2$ kcal/mol, and $\Delta S^\ddagger = 2.4 \pm 0.2$ eu. The activation free energies for internal electron transfer in $(NC)_5FeLCo(NH_3)_5$ and $(NH_3)_4(H_2O)RuLCo(NH_3)_5$, where L = imidazolate, pyrazine, 4,4′-bipyridine, and *trans*-1,2-(4-pyridyl)ethylene, are inversely proportional to the distance between the metal ions. If the inner-sphere reorganization and thermodynamic contributions to the barriers for electron transfer are relatively constant in the series of complexes, then the observed distance dependence is ascribed to the outer-sphere reorganization term, e.g., solvent polarization.

Introduction

Imidazole (ImH) and its conjugate base are important ligands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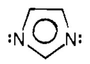
Im$^-$

in chemistry and in biology.[2,3] In particular, derivatives of the imidazolate anion (Im$^-$) have been shown[4] or postulated[5] to act as bridging ligands in enzymes containing heterobimetallic (Cu(II)–Zn(II) or Fe(III)–Cu(II)) units. In a continuation of our work on intramolecular electron transfer[6–8] from $Fe(CN)_5^{3-}$ to $Co(NH_3)_5^{3+}$ in binuclear complexes featuring ligands linking the Fe(II) and Co(III) centers, we wish to report results of our studies with the imidazolate bridged species I. An additional impetus


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for the work was the reported[9] intramolecular electron transfer in $(SO_4)(NH_3)_4Ru^{II}ImCo^{III}(NH_3)_5^{2+}$.

Experimental Section

Materials. The water used in all experiments was house-distilled water passed through a Barnstead ion-exchange demineralizer and distilled in a modified, all-glass Corning Model AG-1b apparatus. Lithium perchlorate was recrystallized from water. The argon used to maintain anaerobic conditions was purified by passing it through a column of BTS catalyst kept at 110 °C.

N-Methylpyrazinium iodide was prepared in 90% yield by the method of Bahner and Norton.[10] The corresponding perchlorate was obtained in 51% yield by metathesis of the iodide salt with sodium perchlorate in methanol. Sodium amminepentacyanoferrate(II) trihydrate was prepared and purified as described before.[7] The product was stored at −10 °C.

Imidazolepentaamminecobalt(III) perchlorate was prepared in 15% yield by a slight modification of the literature method.[11] A preliminary separation of the desired complex from the other reaction products was carried out by using Sephadex CM cation-exchange resin. Anal.[12] Calcd for $[Co(NH_3)_5C_3H_4N_2](ClO_4)_3$: Co, 11.54. Found: Co. 11.47, 11.61.

Instrumentation. All kinetic measurements were performed on a Durrum D-110 stopped-flow instrument interfaced to an IBM 1800 computer. Spectrophotometric measurements were obtained from either a Cary 17 or a Cary 118 spectrophotometer. pH measurements were obtained from either an Orion ionalyzer, Model 801, or a Radiometer Model 26 pH meter.

Kinetic and Stoichiometric Measurements. All measurements were carried out under anaerobic conditions by using solutions saturated with argon. Solutions of $Fe(CN)_5OH_2^{3-}$ were obtained by aquation of $Fe(CN)_5NH_3^{3-}$ at pH ~5 (acetate buffer) for about 5 min. Aliquots of these solutions were withdrawn, and all desired measurements were obtained as rapidly as possible, usually within 5 min.

Rates of formation of the binuclear complex $(NC)_5FeImCo(NH_3)_5^-$ were determined by a competition method by using *N*-methylpyrazinium ($MePz^+$) as an indicator. Solutions of $Co(NH_3)_5ImH^{3+}$ and $Co(NH_3)_5Im^{2+}$ at the desired pH and ionic strength and containing the desired concentration of $MePz^+$ were mixed in the stopped-flow apparatus with *freshly* prepared solutions of $Fe(CN)_5OH_2^{3-}$ at the desired pH and ionic strength. The absorbance of the $Fe(CN)_5MePz^{2-}$ formed was monitored at its 658-nm absorption maximum. Values of k_{obsd} were obtained from the linear (3 half-lives) plots of ln $(A_\infty - A_t)$ vs. t.

Rates of internal electron transfer in $(NC)_5FeImCo(NH_3)_5^-$ were measured in the presence of ethylenediamine tetraacetate to prevent precipitation of Co^{2+} with iron cyanide complexes. With use of the stopped-flow method, the absorbance changes at 440 mm occurring upon mixing solutions of $Fe(CN)_5OH_2^{3-}$ and of $Co(NH_3)_5Im^{2+}$ were monitored. The traces showed first a small decrease associated with the formation of the binuclear complex and then a sizeable increase associated with the internal electron transfer and formation of $Fe(CN)_5Im^{3-}$.[13] In order to prevent interference of the first reaction in the determination

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of the rate of the second, we did not collect absorbance values until more than 10 half-lives of the first reaction had elapsed. Rate constants were obtained from $\ln(A_\infty - A_t)$ vs. t plots.

Stoichiometric measurements were designed to measure the amounts of $Fe(CN)_5OH_2^{2-}$ and $Fe(CN)_5Im^{3-}$ formed in the $Fe(CN)_5OH_2^{3-}$–$Co(NH_3)_5Im^{2+}$ reaction. Following completion of the internal electron transfer in $(NC)_5FeImCo(NH_3)_5^-$, the resulting solution was treated with acetate buffer to bring the pH to ~5 and an excess of $MePz^+$ was added. The absorbance at 658 nm was measured, and then ascorbic acid was added. The instantaneous absorbance increase was a measure of the $Fe(CN)_5OH_2^{2-}$ concentration. The subsequent, slow absorbance increase was a measure of the $Fe(CN)_5Im^{3-}$ concentration.[14]

Equilibrium Measurements. The pK_a of $Co(NH_3)_5ImH^{3+}$ was determined by titration of the cobalt complex with standard potassium hydroxide at constant ionic strength (0.100 M maintained with potassium nitrate) and measuring the pH of the solution after each addition.

Results and Discussion

The reaction of equilibrium mixtures of $Co(NH_3)_5ImH^{3+}$ and $Co(NH_3)_5Im^{2+}$ at pH ~10 with $Fe(CN)_5OH_2^{3-}$ proceeds in two stages. The first stage corresponds to the formation of the binuclear complex I (eq 1) and is followed by the intramolecular electron transfer reaction of I (eq 2). As will be shown below,

$$Fe(CN)_5OH_2^{3-} + Co(NH_3)_5Im^{2+} \rightarrow (NC)_5FeImCo(NH_3)_5^- \qquad (1)$$

$$(NC)_5FeImCo(NH_3)_5^- \rightarrow Fe(CN)_5Im^{3-} + \underset{\hookrightarrow CoEDTA^{2-}}{Co^{2+}} + NH_3 \quad k_{et} \qquad (2)$$

only the deprotonated form of the cobalt complex is reactive, and this finding has been incorporated in the formulation of eq 1. The $Fe(CN)_5Im^{3-}$ produced in eq 2 was identified by its absorption maximum at 440 nm.[13] Four stoichiometric experiments with $[Fe(CN)_5OH_2^{3-}] = (1.00\text{–}1.05) \times 10^{-5}$ M, $[Co(NH_3)_5ImH^{3+}] + [Co(NH_3)_5Im^{2+}] = (2.11\text{–}20.3) \times 10^{-4}$ M, pH 9.63–9.98, 25 °C, and ionic strength of 0.100 M showed that 95.6–97.3% of $Fe(CN)_5Im^{3-}$ was produced, the remaining iron being present as $Fe(CN)_5OH_2^{2-}$. Therefore, we infer that the $Co(NH_3)_5Im^{2+}$–$Fe(CN)_5OH_2^{3-}$ reaction proceeds predominantly by an inner-sphere mechanism.

The increase in absorbance at 440 nm (the wavelength maximum for $Fe(CN)_5Im^{3-}$) could be easily determined (molar absorbance ≈ 1.6×10^3) in the stopped-flow apparatus. In contrast, we could not obtain a good spectrum of the precursor complex I. At the small iron concentrations (~10^{-5} M) necessary to prevent dimerization[15] and recognizing that $Fe(CN)_5ImH^{3-}$ has small molar absorbances in the useful spectroscopic region (for example, 463 M^{-1} cm^{-1} at its 382-nm absorption maximum[13]), it can be seen that the changes in absorbance associated with reaction 1 were near the detection limit of the stopped-flow instrument. Nevertheless, a decrease in absorbance at 440 nm (the wavelength maximum for $Fe(CN)_5OH_2^{3-}$) and an increase in absorbance at 380 nm (near the wavelength maximum for $Fe(CN)_5ImH^{3-}$) could be discerned, and it is apparent that the spectrum of the binuclear, precursor complex I closely resembles that of the corresponding mononuclear iron(II) complex.

In view of the small absorbance changes associated with reaction 1, the rate of the reaction was determined by a competition method that utilized $MePz^+$ as an indicator. The choice of $MePz^+$ was based on the reported[16] wavelength maximum (658 nm) for $Fe(CN)_5MePz^{2-}$. At this wavelength, the subsequent internal redox reaction of I resulted in no absorbance changes, and therefore good measurements of the rate of disappearance of $Fe(CN)_5OH_2^{3-}$ could be obtained. Two sets of measurements were carried out, one at pH 4.82 ± 0.02 (acetate buffer) and another at pH 9.68–9.89. At the lower pH, the cobalt complex is present almost exclusively in the protonated form, whereas at the higher pH about equal amounts of $Co(NH_3)_5ImH^{3+}$ and $Co(NH_3)_5Im^{2+}$ are present. The pK_a of $Co(NH_3)_5ImH^{3+}$, determined in the present work at 25 °C and ionic strength of 0.100 M, is 9.64 ± 0.05, in good agreement with the previously[11] reported value of 10.02 ± 0.04 at ionic strength of 1.00 M.

Table I. Observed Rate Constants for the Reaction between $Fe(CN)_5OH_2^{3-}$ and $MePz^+$ in the Presence of $Co(NH_3)_5ImH^{3+}/Co(NH_3)_5Im^{2+}$ [a]

$10^4[Co^{III}]_t$,[b] M	pH[c]	k_{obsd},[d] s^{-1}
0.00	5–10	1.09 ± 0.05 (1.09)
2.25	4.81	1.00 ± 0.05 (1.02)
4.80	4.83	0.92 ± 0.01 (0.95)
10.1	4.83	0.81 ± 0.01 (0.84)
20.2	4.82	0.67 ± 0.01 (0.68)
1.06	9.89	1.21 ± 0.02 (1.24)
1.11	9.87	1.27 ± 0.02 (1.25)
2.12	9.88	1.41 ± 0.03 (1.38)
2.15	9.87	1.41 ± 0.04 (1.38)
5.06	9.83	1.68 ± 0.05 (1.66)
5.17	9.82	1.59 ± 0.02 (1.66)
9.85	9.77	1.87 ± 0.04 (1.96)
11.3	9.78	2.20 ± 0.02 (2.04)
15.1	9.82	2.22 ± 0.07 (2.29)
15.6	9.83	2.34 ± 0.04 (2.31)
19.9	9.70	2.19 ± 0.04 (2.30)
20.5	9.68	2.56 ± 0.11 (2.29)

[a] Measurements at 25 °C, ionic strength of 0.100 M (lithium perchlorate), $[MePz^+] = 4.01 \times 10^{-4}$ M, $[EDTA^{2-}] = 5.0 \times 10^{-4}$ M, $[Fe(CN)_5OH_2^{3-}] = (0.99\text{–}1.07) \times 10^{-5}$ M. [b] Total cobalt(III) concentration = $[Co(NH_3)_5ImH^{3+}] + [Co(NH_3)_5Im^{2+}]$. [c] Acetate buffer for the first 5 experiments; carbonate buffer for last 12 experiments. [d] Average and standard deviation of 3–5 replicate experiments. Values in parentheses calculated by using parameters given in text.

Table II. Rate Constants for Intramolecular Electron Transfer of $(NC)_5FeImCo(NH_3)_5^-$ [a]

10^5-$[(NC)_5$-$FeImCo(NH_3)_5^-]$,[b] M	10^4-$[Co^{III}]_t$,[c] M	$10k_{et}$,[d] s^{-1}
2.53	5.02	1.61 ± 0.03
2.60	5.29	1.36 ± 0.15
2.50	10.6	1.82 ± 0.11
2.51	10.5	1.76 ± 0.13
4.92	10.0	1.80 ± 0.03
4.49	10.7	1.64 ± 0.08
5.01	21.1	1.53 ± 0.08
5.08	20.0	1.64 ± 0.03
2.64	5.34	0.89 ± 0.06[e]
2.68	5.28	0.97 ± 0.06[e]
2.58	5.24	2.8 ± 0.2[f]
2.63	5.32	2.8 ± 0.1[f]
2.62	5.37	4.9 ± 0.5[g]
2.67	5.24	4.9 ± 0.4[g]

[a] Ionic strength of 0.100 M (lithium perchlorate), pH 9.68–9.85 (carbonate buffer), $[Na_2EDTA] = 5.0 \times 10^{-4}$ M, 25 °C except where noted. [b] Assumed to be equal to the initial $[Fe(CN)_5OH_2^{3-}]$. [c] Total excess cobalt(III), $[Co(NH_3)_5ImH^{3+}] + [Co(NH_3)_5Im^{2+}]$. [d] Average and standard deviation of 3–4 replicate measurements. [e] At 20 °C. [f] At 30 °C. [g] At 35 °C.

The results of the measurements at pH 4.82 are listed in Table I (first 5 experiments). It will be seen that as the concentration of $Co(NH_3)_5ImH^{3+}$ increases, the rate constant for the formation of $Fe(CN)_5MePz^{2-}$ decreases. The inhibitory effect of $Co(NH_3)_5ImH^{3+}$ is ascribed to the formation of an unreactive ion pair with $Fe(CN)_5OH_2^{3-}$, the mechanism being given by eq 3 and 4, with $k_{obsd} = k_4[MePz^+]/1 + Q_p[Co(NH_3)_5ImH^{3+}]$. From the

$$Fe(CN)_5OH_2^{3-} + Co(NH_3)_5ImH^{3+} \rightleftharpoons Fe(CN)_5OH_2^{3-}\cdot Co(NH_3)_5ImH^{3+} \quad Q_p \qquad (3)$$

$$Fe(CN)_5OH_2^{3-} + MePz^+ \rightarrow Fe(CN)_5MePz^{2-} + H_2O \quad k_4 \qquad (4)$$

values of k_{obsd} in Table I, we obtain $k_4 = (2.68 \pm 0.08) \times 10^3$ M^{-1}

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(14) Addition of ascorbic acid to $Fe(CN)_5OH_2^{2-}$ and $Fe(CN)_5Im^{3-}$ results in the rapid formation of the corresponding Fe(II) complexes. The $Fe(CN)_5OH_2^{3-}$ reacts rapidly (a few seconds) with $MePz^+$, whereas $Fe(CN)_5ImH^{3-}$ reacts slowly (a few thousand seconds).

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s^{-1} and $Q_p = (3.02 \pm 0.08) \times 10^2$ M^{-1}. Previous measurements of k_4 for reaction 4 are $(2.41 \pm 0.08) \times 10^3$ M^{-1} s^{-1} at pH 6–8.5[16] and $(2.35 \pm 0.11) \times 10^3$ M^{-1} s^{-1} from the dependence of the reaction rate upon pH in the range 1.0–7.52.[17]

The results of the measurements at pH 9.68–9.89 are listed in Table II (last 12 experiments). In contrast with the measurements at pH 4.82, it will be seen that k_{obsd} increases with increasing cobalt concentration. Under the conditions of the experiments listed in Table II, the cobalt complex exists as a mixture of protonated and deprotonated forms. The former, $Co(NH_3)_5ImH^{3+}$, forms an unreactive ion pair with $Fe(CN)_5OH_2^{3-}$. Therefore, the increase in rate with increasing cobalt concentration must be ascribed to the deprotonated form, $Co(NH_3)_5Im^{2+}$, being reactive toward replacement of the water in $Fe(CN)_5OH_2^{3-}$. However, before examining the pH and cobalt concentration dependences in detail, it is necessary to consider the possible importance of the acid–base equilibrium represented by eq 5. There is conflicting evidence

$$Fe(CN)_5OH_2^{3-} \rightleftharpoons Fe(CN)_5OH^{4-} + H^+ \qquad (5)$$

in the literature about this point. Davies and Garafalo[18] reported that the reactions of $Fe(CN)_5OH_2^{3-}$ with various nucleophiles were independent of pH in the range 6–12.2. Malin and Koch[17] reported that the reaction of $Fe(CN)_5OH_2^{3-}$ with $MePz^+$ is independent of pH in the range 6–7.5.[19] On the other hand, Macartney and McAuley,[20] in a study of the reaction of $Fe(CN)_5OH_2^{3-}$ with thiourea, report a marked diminution in rate in the range 6–9 and claim a pK_a of 7.9 for eq 5. Unless the reactions of $Fe(CN)_5OH_2^{3-}$ and of $Fe(CN)_5OH^{4-}$ with each of the nucleophiles studied by Davies and Garafalo and by Malin and Koch proceed at identical rates, a highly unlikely occurrence considering the diversity of ligands used (pyrazine, *N*-methylpyrazinium, thiourea, isonicotinamide, acetonitrile), the pH independence observed by these workers imply that the pK_a for eq 5 cannot be smaller than 12. Our own studies with 4-cyanopyridine corroborate this conclusion. With $[Fe(CN)_5OH_2^{3-}] = (3.0–3.1) \times 10^{-5}$ M, [4-cyanopyridine] $= (2.07–2.23) \times 10^{-2}$ M, 25 °C, and ionic strength of 0.100 M, values of the second-order rate constant were $(6.7 \pm 0.1) \times 10^2$ and $(6.6 \pm 0.6) \times 10^2$ M^{-1} s^{-1} at pH 10 and 11, respectively, to be compared with our previous value[1b,21] of $(6.2 \pm 0.4) \times 10^2$ M^{-1} s^{-1} at pH 5 and 8. Moreover, Davies and Garafalo[22] have concluded that the observations reported by Macartney and McAuley are artifacts associated with polymerization and/or oxidation of $Fe(CN)_5OH_2^{3-}$ rather than the manifestation of the chemical equilibrium represented by eq 5. Based on all of the above considerations,[23] we conclude that the pH dependence of the $Co(NH_3)_5ImH^{3+}$–$Fe(CN)_5OH_2^{3-}$ reaction in the range of ~5 to ~10 is associated with deprotonation of the former species rather than of the $Fe(CN)_5OH_2^{3-}$ ion.

The high pH measurements in Table I are interpreted on the basis of eq 4, 6, and 7. In contrast with the unreactive protonated

$$Fe(CN)_5OH_2^{3-} + Co(NH_3)_5Im^{2+} \rightleftharpoons Fe(CN)_5OH_2^{3-}\cdot Co(NH_3)_5Im^{2+} \quad Q_{DP} \qquad (6)$$

$$Fe(CN)_5OH_2^{3-}\cdot Co(NH_3)_5Im^{2+} \rightarrow (NC)_5FeImCo(NH_3)_5^{-} \quad k_{IS} \qquad (7)$$

ion pair formed in eq 3, the deprotonated ion pair formed in eq 6 is thought to be reactive toward substitution, the rate constant for substitution of the inner sphere water being defined as k_{IS}. On the basis of the kinetic scheme which includes eq 3, 4, 6, and 7 and the rapid acid base equilibrium between protonated and deprotonated ion pairs, the observed pseudo-first-order rate constant is given by eq 8. [Co(III)] represents the total cobalt

$$k_{obsd} = \frac{(k_{IS}Q_{DP}K_a/(K_a + [H^+]))[Co^{III}] + k_4[MPz^+]}{1 + [Co^{III}](Q_p[H^+] + Q_{DP}K_a)/(K_a + [H^+])} \qquad (8)$$

concentration, $[Co(NH_3)_5ImH^{3+}] + [Co(NH_3)_5Im^{2+}]$, and K_a is 2.09×10^{-10}, the acid dissociation constant of the protonated cobalt complex. The measured values of k_{obsd} were fitted to eq 8 by means of a nonlinear least-squares program that treated $[H^+]$ and $[Co^{III}]$ as independent variables, K_a, Q_p, and $k_4[MePz^+]$ as constant parameters, and Q_{DP} and k_{IS} as floating parameters. The value of Q_p was obtained from the low pH measurements (vide supra) and $k_4[MePz^+]$ was taken as k_{obsd} in the absence of cobalt. The resulting values of k_{IS} and Q_{DP} are 4.9 ± 1.6 s^{-1} and 670 ± 390 M^{-1}, respectively. It will be seen that these parameters reproduce quite well the experimental k_{obsd} values: the average difference between experimental and calculated values being less than 4%.

Some comments about the magnitudes of the values of Q_p, Q_{DP}, and k_{IS} are in order. The value of Q_p, 3.0×10^2 M^{-1}, is in acceptable agreement with the value 1.0×10^2 M^{-1} calculated from eq 9.[23] Definitions: a is the distance of closest approach

$$K_0 = (2.523 \times 10^{21})\, a^3 \exp\left(-\frac{(7.131 \times 10^{-8})Z_1Z_2}{a(1 + (3.285 \times 10^7)\,\mu^{1/2}a)}\right) \qquad (9)$$

between the ions, Z_1 and Z_2 are the charges of the positive and negative ions, respectively, μ is the ionic strength, and the constants are applicable to aqueous solutions at 25 °C. The radii of $Fe(CN)_5OH_2^{3-}$ and $Co(NH_3)_5ImH^{3+}$ were taken as 4.5×10^{-8} and 3.5×10^{-8} cm, respectively. The value of Q_p is also in excellent agreement with the value 3.5×10^2 M^{-1} measured[24] for the ion pair formed between $Co(NH_3)_5OS(CH_3)_2^{3+}$ and $Fe(CN)_5OH_2^{3-}$. In contrast, the value of Q_{DP}, 6.7×10^2 M^{-1}, is in poor agreement with the value 2.4×10^1 M^{-1} calculated from eq 9. Moreover, Q_{DP} is *larger* than Q_p, whereas the opposite trend would have been predicted on the basis of simple electrostatic considerations. Perhaps, the increased stability constant of the ion pair $Fe(CN)_5OH_2^{3-}\cdot Co(NH_3)_5Im^{2+}$ may be associated with specific effects such as hydrogen bonding between the oxygen of $Fe(CN)_5OH_2^{3-}$ and the remote imidazolate nitrogen of $Co(NH_3)_5Im^{2+}$.[25] The value 4.9 s^{-1} measured in the present work for eq 7 is in good agreement with the only other value measured for the inner-sphere substitution of the water in $Fe(CN)_5OH_2^{3-}$ within an ion pair, namely, 20 s^{-1} for the formation of the dimethyl sulfoxide bridged binuclear complex from $Fe(CN)_5OH_2^{3-}\cdot Co(NH_3)_5OS(CH_3)_2^{3+}$.[24] The small difference between the rates for the nucleophilic replacements by S and N conforms to the dissociative mechanism demonstrated[16,21] for the substitution of the water in $Fe(CN)_5OH_2^{3-}$.

The rate constants k_{et} for the intramolecular electron reaction of I (eq 2) measured under a variety of conditions are listed in Table II. As required for a true intramolecular transfer process, the value of k_{et} is independent of the initial concentration of I and of excess Co(III). From the temperature dependence of k_{et}, we calculate $\Delta H^* = 19.2 \pm 0.2$ kcal/mol and $\Delta S^* = 2.4 \pm 0.2$ cal/(mol deg).

Rate constants for intramolecular electron transfer in a series of related Ru–Co and Fe–Co binuclear complexes containing a variety of bridging ligands are presented in Table III. Except for the case of bis(4-pyridyl)ethane as a bridge which will be discussed below, the ruthenium complexes react somewhat faster than the iron complexes, the reactivity ratio varying between 5.5 and 36. In trying to understand the difference between ruthenium

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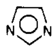
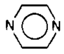
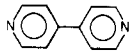
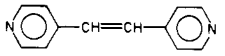
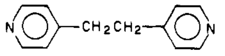
Table III. Comparison of Rate Constants for Intramolecular Electron Transfer in $(NC)_5FeLCo(NH_3)_5$ and $(NH_3)_4(H_2O)RuLCo(NH_3)_5$[a]

L	k_{et} for Fe, s^{-1}	k_{et} for Ru, s^{-1}	R[b]	d,[c] nm
	1.65×10^{-1}	6×10[d]	36	0.60
	5.5×10^{-2}[e]	3×10^{-1}[f]	5.5	0.69
	2.6×10^{-3}[g]	4.4×10^{-2}[h]	17	1.11
	1.4×10^{-3}[i]	1.87×10^{-2}[h]	13	1.32
	2.1×10^{-3}[i]	1.0×10^{-3}[h]	0.48	

[a] At 25 °C and ionic strength of 0.10 M. [b] Ratio of k_{et} for Ru to k_{et} for Fe. [c] Distance between metal ions from ref 38. [d] Reference 9; it is not certain whether water or sulfate is bound to the ruthenium. [e] Reference 33. [f] Unpublished work by S. Isied, quoted in "Tunneling in Biological Systems"; Chance, B., Marcus, R. A., DeVault, D. C., Schrieffer, J. R., Frauenfelder, N., Sutin, N., Eds.; Academic Press: New York, 1979; p 229. [g] Reference 6. [h] Reference 32. [i] Reference 8.

and iron, it must be recognized that the electron-transfer process represented by eq 2 (as well as the corresponding process for ruthenium) is in fact a sequence of at least two elementary steps, eq 10 and 11, each of which can be rate determining.[26] If eq

$$(NC)_5Fe^{II}ImCo^{III}(NH_3)_5^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (NC)_5Fe^{III}ImCo^{II}(NH_3)_5^- \qquad (10)$$

$$(NC)_5Fe^{III}ImCo^{II}(NH_3)_5^- \xrightarrow{k_2} \text{products} \qquad (11)$$

11 is rate determining,[26] then the measured rate constant k_{et} is equal to K_1k_2 ($K_1 \equiv k_1/k_{-1}$). Under these circumstances, the differences in reactivity between Ru and Fe should closely parallel the differences in redox potentials.[26] The differences in the reduction potentials of pentacyanoferrate(III) and pentaammineruthenium(III) couples are 0.12, 0.23, and 0.10 for 4,4′-bipyridine,[27] imidazolate,[28,29] and pyrazine,[16,30] respectively. The calculated reactivity ratios (Ru to Fe) are 1.1×10^2 (4,4′-bipyridine), 7.7×10^3 (imidazolate), and 49 (pyrazine). The observed ratios are 17, 36, and 5.5, respectively, and thus, the previous conclusion[8,26] that dissociation and/or spin change (eq 11) cannot determine the reaction rate is reinforced. If the forward reaction in eq 10 is rate determining, then a half-power dependence of the observed rate constant k_{et} with respect to K_1 would be anticipated on the basis of the Marcus cross-relation applied to inner-sphere reactions. The calculated ratios on this basis[31] (Ru to Fe) are 10, 87, and 7 for 4,4′-bipyridine, imidazolate, and pyrazine, respectively. The good agreement between calculated and observed values strengthens the conclusion[8,26] that k_1 is the value being measured under intramolecular electron-transfer conditions.

For bis(4-pyridyl)ethane, the reactivity ratio of Ru to Fe does not follow the difference in reduction potentials nor the square-root dependence upon K_1, and in fact a reversal in reactivity is observed. It was suggested previously,[8,32] on the basis of rate comparisons within a series of ruthenium or iron complexes, that, with bis(4-pyridyl)ethane as the bridging ligand, outer-sphere electron transfer obtains in a conformation of the binuclear complexes which brings the two metals close to each other. The rate comparisons in Table III reinforce this interpretation. The higher reactivity of Fe vs. Ru for this ligand as compared to the reverse trend for the other ligands is ascribed to the difference in electrical charges of the ruthenium and iron complexes. For the latter, the binuclear complex has 3+ and 3− moieties linked by the flexible bridging ligand, and thus the closed, reactive structure which brings the two oppositely charged metal complexes together is preferred. For Ru, the binuclear complex has 3+ and 2+ moieties, and an open, unreactive conformation is adopted.

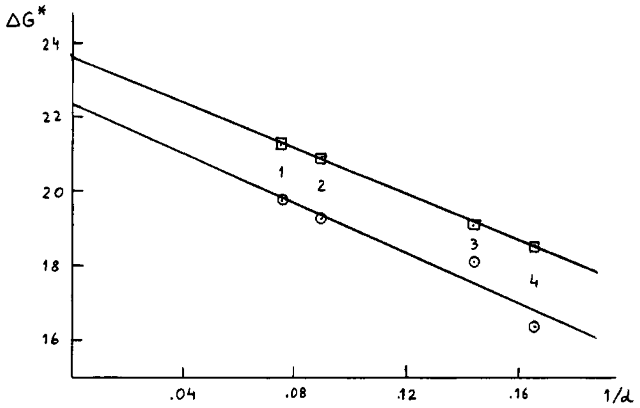


Figure 1. Free energy of activation (in kcal/mol) for intramolecular electron transfer in $(NC)_5FeLCo(NH_3)_5$ (squares) or $(NH_3)_4(OH_2)$-$RuLCo(NH_3)_5^{5+}$ (circles) as a function of the inverse of the distance (in angstroms) between metal ions: (1) *trans*-1,2-bis(4-pyridyl)ethylene; (2) 4,4′-bipyridine; (3) pyrazine; (4) imidazolate. Solid lines are least-squares equations $22.4 - 33.4/d$ (ruthenium) and $23.7 - 30.9/d$ (iron).

It is noteworthy that, although imidazolate is the poorest π-acceptor ligand[29] in Table III, it is the most efficient in promoting electron transfer. This observation is particularly significant because in previous work[7,8,33] it was found that delocalization of t_{2g} electron density from the reductant to the π system of the pyridine ring attached to the oxidant was important in determining relative reactivities. However, it is not known, quantitatively, the extent of delocalization needed for electron transfer, and it may be that even weak coupling[32] is sufficient for efficient electron transfer. If this is the case, then the higher reactivity of the imidazolate-bridged complexes can be ascribed[9,33] to the smaller intermetallic distance as compared to the complexes with other bridges. In fact, a linear dependence of $\Delta G^{\ddagger}$ upon $-1/d$ is found experimentally as displayed in Figure 1 for both iron and ruthenium complexes. A similar $-1/d$ dependence was found previously[34] for optical intervalence transitions in a series of binuclear complexes $(bpy)_2ClRuLRuCl(bpy)_2^{3+}$. Such a $-1/d$ dependence is expected on the basis of the Marcus-Hush theory for both thermal electron transfer and optical intervalence transfer. The pertinent relationship for the Marcus free-energy barrier[35,36] to electron transfer in an outer-sphere reaction is given by eq 12.

$$\Delta G^* = w + \frac{\lambda_i + \lambda_o}{4} + \frac{(\Delta G^\circ + w_p - w)}{2} + \frac{(\Delta G^\circ + w_p - w)^2}{4(\lambda_i + \lambda_o)} \qquad (12)$$

Definitions: w is the work necessary to bring the reactants together; w_p is the corresponding term for the products; ΔG° is the standard free-energy change; λ_i and λ_o are energy terms related to the reorganization of the inner and outer coordination shells of the reactants. Equation 12 reduces to eq 13 for an inner-sphere

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(31) Since the rate constants for self-exchange in $Ru(NH_3)_5py^{3+/2+}$ and $Fe(CN)_5py^{2-/3-}$ couples are essentially identical,[26] the ratio of the rate constants for Ru to Fe is simply the ratio of the square roots of the equilibrium constants.

(32) Fischer, H.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 5512.

(33) Malin, J.; Ryan, D. A.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1978**, *100*, 2097.

(34) Powers, M. J.; Salmon, D. J.; Callahan, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 6731.

(35) The Marcus free-energy barrier and the free energy of activation are related by the expression $\Delta G^* = \Delta G^{\ddagger} + RT \ln (hZ/k_BT)$.

(36) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.

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$$\Delta G^* = \frac{\lambda_i + \lambda_o}{4} + \frac{\Delta G^\circ_r}{2} + \frac{(\Delta G^\circ_r)^2}{4(\lambda_i + \lambda_o)} \qquad (13)$$

reaction where the redox partners are preassembled. ΔG°_r is the standard free energy change for internal electron transfer within the binuclear complex. The solvent reorganization term is given by eq 14,[34] where e is the electronic charge, a_1 and a_2 are the radii

$$\lambda_o = e^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \qquad (14)$$

of the two reactants (assumed to be spherical), r is the distance between the metal ions in the transition state, and D_{op} and D_s are the optical and static dielectric constants of the medium, respectively. If λ_i, ΔG_r°, a_1, and a_2 do not change much along a series of compounds and the third term in eq 13 is small compared to $(\lambda_i/4) + (\Delta G_r^\circ/2)$, then it can be shown that eq 15 should be

$$\Delta G^* = \text{int} - \text{slope}/d \qquad (15)$$

obeyed where slope = 45 kcal if d is expressed in angstroms.[37] The experimental values of the slopes are 33.4 and 30.9 kcal for ruthenium and iron, respectively. For optical electron transfer in $(bpy)_2ClRuLRuCl(bpy)_2^{3+}$, the slope found previously was 27.7 kcal in acetonitrile (theoretical value 43.5 kcal).[38] The disagreement between theory and experiment is not unexpected in view of all the approximations used in deriving eq 15. Undoubtedly, other factors such as changes in the redox potentials of the metal centers and differences in inner-shell reorganization energies as the bridging ligand varies also contribute to the variation in rate. However, when the contributions of these factors are relatively constant for a series of related compounds, then the outer-sphere reorganization terms, although small compared to the inner-sphere terms of cobalt–ammine complexes, appear to determine the relative rate constants of intramolecular electron transfer.

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Studies of the Photochemical Behavior of $Fe_3(CO)_{11}^{2-}$ in Solution

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Abstract: Irradiation (λ = 504 nm) of $Fe_3(CO)_{11}^{2-}$ in the presence of PPh_3 in CH_3CN solution yields $Fe(CO)_4^{2-} + Fe(CO)_3(PPh_3)_2 + CO$. The reaction is inhibited in the presence of excess CO. The mechanism of the photoreaction is proposed to involve loss of CO to give $Fe_3(CO)_{10}^{2-}$; in the presence of PPh_3, $Fe_3(CO)_{10}^{2-}$ reacts to give $2Fe(CO)_3(PPh_3)_2 + Fe(CO)_4^{2-}$. The fact that the primary photoprocess does not involve cluster fragmentation is attributed to the presence of the face-bridging CO ligands in $Fe_3(CO)_{11}^{2-}$, which inhibit geometrical rearrangement of photogenerated diradical species and facilitate metal–metal bond formation. Ultraviolet irradiation ($\lambda \leq 313$ nm) of $Fe_3(CO)_{11}^{2-}$ in 1 M NaOH solutions gives the following reaction: $Fe_3(CO)_{11}^{2-} \rightarrow Fe(CO)_4^{2-} + 2Fe(OH)_2 + 2H_2 + 7CO$. The first step in the mechanism of this photoreaction is not known; one possibility is that the metal cluster fragments directly at these higher excitation energies; alternatively, initial Fe–CO dissociation may precede fragmentation. In either case, it is proposed that photogenerated $Fe(CO)_n$ (n = 3 or 4) fragments are oxidized to $Fe(OH)_2$ in the basic aqueous medium, thereby producing H_2.

Introduction

Ultraviolet irradiation of hydrido transition-metal complexes in solution often leads to hydrogen production.[1] A system of this type that attracted our interest was reported by Hieber and Schubert in 1965.[2]

$$3HFe(CO)_4^- + H_2O \xrightarrow{UV} 2H_2 + Fe_3(CO)_{11}^{2-} + CO + OH^- \qquad (1)$$

It occurred to us that a study of the solution photochemistry of $Fe_3(CO)_{11}^{2-}$ might allow us to find conditions whereby the trinuclear species could be photofragmented to three molecules of $HFe(CO)_4^-$ (for $H_2Fe(CO)_4$, $pK_a(1) = 4.4$; $pK_a(2) = 14$),[3] as in eq 2. The CO_2 and two of the $HFe(CO)_4^-$ ions in eq 3 presumably

$$Fe_3(CO)_{11}^{2-} + 3CO + OH^- + \xrightarrow{h\nu} 3HFe(CO)_4^- + 2CO_2 \qquad (2)$$

would come from the known reaction of $Fe(CO)_5$ with OH^-.[4] Coupling the reactions described by eq 1 and 2 would result in a photochemical water-gas shift cycle (eq 3).

$$H_2O + CO \xrightarrow[Fe_3(CO)_{11}^{2-}]{h\nu} H_2 + CO_2 \qquad (3)$$

With this goal in mind, we began an investigation of the photochemical behavior of $Fe_3(CO)_{11}^{2-}$ in aqueous and nonaqueous solutions. Although we have not achieved the desired cyclic photoprocess (eq 3), we have found that the solution photochemistry of $Fe_3(CO)_{11}^{2-}$ is rich; visible irradiation of the trinuclear species in the presence of PPh_3 gives $Fe(CO)_4^{2-}$ and $Fe(CO)_3(PPh_3)_2$; and H_2, $Fe(CO)_4^{2-}$, $Fe(OH)_2$, and CO are produced by ultraviolet irradiation of the cluster dianion in basic aqueous solution. In this paper we report the characterizations of these and related photoreactions as well as a brief discussion of their probable mechanisms.

Experimental Section

The iron–carbonyl anions decompose when exposed to air. All manipulations were carried out in a nitrogen atmosphere glovebox or on a vacuum line. Solvents were rigorously dried by standard techniques.[5]

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