**Figure 3.** Temperature-dependent ¹H NMR spectra of W(CO)₅(THT) (**2**) in CDCl₃.

Typically, a decrease in $\Delta G^{\ddagger}$ of 10–12 kJ/mol is observed in the conjugated systems. Evidence for $\pi$-conjugation effects are also seen in inversion barriers from examination of phospholes,[29] Chart I. In compounds where the phosphorus lone pair can delocalize

in an aromatic ring, inversion barriers are substantially lower than for other systems. The increase in the barrier to inversion in the saturated ring systems (C and D in Chart I) reflects the disruption of the "aromaticity" of the phospholene ring. In order to probe further the effect of the olefinic bond in **1** and W(CO)₅(2,5-DHT) on the inversion barrier, we undertook a variable-temperature ¹H NMR study (Figure 3) of **2**, W(CO)₅(THT), with the saturated tetrahydrothiophene ligand. The free energy barrier calculated by using eq 6 is 43.9 kJ/mol ($T_c$ = 218 K). Thus, the trend in inversion barriers for **1**, W(CO)₅(2,5-DHT), and **2**, is 48.5, 45.6, and 43.9 kJ/mol, respectively, and can be explained by considering the effect of ring strain. For the series of Pd(II) complexes,

*trans*-PdCl₂[S(CH₂)ₓCH₂]₂, where $x$ = 2, 3, or 4, the barrier to inversion increases with increasing ring strain. The decrease in ring size (i.e., the C–S–C bond angle) presumably constrains access to the planar transition state required for inversion.[20] The ring strain energies for 2,3-DHT, 2,5-DHT, and THT are 18.0, 15.8, and 8.3 kJ/mol,[30] exactly the trend observed for the inversion barriers in the analogous W(CO)₅L complexes. It therefore appears that ring strain is the most important factor determining the rates of inversion in the W(CO)₅L complexes of 2,3-DHT, 2,5-DHT, and THT.

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# Large Positive Activation Volume (+38 cm³ mol⁻¹) for the Intramolecular Electron-Transfer Reaction from Iron(II) to Cobalt(III) in (μ-Pyrazine-*N*,*N′*)(pentaamminecobalt(III))pentacyanoiron(II) in Aqueous Solution

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The title reaction gave an activation volume ($\Delta V^{\ddagger}$) of +38 ± 1 cm³ mol⁻¹ (pH 5.0 (0.015 M phosphate buffer), $I$ = 0.10 M (NaClO₄), 25 °C, 0.1–70 MPa), which is among the largest positive activation volumes ever observed for electron-transfer reactions of metal complexes. While the first-order rate constants differ appreciably on changing added electrolytes (4.9 × 10⁻², 4.1 × 10⁻², and 8.9 × 10⁻² s⁻¹ for 0.1 M NaClO₄, NaCl, and (C₂H₅)₄NClO₄, respectively), $\Delta V^{\ddagger}$, as well as $\Delta H^{\ddagger}$ (ca. 130 kJ mol⁻¹), and $\Delta S^{\ddagger}$ (ca. +165 J K⁻¹ mol⁻¹), is essentially unchanged. The large positive activation volume cannot be accounted for by the sum of the intrinsic volume change (theoretical estimation, <20 cm³ mol⁻¹) and the solvational volume change due to the change in electrostriction (<6.51 cm³ mol⁻¹). The hydrogen-bonding interactions between the ligands and the solvent water molecules may play a significant role in determining the activation volume. The salt effect, which is not great enough to affect the activation parameters, may be explained by the difference in the extent of stabilization between the initial and the transition state.

## Introduction

It is increasingly realized that activation volume ($\Delta V^{\ddagger}$) is one of the most useful tools in elucidating the transition state of electron-transfer reactions of metal complexes in solution.[2-11] It
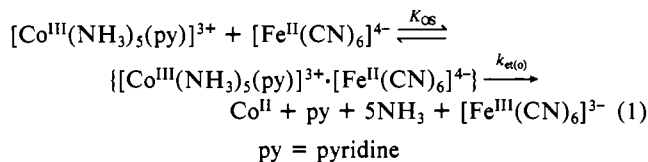
is a measure of the volume difference between the initial and the transition state and involves contributions from both the solvation sphere and the reactants themselves.[12] Outer-sphere electron-transfer reactions proceed through encounter complex formation (formation constant, $K_{OS}$) and net electron-transfer within it (rate

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(2) For references that appeared before 1983, see those cited in ref 3–11.
(3) Tanaka, H. K.; Sasaki, Y.; Saito, K. *Sci. Pap. Inst. Phys. Chem. Res.* (*Jpn.*) **1984**, *78*, 92–96; *Chem. Abstr.* **1985**, *103*, 169703n.
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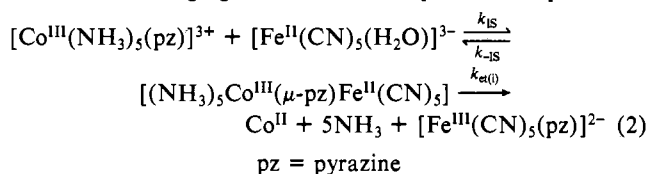
constant, $k_{et(o)}$). Direct information on net electron transfer is preferable to that on the overall reaction for a detailed understanding of the electron-transfer action. Individual observation of the two terms is possible, however, only when $K_{OS}$ is sufficiently large.[13,14] Otherwise only the product $K_{OS}k_{et(o)}$ is measurable.

We have observed $\Delta V^*$ for the net electron-transfer process of reaction 1[15,16] and two other systems[15,17] and concluded that the

$$[Co^{III}(NH_3)_5(py)]^{3+} + [Fe^{II}(CN)_6]^{4-} \xrightarrow{K_{OS}}$$

$$\{[Co^{III}(NH_3)_5(py)]^{3+}\cdot[Fe^{II}(CN)_6]^{4-}\} \xrightarrow{k_{et(o)}}$$
$$Co^{II} + py + 5NH_3 + [Fe^{III}(CN)_6]^{3-} \quad (1)$$

$$py = pyridine$$

intrinsic volume change of reactants contributes significantly to $\Delta V^*$ (either for $k_{et(o)}$ or $K_{OS}k_{et(o)}$) whenever reduction of Co$^{III}$ to Co$^{II}$ is involved.[15]

Inner-sphere electron-transfer reactions usually give second-order rate constants that include the formation constant of an inner-sphere bridging complex. There are several systems, however, that enable direct measurement of first-order rate constants.[18,19] Such systems should provide an important comparison with the outer-sphere electron transfer within the precursor ion pair. Thus we have studied the pressure effect on the intramolecular electron transfer ($k_{et(i)}$) of reaction 2,[16] in which the formation of bridging intermediate is rapid and complete.[18]

$$[Co^{III}(NH_3)_5(pz)]^{3+} + [Fe^{II}(CN)_5(H_2O)]^{3-} \underset{k_{-IS}}{\overset{k_{IS}}{\rightleftharpoons}}$$

$$[(NH_3)_5Co^{III}(\mu\text{-}pz)Fe^{II}(CN)_5] \xrightarrow{k_{et(i)}}$$
$$Co^{II} + 5NH_3 + [Fe^{III}(CN)_5(pz)]^{2-} \quad (2)$$

$$pz = pyrazine$$

## Experimental Section

**1. Preparation of the Complexes. (a) Pentaammine(pyrazine)cobalt(III) Chloride Dihydrate, [Co$^{III}$(NH$_3$)$_5$(pz)]Cl$_3$·2H$_2$O.** This complex was prepared essentially by the method described earlier,[20] from [Co$^{III}$(NH$_3$)$_5$(H$_2$O)](ClO$_4$)$_3$ (5.8 g, 0.01 mol), pyrazine (5 g, 0.06 mol), and dimethylacetamide (DMA) (10 cm$^3$). The pyrazine complex was isolated as the perchlorate salt by adding 60% HClO$_4$ dropwise in an ice bath to the solution of the crude pyrazine complex after the appropriate preparative procedures.[20] The precipitate (ca. 5 g; a mixture of red and orange materials) was filtered off and recrystallized twice from ca. 15 cm$^3$ of DMA by adding 7 M (1 M = 1 mol$^{-1}$ dm$^{-3}$) aqueous NaClO$_4$ solution, and finally from 0.01 M HClO$_4$ (3 cm$^3$/g). The yield of orange crystals was 2.5 g. Anal. Calcd for [Co$^{III}$(NH$_3$)$_5$(pz)](ClO$_4$)$_3$·DMA: C, 15.8; H, 4.63; N, 18.4. Found: C, 15.7; H, 4.85; N, 18.4. The $^1$H NMR spectrum of the perchlorate in D$_2$O shows signals at 2.10, 2.92, 3.08, 8.76 and 9.13 ppm (vs. DSS) with an integrated ratio of 3:3:3:2:2. The first three signals coincide with those of free DMA. The latter two are due to the coordinated pyrazine.

The perchlorate was dissolved in 0.01 M HCl and treated with an SP-Sephadex C-25 cation-exchange column in Na$^+$ form. The orange band was eluted with 1 M HCl. Evaporation of the eluate under reduced pressure gave orange needles of the chloride. The yield was ca. 1 g. Anal. Calcd for [Co$^{III}$(NH$_3$)$_5$(pz)]Cl$_3$·2H$_2$O: C, 13.1; H, 6.32; N, 26.8. Found: C, 13.0; H, 6.75; N, 26.5.

The visible absorption spectrum of the chloride in water shows an absorption peak at 473 nm with $\epsilon$ = 63 M$^{-1}$ cm$^{-1}$, which is exactly

reproduced by the use of the perchlorate, [Co$^{III}$(NH$_3$)$_5$(pz)](ClO$_4$)$_3$·DMA. The previously reported $\epsilon$ value is 53.9 at $\lambda_{max}$ = 473 nm.[18]

**(b) Sodium Amminepentacyanoferrate(II) Trihydrate, Na$_3$[Fe$^{II}$(C-N)$_5$(NH$_3$)]·3H$_2$O.** Commercial crude material was purified as described by Toma and Malin.[21]

**(c) Other Materials.** Commercial anhydrous sodium perchlorate was recrystallized from water and dried at 160 °C under reduced pressure (1 mmHg) for 2 days. (C$_2$H$_5$)$_4$NClO$_4$, NaH$_2$PO$_4$·2H$_2$O, Na$_2$HPO$_4$·12H$_2$O, and potassium hydrogen phthalate were recrystallized from water and dried in vacuo. Sodium chloride (special grade) was used as received.

**2. Kinetic Measurements.** Kinetic runs at ambient pressure were carried out by the use of a Union-Giken RA-401 stopped-flow spectrophotometer. For the measurements at elevated pressures, a FIT 3A high-pressure stopped-flow apparatus[22] from Hikari Koatsu (Hiroshima, Japan) was connected to the above spectrophotometer. A solution of the cobalt complex (chloride), containing the appropriate buffer components and electrolyte, was mixed with a solution of the reductant to start kinetic runs. Both solutions were prepared with deoxygenated water, which was kept at the kinetic temperature in advance. A solution of the iron complex was prepared immediately before use because it tends to degrade slowly (possibly by dimerization).[21] Reaction temperature was carefully controlled because the reaction is very sensitive to temperature, and it was kept within ±0.1 °C. Reaction pressures were monitored by a Toyo Baldwin HT-3500 pressure cell connected with a Unipulse AM10 DC amplifier and are subject to ca. 5% uncertainty.

It was reported that the intramolecular electron transfer ($k_{et(i)}$) is catalyzed by light.[18] Our stopped-flow spectrophotometer has two slits before and after the monochromator. Each slit was adjusted by inserting a slit plate of appropriate width (indicated as 0.35, 0.7, 1.4, 3.5, and 7.0 nm). The rate increased with increase in the slit width but was almost constant within experimental error when each of the slit widths was less than 1.4 nm. All the kinetic runs were carried out by using slit widths less than 1.4 nm. The photosensitivity appears to be lower at lower pH, where most runs were carried out. The effect of light is negligible for the kinetic results reported below.

**3. Other Measurements.** Absorption spectra were recorded on a Hitachi 330 automatic recording spectrophotometer. Rapid-scanning spectrophotometry using an RA-401 spectrophotometer was applied to the measurement of transient absorption spectra during the reaction. A proton NMR spectrum was measured by a Varian T-60 NMR spectrometer. A TOA HM-20 pH meter was used for the pH measurements.

## Results and Discussion

**1. Kinetic Studies at Atmospheric Pressure. (a) Summary of the Previous Study.**[18] The previous study clearly indicated that reaction 2 was observed. The [Fe$^{II}$(CN)$_5$(NH$_3$)]$^{3-}$ ion is aquated immediately on dissolution to give [Fe$^{II}$(CN)$_5$(H$_2$O)]$^{3-}$. When the solutions of the two reactants were mixed, a strong peak appeared at around 630 nm, which was assigned to the formation of the pyrazine bridged binuclear species [(NH$_3$)$_5$Co$^{III}$($\mu$-pz)-Fe$^{II}$(CN)$_5$]. The bimolecular formation rate constant at pH 6.5 and at $I$ = 0.15 M was reported to be 7.03 × 10$^3$ M$^{-1}$ s$^{-1}$ at 25 °C. The absorption peak at 630 nm subsequently disappeared. Since the first-order rate constant for the disappearance was independent of the initial concentrations of the two reactants, it was concluded that the formation of the intermediate was quantitative.

The reaction has been carefully reexamined, since the pyrazine complex used in the previous study was indicated to be contaminated.[18] All the observations described below are qualitatively similar to those reported previously[18] but are appreciably different quantitatively.

**(b) Transient Absorption Spectrum.** The change in the absorption spectrum when the solutions of [Co$^{III}$(NH$_3$)$_5$(pz)]$^{3+}$ and [Fe$^{II}$(CN)$_5$(NH$_3$)]$^{3-}$ were mixed was followed by rapid-scanning spectrophotometry. A strong peak developed at 585 nm, the intensity reaching a maximum 500–700 ms after the mixing ([Co$^{III}$] = 1.0 × 10$^{-3}$ M, [Fe$^{II}$] = 4.0 × 10$^{-5}$ M, $I$ = 0.15 M (NaClO$_4$), pH 6.4 (0.015 M phosphate buffer), 25 °C). This transient absorption peak disappeared subsequently. The $\epsilon$ value at $\lambda_{max}$ = 585 nm for the binuclear intermediate determined at 482–742 ms after the mixing is 16 300 M$^{-1}$ cm$^{-1}$ based on Fe$^{II}$.

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(21) Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1973**, 12, 1039–1045.
(22) A FIT 3A high-pressure stopped-flow apparatus was partly modified from that reported previously: Ishihara, T.; Funahashi, S.; Tanaka, M. *Rev. Sci. Instrum.* **1982**, 53, 1231–1234.

**Table I.** First-Order Rate Constant $(k_{et(i)})$ for the Intramolecular Redox Reaction of $[(NH_3)_5Co^{III}(\mu\text{-pz})Fe^{II}(CN)_5]$ in Aqueous Solution[a]

| temp/°C | $10^3[Co^{III}]$/M | $10^5[Fe^{II}]$/M | pH[b] | [NaClO₄]/M | $10^2 k_{et(i)}$/s⁻¹ | other conditions[c] |
|---|---|---|---|---|---|---|
| 25.0 | 1.0 | 4.0 | 6.4 | 0.15 | 4.04 ± 0.05 | |
|  | 1.0 | 4.0 | 6.0 | 0.15 | 4.51 ± 0.06 | |
|  | 1.0 | 4.0 | 5.5 | 0.15 | 4.77 ± 0.03 | |
|  | 1.0 | 4.0 | 5.1 | 0.15 | 4.91 ± 0.08 | |
|  | 1.0 | 4.0 | 4.9 | 0.15 | 4.95 ± 0.07 | |
|  | 1.0 | 4.0 | 5.1 | 0.15 | 4.92 ± 0.20 | monitored at 640 nm |
|  | 1.0 | 4.0 | 5.1 | 0.15 | 4.84 ± 0.10 | monitored at 660 nm |
|  | 1.0 | 4.0 | 5.1 | 0.10 | 4.74 ± 0.09 | |
|  | 2.0 | 4.0 | 5.0 | 0.10 | 4.63 ± 0.05 | |
|  | 1.0 | 6.3 | 5.1 | 0.10 | 4.85 ± 0.07 | |
|  | 1.0 | 4.0 | 5.2 | 0.10 | 5.03 ± 0.05 | [phosphate] = 0.0075 M |
|  | 1.0 | 4.0 | 5.0 | 0.10 | 4.60 ± 0.07 | [phosphate] = 0.02 M |
|  | 1.0 | 4.0 | 5.0 | 0.038 | 4.89 ± 0.19 | |
|  | 1.0 | 4.0 | 5.1 | 0.113 | 4.59 ± 0.05 | [NaCl] = 0.038 M |
|  | 1.0 | 4.0 | 5.1 | 0.075 | 4.35 ± 0.06 | [NaCl] = 0.078 M |
|  | 1.0 | 4.0 | 5.1 | 0 | 3.85 ± 0.05 | [NaCl] = 0.15 M |
|  | 1.0 | 4.0 | 5.1 | 0.05 | 4.45 ± 0.05 | [NaCl] = 0.05 M |
|  | 1.0 | 4.0 | 5.1 | 0.10 | 4.08 ± 0.06 | [NaCl] = 0.10 M |
|  | 1.0 | 4.0 | 5.1 | 0 | 8.89 ± 0.16 | $[(C_2H_5)_4NClO_4]$ = 0.15 M |
|  | 1.0 | 4.0 | 5.1 | 0.10 | 3.98 ± 0.05 | phthalate buffer |
| 35.0 | 1.0 | 4.0 | 5.1 | 0.10 | 27.8 ± 0.5 | |
| 45.0 | 1.0 | 4.0 | 5.1 | 0.10 | 137 ± 4 | |
| 26.3 | 1.0 | 4.0 | 5.1 | 0 | 5.13 ± 0.10 | |
| 35.1 | 1.0 | 4.0 | 5.1 | 0 | 23.1 ± 0.3 | |
| 40.3 | 1.0 | 4.0 | 5.1 | 0 | 54.8 ± 0.4 | [NaCl] = 0.10 M |
| 44.7 | 1.0 | 4.0 | 5.1 | 0 | 113 ± 2 | |
| 25.0 | 1.0 | 4.0 | 5.1 | 0 | 7.45 ± 0.22 | |
| 25.9 | 1.0 | 4.0 | 5.1 | 0 | 8.60 ± 0.12 | |
| 30.6 | 1.0 | 4.0 | 5.1 | 0 | 19.5 ± 0.05 | |
| 34.7 | 1.0 | 4.0 | 5.1 | 0 | 38.8 ± 1.4 | $[(C_2H_5)_4NClO_4]$ = 0.10 M |
| 39.9 | 1.0 | 4.0 | 5.1 | 0 | 92.8 ± 1.0 | |
| 45.4 | 1.0 | 4.0 | 5.1 | 0 | 221 ± 9 | |

[a] Monitored at 620 nm. [b] Phosphate buffer (0.015 M) was used. [c] $[Cl^-]$ = 3$[Co^{III}]$.

Since the maximum percent yield of the intermediate is calculated to be 96.6% at 713 ms by the use of the formation (7.03 × 10³ $M^{-1}$ $s^{-1}$) and the decay rate constants (4.85 × 10⁻² $s^{-1}$ (vide infra)),[23] the ε value for the intermediate is estimated to be 16 870 $M^{-1}$ $cm^{-1}$. The reported value for this intermediate is ε = 14250 $M^{-1}$ $cm^{-1}$ at $\lambda_{max}$ = 630 ± 20 nm.[18]

**(c) Kinetic Studies of the Intramolecular Electron Transfer.** We have examined only the decay of the intermediate absorption peak due to the intramolecular electron-transfer. The reaction was monitored mostly at 620 nm where the absorption due to other chemical species than the bridged complex can be ignored. First-order plots of ln $D_t$ vs. $t$ ($D_t$ = absorbance at time $t$) gave a straight line over at least 4 half-lives.

First-order rate constants $(k_{et(i)})$ under various conditions are listed in Table I. As expected $k_{et(i)}$ is independent of the initial concentrations of the cobalt and the iron complex. The $k_{et(i)}$ depends, however, on various factors, including pH, buffer component, kind of inert electrolyte, and ionic strength. Such dependences of $k_{et(i)}$ were not noted previously. The intramolecular electron-transfer rate was claimed to be independent of pH (2.45–6.25; phosphate and acetate buffers) and ionic strength[18] on the basis of rather limited kinetic data. Our $k_{et(i)}$ value at pH 6.4 (4.04 × 10⁻² $s^{-1}$) is considerably smaller than the reported value (5.7 × 10⁻² $s^{-1}$).[18] Our values are reasonably reproducible and self-consistent with the set of data in Table I. $k_{et(i)}$ increases with decrease in pH but is almost constant in the pH range 4.9–5.3 at a given buffer concentration. $k_{et(i)}$ decreases with decrease in buffer concentration at a given pH. There is no protonation or deprotonation site in the bridged complex in the given pH range. Thus the pH dependence of $k_{et(i)}$ is more likely due to the change in $HPO_4^{2-}$ concentration rather than [H⁺] (see discussions on the medium effect).

**(d) Temperature Dependence.** Activation parameters $\Delta H^*$ and $\Delta S^*$ were obtained at pH 5.1 with various added electrolytes, NaClO₄, NaCl, or $(C_2H_5)_4NClO_4$ (Table II). Differences in $\Delta H^*$

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**Table II.** Activation Parameters for the Intramolecular Electron Transfer of $[(NH_3)_5Co^{III}(\mu\text{-pz})Fe^{II}(CN)_5]$ in Aqueous Solutions Containing Various Electrolytes

| electrolyte (0.10 M) | $\Delta H^*$/ kJ mol⁻¹ | $\Delta S^*$/ J K⁻¹ mol⁻¹ | $\Delta V^*$/ cm³ mol⁻¹ |
|---|---|---|---|
| NaClO₄ | 135 ± 1 | +167 ± 2 | +38 ± 1 |
| NaCl | 130 ± 2 | +165 ± 5 | +36 ± 1 |
| $(C_2H_5)_4NClO_4$ | 129 ± 1 | +166 ± 2 | +37 ± 1 |

**Table III.** First-Order Rate Constant $(k_{et(i)})$ for the Intramolecular Redox Reaction of $[(NH_3)_5Co^{III}(\mu\text{-pz})Fe^{II}(CN)_5]$ in Aqueous Solution at Various Pressures[a]

| medium (0.10 M) | $p^b$/ MPa | $10^2 k_{et(i)}^c$/s⁻¹ | medium (0.10 M) | $p^b$/ MPa | $10^2 k_{et(i)}^c$/s⁻¹ |
|---|---|---|---|---|---|
| NaClO₄ | 1 | 4.62 ± 0.10 | NaCl | 10.5 | 3.49 ± 0.08 |
|  | 12 | 3.94 ± 0.11 |  | 20 | 2.96 ± 0.07 |
|  | 21 | 3.33 ± 0.05 |  | 30 | 2.55 ± 0.04 |
|  | 32 | 2.83 ± 0.04 |  | 41 | 2.23 ± 0.05 |
|  | 41 | 2.48 ± 0.07 |  | 50.5 | 1.91 ± 0.05 |
|  | 46 | 2.32 ± 0.04 | $(C_2H_5)_4NClO_4$ | 10 | 6.51 ± 0.05 |
|  | 50 | 2.20 ± 0.07 |  | 20 | 5.51 ± 0.06 |
|  | 55 | 2.05 ± 0.15 |  | 30 | 4.78 ± 0.05 |
|  | 66 | 1.73 ± 0.04 |  | 50 | 3.52 ± 0.05 |
|  | 71 | 1.58 ± 0.06 |  |  |  |

[a] Conditions: $[Co^{III}]$ = 1.0 × 10⁻³ M; $[Fe^{II}]$ = 4.0 × 10⁻⁵ M; pH 5.0 (NaClO₄) and 5.1 (NaCl and $(C_2H_5)_4NClO_4$) adjusted with 0.015 M phosphate buffer; 25.0 °C. [b] ±5%. [c] Average of two to six repeated measurements.

and $\Delta S^*$ are small, and it is not possible to conclude which parameters are responsible for the difference in $k_{et(i)}$. The effect of electrolyte is unlikely to have mechanistic significance.

**2. Kinetic Studies at Elevated Pressures.** Conditions for the studies of pressure effect were chosen as follows on the basis of the studies at atmospheric pressure: $[Co^{III}]$ = 1.0 × 10⁻³ M; $[Fe^{II}]$ = 4.0 × 10⁻⁵ M; $I$ = 0.10 M (NaClO₄, NaCl, or $(C_2H_5)_4NClO_4$); pH 5.0–5.1 (0.015 M phosphate buffer); 25.0 °C. Table III lists the first-order rate constants $k_{et(i)}$ at 0.1–71 MPa (values at 0.1 MPa are given in Table I).[24,25] The plots of ln $k_{et(i)}$ vs. $p$ in the

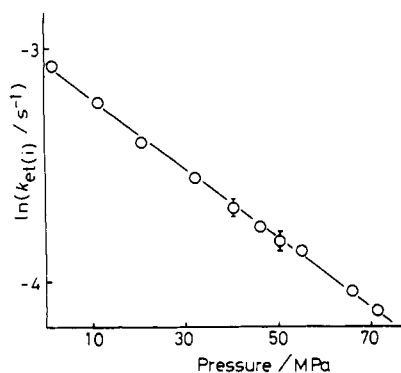**Figure 1.** Dependence of ln $k_{et(i)}$ on pressure for the intramolecular electron transfer of [(NH$_3$)$_5$Co$^{III}$($\mu$-pz)Fe$^{II}$(CN)$_5$] in 0.10 M NaClO$_4$ at 25 °C (pH 5.0; 0.015 M phosphate buffer).
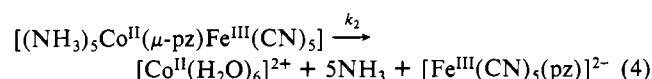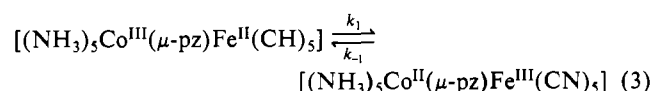
**Table IV.** Activation Volumes of Electron-Transfer Reactions Involving Co$^{III}$ to Co$^{II}$ Reduction

| | $\Delta V^*/$ cm$^3$ mol$^{-1}$ | ref |
|---|---|---|
| (A) Intramolecular Electron-Transfer | | |
| [(NH$_3$)$_5$Co$^{III}$($\mu$-pz)Fe$^{II}$(CN)$_5$] | +38 | this work |
| [Co$^{III}$(NH$_3$)$_5$(SO$_3$)]$^+$ | +34 | 45 |
| [(en)$_2$NH$_3$Co$^{III}$($\mu$-O$_2$$^{(2-)}$)Co$^{III}$NH$_3$(en)$_2$]$^{4+}$$^a$ | +24 | 15 |
| (B) Outer-Sphere Electron Transfer within the Ion Pair | | |
| [Co$^{III}$(NH$_3$)$_5$(H$_2$O)]$^{3+}$ + [Fe$^{II}$(CN)$_6$]$^{4-}$ | +38 | 10 |
| | +26$^b$ | 6 |
| [Co$^{III}$(NH$_3$)$_5$(py)]$^{3+}$ + [Fe$^{II}$(CN)$_6$]$^{4-}$ | +24 | 15 |
| | +30$^b$ | 6 |
| [Co$^{III}$(NH$_3$)$_5$(Me$_2$SO)]$^{3+}$ + [Fe$^{II}$(CN)$_6$]$^{4-}$ | +34$^b$ | 6 |
| [Co$^{III}$(NH$_3$)$_5$Cl]$^{2+}$ + [Fe$^{II}$(CN)$_6$]$^{4-}$ | +26 | 8 |

$^a$ Two other related systems gave similar $\Delta V^*$ values.[15] $^b$ Comments on these values are given in ref 10.

three electrolytes give straight lines (Figure 1), and the $\Delta V^*$ values (Table II) were obtained directly from their slopes. They are essentially constant. The observed activation volume is among the largest positive values ever reported for electron-transfer reactions (Table IV).

**3. Interpretation of the Activation Volume. (a) Rate-Determining Step.** The $k_{et(i)}$ term may be composed of two consecutive steps 3 and 4.[26] The electron-transfer step 3 rather than the

$$[(NH_3)_5Co^{III}(\mu\text{-}pz)Fe^{II}(CH)_5] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$
$$[(NH_3)_5Co^{II}(\mu\text{-}pz)Fe^{III}(CN)_5] \quad (3)$$

$$[(NH_3)_5Co^{II}(\mu\text{-}pz)Fe^{III}(CN)_5] \overset{k_2}{\longrightarrow}$$
$$[Co^{II}(H_2O)_6]^{2+} + 5NH_3 + [Fe^{III}(CN)_5(pz)]^{2-} \quad (4)$$

subsequent decomposition of the successor complex has been concluded to be rate-determining for various intramolecular electron-transfer reactions[14,26–29] including the present reaction 2.[29] Thus, $k_{et(i)}$ is expressed by eq 5. The observed $\Delta V^*$ is thus

$$k_{et(i)} = k_1 \quad (5)$$

considered to represent that of the electron-transfer step.

**(b) Controlling Factors of Activation Volume.** Activation volume ($\Delta V^*$) is considered as a sum of the contribution from intrinsic volume change of the reactant ($\Delta V^*_{int}$) and that from the solvational volume change ($\Delta V^*_{solv}$).

$$\Delta V^* = \Delta V^*_{int} + \Delta V^*_{solv} \quad (6)$$

**(c) Contribution of the Intrinsic Volume Change ($\Delta V^*_{int}$).** The volume difference of the binuclear species before and after the electron transfer (intrinsic part of the reaction volume, $\Delta V^\circ_{int}$) sets the upper limit of $\Delta V^*_{int}$. Since direct determination of $\Delta V^\circ_{int}$ is not possible for the bridged species, we take the hexaamminecobalt and hexacyanoferrate units as models. The Co–N distances for [Co$^{III}$(NH$_3$)$_6$]$^{3+}$ and [Co$^{II}$(NH$_3$)$_6$]$^{2+}$ are 1.96[30,31] and 2.16 Å,[32] respectively. The N–H distance and Co–N–H angle are commonly taken as 0.79 Å and 107.3°, respectively, from the structural data of [Co$^{III}$(NH$_3$)$_6$]$^{3+}$.[30] The van der Waals radius of hydrogen atom is taken as 1.2 Å.[33] Assuming a spherical model, the volume difference between the two complex ions is calculated to be +18.8 cm$^3$ mol$^{-1}$. The Fe–N distance in [Fe$^{II}$(CN)$_6$]$^{4-}$ is reported to be 3.069 Å.[34] The corresponding value for [Fe$^{III}$(CN)$_6$]$^{3-}$ ranges from 3.074 to 0.379 Å.[35] The difference between the distances for the two ions is small, and the calculated volume difference including the van der Waals radius of 1.5 Å for the nitrogen atoms[33] is only 0.8–1.6 cm$^3$ mol$^{-1}$. By the use of two model systems, we can obtain an approximate value for the intrinsic volume change ($\Delta V^\circ_{int}$) in the binuclear species of ca. +20 cm$^3$ mol$^{-1}$, which is the maximum possible value for $\Delta V^*_{int}$. It is clear that the observed activation volume cannot be accounted for by the intrinsic volume change alone. $\Delta V^*_{solv}$ should be at least +18 cm$^3$ mol$^{-1}$.

**(d) Contribution of the Solvational Change ($\Delta V^*_{solv}$) due to Electrostriction.** The solvational change is considered to be the reflection of the change in the extent of electrostriction around the charged reacting species. The charges of the redox centers are mutually cancelled for the bridged species [(NH$_3$)$_5$Co$^{III}$($\mu$-pz)Fe$^{II}$(CN)$_5$]. Nevertheless, the bridged species has a considerable dipole moment with a positive charge at the cobalt(III) side and a negative charge at the iron(II) side. Such a dipole moment would become smaller at the transition state where the cobalt center is less positive and the iron center less negative. The electrostriction of the surrounding solvent molecules would be stronger for the more polar initial state, as compared with the less polar transition state. Thus the transition state would have a less compressed solvation sphere.

The contribution of the change in electrostriction is estimated by the use of the treatment of Hartmann and his co-workers,[36] in which the volume decrease due to electrostriction by dissolving a rigid molecule with dipole moment $\mu$ is expressed by eq 7.[37]

$$\Delta V_{el} = -3\{(N\mu^2/a^3)/(2\epsilon + 1)^2\}(d\epsilon/dp) \quad (7)$$

Here $N$, $a$, and $\epsilon$ are Avogadro's number, the radius of the molecule, and the solvent dielectric constant, respectively. $\{1/(2\epsilon + 1)^2\}d\epsilon/dp$ for water at 25.0 °C and 1 bar is $-1.481 \times 10^{-7}$ bar$^{-1}$.[39] The dipole moment of the present binuclear species is estimated to be 97.3 D by assuming +3 and −3 point charges at the metal centers at a 6.75-Å distance. The $a$ value is estimated to be 6.0 Å as the average of the long and the short distances of the ellipsoidal molecule.[40] The $\Delta V_{el}$ value is calculated to be 11.68

(24) Reaction was not followed at pressures >100 MPa, because it was too slow to obtain stable traces of absorbance change with our apparatus. With a conventional spectrophotometer, the reaction proceeded significantly before the pressure was adjusted to the desired one at >100 MPa.

(25) For the studies under high pressure, concentrations should be expressed more appropriately by the unit mol kg$^{-1}$. In this paper, we indicate concentrations at atmospheric pressure by the unit mol dm$^{-3}$.

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$cm^3 mol^{-1}$. The corresponding value for the species after electron transfer is calculated to be 5.26 $cm^3 mol^{-1}$ by the use of the estimated dipole moment, 65.3 D, with +2 and −2 point charges at a 6.80-Å distance. Thus the calculated volume difference due to electrostriction is 6.42 $cm^3 mol^{-1}$, which set the maximum possible value of $\Delta V^{\ddagger}_{solv}$ due to electrostriction.[40] It is thus concluded that the $\Delta V^{\ddagger}_{solv}$ of at least +18 $cm^3 mol^{-1}$ cannot be accounted for by the change in the extent of electrostriction.

**(e) Alternative Interpretation for the Solvational Volume Change ($\Delta V^{\ddagger}_{solv}$).** Some local interactions between the ligands and the solvent molecules in the first solvation sphere should be considered in order to account for the large solvational volume change of the present system.

The ligands may form hydrogen bonds with the water molecules in the first solvation sphere. The $pK_a$ value of the ligands may be taken as a measure of the potential of forming the hydrogen bond. The $pK_a$ value for the first protonation is much larger for $[Fe^{II}(CN)_6]^{4-}$ than for $[Fe^{III}(CN)_6]^{3-}$.[41,42] Thus the interaction through the hydrogen bond would be much more extensive for the former. The oxidation of $Fe^{II}$ to $Fe^{III}$ would cause a further increase in the volume of the solvation sphere due to the breaking of some hydrogen bonds in addition to the contribution from the decrease in electrostatic interaction. In fact the observed molar volumes of $[Fe^{II}(CN)_6]^{4-}$ and $[Fe^{III}(CN)_6]^{3-}$ are 89.7 and 132.6 $cm^3 mol^{-1}$, respectively, and the difference in the volumes of 42.9 $cm^3 mol^{-1}$ [6] is much larger than the value expected from simple electrostatic consideration (ca. 10 $cm^3 mol^{-1}$)[36] or from the empirical equation (<10 $cm^3 mol^{-1}$)[43] for 4− and 3− ions with almost identical intrinsic volumes. It is possible that the solvation sphere around the $Fe(CN)_5$ moiety in the binuclear complex would expand more than electrostatic considerations predicted on going from $Fe^{II}$ to $Fe^{III}$.

A similar discussion is feasible for the $Co(NH_3)_5$ moiety. The coordinated $NH_3$'s in $[Co^{III}(NH_3)_6]^{3+}$ form distinctive hydrogen bonds with $Cl^-$ in the crystals of $[Co^{III}(NH_3)_6][CdCl_5]$.[30] Since the hydrogen-bond formation would be more extensive for $Co^{III}$ than for $Co^{II}$, the reduction of the $Co^{III}(NH_3)_5$ moiety would possibly cause more solvent release than the electrostatic consideration would predict, although the extent would be less than that from the Fe moiety.

**(f) Conclusion.** The large activation volume ($\Delta V^{\ddagger}$) for $k_{et(i)}$, which can not be explained by the change in the intrinsic volume and the electrostriction, may be accounted for by considering some special interactions between the ligands and the solvent water molecules at the first solvation sphere. The hydrogen-bonding interaction is a possibility, although by no means unequivocal at present.[44]

**(g) Comparison with the $\Delta V^{\ddagger}$ of Other Electron-Transfer Reactions.** The present result is compared with some relevant results in Table IV. The present activation volume is significantly larger than that for the outer-sphere electron-transfer reaction within the ion pair of $[Co^{III}(NH_3)_2(py)]^{3+}$ and $[Fe^{II}(CN)_6]^{4-}$ ($\Delta V^{\ddagger}$ = +24 $cm^3 mol^{-1}$).[15] The difference in $\Delta V^{\ddagger}$ may be accounted for, at least partly, by the difference in the redox potential of $[Fe^{II}(CN)_6]^{4-}$ and $[Fe^{II}(CN)_5(pz)]^{3-}$ (the latter represents the reductant moiety of the bridged binuclear species). The potential for the hexacyano and the pentacyano couples are +0.36[41] and +0.55 $V^{21}$ vs. NHE at 25 °C, respectively. Thus the driving force for the electron transfer is bigger for the outer-sphere electron transfer than for the present intramolecular electron transfer, provided that the redox potentials for the cobalt moieties are not significantly different. This means that the transition state of the intramolecular electron transfer should be closer to the final state than is observed in the outer-sphere reaction. If the volume increases smoothly on going from the initial to the final state through the transition state, the present intramolecular electron transfer requires bigger volume change to reach the transition state.

The difference in the driving forces of the two reactions do not appear to be big enough to account for the difference in $\Delta V^{\ddagger}$, however. Furthermore, the effect of electrostriction would be more significant in the ion pair, since charges are more distinctively separated in the ion pair as compared with the binuclear species. It may be that the possible difference in the solvation state in the first solvation sphere would be important. The $[Co(NH_3)_5(py)]^{3+}$ ion in the outer-sphere electron-transfer reaction has an exposed hydrophobic group, whereas the hydrophobic pyrazine moiety in the binuclear species is hidden inside the molecule. The intramolecular electron-transfer reactions from bridging peroxide to cobalt(III) in the binuclear complexes with surrounding hydrophobic alkylpolyamine ligands give $\Delta V^{\ddagger}$ values of ca. +20 $cm^3 mol^{-1}$,[15] while the outer-sphere redox reaction between $[Fe^{II}(CN)_6]^{4-}$ and $[Co^{III}(NH_3)_5(H_2O)]^{3+}$ with no hydrophobic group attached give $\Delta V^{\ddagger}$ = ca. +38 $cm^3 mol^{-1}$.[10] A fairly large $\Delta V^{\ddagger}$ value (+34 $cm^3 mol^{-1}$) is reported for the redox decomposition of $[Co^{III}(NH_3)_5(SO_3)]^+$, although some mechanistic uncertainties remain in this case.[45] Certainly more systematic studies are required to clarify the role of the first solvation sphere to $\Delta V^{\ddagger}$.

**4. Interpretation of the Medium Effect.**[46] The rate constant at [NaCl] = 0.10 or 0.15 M is nearly 20% smaller than that in $NaClO_4$ at the same concentration. The rate constant is nearly doubled when 0.10 M $NaClO_4$ is replaced by 0.10 M $(C_2H_5)_4N$-$ClO_4$. Thus addition of smaller ions, whether cationic or anionic, seems to cause appreciable decrease in the rate constant. Smaller ions have higher charge densities than bigger ions of the same charge and would cause stronger electrostatic interaction with the bridged dipolar complex. It is expected that electrostatic interaction with surrounding ionic species to increase the stability would be stronger at the initial state than the transition state. Small ions such as $Cl^-$ and $Na^+$ would stabilize both states more than $ClO_4^-$ and $(C_2H_5)_4N^+$, respectively, do, in such a way that the extent of stabilization is bigger for the initial state with higher dipole moment. Therefore the small ions cause a larger energy separation between the initial state and the transition state. The effect is not sufficiently large to cause appreciable change in activation parameters. In fact, a 2-fold difference in rate constant would cause only ca. 3.6 kJ $mol^{-1}$ difference in the $\Delta G^{\ddagger}$ value. The medium effect discussed here is thus minor as compared with the various effects discussed in the previous section.

(40) In the real binuclear molecule, charges should be delocalized on the ligand environment. Thus the dipole moment is likely to be much less than the estimated value. Also, if the *a* value is taken to be bigger than 6.0 Å to be close to the value at longer axis, then the dipole moment is again less than the estimated value. Therefore the change in the extent of electrostriction in the real molecule is highly unlikely to exceed the calculated value.

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(42) It should be noted that the difference in the $pK_a$ value is not only the reflection of the total electronic charge of the complex ions but also of the different electronic state of the coordinated $CN^-$ (strong back-donation in the $Fe^{II}$ complex would make protonation even more favorable).

(43) Kitamura, Y.; van Eldik, R. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 418–422. This paper gives an empirical equation for the neutralization, which may be extended to the estimation of $\Delta V_{el}$ by considering appropriate corrections for the deprotonation and the intrinsic effects.

(44) Cobalt(II) often prefer a coordination number of 5, and one may argue that the electron-transfer process might be accompanied by the loss of one cobalt-bound ammonia molecule to give a positive contribution to $\Delta V^{\ddagger}$. Such a contribution may be important for the complexes with special ligands such as $CN^-$, but would be less likely to be significant in the present case. With ligands such as $NH_3$ and $H_2O$, cobalt(II) is normally hexacoordinated.

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