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Kinetics of Substitution of Hexacyanometalates Trans to the Carbon-Cobalt Bond in Ethylaquobis(dimethylglyoximate)cobalt¹

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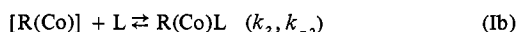
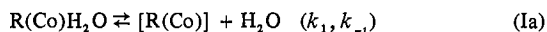
Kinetic and equilibrium measurements, the former based upon stopped-flow determinations, are reported for the formation of a 1:1 adduct between $C_2H_5Co(dmgH)_2H_2O$ and $M(CN)_6^{n-}$ complexes for $M = Fe(II), Co(III), Fe(III),$ and $Cr(III)$. The product in each case corresponds simply to displacement of water, $[C_2H_5Co(dmgH)_2NCM(CN)_6^{n-}]$, except that a slower secondary process was noted for $Cr(CN)_6^{3-}$. The kinetic results are not consistent with a limiting SN_1 mechanism for all four reactions. A mechanism which is applicable to all the reactions involves the prior outer-sphere association of the alkylcobaloxime with $M(CN)_6^{n-}$, followed by rate-determining loss of water.

Introduction

It has been recognized for some time that the ligand trans to a σ -bonded alkyl substituent undergoes substitution at rates considerably higher than the same ligand in similar compounds lacking the M-C bond.²⁻⁹ The compounds which have received the greatest attention to date are monoalkylcobalt complexes of planar, four-coordinate macrocyclic ligands including corrins,^{3,4} bis(dimethylglyoximate) complexes,⁵⁻⁷ and structurally related chelates.^{8,9} A related process is the reaction in noncoordinating solvents of the dimeric $[MeCo(dmgH)_2]_2$ with nucleophiles B, converting the former to 2 $MeCo(dmgH)_2B$.¹⁰

In some cases⁹ the kinetic expressions¹¹ take the form consistent with a limiting SN_1 expression (Scheme I), par-

Scheme I. The Limiting SN_1 Mechanism and Kinetic Equation

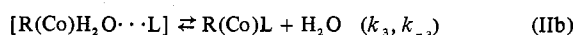
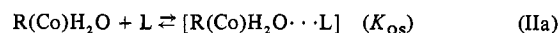


$$k_{obsd} = \frac{(k_1 k_2 / k_{-1})[L] + k_{-2}}{1 + (k_2 / k_{-2})[L]} \quad (Ic)$$

ticularly the saturation of rate with respect to the concentration of incoming ligand. Even in such cases the mechanism cannot be assigned with certainty, and the kinetic data are consistent also with an outer-sphere complexation mecha-

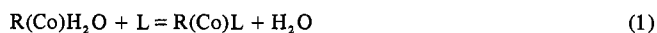
nism (Scheme II). As indicated these have equivalent algebra-

Scheme II. The Outer-Sphere Complexation Mechanism and Kinetic Equation



$$k_{obsd} = \frac{(k_3 + k_{-3})K_{Os}[L] + k_{-3}}{1 + K_{Os}[L]} \quad (IIc)$$

ic forms. In many of the reactions reported in the literature the experimental kinetic data for the equilibrium

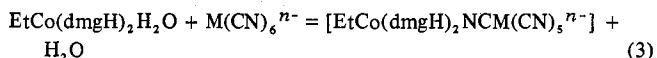


take an even simpler form

$$k_{obsd} = k_f[L] + k_r \quad (2)$$

Comparison of this equation with those given in Schemes I and II indicates that eq 2 may result as a simplified version of either Scheme I (with $1 \gg (k_2/k_{-2})[L]$) or Scheme II (with $1 \gg K_{Os}[L]$). Moreover the simpler expression is consistent also with a "direct" replacement of H_2O by L such as in the SN_2 mechanism. Kinetic determinations in such cases cannot be used to distinguish these mechanisms; comparison among such results, however, may make some mechanistic conclusions possible.

In the present work we report the results of a kinetic study of the association of ethylaquobis(dimethylglyoximate)cobalt(III) with hexacyanometalate anions, namely, $Fe(CN)_6^{3-}$, $Co(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, and $Cr(CN)_6^{3-}$, as in the reaction



A similar reaction was found by George and coworkers¹² to occur between methylcobalamin and the first three of these cyanides. For the cobalamins the bonding to cobalt is through the nitrogen of one cyanide, as shown by spectral shifts similar to those found for other nitrogen donor ligands; it is quite dissimilar, for example, from the effect of coordinating free cyanide ions which occurs at the carbon position.

Experimental Section

Materials. Ethylpyridinecobaloxime¹³ was prepared by the method of Schrauzer¹⁴ and converted to the ethylaquo compound

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(13) Cobaloxime is the trivial name for $Co(dmgH)_2$, bis(dimethylglyoximate)cobalt.

(14) G. N. Schrauzer, *Inorg. Syn.*, **11**, 61 (1968).

(1) Based in part on the M.S. thesis of R. R., Iowa State University, Aug 1973.

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(10) (a) T. L. Brown, L. M. Ludwick, and R. S. Stewart, *J. Amer. Chem. Soc.*, **94**, 834 (1972); (b) L. M. Ludwick and T. L. Brown, *ibid.*, **91**, 5188 (1969).

(11) The kinetic expressions for reversible reactions are most conveniently given for experiments with $[L] \gg [R(Co)H_2O]$ in terms of " k_{obsd} " the pseudo-first-order rate constant for the approach to equilibrium, $-d \ln \{ [R(Co)H_2O] - [R(Co)H_2O]_{eq} \} / dt$, which is the quantity most closely related to the raw experimental data.

by heating it to boiling in dilute acid for 10 min. The preparations as well as subsequent solutions used for equilibrium and kinetic determinations were handled in the dark to avoid photodecomposition.

Potassium ferricyanide was recrystallized twice from water. Potassium chromicyanide was prepared from $\text{Cr}(\text{ClO}_4)_3$ and KCN according to the method of Schaap;¹⁵ $\text{K}_3\text{Cr}(\text{CN})_6$ was purified by recrystallization from water-methanol. Potassium cobalticyanide was prepared from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and excess KCN, boiling these components in the presence of air as described by Benedetti-Pichler.¹⁶ The precipitate of $\text{K}_3\text{Co}(\text{CN})_6$ was recrystallized twice from water. Potassium ferrocyanide was recrystallized before use. In some experiments the sodium salt was used instead; this was prepared by extracting ferrocyanic acid into ether and subsequently forming $\text{Na}_4\text{Fe}(\text{CN})_6$ by adding sodium hydroxide which was precipitated with methanol.¹⁷ Sodium perchlorate was recrystallized twice from water.

Solutions of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ were analyzed spectrophotometrically¹⁸ as $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, converting the cyano complexes by fuming in perchloric acid. Cobalt and chromium in their hexacyano complexes were also converted to $\text{Co}_{\text{aq}}^{2+}$ and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, respectively, by fuming with perchloric acid. They were subsequently analyzed as $\text{Co}(\text{NCS})_2^{2-}$ in 50% acetone (λ 623 nm, ϵ 1843 $M^{-1}\text{cm}^{-1}$)¹⁹ and as CrO_4^{2-} in alkaline peroxide (λ 372 nm, ϵ 4830 $M^{-1}\text{cm}^{-1}$).²⁰

Procedures and Measurements. Solutions of the cobaloxime and of the metal cyanides were prepared fresh each day. Solutions of the potassium salts were converted to the sodium form by passage through a column of Dowex 50W-X8 cation-exchange resin in the sodium form. Not only does this avoid precipitation of potassium perchlorate in the reaction solutions, but it also provides a more constant reaction medium since sodium perchlorate was added to maintain ionic strength at 1.0 M . Most experiments were carried out in neutral, unbuffered water with occasional measurements at pH 4–10 to demonstrate the absence of any effect of pH upon the reaction rates.

Spectral measurements were made using Cary 12 and Cary 14 spectrophotometers with a water-filled thermostated sample compartment in which the quartz sample cells were immersed. Stopped-flow kinetic measurements were made using a Durrum instrument with a Kel-F mixing block and a 20-mm optical path. A Beckman expanded pH meter was used with calibration using solutions of unit ionic strength at pH 4, 7, and 11.

The complexation equilibria are established within the time of mixing and are accompanied by easily measured spectral changes. The equilibrium constants for the various $\text{M}(\text{CN})_6^{n-}$ complexes in eq 3 were determined from the spectral changes accompanying the stopped-flow kinetic determinations. For $\text{Fe}(\text{CN})_6^{4-}$ values of K were also determined from the spectra of equilibrated samples in comparison with the spectra of the unreacted components.

Ethylaquocobaloxime has absorption maxima at λ 450 nm (ϵ $1.49 \times 10^3 M^{-1}\text{cm}^{-1}$) and 390 nm ($1.74 \times 10^3 M^{-1}\text{cm}^{-1}$). The addition of $\text{M}(\text{CN})_6^{3-}$ causes small wavelength shifts and particularly an intensity decrease in the first band and either a smaller increase or decrease in the second. This is illustrated in Figure 1 by the spectra of ethylaquocobaloxime with and without $\text{Cr}(\text{CN})_6^{3-}$ and $\text{Co}(\text{CN})_6^{3-}$. One spectrum is that of $\text{EtCo}(\text{dmgH})_2\text{H}_2\text{O}$ alone, another represents that with $3.6 \times 10^{-3} M$ $\text{Cr}(\text{CN})_6^{3-}$ (which corresponds to ca. 36% conversion to the mixed cyano adduct), and the third contains $3.3 \times 10^{-3} M$ $\text{Co}(\text{CN})_6^{3-}$ (corresponding to ca. 19% conversion).

The equilibrium constant can be determined from the spectral changes so measured by use of the relation

$$\bar{\epsilon} = \epsilon_1 + (\epsilon_0 - \bar{\epsilon})/[L]K \quad (4)$$

in which $\bar{\epsilon}$ is computed from the absorbance (D) according to

$$\bar{\epsilon} = D/b[\text{R}(\text{Co})]_T \quad (5)$$

where b represents the optical path length, $[\text{R}(\text{Co})]_T$ is the sum

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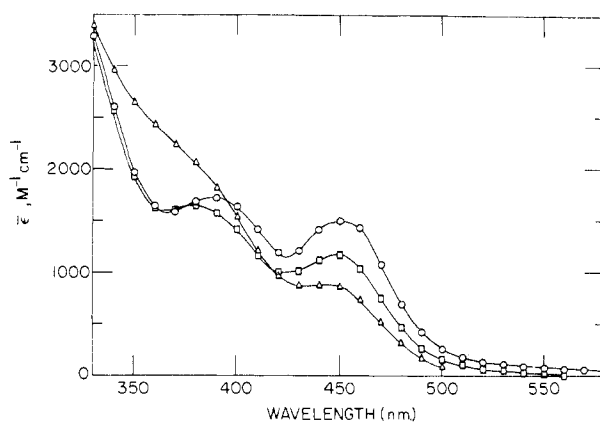


Figure 1. Absorption spectra of $\text{C}_2\text{H}_5\text{Co}(\text{dmgH})_2\text{H}_2\text{O}$ in water (circles), with $3.3 \times 10^{-3} M$ $\text{Co}(\text{CN})_6^{3-}$ (squares), and with $3.6 \times 10^{-3} M$ $\text{Cr}(\text{CN})_6^{3-}$ (triangles).

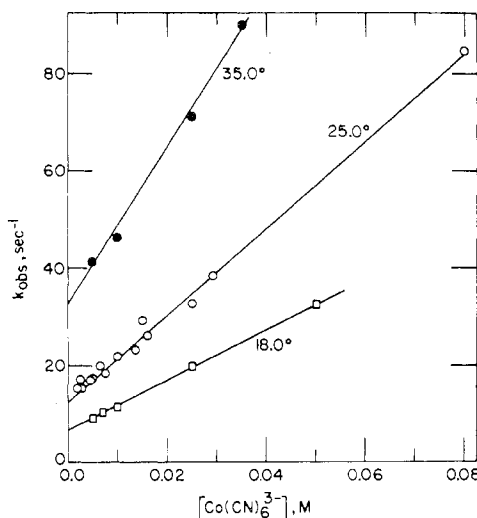


Figure 2. Illustration of the linear dependence of k_{obsd} upon $[\text{Co}(\text{CN})_6^{3-}]$ at each temperature according to eq 7.

$[\text{RCo}(\text{dmgH})_2\text{H}_2\text{O}] + [\text{RCo}(\text{dmgH})_2\text{NCM}(\text{CN})_5^{n-}]$, and ϵ_0 and ϵ_1 are their respective molar absorptivities. The usual measurement made is the absorbance change during the reaction which can be read from the photograph of the oscilloscope trace, although with limited accuracy. In terms of this quantity ($\Delta D = D_{\text{eq}} - D_0$) the relation becomes

$$\frac{\Delta D}{b[\text{R}(\text{Co})]_T} = (\epsilon_0 - \epsilon_1) - \left(\frac{\Delta D}{b[\text{R}(\text{Co})]_T[L]K} \right) \frac{1}{K} \quad (6)$$

Kinetic determinations were carried out with $[\text{L}] \gg [\text{R}(\text{Co})]_T$, such that the kinetic equation is that for opposing pseudo-first-order reactions. A plot of $\log |D_t - D_{\text{eq}}|$ vs. time was constructed for each experiment. These plots were always linear as expected, and from their slopes values of k_{obsd} ¹¹ could be computed directly.

Results

The Reactions of $\text{M}(\text{CN})_6^{3-}$ with $\text{C}_2\text{H}_5\text{Co}(\text{dmgH})_2\text{H}_2\text{O}$. Each of the three reactions were studied with a pseudo-first-order excess of $\text{M}(\text{CN})_6^{3-}$. Typical concentrations of the cobaloxime were $(1-6) \times 10^{-4} M$, with the typical variation of $[\text{M}(\text{CN})_6^{3-}]$ from 0.005 to 0.05 M . At each temperature the apparent first-order rate constant¹¹ k_{obsd} proved to be a linear function of $[\text{L}]$. The data for the three reactions are presented in Figures 2–4 for $\text{Co}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{3-}$, and $\text{Cr}(\text{CN})_6^{3-}$, respectively, in accord with the relation

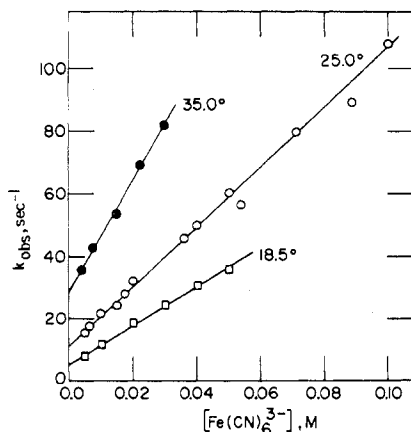
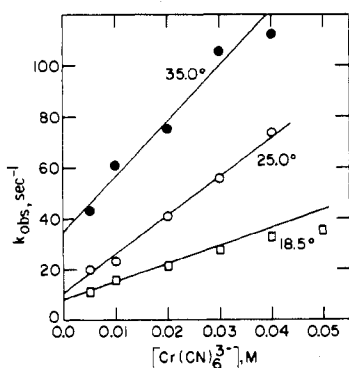
$$k_{\text{obsd}} = k_f[\text{L}] + k_r \quad (7)$$

Table I summarizes the values of k_f and k_r for each of the three reactions at the different temperatures. The variation

Table I. Rate Constants^a for the Reactions of $M(\text{CN})_6^{3-}$ with $\text{C}_2\text{H}_5\text{Co}(\text{dmgH})_2\text{H}_2\text{O}$ in Water at $\mu = 1.0 M$

$M(\text{CN})_6^{3-}$	$k_f, M^{-1} \text{sec}^{-1}$			k_r, sec^{-1}		
	18.5°	25.0°	35.0°	18.5°	25.0°	35.0°
$\text{Co}(\text{CN})_6^{3-}$	522 ± 8	900 ± 15	1510 ± 35	6.6 ± 0.2	12.3 ± 0.4	30.9 ± 0.8
$\text{Fe}(\text{CN})_6^{3-}$	620 ± 16	930 ± 24	1770 ± 52	5.5 ± 0.5	11.9 ± 1.2	28.5 ± 1.0
$\text{Cr}(\text{CN})_6^{3-}$	620 ± 27	1570 ± 70	2010 ± 226	8.9 ± 0.5	9.9 ± 1.7	37.3 ± 5.6

^a The uncertainties represent one standard deviation in the least-squares fit of the data to eq 7.

Figure 3. Plots of k_{obsd} vs. $[\text{Fe}(\text{CN})_6^{3-}]$.Figure 4. Plots of k_{obsd} vs. $[\text{Cr}(\text{CN})_6^{3-}]$.

of rate constants with temperature can best be expressed in terms of an equation which accounts simultaneously for the dependence of k_{obsd} upon $[\text{L}]$ as in eq 7 as well as the variation of k_f and k_r with temperature. This relation is

$$k_{\text{obsd}} = \frac{(RT/Nh)([\text{L}] \exp(-\Delta H_f^\ddagger/RT + \Delta S_f^\ddagger/R) + \exp(-\Delta H_r^\ddagger/RT + \Delta S_r^\ddagger/R))}{K} \quad (8)$$

A nonlinear least-squares fit²¹ of the data to this relation gives the values of the activation parameter for each reaction summarized in Table II.

The reactions of $\text{Co}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{3-}$ did not show a dependence upon pH as illustrated by the data in Table III; this dependence was not examined for $\text{Cr}(\text{CN})_6^{3-}$ although we have no reason to expect any different result.

The equilibrium constant at any temperature can be computed from the quotient k_f/k_r from the data in Table I, or from the relation

$$K = \exp[(\Delta H_r^\ddagger - \Delta H_f^\ddagger)/RT + (\Delta S_f^\ddagger - \Delta S_r^\ddagger)/R] \quad (9)$$

using the activation parameters given in Table II. The overall absorbance changes which were measured for all the kinetic runs can be used to derive an independent value for K via eq 6. The agreement is often reasonable: for $\text{Co}(\text{CN})_6^{3-}$ at

Table II. Activation Parameters for the Reactions of $M(\text{CN})_6^{3-}$ with $\text{C}_2\text{H}_5\text{Co}(\text{dmgH})_2\text{H}_2\text{O}$

	$\text{Co}(\text{CN})_6^{3-}$	$\text{Fe}(\text{CN})_6^{3-}$	$\text{Cr}(\text{CN})_6^{3-}$
$\Delta H_f^\ddagger, \text{kcal mol}^{-1}$	10.5 ± 1.2	10.4 ± 0.8	11.5 ± 1.9
$\Delta S_f^\ddagger, \text{cal mol}^{-1} \text{K}^{-1}$	-9.8 ± 4.1	-10.0 ± 2.6	-6.1 ± 6.3
$\Delta H_r^\ddagger, \text{kcal mol}^{-1}$	16.2 ± 1.0	17.7 ± 0.9	15.3 ± 2.4
$\Delta S_r^\ddagger, \text{cal mol}^{-1} \text{K}^{-1}$	1 ± 3	5 ± 3	-2 ± 8

Table III. Dependence of k_{obsd} (25.0°, $\mu = 1.0 M$) upon pH for the Reactions of $M(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ with $\text{C}_2\text{H}_5\text{Co}(\text{dmgH})_2\text{H}_2\text{O}$

pH	$[\text{Co}(\text{CN})_6^{3-}] = 0.0110 M$	pH	$[\text{Fe}(\text{CN})_6^{3-}] = 0.0300 M$	pH	$[\text{Fe}(\text{CN})_6^{4-}] = 0.0100 M$
	$k_{\text{obsd}}, \text{sec}^{-1}$		$k_{\text{obsd}}, \text{sec}^{-1}$		$k_{\text{obsd}}, \text{sec}^{-1}$
4.4	24.2	3.7	44.7	5.9	1.95
8.0	25.0	6.4	41.7	6.8	1.95
10.3	23.2	11.2	43.5	7.5	1.97
				10.4	1.96

18.0°, $k_f/k_r = 79.3 \pm 3.6 M^{-1}$ compared to $K = 83 \pm 11 M^{-1}$ based on the ΔD measurements and use of eq 6; for $\text{Fe}(\text{CN})_6^{3-}$ at 25.0°, $k_f/k_r = 78 \pm 10 M^{-1}$ compared to $K = 100 \pm 12 M^{-1}$ from eq 6. On the other hand, larger discrepancies were noted, such as for $\text{Cr}(\text{CN})_6^{3-}$ at 25.0°, $k_f/k_r = 160 \pm 34 M^{-1}$ compared to $K = 97 \pm 20 M^{-1}$ from eq 6. The rough agreement of the two determinations appears to substantiate the occurrence of a single, simple equilibrium in accounting for the observations made in the course of this work. The differences between the different determinations of K are probably attributable to the relatively large uncertainties involved. The quantity k_f/k_r has an inherently large uncertainty because it represents the quotient of a slope and intercept of a single line, quantities which show a correlation coefficient of -1.0. On the other hand, the ΔD values needed for application of eq 6 are subject to considerable uncertainty, and values of K determined by this method may show systematic errors as well as sizable random errors, only the latter being reflected in the indicated standard deviations.

For $\text{Co}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{3-}$ the equilibrium shown in eq 3 appears to be the only reaction occurring: the product solutions are stable and their spectra are consistent with only two cobaloxime species. A slower, secondary reaction was noted in the case of $\text{Cr}(\text{CN})_6^{3-}$, occurring roughly 10 times more slowly than the reaction of interest. In view of the much higher rate of loss of CN^- for $\text{Cr}(\text{CN})_6^{3-}$ compared to the others,¹⁵ it could be that the slow reaction corresponds to aquation, with the accompanying formation of $\text{EtCo}(\text{dmgH})_2\text{CN}^-$ and $\text{Cr}(\text{CN})_5(\text{H}_2\text{O})^{2-}$. Another possibility is that the slower process corresponds to the intramolecular isomerization of $[\text{EtCo}(\text{dmgH})_2\text{NCCr}(\text{CN})_5]^{3-}$ to $[\text{EtCo}(\text{dmgH})_2\text{CNCr}(\text{CN})_5]^{3-}$. The nature of this reaction was not resolved.

The Reaction of $\text{Fe}(\text{CN})_6^{4-}$ with $\text{C}_2\text{H}_5(\text{dmgH})_2\text{H}_2\text{O}$. The kinetics of this reaction were studied as a function of concentration ($(1.5-2.6) \times 10^{-4} M$ cobaloxime, 0.005-0.075 M $\text{Fe}(\text{CN})_6^{4-}$), pH (5.9-10.4), and temperature (18.5-35.0°). As in the other reactions the approach to equilibrium followed pseudo-first-order kinetics, k_{obsd} being evaluated from

(21) Based on the program LASL 2367 + Addenda from the Los Alamos Scientific Laboratory.

the slope of a plot of $\log(D - D_\infty)$ vs. time. These values are listed in Table IV. The plot of k_{obsd} vs. $[L]$ was not linear, however, unlike the other reactions as depicted in Figure 5. The direction of curvature suggests that the data may conform to an equation of the form

$$k_{\text{obsd}} = \frac{A[\text{Fe}(\text{CN})_6^{4-}] + B}{1 + C[\text{Fe}(\text{CN})_6^{4-}]} \quad (10)$$

which has the same form as the theoretical expressions for the limiting SN1 mechanism (eq 1c) and the outer-sphere association mechanism (eq 11c).

The values of k_{obsd} at each temperature were fit to eq 10 using a nonlinear least-squares program.²¹ The fit of the data to eq 10 is quite good; the mean deviations between the experimental and calculated rate constants were 1.9, 1.9, and 0.7% at 18.5, 25.0, and 35.0°, respectively. The values of the rate parameters A , B , and C are summarized in Table V. The pH dependence of this reaction is also nil, as shown in Table III.

The value of K for the ferrocyanide reaction was computed at each temperature from the absorbance changes. Values are $24 \pm 3 M^{-1}$ (18.5°), 45 ± 4 (25.0°), and 42 ± 7 (35.0°). Again, these values are semiquantitative at best considering the errors in this measurement. Spectra were determined independently at 25° as a function of $[\text{Fe}(\text{CN})_6^{4-}]$. Application of eq 5 gives the value $K = 28 \pm 3 M^{-1}$ (25.0°).

Interpretation and Discussion

The equilibrium between ethylaquocobaloxime and the cyanometalates corresponds to the formation of a cyano-bridged complex. The spectra of the products exhibit maxima at shorter wavelengths, but are markedly dissimilar from that of $\text{EtCo}(\text{dmgH})_2\text{CN}^-$. Moreover, the equilibrium constant determinations, the form of the kinetic expressions, the rapidity, and the ready reversibility of the reactions all substantiate that the reaction corresponds simply to adduct formation and not, for example, to transfer of cyanide from $\text{M}(\text{CN})_6^{3-}$ to the cobaloxime. The products are analogous to those formed in the reactions of cobalamins.¹²

The Limiting SN1 Mechanism. The algebraic form of the rate law for the $\text{Fe}(\text{CN})_6^{4-}$ reaction in eq 10 is consistent with the expression for the limiting SN1 mechanism given in eq 1c. The parameters are identified as $A = k_1 k_2 / k_{-1}$, $B = k_{-2}$, and $C = k_2 / k_{-1}$. The values at 25.0° are $k_1 = 14.1 \pm 1.0 \text{ sec}^{-1}$, $k_{-2} = 1.00 \pm 0.04 \text{ sec}^{-1}$, and $k_2 / k_{-1} = 6 \pm 3 M^{-1}$. In themselves these values are not unreasonable. Certain complications become apparent, however, if it is assumed all four reactions proceed by this mechanism. The simpler rate expression for the $\text{M}(\text{CN})_6^{3-}$ reactions given by eq 7 is derived from eq 1c under the limiting condition

$$(k_2 / k_{-1})[\text{M}(\text{CN})_6^{3-}] \ll 1 \quad (11)$$

in which case the parameters of eq 2 are $k_f = k_1 k_2 / k_{-1}$ and $k_r = k_{-2}$. According to this mechanism the values of k_1 and k_{-1} are unique to the cobaloxime and are identical for any entering ligand. That being the case the k_1 value found for $\text{Fe}(\text{CN})_6^{4-}$ together with the value of k_f for each $\text{M}(\text{CN})_6^{3-}$ reaction permits the computation of k_2 / k_{-1} for each reaction. At 25.0°, for example, the computed values of k_2 / k_{-1} are 64, 66, and $110 M^{-1}$ for $\text{Co}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{3-}$, and $\text{Cr}(\text{CN})_6^{3-}$, respectively. Clearly these values are inconsistent with the requisite inequality in (11), which was the basis upon which the particular limiting form for these reactions was derived from the general expression of (1c).

This we interpret as indicating that the limiting SN1 mecha-

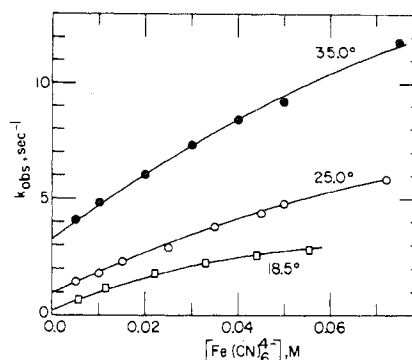


Figure 5. The variation of k_{obsd} with $[\text{Fe}(\text{CN})_6^{4-}]$ does not follow a linear dependence.

Table IV. Values of k_{obsd} for the Reaction of $\text{Fe}(\text{CN})_6^{4-}$ with $\text{C}_2\text{H}_5\text{Co}(\text{dmgH})_2\text{H}_2\text{O}$ at Various Temperatures and $\mu = 1.0 M$

18.5°		25.0°		35.0°	
$[\text{Fe}(\text{CN})_6^{4-}] / M$	$k_{\text{obsd}} / \text{sec}^{-1}$	$[\text{Fe}(\text{CN})_6^{4-}] / M$	$k_{\text{obsd}} / \text{sec}^{-1}$	$[\text{Fe}(\text{CN})_6^{4-}] / M$	$k_{\text{obsd}} / \text{sec}^{-1}$
0.0055	0.65	0.0050	1.45	0.0050	4.12
0.0110	1.15	0.0100	1.77	0.0100	4.77
0.0220	1.73	0.0150	2.31	0.0200	6.02
0.0330	2.20	0.0250	2.90	0.0300	7.34
0.0440	2.63	0.0350	3.78	0.0400	8.42
0.0555	2.86	0.0450	4.39	0.0500	9.24
		0.0500	4.77	0.0700	11.8
		0.0723	5.85		

Table V. Values of the Rate Parameters of Eq 10 for the Reaction of $\text{Fe}(\text{CN})_6^{4-}$ with $\text{C}_2\text{H}_5\text{Co}(\text{dmgH})_2\text{H}_2\text{O}$

$T, ^\circ\text{C}$	$A, M^{-1} \text{sec}^{-1}$	B, sec^{-1}	C, M^{-1}	$A/C, \text{sec}^{-1}$
18.5	115 ± 5	0.10 ± 0.04	22.5 ± 2.5	4.9 ± 1.6
25.0	85 ± 3	1.00 ± 0.04	6.0 ± 3.1	14.1 ± 1.0
35.0	130 ± 3	3.40 ± 0.06	3.7 ± 0.8	34.9 ± 2.3

nism cannot be applicable to all four reactions and hence is most probably applicable to none in that it seems probable though of course not mandatory that the reactions proceed by a common mechanism.

The Outer-Sphere Complexation Mechanism. According to the equations given in Scheme II the parameters of the rate equation for the ferrocyanide reaction, eq 10, are identified as $A = (k_3 + k_{-3})K_{\text{os}}$, $B = k_{-3}$, and $C = K_{\text{os}}$. The limiting form for the other reactions as in eq 7 can be realized *via* the inequality

$$K_{\text{os}}[\text{M}(\text{CN})_6^{3-}] \ll 1 \quad (12)$$

whence $k_f = (k_3 + k_{-3})K_{\text{os}}$ and $k_r = k_{-3}$.

Applying these ideas to $\text{Fe}(\text{CN})_6^{4-}$ the parameters in Table V at 18.5, 25.0, and 35.0°, respectively, are $k_3 = 4.8, 13.1,$ and 31.5 sec^{-1} , $k_{-3} = 0.1, 1.0,$ and 3.4 sec^{-1} , and $K_{\text{os}} = 23, 6,$ and $4 M^{-1}$. The data for the three remaining reactions permit the evaluation only of k_{-3} and of the quantity $(k_3 + k_{-3})K_{\text{os}}$. The applicability of the inequality in (12) gives for all three reactions the limit $K_{\text{os}} < ca. 1 M^{-1}$, considering the range of $\text{M}(\text{CN})_6^{3-}$ concentrations studied. On that basis the values of k_3 , at 25° for example, are $\geq 9 \times 10^2, \geq 9 \times 10^2,$ and $\geq 1.6 \times 10^3 \text{ sec}^{-1}$ for $\text{Co}(\text{CN})_6^{3-}, \text{Fe}(\text{CN})_6^{3-},$ and $\text{Cr}(\text{CN})_6^{3-}$, respectively.

The value of K_{os} for $\text{Fe}(\text{CN})_6^{4-}$ is considerably larger than that for the $\text{M}(\text{CN})_6^{3-}$ ions, which appears reasonable in that the former in view of its greater negative charge might be expected to have a larger binding constant toward the aquo-cobaloxime. A possible mode of such interaction, but not a

unique one, is a hydrogen bond between the coordinated water molecule and the nitrogen of a cyanide.

Likewise the values of k_{-3} appear reasonable in terms of the interchange processes represented by reaction IIb. The approximate constancy of k_{-3} (and of the associated activation parameters) for the three $M(CN)_6^{3-}$ ions is noted in Tables I and II, and these values are *ca.* 10 times larger than that for k_{-3} in the case of $Fe(CN)_6^{4-}$. Similar electrostatic and polarization arguments are applicable.

The approximate constancy for the $M(CN)_6^{3-}$ reactions of the quantity $k_{\ddagger} = (k_3 + k_{-3})K_{os}$ suggests approximately constant values of k_3 for each reaction as well. The very reasonable assumption is made that K_{os} has approximately the same value for each $M(CN)_6^{3-}$ reaction, based on the concept that outer-sphere association should be quite non-specific for reactants of similar charge types, formulas, and structures.

Consequently, as is often the case in octahedral substitutions, the reaction rates are "dissociatively controlled." That is, the transition state for reaction IIb, although it contains $M(CN)_6^{3-}$, reflects primarily cobalt-water bond breaking. That k_3 for $M(CN)_6^{3-}$ should be $> \sim 10k_3$ for $Fe(CN)_6^{4-}$ is possibly explained by the greater difficulty in dissociation of the water molecule which experiences not only the cobalt-oxygen bond but also hydrogen bonding (or other association) to the entering ferrocyanide.

Mechanistic Comparisons. It appears helpful to consider the results and conclusions of the present study in comparison with certain published results on mechanisms assigned to octahedral substitutions. The most pertinent studies relate to alkylcobaloximes^{5,6} and to other alkyl complexes of related macrocyclic ligands,⁹ although note must be taken of the recent study of the anation of $(H_2O)_5RhCl^{2+}$ by Cl^- .²²

These authors consider the mechanisms given in Schemes I and II, which often are indistinguishable, and succeed in rejecting II in this case.

The usual situation for the reactions of alkylaquocobalt complexes is that the value of k_{obsd} is a linear function of the concentration of the entering ligand L, as in the $M(CN)_6^{3-}$ reactions here. That being the case, relatively few unambiguous distinctions can be made on that basis alone. In the fewer instances in which curvature of the plots of k_{obsd} vs. [L] was noted the interpretations have varied. Thus the first study^{9a} of the substitution of the $RCo(dpn)H_2O^{+23}$ by various entering groups in acetone containing 1% water was interpreted in terms of the limiting SN1 mechanism of Scheme I. More recently the Me and Et derivatives of the same compound have been studied in aqueous solution.^{9b} In this case the results clearly are not consistent with this mechanism in that the resulting values of the k_1 parameter of Scheme I vary for the different entering ligands. These authors thus assign their reactions to the outer-sphere complexation process of Scheme II, as we also have done in this instance.

Acknowledgment. We are grateful to Professor G. Gordon and Mr. R. Silverman for helpful discussions.

Registry No. $C_2H_5Co(dmgh)_2H_2O$, 26025-30-9; $Co(CN)_6^{3-}$, 14897-04-2; $Fe(CN)_6^{3-}$, 13408-62-3; $Cr(CN)_6^{3-}$, 14875-14-0; $Fe(CN)_6^{4-}$, 13408-63-4.

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(23) The group R represents various alkyls and aryls, and dpn is the monoanion of 1,3-bis(biacetylmonoximeimine), a planar, tetradentate ligand, similar to $(dmgh)_2$, whose structure is depicted in ref 9a.

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Formation and Properties of Some New σ -Aryl Derivatives of Iridium(I) and Iridium(III)

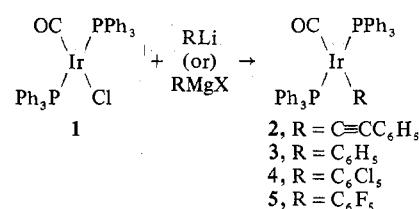
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Several square-planar complexes of the type $Ir(Ar)(CO)(PPh_3)_2$ ($Ar = C_6H_5, C_6F_5, C_6Cl_5$) have been prepared from reactions of $IrCl(CO)(PPh_3)_2$ and appropriate aryllithium reagents or arylmagnesium halides. The σ -pentahaloaryl complexes were found to undergo reversible oxidative addition reactions with hydrogen chloride to form six-coordinate iridium(III) complexes. An attempted exchange reaction of $Ir(\sigma-C_6F_5)(CO)(PPh_3)_2$ and diphenylmethylphosphine has resulted in the formation of σ -pentafluorophenyltris(diphenylmethylphosphine)iridium(I).

Since the first report of the preparation¹ and formulation² of chlorocarbonylbis(triphenylphosphine)iridium(I) (**1**), an enormous amount of interest concerning the properties and reactivities of various halogen and phosphine analogs of (**1**) has been generated.³⁻⁶ It is also now well established that both phosphine and carbonyl ligands tend to facilitate the stabilization of σ -bonded organic derivatives of transition metals.⁷ It is therefore surprising that, up to the present

time, there has been only one report of any organometallic derivatives of these iridium(I) complexes, namely, the formation of σ -phenylethynylcarbonylbis(triphenylphosphine)iridium(I) (**2**).⁸



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