Electron-Transfer Reactions of Pentacyanocobaltate(II) with Various Pentacyanocobaltate(III) Complexes[1]

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Abstract: Various pentacyanocobaltate(III) complexes, $Co^{III}(CN)_5X$ ($X = OH_2, OH^-, Cl^-, Br^-, I^-, N_3^-$, and SCN^-) were found to react with CN^-, in the presence of $Co(CN)_5{}^{3-}$, to form $Co(CN)_6{}^{3-}$ (eq 3). The reactions were found to be catalyzed by $Co(CN)_5{}^{3-}$, the principal contribution to the rate law, in each case, having the form, $k_2[Co^{III}(CN)_5X][Co(CN)_5{}^{3-}]$. Values of k_2, determined at 25° and ionic strength 0.50 M, ranged from 0.86 M^{-1} sec^{-1} for $Co(CN)_5OH_2{}^{2-}$ to 9.8×10^{-3} M^{-1} sec^{-1} for $Co(CN)_5OH^{3-}$. The results are interpreted in terms of an indirect substitution mechanism involving an inner-sphere electron transfer between $Co(CN)_5{}^{3-}$ and $Co^{III}(CN)_5X$ through a bridging cyanide ligand (eq 4–6).

In the course of extending[2] our studies on the oxidation of pentacyanocobaltate(II) by organic halides[3] ($R = CH_3$, etc.) according to the reaction

$$2Co(CN)_5{}^{3-} + RI \longrightarrow Co(CN)_5I^{3-} + Co(CN)_5R^{3-} \qquad (1)$$

we observed that, in the presence of excess $Co(CN)_5{}^{3-}$ and CN^-, the product $Co(CN)_5I^{3-}$ underwent further substitution to yield $Co(CN)_6{}^{3-}$ in accord with eq 2.

$$Co(CN)_5I^{3-} + CN^- \longrightarrow Co(CN)_6{}^{3-} + I^- \qquad (2)$$

This paper describes a kinetic study of this reaction and of the corresponding substitution reactions of other pentacyanocobaltate(III) complexes, *i.e.*

$$Co^{III}(CN)_5X + CN^- \longrightarrow Co(CN)_6{}^{3-} + X \qquad (3)$$

where $X = H_2O, OH^-, Cl^-, Br^-, N_3^-$, and SCN^-. In each case the reaction was found to be catalyzed by $Co(CN)_5{}^{3-}$, a result which is interpreted in terms of an indirect substitution mechanism involving an inner-sphere electron transfer between $Co(CN)_5{}^{3-}$ and $Co^{III}(CN)_5X$ through a bridging cyanide ligand (eq 4–6).

$$\begin{array}{lr}
Co^{III}(CN)_5X + Co(CN)_5{}^{3-} \longrightarrow & \\
\qquad [X(NC)_4\underset{\overset{\curvearrowleft}{e^-}}{Co^{III}\text{—}CN\text{—}Co^{II}(CN)_5}] \longrightarrow & \\
\qquad Co^{II}(CN)_4X + Co(CN)_5(NC)^{3-} \text{ (rate-determining)} & (4) \\
\qquad Co(CN)_5(NC)^{3-} \longrightarrow Co(CN)_6{}^{3-} & (5) \\
\qquad Co^{II}(CN)_4X + CN^- \longrightarrow Co(CN)_5{}^{3-} + X & (6) \\
\hline
\qquad Co^{III}(CN)_5X + CN^- \longrightarrow Co(CN)_6{}^{3-} + X & (3)
\end{array}$$

The reactions described here undoubtedly account, in part at least, for the formation of $Co(CN)_6{}^{3-}$ observed by other workers to accompany the oxidation of $Co(CN)_5{}^{3-}$ by oxidants such as chlorine,[4] oxygen,[5] and water.[6,7]

Experimental Section

Materials. The various pentacyanocobaltate(III) complexes, $Co^{III}(CN)_5X$, were prepared by reaction of cyanide ion with the perchlorate salts of the corresponding pentaamminecobalt(III) complexes.[8] The latter complexes were prepared by published procedures.[9] The sulfito complex, $Na_4Co(CN)_5SO_3 \cdot 2H_2O$, was prepared by the method of Wilmarth.[10] A stock solution of sodium perchlorate, used to maintain ionic strength constant at 0.50 M, was prepared from G. F. Smith sodium perchlorate, which had been recrystallized three times from distilled water. The solution was analyzed by ion-exchange titration. All other materials were of reagent grade. Solutions were prepared with distilled water and were analyzed by accepted procedures.

Kinetic Measurements. The kinetics of these reactions were measured spectrophotometrically, the disappearance of $Co^{III}(CN)_5X$ being followed at a wavelength near its visible absorbance maximum.[11] The measurements were made on a Cary 14 or Beckman DB recording spectrophotometer with a thermostated cell compartment. The reaction vessels were 1.0-cm spectrophotometer cells purged with nitrogen and capped with rubber serum caps.

To minimize hydrolysis, solutions of the cobalt(III) complexes were prepared immediately before use by reaction of the corresponding solid $Co^{III}(NH_3)_5X$ salts with sodium cyanide solution under nitrogen. Reagent solutions, previously purged with purified nitrogen, were transferred to the spectrophotometer cells with a nitrogen-flushed syringe and needle. The last reagent added was Co^{2+}, which rapidly reacts with CN^- to form $Co(CN)_5{}^{3-}$.

Data Treatment. Aqueous solutions of $Co(CN)_5{}^{3-}$ are somewhat unstable,[7] as a result of a pseudo-second-order reaction between $Co(CN)_5{}^{3-}$ and water ($k \sim 3.3 \times 10^{-3}$ M^{-1} sec^{-1})[7] to form $Co(CN)_5H^{3-}$ and $Co(CN)_5OH^{3-}$. To minimize complications due to this, the kinetic data were treated in the following manner. Guggenheim plots[12] of $\ln (A_t - A_{t+\tau})$ *vs.* t (where A is absorbance at the indicated time, and τ is a constant time interval) were made, using two or more values of $\tau \leq$ one half-life. The small values of τ were used to minimize the effect of $Co(CN)_5{}^{3-}$ decay and, in the case of the reaction with mixtures of $Co(CN)_5OH_2{}^{2-}$ and $Co(CN)_5OH^{3-}$, to eliminate nonlinearity which could be introduced by changes in pH at longer times. Half-lives calculated from the Guggenheim plots were independent of the value of τ, and the plots were usually linear for at least two half-lives.

The OH^- concentrations of solutions containing $Co(CN)_5OH^{3-}$, $Co(CN)_5OH_2{}^{2-}$, and CN^- were calculated by successive approximations using the relations

$$K_{Co} = [Co(CN)_5OH^{3-}][H^+][Co(CN)_5OH_2{}^{2-}]^{-1} = 1.6 \times 10^{-10}\ M\ ^{13} \qquad (7)$$

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[1] This research was supported by grants from the National Science Foundation and the Advanced Research Projects Agency.

[2] P. B. Chock and J. Halpern, to be published.

[3] J. Halpern and J. P. Maher, *J. Am. Chem. Soc.*, **86**, 2311 (1964); **87**, 5361 (1965).

[4] A. W. Adamson, *ibid.*, **78**, 4260 (1956).

[5] A. Haim and W. K. Wilmarth, *ibid.*, **83**, 509 (1961).

[6] N. K. King and M. E. Winfield, *ibid.*, **83**, 3366 (1961).

[7] M. G. Burnett, P. J. Connolly, and C. Kemball, *J. Chem. Soc.*, 800 (1967). This paper also notes that the conversion of $Co(CN)_5OH_2{}^{2-}$ and of $Co(CN)_5OH^{3-}$ to $Co(CN)_6{}^{3-}$ is catalyzed by $Co(CN)_5{}^{3-}$.

[8] J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, **85**, 2517 (1963); S. Nakamura, Ph.D. Dissertation, University of Chicago, 1964.

[9] We are grateful to Drs. J. P. Candlin, D. N. Hague, and S. Nakamura for preparation of the pentaamminecobalt(III) complexes. References to the preparations may be found in J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

[10] H. H. Chen, M. S. Tsao, R. W. Gaver, P. H. Tewari, and W. K. Wilmarth, *Inorg. Chem.*, **5**, 1913 (1966).

[11] For the complexes $Co^{III}(CN)_5X$; λ_{max} 380 mμ (ϵ 288 M^{-1} cm^{-1}), $X = H_2O$; 375 (240), OH^-; 388 (220), Cl^-; 395 (200), Br^-; 502 (100), I^-; 383 (685), N_3^-; 378 (195), SCN^-; 310 (195), CN^-.

[12] E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

$$K_{CN} = [CN^-][H^+][HCN]^{-1} = 6.17 \times 10^{-10}\ M\ ^{14} \quad (8)$$

$$K_w = [H^+][OH^-] = 2.0 \times 10^{-14}\ M \quad (\text{in } 0.5\ M\ NaClO_4)^{15} \quad (9)$$

Variation of the values of these equilibrium quotients by factors of 2 to 5 had only a small effect on the OH^- concentration calculated for a typical experiment.

For the reactions of $Co(CN)_5Cl^{3-}$ and $Co(CN)_5I^{3-}$ which obeyed a multiterm rate law, the rate constants were obtained from the least-squares fit of the data to the appropriate rate equation.

Results and Discussion

Stoichiometry. The stoichiometry of the reaction of CN^- with a mixture of $Co(CN)_5OH_2^{2-}$ and $Co(CN)_5OH^{3-}$ complexes in the presence of $Co(CN)_5^{3-}$ was determined quantitatively as follows. Aliquots of the reaction solution were quenched periodically by delivery into 1 *M* $HClO_4$ under nitrogen. A small amount of precipitate, presumably $Co(CN)_2$, was removed by filtration after the quenched solution was diluted quantitatively with 1 *M* $HClO_4$. A blank experiment was made to correct for any absorbance due to products of decomposition of $Co(CN)_5^{3-}$ using the same procedure for a solution containing CN^- and $Co(CN)_5^{3-}$ but no $Co(CN)_5OH_2^{2-}$ or $Co(CN)_5OH^{3-}$.

In each case the visible and near-ultraviolet spectrum of the filtered solution was measured and found to contain two absorption maxima: one at 380 mμ which decreased in intensity with time, and a second at 310 mμ which increased. These wavelengths are characteristic of the absorption maxima of $Co(CN)_5OH_2^{2-}$ and $Co(CN)_6^{3-}$, respectively.[11] Concentrations of these species in each quenched solution were calculated from the measured absorbances (corrected for the blank experiment) at 380 and 310 mμ and the known extinction coefficients at these wavelengths. The results are presented in Table I.

Table I. Stoichiometry of the $Co(CN)_5^{3-}$-Catalyzed Reaction between $Co(CN)_5OH_2^{2-}$ and CN^- [a]

Time, min	$10^3[Co(CN)_5OH_2^{2-}]$, *M*	$10^3[Co(CN)_6^{3-}]$, *M*	$10^3[Co(III)]_{tot}$, *M*
0.0	4.85	. . .	4.85
0.75	4.15	0.73	4.88
2.1	3.60	1.45	5.05
5.0	2.89	1.97	4.86
10.0	2.16	2.40	4.56
20.0	1.65	3.10	4.75
60.0	1.17	4.00	5.17
			Av = 4.88 ± 0.16

[a] Reaction solution contained initially 0.05 *M* $Co(CN)_5OH_2^{2-}$, 0.02 *M* $Co(CN)_5^{3-}$, 0.4 *M* CN^-, and 2.7×10^{-3} *M* OH^-. Concentrations listed in the table were determined after quenching and tenfold dilution with 1 *M* $HClO_4$.

The constancy of the sum of the concentrations of $Co(CN)_5OH_2^{2-}$ and $Co(CN)_6^{3-}$ confirms that the stoichiometry of the reaction is given by

$$Co(CN)_5OH_2^{2-} + CN^- \longrightarrow Co(CN)_6^{3-} + H_2O \quad (10)$$

For the other $Co^{III}(CN)_5X$ complexes ($X = Cl^-$, Br^-, I^-, N_3^-, and SCN^-), the spectral changes accompanying the formation of $Co(CN)_6^{3-}$ are not quite so favorable (because of excessive interference of $Co^{III}(CN)_5X$ with the estimation of $Co(CN)_6^{3-}$), and the stoichiometries of the reactions of these complexes were not established quantitatively. However, qualitatively, it was confirmed in each case that the absorbance at the long wavelength maximum of the $Co^{III}(CN)_5X$ complex decreased during the reaction while the absorbance in the region of 310 mμ (corresponding to the absorbance maximum of $Co(CN)_6^{3-}$) increased. These absorbance changes, and the rates of change, were much larger than those observed for hydrolysis of the $Co^{III}(CN)_5X$ complex. These observations are consistent with the formation of $Co(CN)_6^{3-}$ according to eq 3.

Kinetics. Kinetic measurements were made at 25° over the following initial concentration ranges, the ionic strength being maintained at 0.50 *M* with $NaClO_4$: 0.0007–0.008 *M* $Co^{III}(CN)_5X$, 0.002–0.3 *M* $Co(CN)_5^{3-}$, 0.008–0.40 *M* excess CN^-, and 0.002–0.05 *M* OH^-.

Except for the reactions of $Co(CN)_5Cl^{3-}$ and $Co(CN)_5I^{3-}$ (for which, as explained below, the rate law apparently contained an additional minor $Co(CN)_5^{3-}$-independent term), the kinetics of the observed absorbance changes were adequately described by the rate law

$$-d \ln (A_t - A_{t+\tau})/dt = -d \ln [Co^{III}(CN)_5X]/dt = k_{obsd} \quad (11)$$

where

$$k_{obsd} = k_2[Co(CN)_5^{3-}] \quad (12)$$

Since $Co(CN)_5^{3-}$ functions only as a catalyst and is not consumed in the reaction, each experiment exhibited pseudo-first-order kinetic behavior (eq 11). Values of k_{obsd}, determined from the Guggenheim plots as described earlier, are listed in Table II and the values of k_2 derived from them, in Table III.

The reproducibility of the measurements is reflected in the duplicate values of k_{obsd} listed in Tables II and IV. This reproducibility was generally in the range ±10%, except in a few experiments, notably those at low $Co(CN)_5^{3-}$ concentrations where complications due to decomposition of $Co(CN)_5^{3-}$ during the long reaction periods involved were more severe.

For $Co(CN)_5Cl^{3-}$ and $Co(CN)_5I^{3-}$, but not for the other complexes, the fit of the data could be significantly improved by the addition of a further $Co(CN)_5^{3-}$-independent term, k_1, to the rate law, *i.e.*

$$k_{obsd} = k_1 + k_2[Co(CN)_5^{3-}] \quad (13)$$

where $k_1 = (8.4 \pm 1.9) \times 10^{-5}\ sec^{-1}$ for $Co(CN)_5Cl^{3-}$ and $(1.45 \pm 0.86) \times 10^{-4}\ sec^{-1}$ for $Co(CN)_5I^{3-}$. Even for these complexes, the contributions from the path involving k_1 was a minor one except at very low $Co(CN)_5^{3-}$ concentrations, and it cannot be asserted with certainty that this contribution arises from the same over-all reaction (*i.e.*, conversion of $Co^{III}(CN)_5X$ to $Co(CN)_6^{3-}$), rather than from a secondary reaction such as hydrolysis to $Co(CN)_5OH_2^{3-}$ (see below). The instability of $Co(CN)_5^{3-}$ over the very long periods required to study the reactions at low $Co(CN)_5^{3-}$ concentrations makes it difficult to elucidate the nature of these reactions in greater detail.

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(14) R. M. Izatt, J. J. Christensen, R. T. Pack, and R. Bench, *ibid.*, **1**, 828 (1962).

(15) G. Lagerström, *Acta Chem. Scand.*, **13**, 722 (1959).

Table II. Kinetic Data for the Reaction $Co^{III}(CN)_5X$ + $CN^- \longrightarrow Co(CN)_6^{3-}$ + X at 25°, Ionic Strength 0.50 *M*[a]

X	$[Co(CN)_5^{3-}]$, *M*	$10^3[Co(CN)_5X^{3-}]$,[b] *M*	Excess $[CN^-]$,[b] *M*	10^4k, sec^{-1} Obsd	10^4k, sec^{-1} Calcd[d]
Cl^-	0.0020	5.27	0.453	1.94	1.8[e]
	0.0050	3.12	0.00833	3.14	3.3[e]
	0.0050	2.73	0.438	3.25	3.3[e]
	0.0100	5.75	0.0100	5.83	5.8[e]
	0.0100	7.22	0.377	6.11	5.8[e]
	0.0100	3.41	0.400	5.61	5.8[e]
	0.0100	3.32	0.400	5.72[c]	5.8[e]
	0.0200	3.90	0.0100	11.1	10.8[e]
	0.0200	4.19	0.100	11.0	10.8[e]
	0.0200	4.39	0.313	10.8	10.8[e]
	0.0300	2.44	0.0100	15.0	15.8[e]
	0.0300	2.54	0.243	16.3	15.8[e]
Br^-	0.0020	3.23	0.0739	1.05	1.3
	0.0050	2.29	0.0136	3.12	3.2
	0.0100	3.39	0.00972	7.40	6.5
	0.0200	2.05	0.00975	13.4	12.9
	0.0200	3.55	0.0989	13.9	12.9
	0.0200	2.37	0.322	13.9	12.9
	0.0300	2.84	0.0491	17.5	19.4
I^-	0.0020	4.82	0.446	1.86	2.3[f]
	0.0050	4.33	0.0100	4.62	3.6[f]
	0.0100	7.95	0.0103	4.62	5.6[f]
	0.0100	2.77	0.400	6.08	5.6[f]
	0.0200	4.33	0.0117	11.3	9.8[f]
	0.0200	5.39	0.296	8.08	9.8[f]
	0.0300	4.11	0.226	14.3	14.0[f]
N_3^-	0.0050	1.64	0.0101	0.88	1.4
	0.0100	1.30	0.0102	3.21	2.7
	0.0100	0.87	0.412	2.75	2.7
	0.0200	0.69	0.0999	5.66	5.5
	0.0300	1.13	0.251	9.79	8.2
SCN^-	0.0100	1.99	0.0101	4.31	5.0
	0.0100	3.82	0.0109	4.75	5.0
	0.0100	2.41	0.401	3.85	5.0
	0.0200	4.65	0.0101	9.47	10.0
	0.0200	3.08	0.315	12.8	10.0
	0.0300	2.24	0.00880	17.8	15.0

[a] $[OH^-]$ = 0.0035–0.0049 *M* in most experiments. [b] Initial concentrations. [c] $[OH^-]$ = 0.0473 *M*. [d] Unless otherwise indicated, computed from eq 12 using the values of k_2 in Table III. [e] Computed from eq 13 using $k_1 = 8.4 \times 10^{-5}$ sec^{-1}. [f] Computed from eq 13 using $k_1 = 1.45 \times 10^{-4}$ sec^{-1}.

Table III. Summary of Rate Constants[a]

X	k_2, M^{-1} sec^{-1}	k_3, M^{-2} sec^{-1}
H_2O	$(8.63 \pm 0.46) \times 10^{-1}$ [b]	
OH^-	$(9.8 \pm 1.5) \times 10^{-3}$ [b]	
Cl^-	$(4.98 \pm 0.11) \times 10^{-2}$ [c]	$<2 \times 10^{-3}$
Br^-	$(6.47 \pm 0.60) \times 10^{-2}$ [d]	$<3 \times 10^{-3}$
I^-	$(4.20 \pm 0.52) \times 10^{-2}$ [c]	$<2 \times 10^{-2}$
N_3^-	$(2.74 \pm 0.48) \times 10^{-2}$ [d]	$<6 \times 10^{-3}$
SCN^-	$(5.00 \pm 0.78) \times 10^{-2}$ [d]	$<8 \times 10^{-3}$
CN^-	$<1 \times 10^{-5}$	
SO_3^{2-}	$<9 \times 10^{-4}$	

[a] At 25°, ionic strength 0.50 *M*. [b] From least-squares fit of data to eq 17. [c] From least-squares fit of data to eq 13, yielding $k_1 = (8.4 \pm 1.9) \times 10^{-5}$ sec^{-1} for $Co(CN)_5Cl^{3-}$ and $(1.45 \pm 0.86) \times 10^{-4}$ sec^{-1} for $Co(CN)_5I^{3-}$. [d] From least-squares fit of data to eq 12.

Table IV. Kinetic Data for the Reactions of $Co(CN)_5OH_2^{2-}$ and $Co(CN)_5OH^{3-}$ at 25°, Ionic Strength 0.50 *M*

$[Co(CN)_5^{3-}]$, *M*	$10^3[Co(CN)_5OH_2^{2-}]_{tot}$,[a] *M*	Excess $[CN^-]$,[a] *M*	$[OH^-]$,[a] *M*	10^4k, sec^{-1} Obsd	10^4k, sec^{-1} Calcd[b]
0.0020	2.00	0.0198	0.00312	0.638	0.85
0.0020	2.00	0.0199	0.00989	0.340	0.38
0.0050	2.50	0.0276	0.00435	1.39	1.7
0.0050	2.50	0.403	0.00493	1.05	1.5
0.0050	2.50	0.405	0.0108	1.28	1.0
0.0050	2.50	0.406	0.0247	0.77	0.71
0.0050	2.50	0.406	0.0494	0.55	0.60
0.0100	5.00	0.00805	0.000943	13.3	12.4
0.0100	5.00	0.371	0.00321	3.30	4.3
0.0100	5.00	0.00827	0.00435	3.73	3.5
0.0100	5.00	0.0976	0.00477	3.30	3.2
0.0100	5.00	0.373	0.00608	2.67	2.7
0.0100	5.00	0.374	0.0119	1.70	2.0
0.0100	5.00	0.374	0.0187	2.20, 2.27	1.6
0.0100	2.50	0.395	0.00468	3.12	3.2
0.0100	1.00	0.410	0.00579	2.51	2.8
0.0200	2.50	0.0271	0.00199	12.3	12.8
0.0200	2.50	0.152	0.00312	10.5	8.9
0.0200	2.50	0.316	0.00401	6.79	7.3
0.0200	2.50	0.0274	0.00759	4.12	4.8
0.0200	2.50	0.154	0.00761	3.90	4.8
0.0200	2.50	0.0506	0.00781	4.17, 5.78	4.7
0.0200	2.50	0.317	0.00880	4.83	4.4
0.0200	2.50	0.154	0.0176	3.44	3.2
0.0200	2.50	0.0507	0.0177	4.87, 3.98	3.2
0.0200	2.50	0.317	0.0182	4.62	3.1

[a] Initial concentrations. [b] Computed from eq 17.

The reaction of $Co(CN)_5OH_2^{2-}$ was complicated by the hydrolysis equilibrium

$$Co(CN)_5OH_2^{2-} + OH^- \rightleftarrows Co(CN)_5OH^{3-} + H_2O \quad (14)$$

Assuming that $Co(CN)_5OH_2^{2-}$ and $Co(CN)_5OH^{3-}$ each reacts to form $Co(CN)_6^{3-}$ according to the simple second-order rate law described by eq 12, the over-all rate law becomes

$$-d[Co(CN)_5OH_2^{2-}]_{tot}/dt = (k_{OH_2}[Co(CN)_5OH_2^{2-}] + k_{OH}[Co(CN)_5OH^{3-}])[Co(CN)_5^{3-}] \quad (15)$$

$$-d[Co(CN)_5OH_2^{2-}]_{tot}/dt = \left(\frac{k_{OH_2} + k_{OH}K_b[OH^-]}{1 + K_b[OH^-]}\right)[Co(CN)_5OH_2^{2-}]_{tot}[Co(CN)_5^{3-}] \quad (16)$$

Hence

$$k_{obsd} = -d \ln [Co(CN)_5OH_2]_{tot}/dt = \left(\frac{k_{OH_2} + k_{OH}K_b[OH^-]}{1 + K_b[OH^-]}\right)[Co(CN)_5^{3-}] \quad (17)$$

where $[Co(CN)_5OH_2^{2-}]_{tot} = [Co(CN)_5OH_2^{2-}] + [Co(CN)_5OH^{3-}]$, K_b is the base constant of $Co(CN)_5OH_2^{2-}$ (8×10^3 M^{-1}),[13,15] and k_{OH_2} and k_{OH} are the values of the rate constant k_2 for $Co(CN)_5OH_2^{2-}$ and $Co(CN)_5OH^{3-}$, respectively.

The values of k_{obsd}, determined for various concentions of $Co(CN)_5OH_2^{2-}$, $Co(CN)_5^{3-}$, CN^-, and OH^-, are listed in Table IV. When fitted to eq 17, they exhibited appreciable scatter (reflected in the comparison of k_{obsd} and k_{calcd} in Table IV), within limits consistent with the experimental accuracy, but no systematic departure from eq 17 was apparent despite the 10-fold variation in the $Co(CN)_5^{3-}$ concentration, 40-fold variation in the CN^- concentration, and 50-fold variation in the OH^- concentration spanned by the data. A least-squares fit yielded the values (listed as k_2 in Table III) $k_{OH_2} = 0.863 \pm 0.046$ and $k_{OH} = (9.8 \pm 1.5) \times 10^{-3}$ M^{-1} sec^{-1}.

In addition to the complexes for which kinetic data have been presented above, some experiments were also performed on $Co(CN)_5SO_3^{4-}$ and $Co(CN)_5NO_2^{3-}$. With $Co(CN)_5SO_3^{4-}$, a negligible absorbance change (less than 5% of that expected for complete conversion to $Co(CN)_6^{3-}$) was observed in 80 min, in the presence of 0.01 M $Co(CN)_5^{3-}$ and excess CN^-, permitting only an upper limit to be placed upon k_2 (Table III). Under the same conditions $Co(CN)_5NO_2^{3-}$ also exhibited only a small absorbance decrease (at 345 mμ, a shoulder in the spectrum of $Co(CN)_5NO_2^{3-}$), much smaller (<20%) in fact than that expected simply due to hydrolysis under the same conditions. The rate of this absorbance change was apparently independent of the $Co(CN)_5^{3-}$ concentration and unrelated to the $Co(CN)_5^{3-}$-catalyzed formation of $Co(CN)_6^{3-}$ observed for the other complexes.

Mechanism. The predominant reaction path for the formation of $Co(CN)_6^{3-}$ from each of the $Co^{III}(CN)_5X$ complexes obeys a second-order rate law, $k_2[Co^{III}(CN)_5X][Co(CN)_5^{3-}]$, where k_2 is independent of the excess CN^- concentration and of the OH^- concentration (provided that account is taken of the pH dependence of the $Co(CN)_5OH_2^{2-}$ hydrolysis equilibrium and of the different reactivities of $Co(CN)_5OH_2^{2-}$ and $Co(CN)_5OH^{3-}$).

This kinetic behavior is most plausibly accounted for in terms of the mechanism depicted by eq 4–6, involving inner-sphere electron transfer between $Co(CN)_5^{3-}$ and $Co^{III}(CN)_5X$ through a bridging CN^- ligand with accompanying transfer of the latter. This mechanism is analogous to the mechanisms that have previously been proposed for several other catalyzed substitution reactions which are also believed to proceed through electron-transfer paths, *e.g.*, $Co^{III}(NH_3)_5X + 5CN^- \rightarrow Co^{III}(CN)_5X + 5NH_3$, catalyzed by $Co(CN)_5^{3-}$;[8] $Cr^{III}(NH_3)_5X + 5H_2O \rightarrow Cr^{III}(OH_2)_5X + 5NH_3$, catalyzed by $Cr^{2+}{}_{aq}$;[16] $Fe(OH_2)_5Cl^{2+} + H_2O \rightarrow Fe(OH_2)_6^{3+} + Cl^-$, catalyzed by $Fe_{aq}{}^{2+}$;[17] $Cr^{III}(OH_2)_5X + H_2O \rightarrow Cr(OH_2)_6^{3+} + X$, catalyzed by $Cr_{aq}{}^{2+}$.[18]

The isocyano intermediate, $Co(CN)_5(NC)^{3-}$ (eq 4 and 5), is postulated by analogy with other inner-sphere electron-transfer reactions[19,20] in which transfer of a bridging cyanide ligand has been shown to yield an isocyano complex which subsequently rearranges to the more stable cyano isomer. One such reaction, namely that between $Co(CN)_5^{3-}$ and $Co(NH_3)_5CN^{2+}$, actually leads to the same intermediate as postulated here, $Co(CN)_5(NC)^{3-}$, which has been detected spectrophotometrically and shown to rearrange to $Co(CN)_6^{3-}$ (eq 6) with a half-life of 1.6 sec.[19]

In addition to the values of k_2 determined in these studies, an upper limit may also be deduced for the value of k_2 for the corresponding electron-transfer reaction between $Co(CN)_5^{3-}$ and $Co(CN)_6^{3-}$ (*i.e.*, X = CN^-) from measurements by Adamson[21] on the isotopic exchange between $Co(CN)_6^{3-}$ and labeled CN^- in the presence of $Co(CN)_5^{3-}$. From the observation that less than 10% exchange of $Co(CN)_6^{3-}$ with labeled CN^- occurred in 100 hr at 25°, in a solution containing 0.01 M $Co(CN)_5^{3-}$ and 0.0207 M $Co(CN)_6^{3-}$, an upper limit of 1×10^{-5} M^{-1} sec^{-1} (recorded in Table III) can be deduced for the rate constant (k_2) of the reaction

$$Co(CN)_6^{3-} + Co(^*CN)_5^{3-} \longrightarrow [(NC)_5\underset{\curvearrowleft\ e^-}{Co^{III}—CN—Co^{II}}(^*CN)_5] \longrightarrow Co(^*CN)_5CN^{3-} + Co(CN)_5^{3-} \quad (18)$$

The results reported in this paper, including the last result, are of interest in that they depict the variation in rate of a series of related inner-sphere electron-transfer reactions between $Co(CN)_5^{3-}$ and $Co^{III}(CN)_5X$, differing only in the identity of one of the nonbridging ligands, X. The sequence found for the dependence of the rate on X is $H_2O \gg Br^- > SCN^- \sim Cl^- > N_3^- > OH^- \gg SO_3^{2-}, CN^-$. With the exception of X = CN^-, for which the rate is appreciably lower than for the other complexes of the same charge type, the major differences in rate appear to reflect the variation in the charge of the complex. Thus, apart from CN^-, the variation in rate among complexes of the same charge type (X = Br^-, Cl^-, I^-, OH^-, etc.) is remarkably small, encompassing only a sevenfold range. This is much smaller, for example, than has been found[18] for the Cr^{2+}-catalyzed aquations of $Cr^{III}(H_2O)_5X$ complexes, which probably proceed by electron transfer through an OH^--bridged intermediate, *i.e.*, $[X(H_2O)_4Cr^{III}\text{-}OH\text{-}Cr^{II}(OH_2)_5]$, and which follow the rate sequence X = $I^- > Br^- > Cl^- > CN^-$, the decrease in rate in going from X = I^- to X = Cl^- being about 100-fold. The sequence of rates in the latter case corresponds to the sequence of increasing ligand field strengths and, presumably, decreasing thermodynamic driving force for the transformation of $Cr^{III}(OH_2)_5X$ to $Cr(OH_2)_6^{3+}$. The much smaller differences between the rates of reaction of $Co(CN)_5^{3-}$ with $Co(CN)_5Cl^{3-}$, $Co(CN)_5Br^{3-}$, and $Co(CN)_5I^{3-}$ may well reflect the transition from class A to class B character[22] of the metal ion in going from $Cr^{III}(OH_2)_5X$ to $Co^{III}(CN)_5X$.

As noted earlier, for the reactions of $Co(CN)_5Cl^{3-}$ and, less strikingly, $Co(CN)_5I^{3-}$, there appears, in each case, to be an additional contribution to the rate law from a CN^--independent term, k_1 (eq 13). One possible origin of this contribution is from hydrolysis of $Co^{III}(CN)_5X$ to $Co(CN)_5OH_2^{2-}$ (which may in turn react to give $Co(CN)_6^{3-}$ by the $Co(CN)_5^{3-}$-catalyzed path), although a comparison of k_1 for $Co(CN)_5I^{3-}$ (1.45×10^{-4} sec^{-1} at 25°) with the corresponding hydrolysis rate constant (7.5×10^{-6} sec^{-1} at 40°)[23] casts some doubt upon this interpretation. No really convincing explanation of the k_1 term can be offered at the present time.

In addition to the mechanism described, two other possible mechanisms of electron transfer between $Co(CN)_5^{3-}$ and $Co^{III}(CN)_5X$ complexes merit consideration. One of these, namely inner-sphere electron transfer through the bridging ligand X, does not lead to any net chemical change and would thus require isotopic labeling for detection. Since, on the basis of

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other such comparisons,[8,19,20] ions such as OH^-, Cl^-, Br^-, I^-, and N_3^- are expected to be at least as effective as CN^- as bridging ligands for inner-sphere electron transfer, such electron transfer presumably is occurring under the conditions of our reactions but is undetected.

The other mechanism of electron transfer, which might be expected to operate in these systems, is outer-sphere electron transfer between $Co(CN)_6^{4-}$ (generated by the equilibrium, $Co(CN)_5^{3-} + CN^- \rightleftarrows Co(CN)_6^{4-}$) and $Co^{III}(CN)_5X$, analogous to the outer-sphere oxidation of $Co(CN)_5^{3-}$ by $Co(NH_3)_6^{3+}$ and other cobalt(III) ammine complexes.[8] Such a reaction would also show up as a $Co(CN)_5^{3-}$-catalyzed conversion of $Co^{III}(CN)_5X$ to $Co(CN)_6^{3-}$ but with a CN^--dependent rate law, *i.e.*, $k_3[Co^{III}(CN)_5X][Co(CN)_5^{3-}][CN^-]$. The absence of any observed CN^- dependence permits upper limits to be placed upon the values of k_3 (listed in Table III) for each of the $Co^{III}(CN)_5X$ complexes. The values of these upper limits ($<2 \times 10^{-2}$ M^{-2} sec^{-1}) are much lower than the values of the corresponding rate constants (ranging from 5.2×10^2 M^{-2} sec^{-1} for $Co(NH_3)_5PO_4$ to 8×10^4 M^{-2} sec^{-1} for $Co(NH_3)_6^{3+}$) reported for the analogous CN^--dependent reactions between $Co(CN)_5^{3-}$ and various cobalt(III) ammine complexes.[8] The difference is unexpectedly large but in the direction expected on the basis of the observed dependence on the charge of the cobalt(III) complex.

Bis(1-substituted 5-tetrazolyl)nickel(II) Complexes

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Abstract: The complexes bis(1-methyl-5-tetrazolyl)nickel(II) and bis(1-cyclohexyl-5-tetrazolyl)nickel(II) have been prepared and are insoluble in all common solvents (thus suggesting a polymeric structure), decompose when heated, and are sensitive to the atmosphere. The reflectance spectra indicate that nickel is in an octahedral environment. The observed d–d transitions are 8.06×10^3 and 14.7×10^3 cm^{-1}, and 8.33×10^3 and 14.7×10^3 cm^{-1}, respectively. The transition $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ was observed at approximately 25.0×10^3 cm^{-1} for bis(1-methyl-5-tetrazolyl)nickel(II) and at approximately 26.6×10^3 cm^{-1} for bis(1-cyclohexyl-5-tetrazolyl)nickel(II). Charge-transfer bands were observed at 30.9×10^3 cm^{-1} for the 1-methyl complex and at 35.1×10^3 and 42.9×10^3 cm^{-1} for the 1-cyclohexyl complex. Bands were observed at 595, 456, and 298 cm^{-1} which may be attributed to the Ni–C bend, Ni–C stretch, and a Ni–N bond, respectively, for bis(1-methyl-5-tetrazolyl)nickel(II). The Ni–C bend at 581 cm^{-1} and a band at 316 cm^{-1} which may be attributed to a Ni–N bond were observed for the 1-cyclohexyl complex. The observed magnetic moments, 2.90 and 2.98 BM, for the 1-methyl and 1-cyclohexyl complexes indicate two unpaired electrons.

The preparation of bis(1-methyl-5-tetrazolyl)nickel(II) in this laboratory was discussed in a preliminary communication.[1] Recently Beck and Fehlhammer[2] have prepared tetraphenylarsonium tetrakis(1-cyclohexyl-5-tetrazolyl)gold(III) by the reaction of tetraphenylarsonium tetrazidogold(III) with cyclohexylisonitrile in dichloromethane at 0°. The infrared spectrum of the 1-cyclohexyl-5-tetrazolyl ligand is essentially the same as that for 1-cyclohexyltetrazole.

The formation of a solid complex, tetrachlorobis(1-ethyltetrazole)platinum(IV), has been reported by Oliveri-Mandala and Alagna.[3] A number of complexes of various 1-substituted tetrazoles and several metal ions have been prepared and, except for the zinc complexes,[4] appear to be insoluble in all common solvents. The present work concerns the preparation of solid bis(1-substituted 5-tetrazolyl)nickel(II) complexes.

Experimental Section

Materials. Reagent grade chemicals were used throughout this investigation. The tetrazoles were prepared by the methods described previously for 1-phenyltetrazole[5] and for 1-methyl- and 1-cyclohexyltetrazole.[4]

The tetrazoles were purified by sublimation under reduced pressure. Purity was confirmed by comparing melting points and infrared spectra with previously reported values.[4,5]

Reagent grade diethyl ether (Et_2O) and tetrahydrofuran (THF) were purified by allowing them to reflux with lithium aluminum hydride under prepurified nitrogen and distilling off the ether. The fractions which boiled at 34.5 and 65°, respectively, were collected and stored under nitrogen and over sodium metal in sealed vessels.

Reagent grade acetone was purified by allowing the solvent to stand over anhydrous calcium chloride for at least 3 weeks. The acetone was subsequently refluxed with Drierite and distilled under nitrogen directly into the flask in which it was used.

Nickel(II) chloride and iron(III) chloride were prepared by dehydration of the hexahydrates by reaction with a slight excess of thionyl chloride[6] and then removing the remaining thionyl chloride under vacuum. Iron(II) chloride was prepared by reaction of chlorobenzene with iron(III) chloride.[7] Dichlorobis(triethylphosphine)nickel(II) was prepared by the reaction of triethylphosphine with an ethanolic solution of hydrated nickel(II) chloride.[8]

Analytical Methods. Nickel was determined by decomposing the complex (about 50–80 mg) with 30 ml of 6 M hydrochloric acid. The solution was heated to boiling to expel any hydrogen cyanide

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