

The discrepancy in the effect of inserting CH_2 on the rates in the two series does, however, not vitiate the conclusions which have been reached about the Co(III)-Ru(II) system. In other work it has been observed that breaking conjugation by inserting a CH_2 group diminishes the rate by a factor of only 1.5.¹⁵ While changes in coupling when gross changes in structure occur can probably be predicted qualitatively, the subject is not at all well understood, nor for that matter is the coupling mechanism when a group such as CH_2 separates the pyridine rings known. Is there direct $\pi-\pi$ ($\pi-\pi^*$) overlap, or is the effect transmitted through the bond system? The mixed valence species provide an especially convenient approach to illuminating this issue.

Acknowledgments. Fellowship support for Konrad Rieder by the Swiss National Foundation is gratefully acknowledged, as is balance of support of this research by the National Science Foundation (Grant GP24726).

References and Notes

- (1) Parts 1 and 2 are comprised by ref 2 and 5.
- (2) S. Isied and H. Taube, *J. Am. Chem. Soc.*, **95**, 8198 (1973).
- (3) D. Gaswick and A. Haim, *J. Am. Chem. Soc.*, **96**, 7845 (1974).
- (4) J. J. Jwo and A. Haim, Abstracts, Centennial Meeting of the American Chemical Society, New York, N.Y., April 1976, No. INOR-15.
- (5) H. Fischer, G. M. Tom, and H. Taube, *J. Am. Chem. Soc.*, **98**, 5512 (1976).
- (6) L. M. Jampolsky, M. Baum, S. Kaiser, L. H. Sternback, and M. W. Goldberg, *J. Am. Chem. Soc.*, **74**, 5222 (1952).
- (7) P. L. Gaus, A. Haim, and F. Johnson, *J. Org. Chem.*, **42**, 564 (1977).
- (8) E. R. Dockal and E. S. Gould, *J. Am. Chem. Soc.*, **94**, 6673 (1972).
- (9) F. L. Minn, A. L. Trichilo, A. R. Hurt, and N. Filipesa, *J. Am. Chem. Soc.*, **92**, 3600 (1970).
- (10) C. R. Smith, *J. Am. Chem. Soc.*, **52**, 397 (1930).
- (11) J. L. Cramer, Ph.D. Thesis, University of North Carolina, 1975, p 217.
- (12) N. S. Hush, *Prog. Inorg. Chem.*, **8**, 391 (1971).
- (13) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039 (1973).
- (14) J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, **39**, 778 (1963).
- (15) S. Zawacky, research in progress. This represents a correction on a conclusion reached on the basis of the results reported in ref. 2. The validity of the correction has been checked by S. Isied.
- (16) **Note Added in Proof.** Dr. A. Haim as referee has advanced arguments which make it unlikely that if reaction 1 is maintained as an equilibrium, the intermediate in question is normal high-spin cobalt(II). Using for k_2 a value of 10^6 sec^{-1} [M. Simic and J. Lillie, *J. Am. Chem. Soc.*, **96**, 291 (1974); R. Murray, S. F. Lincoln, H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **8**, 554 (1969)] and taking account of the value of E_i for the Ru(III)/Ru(II) couple, it can be shown that the measured value of k_2K_1 would require E_i for the Co(III)/Co(II) couple to be less than -0.15 V . Note that E° for $\text{Co(NH}_3)_5\text{H}_2\text{O}^{3+} + e^- = [\text{Co(NH}_3)_5\text{H}_2\text{O}]^{2+}$ has been estimated at 0.35 V [R. G. Yalman, *Inorg. Chem.*, **1**, 16 (1962)].

The Pentacyanocobaltate(II)-Catalyzed Reactions of μ -Cyano- and μ -Isocyano-pentacyanopentaamminedicobalt(III,III) with Cyanide Ion¹

Larry O. Spreer, Dennis Gaswick, and Albert Haim*

Contribution from the Department of Chemistry, State University of New York, Stony Brook, New York 11794. Received May 13, 1977

Abstract: The Co(CN)_5^{3-} -catalyzed reactions of $(\text{NC})_5\text{CoCNC}(\text{NH}_3)_5$ and $(\text{NC})_5\text{CoNCC}(\text{NH}_3)_5$ with cyanide ion yield 2 mol of Co(CN)_6^{3-} per mol of binuclear complex. The rate law for the reactions has the form $k_{0S}[\text{Co}_2(\text{NH}_3)_5(\text{CN})_6] \cdot [\text{Co(CN)}_5^{3-}][\text{CN}^-]$ with $k_{0S} = (1.82 \pm 0.04) \times 10^4$ and $(3.22 \pm 0.17) \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$ at 25°C and ionic strength 0.50 M for $(\text{NC})_5\text{CoCNC}(\text{NH}_3)_5$ and $(\text{NC})_5\text{CoNCC}(\text{NH}_3)_5$, respectively. The rate-determining step involves the outer sphere reaction of Co(CN)_6^{4-} with the binuclear reactant. By comparing the observed rate constants with those for the corresponding reactions of mononuclear pentaamminedicobalt(III) and pentacyanocobaltate(III) complexes, it is suggested that an electron is transferred from Co(CN)_6^{4-} to the $\text{Co(NH}_3)_5^{3+}$ moiety to yield the mixed valence intermediates $(\text{NC})_5\text{Co}^{\text{III}}\text{CNC}(\text{NH}_3)_5^{\text{II}}$, $(\text{NH}_3)_5^-$ and $(\text{NC})_5\text{Co}^{\text{III}}\text{NCC}(\text{NH}_3)_5^-$. It is postulated that dissociation of these intermediates by bond rupture at the cobalt(II) site produces Co(CN)_6^{3-} and $\text{Co(CN)}_5\text{NC}^{3-}$, respectively. The previously studied Co(CN)_5^{3-} -catalyzed reaction of $\text{Co(NH}_3)_5\text{CN}^{2+}$ with CN^- was reexamined. In agreement with previous work, the rate law was found to be $k_{1S} + k_{0S} \cdot [\text{CN}^-]([\text{Co(NH}_3)_5\text{CN}^{2+}][\text{Co(CN)}_5^{3-}])$, with $k_{1S} = (2.6 \pm 0.3) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{0S} = (4.8 \pm 0.4) \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$. However, an experiment used previously to postulate the intermediacy of $\text{Co(CN)}_5\text{NC}^{3-}$ in the k_{1S} path could not be reproduced, and it is concluded that, if $\text{Co(CN)}_5\text{NC}^{3-}$ is formed, its rate of isomerization is considerably higher than the 1.6-s half-life reported previously.

The syntheses of the title compounds, $(\text{NH}_3)_5\text{CoNC-Co(CN)}_5$ and $(\text{NH}_3)_5\text{CoCNC}(\text{CN})_5$,^{2,3} were designed to yield binuclear complexes containing two oxidizing metal centers in different ligand environments of controlled kinetic and thermodynamic properties with respect to one-electron reduction. The Co(CN)_5^{2-} moiety is conducive to facile inner-sphere electron transfer, but the metal center is thermodynamically a poor oxidant, whereas the $\text{Co(NH}_3)_5^{3+}$ moiety is reduced very slowly by inner-sphere oxidants, but the metal center has a higher reduction potential. In this manner,

it was thought that addition of a good inner-sphere reductant would bring an electron into the Co(CN)_5^{2-} moiety, but the electron would ultimately go to the $\text{Co(NH}_3)_5^{3+}$ moiety. If the rate of electron transfer from external reductant to Co(CN)_5^{2-} is fast compared to the rate of electron transfer from one metal center to the other in the binuclear complex, the measurement of intramolecular electron transfer rates becomes feasible.⁴

We have applied this approach, alas unsuccessfully, to the reactions of $(\text{NH}_3)_5\text{CoNCC}(\text{CN})_5$ and $(\text{NH}_3)_5\text{CoCNC-Co(CN)}_5$ with chromium(II) and with pentacyanobaltate(II).

Upon mixing chromium(II) with either binuclear complex, immediate precipitation occurred (presumably cobalt(II) hexacyanocobaltate(III)), and therefore homogeneous kinetic studies were precluded. Reduction of the binuclear complexes by $\text{Co}(\text{CN})_5^{3-}$ by-passed the possible inner-sphere path,⁵ and outer-sphere reduction via $\text{Co}(\text{CN})_6^{4-}$ obtained.⁵ Although an outer-sphere oxidant could deposit an electron initially in the $\text{Co}(\text{CN})_5^{2-}$ moiety and be followed by intramolecular electron transfer, the evidence we obtained favors direct electron transfer to the $\text{Co}(\text{NH}_3)_5^{3+}$ moiety.

Experimental Section

Materials. House distilled water was passed through a Barnstead ion exchange demineralizer, and then distilled in a modified Corning AG-1b distilling apparatus. Sodium perchlorate was prepared by neutralization of sodium carbonate with perchloric acid. The argon, used to carry out manipulations with oxygen-sensitive solutions, was purified by passing it over a column of BTS catalyst (B.A.S.F. Colors and Chemicals, Inc.). Solutions of $\text{Co}(\text{CN})_5^{3-}$ were prepared by adding the appropriate amounts of cobalt(II) perchlorate solutions to solutions containing the desired quantities of sodium cyanide and sodium hydroxide.

The complex μ -cyano-pentacyanopentaamminedicobalt(III,III) was prepared by a slight modification⁶ of the method reported previously.² The solid material was obtained by concentration of the effluent from the cation and anion exchange resins instead of addition of ethanol. Anal. Calcd for $(\text{NC})_5\text{CoCNC}(\text{NH}_3)_5$: C, 20.06; H, 4.21; N, 42.86. Found: C, 19.99; H, 4.28; N, 42.60. An aqueous solution of the complex exhibits maxima at 475 and 313 nm with molar absorptivities 69 and $252 \text{ M}^{-1} \text{ cm}^{-1}$, in excellent agreement with values reported previously.²

The complex μ -isocyano-pentacyanopentaamminedicobalt(III,III) was prepared as reported earlier.³ Anal. Calcd for $(\text{NC})_5\text{CoNC}(\text{NH}_3)_5 \cdot \text{H}_2\text{O}$: C, 19.11; H, 4.54; N, 40.85. Found: C, 19.19; H, 4.46; N, 40.40. An aqueous solution of the complex exhibits maxima at 440 and 342 nm with molar absorptivities 71.5 and $259 \text{ M}^{-1} \text{ cm}^{-1}$, in excellent agreement with values reported previously.³

Cyanopentaamminedicobalt(III) perchlorate hemihydrate was prepared by Siebert's method.⁷ An aqueous solution of the complex exhibits maxima at 440 and 327 nm with molar absorptivities 56.3 and $53.2 \text{ M}^{-1} \text{ cm}^{-1}$, in excellent agreement with values reported previously.⁷

Kinetic Measurements. Kinetic measurements of the reactions of the binuclear complexes were performed in a stopped-flow apparatus⁸ by mixing solutions of the desired complex and sodium perchlorate with solutions of $\text{Co}(\text{CN})_5^{3-}$, excess sodium cyanide and sodium perchlorate. For $(\text{NC})_5\text{CoCNC}(\text{NH}_3)_5$, the reaction was monitored by following the decrease in absorbance at 500, 475, and 440 nm and the increase in absorbance at 310 nm. For $(\text{NC})_5\text{CoNCC}(\text{NH}_3)_5$, the wavelengths of observation were 440 and 358 nm (decrease in absorbance) and 310 nm (increase in absorbance). Voltage vs. time data were collected in an IBM 1800 computer.⁹ Twenty to thirty points were collected during the first 4 half-lives and infinity values were obtained by averaging five readings taken at 1 half-life intervals starting at 9 half-lives. The voltage vs. time readings were treated by a nonlinear least-squares program¹⁰ to obtain first-order rate constants defined by $-\text{d} \ln [\text{binuclear}]/\text{d}t = k_{\text{obsd}}$.⁹

Kinetic measurements of the $\text{Co}(\text{NH}_3)_5\text{CN}^{2+} - \text{Co}(\text{CN})_5^{3-}$ reaction were carried out in the stopped-flow apparatus by mixing solutions of $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ and Co^{2+} with solutions of sodium cyanide, sodium hydroxide, and sodium perchlorate. The concentrations and the experimental conditions approximate as closely as possible those used by Nakamura.¹¹ Some measurements were carried out by mixing solutions of $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ with solutions of preformed $\text{Co}(\text{CN})_5^{3-}$. The two mixing procedures gave identical results. The wavelengths of observation were 440 (decrease in absorbance) and 320 nm (increase in absorbance). Pseudo-first-order rate constants, k_{obsd} , were obtained from $\log(A_t - A_\infty)$ vs. t plots.

Stoichiometric Measurements. These measurements were designed to determine the final cobalt(III) products of the reactions between cyanide ion and the binuclear complexes. A solution of the desired binuclear complex containing a small amount of cobalt(II) was mixed anaerobically (syringe techniques) with a solution of the desired concentrations of sodium cyanide, sodium hydroxide, and sodium perchlorate. The reaction was allowed to proceed to completion and

Table I. Stoichiometries of the Reactions of $(\text{NC})_5\text{CoCNC}(\text{NH}_3)_5$ and $(\text{NC})_5\text{CoNCC}(\text{NH}_3)_5$ with CN^- Catalyzed by $\text{Co}(\text{CN})_5^{3-}$ ^a

$10[\text{CN}^-], \text{M}$	$10^4[\text{binuclear}], \text{M}^b$	A_m^c	A_c^d
0.30	9.52	0.761	0.758
0.30	9.88	0.770	0.786
0.30	10.9	0.880	0.868
3.50	8.95	0.712	0.712
3.50	9.60	0.766	0.764
3.50	11.8	0.939	0.939
0.30	8.62	0.680	0.686
0.30	8.91	0.708	0.709
0.30	10.2	0.782	0.812
3.50	11.0	0.880	0.876
3.50	9.95	0.776	0.792
3.50	9.62	0.769	0.766

^a At 25 °C and $[\text{Co}(\text{CN})_5^{3-}] = 4.87 \times 10^{-5} \text{ M}$. ^b The first six experiments pertain to $(\text{NC})_5\text{CoCNC}(\text{NH}_3)_5$ and the last six to $(\text{NC})_5\text{CoNCC}(\text{NH}_3)_5$. ^c Measured absorbance at 310 nm corrected for absorbance of the blank; 2-cm cell. ^d Calculated from $2 \times [\text{binuclear}] \times 2 \times 199$.

then the catalytic amount of $\text{Co}(\text{CN})_5^{3-}$ was destroyed by addition of a slight excess of peroxydisulfate. After the appropriate dilution, the resulting solution was examined spectrophotometrically in the 500–280-nm region in a Cary 14 recording spectrophotometer. Blank experiments, containing identical concentrations of all reagents except for the binuclear complexes, were performed for each stoichiometric experiment, and the absorbances reported are those of the unknown solutions minus those of the blanks.

The stoichiometry of the $\text{Co}(\text{NH}_3)_5\text{CN}^{2+} - \text{Co}(\text{CN})_5^{3-}$ was determined utilizing two different procedures. In the first, a solution of sodium cyanide was added slowly to a solution containing $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ and Co^{2+} . At the completion of the reaction, excess 0.10 M perchloric acid was added (*Caution:* HCN), a slight amount of precipitate was filtered out, and the resulting solution was examined spectrophotometrically. Blank experiments were performed under identical conditions except that the $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ was omitted. In the second procedure, a solution containing $\text{Co}(\text{CN})_5^{3-}$ and CN^- was added rapidly to a solution containing $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$. At the completion of the reaction excess 1.0 M perchloric acid was added, and the spectrum of the solution was recorded.

Analytical Methods. Sodium cyanide was standardized by titration with silver(I) in the presence of iodide ion as an indicator.¹² Solutions of cobalt(II) perchlorate were standardized against disodium dihydrogen ethylenediaminetetraacetate dihydrate using murexide as an indicator.¹³ Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories.

Results

Stoichiometry. The results of the experiments designed to determine the stoichiometries of the reactions of $(\text{NC})_5\text{CoCNC}(\text{NH}_3)_5$ and $(\text{NC})_5\text{CoNCC}(\text{NH}_3)_5$ with cyanide ion in the presence of $\text{Co}(\text{CN})_5^{3-}$ are summarized in Table I. The product solutions exhibit absorption maxima at 310 nm and the values of the measured absorbances (corrected for the blank) are given in column 3. The 310-nm wavelength is characteristic of the absorption maximum of $\text{Co}(\text{CN})_6^{3-}$.⁷ Using the known⁷ molar absorbance of $\text{Co}(\text{CN})_6^{3-}$ and assuming that both cobalt(III) centers in the binuclear complexes end up as hexacyanocobaltate(III), values of the absorbances of the product solutions were calculated, and the results are given in column 4. The excellent agreement between measured and calculated absorbance value is taken to indicate that the net stoichiometries of the reactions of the binuclear complexes with cyanide ion are given by

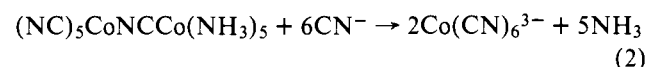
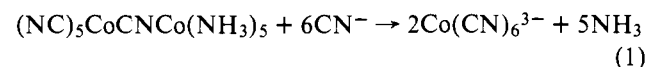
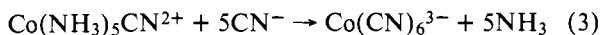


Table II. Kinetics of the $\text{Co}(\text{CN})_5^{3-}$ -Catalyzed Reaction of $(\text{NC})_5\text{CoNC}(\text{NH}_3)_5$ with Cyanide Ion^a

10[CN^-], M	$10^3 k_2, \text{M}^{-1} \text{s}^{-1}$			
	500 nm	475 nm	440 nm	310 nm
0.43 ^b	0.63 ± 0.02	0.61 ± 0.02	0.61 ± 0.03	0.84 ± 0.05
0.43	0.60 ± 0.02	0.62 ± 0.03	0.59 ± 0.03	0.72 ± 0.05
1.00 ^b	1.93 ± 0.08	1.91 ± 0.05	1.86 ± 0.09	2.24 ± 0.19
2.00	3.61 ± 0.12	3.70 ± 0.06	3.73 ± 0.19	4.50 ± 0.25
2.00 ^e	3.66 ± 0.10	3.75 ± 0.08	3.61 ± 0.12	4.60 ± 0.20
3.00	5.36 ± 0.17	5.35 ± 0.17	5.76 ± 0.23	5.55 ± 0.23
3.00 ^e	5.31 ± 0.11	5.24 ± 0.12	5.42 ± 0.19	6.13 ± 0.23
3.00 ^c	5.36 ± 0.12	5.33 ± 0.15	5.49 ± 0.15	5.84 ± 0.45
4.00	7.32 ± 0.19	7.46 ± 0.00	7.23 ± 0.23	8.41 ± 0.45
4.00	7.17 ± 0.15	7.44 ± 0.28	7.61 ± 0.26	7.78 ± 0.62
4.00 ^{d,f}	6.98 ± 0.20	7.24 ± 0.15	7.12 ± 0.22	8.07 ± 0.28

^a At 25 °C and ionic strength 0.50 M (NaClO_4). Unless indicated otherwise, $[\text{Co}_2(\text{NH}_3)_5(\text{CN})_6] = 0.51\text{--}3.3 \times 10^{-3} \text{ M}$, $[\text{OH}^-] = 2.50 \times 10^{-2} \text{ M}$, and $[\text{Co}(\text{CN})_5^{3-}] = 6.49 \times 10^{-4} \text{ M}$. Each entry is the average of at least three replicate experiments with the same pair of solutions. ^b $[\text{Co}(\text{CN})_5^{3-}] = 1.30 \times 10^{-3} \text{ M}$. ^c $[\text{Co}(\text{CN})_5^{3-}] = 2.16 \times 10^{-4} \text{ M}$. ^d $[\text{Co}(\text{CN})_5^{3-}] = 3.25 \times 10^{-4} \text{ M}$. ^e $[\text{OH}^-] = 5.00 \times 10^{-3} \text{ M}$. ^f $[\text{OH}^-] = 5.00 \times 10^{-2} \text{ M}$.

Previous workers^{14,15} have identified $\text{Co}(\text{CN})_6^{3-}$ as the final product of the cobalt(II)-catalyzed reaction between $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ and CN^- . We have confirmed this observation for the cyanide ion independent path¹⁴ of this reaction. In the first experiment, slow, dropwise addition of 25 mL of 0.056 M sodium cyanide to 25 mL of $5.40 \times 10^{-5} \text{ M Co}^{2+}$ and $4.04 \times 10^{-3} \text{ M Co}(\text{NH}_3)_5\text{CN}^{2+}$ followed by addition of 20 mL of 0.10 M perchloric acid (*Caution*: HCN), filtration, and dilution to 100 mL gave a solution which exhibited a maximum at 310 nm with absorbance (corrected for the blank) 1.05 (5-cm cell). The calculated absorbance for quantitative formation of $\text{Co}(\text{CN})_6^{3-}$ is 1.01. The second experiment, 50 mL of a solution $1.0 \times 10^{-4} \text{ M}$ in $\text{Co}(\text{CN})_5^{3-}$, $3.0 \times 10^{-2} \text{ M}$ in CN^- , and $2.0 \times 10^{-2} \text{ M}$ in OH^- was added to 10 mL of a solution $2.07 \times 10^{-2} \text{ M}$ in $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$. At the completion of the reaction (~2 min at ambient temperature), 5 mL of 1.0 M perchloric acid was added (*Caution*: HCN), and dilution to 100 mL resulted in a solution which exhibited a maximum at 310 nm with absorbance (2-cm cell) 0.78. A blank experiment in which the $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ was replaced by an equivalent amount of $\text{Co}(\text{CN})_6^{3-}$ yielded a solution with absorbance 0.81. Therefore, our results confirm the stoichiometry given by



Kinetics. Since there is no net oxidation–reduction in these reactions, the concentration of $\text{Co}(\text{CN})_5^{3-}$ remains constant and this species acts as a catalyst. Therefore, every kinetic experiment was effectively carried out under pseudo-first-order conditions. The pseudo-first-order rate constants, k_{obsd} , for the disappearance of the binuclear complexes divided by the concentration of $\text{Co}(\text{CN})_5^{3-}$ yield second-order rate constants k_2 which are presented in Tables II and III for $(\text{NC})_5\text{CoNC}(\text{NH}_3)_5$ and $(\text{NC})_5\text{CoNCCo}(\text{NH}_3)_5$, respectively. It will be seen that k_2 is independent of $\text{Co}(\text{CN})_5^{3-}$ (cf. expt 1 and 2, 6 and 8, 9, 10, and 11 of Table II; expt 2 and 4, 9 and 11 of Table III) and hydroxide ion (cf. expt 4 and 5, 6 and 7, 9, 10, and 11 of Table II; expt 2 and 3, 6, 7, and 8, 9 and 10 of Table III).

At a particular cyanide ion concentration, it will be seen that the values of k_2 are independent of the wavelength of observation except for the measurements at 310 nm, where values of k_2 are 10–15% higher. Moreover, the scatter of the rate constants measured at 310 nm is somewhat higher than at the longer wavelengths. Since pentacyanocobaltate is oxidized rapidly by oxygen,^{16,17} we considered the possibility that the

Table III. Kinetics of the $\text{Co}(\text{CN})_5^{3-}$ -Catalyzed Reaction of $(\text{NC})_5\text{CoNCCo}(\text{NH}_3)_5$ with Cyanide Ion^a

10[CN^-], M	$10^2 k_2, \text{M}^{-1} \text{s}^{-1}$		
	440 nm	358 nm	310 nm
0.43 ^b	1.34 ± 0.06	1.23 ± 0.04	1.36 ± 0.10
1.00 ^b	3.04 ± 0.09	2.92 ± 0.04	3.88 ± 0.12
1.00 ^{b,c}	3.00 ± 0.08	3.12 ± 0.07	3.88 ± 0.14
2.00	3.12 ± 0.14	2.90 ± 0.15	3.67 ± 0.25
2.00	6.55 ± 0.25	6.27 ± 0.28	7.43 ± 0.35
3.00	9.54 ± 0.48	9.37 ± 0.39	10.9 ± 0.3
3.00 ^c	9.65 ± 0.44	9.35 ± 0.29	10.5 ± 0.5
3.00	9.72 ± 0.40	9.09 ± 0.35	9.80 ± 0.55
4.00	13.1 ± 0.3	13.1 ± 0.4	15.0 ± 1.0
4.00 ^d	13.1 ± 0.5	12.9 ± 0.4	14.6 ± 0.9
4.00 ^e	13.5 ± 0.5	12.9 ± 0.6	14.5 ± 1.0

^a At 25 °C and ionic strength 0.50 M (NaClO_4). Unless indicated otherwise, $[\text{Co}_2(\text{NH}_3)_5(\text{CN})_6] = 0.48\text{--}3.8 \times 10^{-3} \text{ M}$, $[\text{OH}^-] = 2.50 \times 10^{-2} \text{ M}$, and $[\text{Co}(\text{CN})_5^{3-}] = 6.49 \times 10^{-4} \text{ M}$. Each entry is the average of at least three replicate experiments with the same pair of solutions. ^b $[\text{Co}(\text{CN})_5^{3-}] = 1.30 \times 10^{-3} \text{ M}$. ^c $[\text{OH}^-] = 5.00 \times 10^{-3} \text{ M}$. ^d $[\text{OH}^-] = 5.00 \times 10^{-2} \text{ M}$. ^e $[\text{Co}(\text{CN})_5^{3-}] = 2.16 \times 10^{-4} \text{ M}$.

apparent wavelength dependence was associated with contamination by oxygen. Blank experiments in which the binuclear complexes were omitted exhibited absorbance increases at 310 nm equal to 1–10% of the absorbance decreases observed in the presence of the binuclear complexes. The time scale for the changes in the blank measurements was 10–20 s compared to 2.0–30 s for the measurements with the binuclear complexes. No changes in absorbance were noted for the blank experiments at wavelengths longer than 340 nm. Based on these observations, we tend to disregard the wavelength dependence as a manifestation of intrinsic chemical changes in the system, and we conclude that the higher rates at 310 nm are the result of contamination by traces of oxygen. However, since $\text{Co}(\text{CN})_5\text{NC}^{3-}$ is a possible intermediate in the reaction of $(\text{NC})_5\text{CoNCCo}(\text{NH}_3)_5$ and is reported¹⁴ to absorb strongly at 320 nm, we considered the possibility that the higher rates observed at 310 nm were associated with the presence of this intermediate in our system. In order to test this hypothesis we carried out an experiment identical with the fourth experiment in Table III except that the solution of the binuclear complex also contained $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ at $\sim 1 \times 10^{-3} \text{ M}$. $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ has been reported¹⁴ to react with $\text{Co}(\text{CN})_5^{3-}$ to produce the isocyano complex $\text{Co}(\text{CN})_5\text{NC}^{3-}$ which isomerizes to the stable linkage isomer $\text{Co}(\text{CN})_6^{3-}$ with a half-life of 1.6 s.¹⁴ On the basis of the published rates and oscillograms,¹⁴ we expected the absorbance vs. time traces at 320 nm to exhibit a maximum. The first-order plots at 310, 358, and 440 nm were curved and had initial half-lives of the order of 3 s, but no maximum was observed at 320 nm. Therefore, we reexamined the kinetics of the $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ – $\text{Co}(\text{CN})_5^{3-}$ system, and the results are summarized in Table IV. It will be seen that our measurements at 440 nm are in excellent agreement with the previous¹⁴ measurements (also carried out at 440 nm). A least-squares treatment of our data according to the two-term rate law

$$k = k_{1S} + k_{OS}[\text{CN}^-] \quad (4)$$

reported previously¹⁴ gave $k_{1S} = (2.6 \pm 0.3) \times 10^2 \text{ M}^{-1} \text{s}^{-1}$ and $k_{OS} = (4.8 \pm 0.4) \times 10^3 \text{ M}^{-2} \text{s}^{-1}$ compared to $2.9 \times 10^2 \text{ M}^{-1} \text{s}^{-1}$ and $4.5 \times 10^3 \text{ M}^{-2} \text{s}^{-1}$ reported previously.¹⁴ We also carried out measurements at 320 nm, a wavelength where the absorbance vs. time data were reported to go through a maximum.¹⁴ We could not confirm the reported¹⁴ behavior at 320 nm. Our traces show only an exponential increase in absorbance with infinity traces constant on the 1-s sweep used in the previous work.¹⁴ The absorbance changes at 320 nm yielded

Table IV. Kinetics of the $\text{Co}(\text{CN})_5^{3-}$ -Catalyzed Reaction of $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ with Cyanide Ion^a

$10^3[\text{Co}(\text{NH}_3)_5\text{CN}^{2+}]$, M	$10^3[\text{Co}(\text{CN})_5^{3-}]$, M	$10^2[\text{CN}^-]$, M	k_{obsd}^b		$k_{\text{obsd}}^{\text{calcd } c}$
			440 nm	320 nm	
2.00	2.05	3.00	0.89 ± 0.01	0.95 ± 0.05	0.87
1.50	2.00	4.04	1.00 ± 0.04	0.95 ± 0.01	0.94 (0.94)
1.50	2.00	8.02	1.26 ± 0.02	1.29 ± 0.02	1.30 (1.39 ^d)
1.50	1.00	9.03	0.59 ± 0.02	0.62 ± 0.05	0.70 (0.69 ^e)
1.50	2.00	19.0	2.42 ± 0.02	2.46 ± 0.08	2.29 (2.3)

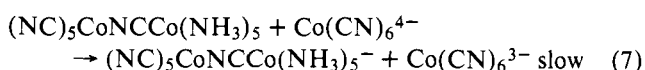
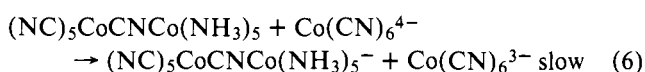
^a At 25 °C and ionic strength 0.20 M maintained with NaClO_4 . ^b $k_{\text{obsd}} = -d(\ln [\text{Co}(\text{NH}_3)_5\text{CN}^{2+}])/dt$ obtained from $\log |(A_t - A_\infty)|$ vs. t plots. ^c Values are calculated from the equation $k_{\text{obsd}} = k_{1S}[\text{Co}(\text{CN})_5^{3-}] + k_{OS}[\text{Co}(\text{CN})_5^{3-}][\text{CN}^-]$ where $k_{1S} = 2.9 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{OS} = 4.5 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$. Values in parentheses are measured values from ref 11 under the same concentration conditions except where noted. ^d At 0.090 M cyanide ion concentration. ^e At 0.095 M cyanide ion concentration.

rates in excellent agreement with the rate measurements at 440 nm. Least-squares values of k_{1S} and k_{OS} for the measurements at 320 nm are $(2.6 \pm 0.3) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and $(4.9 \pm 0.4) \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$, respectively. We have no explanation for the discrepancy between our observations and those reported earlier,¹⁴ but note that contamination by oxygen causes spurious traces at 320 nm that resemble the published¹⁴ oscillogram.

An examination of Tables II and III will show that the values of k_2 increase with increasing cyanide ion concentration. In studies of the $\text{Co}(\text{CN})_5^{3-}$ -catalyzed reactions of pentaamminecobalt(III) complexes with cyanide ion,^{5,14} it was found that the second-order rate constants defined by $-d[\text{Co}(\text{NH}_3)_5\text{X}^{n+}]/dt = k[\text{Co}(\text{NH}_3)_5\text{X}^{n+}][\text{Co}(\text{CN})_5^{3-}]$ were independent of $[\text{CN}^-]$ for some systems ($\text{X} = \text{N}_3^-$, NCS^- , OH^-), first order in $[\text{CN}^-]$ for other systems ($\text{X} = \text{NH}_3$, $\text{C}_2\text{O}_4^{2-}$), or consisted of two terms (eq 4) for still other systems ($\text{X} = \text{F}^-$, NO_2^- , CN^-). Attempts to fit the measured values of k_2 in Tables II and III to eq 4 yielded values of k_{1S} which were small and within experimental uncertainty of zero. Thus, at 440 nm, values of k_{1S} and k_{OS} for $(\text{NC})_5\text{CoCN-Co}(\text{NH}_3)_5$ are $51 \pm 100 \text{ M}^{-1} \text{ s}^{-1}$ and $(1.85 \pm 0.03) \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$, respectively. The corresponding values for $(\text{NC})_5\text{CoNCCo}(\text{NH}_3)_5$ are $10 \pm 62 \text{ M}^{-1} \text{ s}^{-1}$ and $(3.28 \pm 0.16) \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$. Therefore, the values of k_2 in Tables II and III were treated on the basis of the one-term rate law $k_2 = k_{OS}[\text{CN}^-]$, and yielded $k_{OS} = (1.82 \pm 0.04) \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ and $k_{OS} = (3.22 \pm 0.17) \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$ for $(\text{NC})_5\text{CoCN-Co}(\text{NH}_3)_5$ and $(\text{NC})_5\text{CoNCCo}(\text{NH}_3)_5$, respectively.

Discussion

The two-term rate law (eq 4) reported previously^{5,14} for the $\text{Co}(\text{CN})_5^{3-}$ -catalyzed reactions of pentaamminecobalt(III) complexes with cyanide ion was taken to be the manifestation of parallel inner-sphere and outer-sphere reactions of $\text{Co}(\text{CN})_5^{3-}$ and of $\text{Co}(\text{CN})_6^{4-}$ (rapidly formed in small equilibrium concentrations from $\text{Co}(\text{CN})_5^{3-}$ and CN^-) with $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$. We adopt a similar interpretation for the one-term, cyanide-dependent rate law obtained in the present work, and formulate the mechanism on the basis of eq 5 and

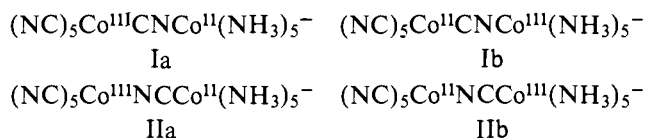


6 or 5 and 7 for the cyano and isocyano complexes, respectively. Reactions 6 and 7 account for only 1 of the 2 mol of $\text{Co}(\text{CN})_6^{3-}$ produced per mol of binuclear complex that reacts, and therefore additional reactions of the intermediates $(\text{NC})_5\text{CoCNC}(\text{NH}_3)_5^-$ and $(\text{NC})_5\text{CoNCCo}(\text{NH}_3)_5^-$ must be considered. However, before doing so, it is instructive to discuss the structures of the intermediates.

Table V. Rate Constants for the Reactions of $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$ and $\text{Co}(\text{CN})_5\text{X}^{n-}$ with $\text{Co}(\text{CN})_6^{4-}$

Cobalt(III) complex	$k_{OS},^a \text{ M}^{-2} \text{ s}^{-1}$	Ref
$\text{Co}(\text{NH}_3)_5\text{PO}_4$	5.2×10^2	<i>b</i>
$\text{Co}(\text{NH}_3)_5\text{CO}_3^+$	1×10^3	<i>b</i>
$\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$	1.0×10^4	<i>b</i>
$\text{Co}(\text{NH}_3)_5\text{O}_2\text{CCH}_3^{2+}$	1.1×10^4	<i>b</i>
$\text{Co}(\text{NH}_3)_5\text{F}^{2+}$	1.7×10^4	<i>b</i>
$\text{Co}(\text{NH}_3)_6^{3+}$	8×10^4	<i>b</i>
$\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$	4.5×10^3	<i>c</i>
$\text{Co}(\text{NH}_3)_5\text{CNC}(\text{CN})_5$	3.2×10^3	<i>d</i>
$\text{Co}(\text{NH}_3)_5\text{NCC}(\text{CN})_5$	1.8×10^4	<i>d</i>
$\text{Co}(\text{CN})_5\text{Br}^{3-}$	$< 2 \times 10^{-3}$	<i>e</i>
$\text{Co}(\text{CN})_5\text{N}_3^{3-}$	$< 6 \times 10^{-3}$	<i>e</i>
$\text{Co}(\text{CN})_5\text{I}^{3-}$	$< 2 \times 10^{-2}$	<i>e</i>

^a At 25 °C, ionic strength 0.20 M. $k_{OS} = (-d[\text{cobalt(III) complex}]/dt)/[\text{Co}(\text{CN})_5^{3-}][\text{CN}^-]$. ^b Reference 5. ^c Reference 19. ^d This work, ionic strength 0.50 M. ^e Reference 19, ionic strength 0.50 M.



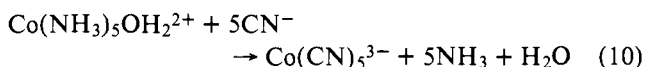
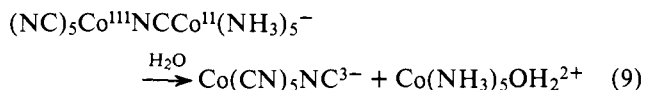
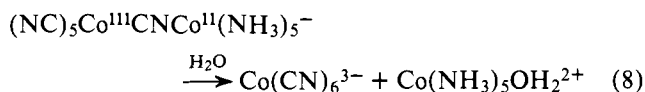
Two formulations for each of these intermediates can be conceived. These are shown as Ia and IIa, and Ib and IIb, for the cyano and isocyano intermediates, respectively. Two related questions can be asked at this point. First, which is the primary binuclear product of the redox reaction between $\text{Co}(\text{CN})_6^{4-}$ and the binuclear reactants? In other words, is Ia or Ib formed in reaction 6? Is IIa or IIb formed in reaction 7? Second, if redox equilibria between Ia and Ib and between IIa and IIb are established rapidly compared to dissociation, which are the thermodynamically favorable forms of I and II? It must be mentioned that these questions appear to be meaningful for mixed valence ions of the type under consideration. Since the amminecobalt(III) and cyanocobalt(III) moieties are noninteracting in the parent complexes,^{2,3} there appears to be little delocalization of molecular orbitals between the cobalt centers, and the binuclear complexes I and II are, undoubtedly, of the trapped valence type.¹⁸

In order to answer the first question raised above, the following indirect approach is proposed. Rate constants for the outer-sphere reductions of a series of $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$ complexes by $\text{Co}(\text{CN})_6^{4-}$ have been measured and found⁵ to show a small dependence on the nature of X. The range of measured rates is 5×10^2 to $8 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ (cf. Table V). In contrast, rate constants for the outer sphere reductions of a series of $\text{Co}(\text{CN})_5\text{X}^{n-}$ complexes by $\text{Co}(\text{CN})_6^{4-}$ are too slow to be measured,¹⁹ and upper limits in the range of 2×10^{-3} to $2 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$ (cf. Table IV) have been assigned to these outer-sphere rate constants.¹⁹ If rate constants in the 10^3 – $10^4 \text{ M}^{-2} \text{ s}^{-1}$ range are taken to be characteristic of pentaammine

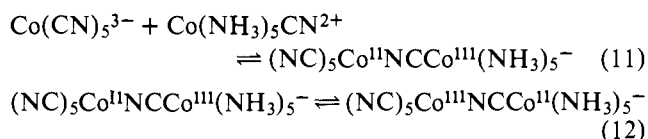
complexes, and upper limits in the 10^{-2} – 10^{-3} $M^{-2} s^{-1}$ range correspond to pentacyano complexes, then the observed values for $(NC)_5CoCNC(NH_3)_5$ and $(NC)_5CoNCCo(NH_3)_5$ (in the 10^3 – 10^4 $M^{-2} s^{-1}$ range) clearly place these complexes in the pentaammine category. In particular, we note the remarkable similarity in rates between $Co(NH_3)_5CN^{2+}$ and $(NC)_5CoNCCo(NH_3)_5$. We infer that the electron is transferred from $Co(CN)_6^{4-}$ to an orbital localized on the $Co(NH_3)_5$ moiety and, therefore, that the primary products formed in reactions 6 and 7 are Ia and IIa, respectively.

The kinetically controlled products Ia and IIa are also thermodynamically favored over the corresponding isomers Ib and IIb. Although reduction of $Co(CN)_6^{3-}$ is not reversible, a value of ~ -0.8 V for the reduction potential appears to be substantially correct.²⁰ Using this value, and the value 0.3 V estimated²¹ for the reduction potential of $Co(NH_3)_5X^{n+}$ complexes, the equilibrium constant for $Ia \rightleftharpoons Ib$ or $IIa \rightleftharpoons IIb$ isomerization is 2.6×10^{-19} . With such an unfavorable equilibrium and with the known²² rate of ligand detachment from cobalt(II) ammine complexes ($> 10^6$ s^{-1}), it seems quite certain that, once an electron is accepted by the pentaamminecobalt moiety, the most likely fate for intermediates Ia and IIa is breaking of the $Co^{III}CN-Co^{II}$ and $Co^{III}NC-Co^{II}$ bonds, respectively.

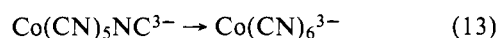
Therefore, following reactions 6 and 7, we must consider reactions 8, 9, and 10. Reaction 10 accounts for the catalytic role of $Co(CN)_5^{3-}$.



Reaction 8 accounts for the second mole of $Co(CN)_6^{3-}$ produced in the $Co(CN)_5^{3-}$ -catalyzed reaction of $(NC)_5CoCNC(NH_3)_5$ with cyanide ion. However, the analogous reaction for $(NC)_5CoNCCo(NH_3)_5$ (eq 9) produces the linkage isomer $Co(CN)_5NC^{3-}$. This isomer was reported¹⁴ as a transient intermediate (half-life of 1.6 s) in the inner-sphere portion of the $Co(NH_3)_5CN^{2+}-Co(CN)_5^{3-}$ reaction, but we have been unable to reproduce the experimental observation¹⁴ which provided the evidence for the intermediacy of $Co(CN)_5NC^{3-}$. Although our kinetic and stoichiometric measurements show that $Co(CN)_5NC^{3-}$ is neither a detectable intermediate nor a stable reaction product, it does seem reasonable, however, that $Co(CN)_5NC^{3-}$ be formed as an (undetectable) intermediate in the inner-sphere $Co(NH_3)_5CN^{2+}-Co(CN)_5^{3-}$ reaction. Using the well-established²³ sequence of precursor complex formation, electron transfer, and successor complex dissociation, the mechanism of the $Co(NH_3)_5CN^{2+}-Co(CN)_5^{3-}$ reaction is given by eq 11, 12, and 9.



It is noteworthy that the successor complex in reaction 12 is identical with the postulated primary binuclear product of reaction 7 (structure Ia). Since adjacent attack in reaction 11 is probably precluded because of the absence of a basic, lone pair of σ electrons on the carbon of the bridging cyanide,²³ remote attack obtains and $Co(CN)_5NC^{3-}$ is the primary, mononuclear cobalt(III) product of the redox reaction. However, it is not detected, presumably because its rate of isomerization, either spontaneous or catalyzed by $Co(CN)_5^{3-}$, is rapid compared to its rate of formation. Assuming that a concentration of $Co(CN)_5NC^{3-}$ equal to $1/10$ that of $Co(NH_3)_5CN^{2+}$ in the first experiment of Table IV would have been detected, a lower limit of $7 s^{-1}$ is estimated for the rate constant for spontaneous isomerization according to reaction 13.



Although at first glance this value might be viewed as unreasonably high for the reaction of a low-spin, d^6 cobalt(III) complex, it is noteworthy that isomerization of $Ru(NH_3)_5NC^{2+}$ to $Ru(NH_3)_5CN^{2+}$, the identical reaction of another low-spin, d^6 complex, has been reported to proceed with a rate constant larger than $0.7 s^{-1}$.²⁴ Therefore, it is postulated that, following reaction 9, reaction 13 proceeds rapidly, and thus the second mole of $Co(CN)_6^{3-}$ produced in the $(NC)_5CoNCCo(NH_3)_5-CN^-$ reaction is accounted for.

References and Notes

- (1) This work was supported by Grants GP-37057 and CHE 76-10449 from the National Science Foundation.
- (2) R. A. de Castello, C. Piriz Mac-Coll, N. B. Egen, and A. Halm, *Inorg. Chem.*, **8**, 699 (1969).
- (3) R. A. de Castello, C. Piriz Mac-Coll, and A. Halm, *Inorg. Chem.*, **10**, 203 (1971).
- (4) S. S. Isied and H. Taube, *J. Am. Chem. Soc.*, **95**, 8198 (1973).
- (5) J. P. Candlin, J. Halpern, and S. Nakamura *J. Am. Chem. Soc.* **85**, 2517 (1963).
- (6) B. C. Wang, W. P. Schaefer, and R. E. Marsh, *Inorg. Chem.*, **10**, 1492 (1971).
- (7) H. Siebert, *Z. Anorg. Allg. Chem.*, **327**, 63 (1964).
- (8) G. Dulz and N. Sutlin, *Inorg. Chem.*, **2**, 917 (1963).
- (9) J. R. Ward and A. Halm, *J. Am. Chem. Soc.*, **92**, 475 (1970).
- (10) Los Alamos Report LA 2367 (March 4, 1960) and Addenda (Jan 14, 1963).
- (11) S. Nakamura, Ph.D. Thesis, University of Chicago, Dec 1964.
- (12) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Analysis", Macmillan, New York, N.Y., 1952, p 526.
- (13) G. Swarzenbach, "Complexometric Titrations", Interscience, New York, N.Y., 1957, p 68.
- (14) J. Halpern and S. Nakamura, *J. Am. Chem. Soc.*, **87**, 3002 (1965).
- (15) J. Burmelster and D. Sutherland, *Chem. Commun.*, 175 (1965).
- (16) A. Halm and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).
- (17) J. H. Bayston, R. N. Beale, N. K. King, and M. E. Winfield, *Aust. J. Chem.*, **16**, 954 (1963).
- (18) M. B. Robln and P. Day, *Adv. Inorg. Chem. Radiochem.*, **10**, 247 (1967).
- (19) J. P. Birk and J. Halpern, *J. Am. Chem. Soc.*, **90**, 305 (1968).
- (20) A. G. Sharpe, "The Chemistry of Cyano Complexes of the Transition Metals", Academic Press, New York, N.Y., 1976, p 171.
- (21) A. Halm and H. Taube, *J. Am. Chem. Soc.*, **85**, 495 (1962).
- (22) J. Lillie, N. Shinohara, and M. G. Simic, *J. Am. Chem. Soc.*, **98**, 6516 (1976).
- (23) A. Halm, *Acc. Chem. Res.*, **8**, 264 (1975).
- (24) S. S. Isied and H. Taube, *Inorg. Chem.*, **14**, 2561 (1975).