

lattice packing forces by those which tend to alter the geometries of the individual molecules.

The various low-temperature magnetic susceptibilities indicate that, dependent on the polymorph, a certain percentage of molecules remains in the  ${}^5T_2$  state even below  $T_c$ . This inference is well supported by infrared spectral observations as discussed above. Usually, a second-order Zeeman effect accounts for the small paramagnetism encountered in low-spin  $d^6$  ions. This contribution to the susceptibility has been estimated by Ballhausen and Asmussen<sup>51</sup> as  $\sim 200 \times 10^{-6}$  cgs/mole or up to about 0.70 BM. Subtracting this temperature-independent paramagnetism from the slightly temperature-dependent moment below  $T_c$ , one arrives at the estimate that, in the polymorphs I, II, and III, the moment observed at 77°K is due to one in 20, 8,<sup>52</sup> and 6 molecules, respectively, being in a  ${}^5T_2$  ground state. There are two possibilities for the distribution of the high-spin molecules throughout the lattice. In the case of random distribution, a considerably disordered structure would have to be anticipated. If the molecules assume lattice positions in an ordered way, a superlattice should be formed.

The reason why the transition does not proceed to 100% of the  ${}^1A_1$  state is not obvious. Of course, a sufficiently large number of impurity ions could produce the same effects as observed. However,  $\sim 18\%$  of  $Fe^{3+}$  ion impurities, for example, would be needed to give the high moment value of 1.61 BM at 77°K in polymorph III and, in any case, the various spectroscopic methods employed would have given evidence

(51) C. J. Ballhausen and R. W. Asmussen, *Acta Chem. Scand.*, **11**, 479 (1957).

(52) If susceptibilities extrapolated to  $H = \infty$  are used, the ratio of  ${}^5T_2$  to  ${}^1A_1$  molecules of polymorph II at 77°K is 1:10.

for any large amounts of such impurities. In particular, the spurious signals observed in paramagnetic resonance are in the ppm range and thus in a much too small concentration to account for the low-temperature magnetic moments, and no indication of signals due to  $Fe^{3+}$  ions (the most likely impurity) has been detected. One possible explanation for the observations is suggested on the basis of infrared spectra. The distortions, which are apparent from these results, could result in larger space requirements of the individual molecules with the possible consequence that the change-over to the low-spin state does not proceed to include all molecules within the lattice. However, a detailed characterization of the observed transition must await at least the results of the structure determinations both above and below  $T_c$ .

In the recently investigated compounds<sup>6</sup>  $[Fe(phen)_2(NCS)_2]$  and  $[Fe(phen)_2(NCSe)_2]$ , it has also been found that more than one value of the low-temperature terminal moment (*viz.* at 77°K) results. In this case, the low-temperature infrared spectra in the region of the CN stretch clearly demonstrate that, below  $T_c$ , the high moment values originate in some percentage of molecules which are in the  ${}^5T_2$  ground state. Thus it is very likely that, in these compounds, several polymorphs may also be formed, and, in this case, the observed transition would be completely analogous to the transition in  $[Fe(dip)_2(NCS)_2]$ .

**Acknowledgments.** One of the authors (E. K.) expresses his gratitude to Professor C. J. Ballhausen for his hospitality at the H. C. Ørsted Institute and acknowledges a NATO fellowship provided by the DAAD. The cooperation of Dr. D. H. Christensen and Dr. E. Lindner in measurements of infrared spectra is gratefully appreciated.

## Linkage Isomerism of Cyanide Ion. Kinetics and Mechanisms of Reactions of Chromium(II) and Cyanocobalt(III) Complexes<sup>1</sup>

James P. Birk and James H. Espenson

*Contribution from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010. Received October 26, 1967*

**Abstract:** The reaction of  $Cr^{2+}$  with  $Co(NH_3)_5CN^{2+}$ , *trans*- $Co(NH_3)_4(H_2O)CN^{2+}$ , and *trans*- $Co(en)_2(H_2O)CN^{2+}$  produces a metastable intermediate common to all three reactions. On the basis of its kinetic, spectral, and Cr-51 tracer behavior, the intermediate is postulated to be the N-bonded isocyano complex  $(H_2O)_5CrNC^{2+}$ , in rapid equilibrium with the acid form  $(H_2O)_5CrNCH^{3+}$ . The isomerization reaction forms quantitative yields of  $(H_2O)_5CrCN^{2+}$  under all conditions, and the rate equation has two terms, one of which corresponds to Cr(II) catalysis of ligand isomerization. Various properties and reactions of the intermediate have been studied in some detail. Results are discussed in terms of the isomeric model, and other formulations are also considered.

The possible existence of linkage isomers of cyanide ion in coordination compounds has been recognized for some time.<sup>2</sup> This phenomenon finds considerable

(1) (a) Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission. Contribution No. 2157. (b) Based on the Ph.D. thesis of J. P. B., Iowa State University, 1967.

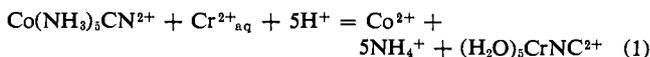
(2) N. V. Sidgwick, "Chemical Elements and their Compounds," Vol. I, Clarendon Press, Oxford England, 1950, p 671.

precedence in organic compounds, and the intramolecular isomerization of isocyanides to the generally more stable nitriles has been studied extensively in solution and in the gas phase.<sup>3</sup> In an earlier communication<sup>4</sup> on

(3) F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **84**, 4215 (1962).

(4) J. H. Espenson and J. P. Birk, *ibid.*, **87**, 3280 (1965).

the reaction of pentaamminecyanocobalt(III) ion and chromium(II), we reported evidence for formation of an isocyanochromium(III) ion as the first step of this reaction (eq 1), and its subsequent isomerization as the second (eq 2).



Until a few years ago the only verified occurrence of linkage isomerism in coordination compounds was for nitro ( $-\text{NO}_2^-$ ) and nitrito ( $-\text{ONO}^-$ ) complexes. Since 1963 this phenomenon has been discovered for other polyatomic ligands, both in the sense of a reversal of stabilities and the discovery of metastable configurations.

Halpern and Nakamura<sup>5</sup> studied the reaction of  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$  with  $\text{Co}(\text{CN})_5^{3-}$ . This reaction occurs in two steps, and the intermediate was presumed to be  $\text{Co}(\text{CN})_5\text{NC}^{3-}$  which reverted in a first-order process to  $\text{Co}(\text{CN})_5^{3-}$  with a half-life of 1.6 sec at 25°. This latter ion is known by neutron diffraction results to have a C-bonded structure.<sup>6</sup>

More recently Haim and Sutin<sup>7</sup> have shown that the S-bonded thiocyanate complex  $(\text{H}_2\text{O})_5\text{CrSCN}^{2+}$  is an important product in the reduction of N-bonded  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$  by  $\text{Cr}^{2+}$ . The S-bonded Cr(III) complex is slowly converted to the more stable N-bonded species  $(\text{H}_2\text{O})_5\text{CrNCS}^{2+}$ . In the case of thiocyanate ion the bonding situation is rather closely balanced, and depending on the metal ion complex, either configuration may be the more stable.<sup>8</sup>

Formation of such a linkage isomer may occur in a ligand-bridged electron-transfer reaction, provided the ligand is polyatomic and ambidentate. The question of whether electron transfer may occur over ligand positions one or more atoms removed from the oxidizing agent is an interesting one, and one that is important in establishing the configuration of the inner-sphere transition state for electron-transfer reactions. Direct observation of reaction intermediates or linkage isomeric products may provide useful insights for these problems.

We have carried out a detailed study of reactions of several monocyano cobalt(III) complexes with chromium(II), and have sought to accumulate as much evidence as possible concerning the intermediate in these reactions. The reactions are formulated in terms of a common intermediate, the N-bonded isocyanochromium(III) ion, but other possibilities are also considered. In addition, a search was made for other complexes in which cyano linkage isomerism might be expected to play an important role.<sup>9</sup> Less extensive studies have been carried out on the reaction of  $\text{Cr}^{2+}$  with the dicyano species  $\text{cis-Co}(\text{en})_2(\text{CN})_2^+$ ; this reaction involves one or more intermediates different from  $\text{CrNC}^{2+}$ .

(5) J. Halpern and S. Nakamura, *J. Am. Chem. Soc.*, **87**, 3002 (1965).

(6) N. A. Curry and W. A. Runciman, *Acta Cryst.*, **12**, 674 (1959).

(7) A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **87**, 4210 (1965); **88**, 434 (1966).

(8) (a) J. L. Burmeister and F. Basolo, *Inorg. Chem.*, **3**, 1587 (1964); (b) F. Basolo, W. H. Baddley, and J. L. Burmeister, *ibid.*, **3**, 1202 (1964); (c) J. L. Burmeister, *ibid.*, **3**, 919 (1964); (d) F. Basolo, J. L. Burmeister, and A. J. Poë, *J. Am. Chem. Soc.*, **85**, 1700 (1963); (e) H.-H. Schmidke, *ibid.*, **87**, 2522 (1965); *Z. Physik. Chem. (Frankfurt)*, **45**, 305 (1965).

(9) In work reported subsequent to completion of these studies, K. Kuroda and P. S. Gentile [*Inorg. Nucl. Chem. Letters*, **3**, 151 (1967)] claim the synthesis of an isocyanocobalt(III) complex,  $\text{cis-}\beta\text{-[Co(NC)}_2\text{(trien)]ClO}_4$ .

## Experimental Section

**Materials.** Chromium(II) perchlorate solutions were prepared by three independent methods. Doubly recrystallized chromium(III) perchlorate was reduced either electrolytically or with amalgamated zinc, and high-purity chromium metal was dissolved in dilute perchloric acid. The detailed procedures of preparation, handling, and analysis of these solutions have been described previously.<sup>10</sup> The analytical procedure for chromium(II) we found most generally useful, especially at low concentration, was based on its reduction of a slight excess of pentaamminechlorocobalt(III). The cobalt(II) so produced was analyzed spectrophotometrically with thiocyanate ion in 50 vol % acetone.

The compounds  $[\text{Co}(\text{NH}_3)_5\text{CN}](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$  and  $\text{trans-}[\text{Co}(\text{NH}_3)_4(\text{OH}_2)\text{CN}]\text{Cl}_2$  were prepared by the method of Siebert<sup>11</sup> and were carefully purified by recrystallization. The procedure of Chan and Tobe<sup>12</sup> was used to prepare  $\text{trans-}[\text{Co}(\text{en})_2(\text{OH})\text{CN}]\text{Cl} \cdot 2\text{H}_2\text{O}$ ; solutions of the aquo ion  $\text{trans-Co}(\text{en})_2(\text{H}_2\text{O})\text{CN}^{2+}$  were prepared by dissolving the solid in dilute perchloric acid. Purification of this complex was not completely successful, and the chloro complex  $\text{trans-Co}(\text{en})_2\text{Cl}(\text{CN})^+$  is a probable impurity.  $\text{cis-}[\text{Co}(\text{en})_2(\text{CN})_2]_2(\text{S}_2\text{O}_8)$  was prepared by the method of Rây and Sarma<sup>13</sup> and converted to the chloride salt by the method of Chan and Tobe.<sup>12</sup> Solutions of cobalt(III) complexes were analyzed spectrophotometrically after reduction with excess chromium(II). The visible and ultraviolet spectra of the cobalt(III) complexes were generally in very close agreement with published values.<sup>14</sup>

Lithium perchlorate was prepared by the dissolution of lithium carbonate in perchloric acid and was recrystallized at least twice from water. Stock solutions were analyzed by titrating with standard base the hydrogen ion released from a column of cation-exchange resin. Water used in all reagent purifications and solutions and in all rate measurements was the product of a double redistillation of laboratory distilled water from alkaline permanganate in a tin-lined Barnstead still. All other reagents were of the best available grade and were used without further purification. Solutions used in volumetric procedures were prepared and analyzed by accepted procedures.

**Kinetics Experiments.** The oxidation-reduction reactions and the decay of the intermediate were studied spectrophotometrically using a Cary Model 14 recording spectrophotometer. Reaction vessels were cylindrical spectrophotometer cells capped with rubber serum caps. Reaction solutions, complete but for one reactant (usually chromium(II), occasionally cobalt(III)), were purged with a stream of nitrogen introduced through a Teflon needle. The purging gas had been purified of traces of oxygen by prior passage through a succession of scrubbing solutions: two chromium(II) solutions, dilute sodium hydroxide, and water. The purging was maintained for at least 20 min, and the solution was then brought to reaction temperature by immersing the cell in a thermostated water bath for a minimum of 30 min prior to injection of the last reagent with a calibrated syringe and needle preflushed with purified nitrogen. Constant temperature was maintained during reaction by circulating constant-temperature water through coils surrounding the water-filled cell holder, described in detail elsewhere.<sup>15a</sup> In studies carried out below room temperature, a continuous stream of dry air was passed through the cell compartment to prevent condensation of water vapor on surfaces in the light path.

The oxidation-reduction reactions of  $\text{Cr}^{2+}$  with  $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CN}^{2+}$  and  $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{CN}^{2+}$  are fairly rapid; very low concentrations of  $\text{Cr}^{2+}$ , from  $10^{-5}$  to  $10^{-4}$  M, were needed to bring the rates into a range measurable by the above procedure. Measurements under these concentration conditions could possibly be seriously in error from partial oxygen oxidation of chromium(II) despite the precautions taken. Agreement with subsequent

(10) J. H. Espenson, *Inorg. Chem.*, **4**, 1025 (1965).

(11) H. Siebert, *Z. Anorg. Allgem. Chem.*, **327**, 63 (1964).

(12) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 966 (1963).

(13) P. R. Rây and B. Sarma, *J. Indian Chem. Soc.*, **28**, 59 (1951).

(14) Values of  $\lambda_{\text{max}}$  ( $\epsilon$ ) for each cobalt(III) complex used in these studies and the literature values, where available, are as follows:  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ , 4400 Å (58  $M^{-1} \text{cm}^{-1}$ ), 3270 (53.5) [lit.<sup>11</sup> 4410 (56.2), 3270 (52.5)];  $\text{Co}(\text{NH}_3)_4(\text{OH}_2)\text{CN}^{2+}$ , 4550 (67.5), 3340 (52.1), 2080 (18,480);  $\text{Co}(\text{en})_2(\text{OH})\text{CN}^{2+}$ , 4450 (79), 3260 (67), 2100 (21,400) [lit.<sup>12</sup> 4500 (80), 3260 (65)]. *Anal.* Calcd for  $[\text{Co}(\text{NH}_3)_5\text{CN}](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ : Co, 15.59. Found: Co, 15.44. Calcd for  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CN}]\text{Cl}_2$ : Co, 24.36. Found: Co, 23.60. Calcd for  $[\text{Co}(\text{en})_2(\text{OH})\text{CN}]\text{Cl} \cdot 2\text{H}_2\text{O}$ : Co, 20.07. Found: Co, 19.54.

(15) (a) J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 5101 (1964); (b) D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **6**, 1370 (1967).

stopped-flow studies proved that such was not the case in these studies although an occasional run gave a widely discrepant rate constant attributed to this cause. Experiments were extended to cover substantially higher chromium(II) concentrations using the stopped-flow technique. Details of the apparatus have been described previously.<sup>15b</sup> Each chromium(II) dilution used in a particular series of stopped-flow reactions was sampled and analyzed periodically during the course of the experiments. In the stopped-flow experiments generally 5–10 repetitive measurements were made on each set of solutions.

The kinetic data were fit to the appropriate integrated rate equation either by a graphical procedure or by a nonlinear least-squares computer program.<sup>16</sup>

**Tracer Experiments.** Isotopically labeled  $\text{Cr}^{2+}$  solutions were prepared from chromium-51 purchased as a solution of chromium(III) in hydrochloric acid. The tracer was added to a  $\text{Cr(III)}$  solution generally before its reduction to  $\text{Cr(II)}$ . Some solutions were prepared by adding  $\text{Cr-51}$  to  $\text{Cr(II)}$ ; the rapid electron exchange reaction of  $\text{Cr(II)}$  and  $\text{CrCl}^{2+}$  ensured equilibrium labeling of  $\text{Cr(II)}$  in this procedure as well.

Separation of  $\text{Cr}^{2+}$  and  $\text{CrCN}^{2+}$  for isotopic assay was carried out by the following procedure. Solutions were quenched in a stream of air, which oxidized  $\text{Cr}^{2+}$  to  $\text{Cr}_2(\text{OH})_2^{4+}$ , and then transferred to columns of Dowex 50W-X8, 50–100 mesh cation resin in the hydrogen ion form, contained in a piece of Tygon tubing about 12 mm  $\times$  8 cm. The resin was then rinsed with 200 ml of 2 *F*  $\text{HClO}_4$ . The first 15–20 ml of acid eluent was collected as the  $\text{CrCN}^{2+}$  fraction and contained most of the  $\text{CrCN}^{2+}$  and  $\text{Co}^{2+}$  produced. The length of resin containing  $\text{Cr}_2(\text{OH})_2^{4+}$  was treated with sodium hydroxide–hydrogen peroxide solution to remove the chromium. The resulting chromium(VI) solution was used as the  $\text{Cr}^{2+}$  fraction.

The specific activity of each fraction was determined by counting a 5-ml sample in a well-type scintillation counter at the energy maximum of the  $\text{Cr-51}$   $\gamma$  radiation and spectrophotometrically analyzing for chromium. The chromium analysis consisted of measurement of the 372-nm chromate absorbance<sup>17</sup> for the  $\text{Cr}^{2+}$  fraction or the diphenylcarbazide method<sup>18</sup> for the  $\text{CrCN}^{2+}$  fraction (since  $\text{Co}^{2+}$  interferes with the alkaline chromate method). No colored species which might interfere with the chromium analysis could be bleached or eluted from the resin.

## Results

**Oxidation–Reduction Reactions.** The immediate product of the reaction of chromium(II) with  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ , *trans*- $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CN}^{2+}$ , and *trans*- $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{CN}^{2+}$  is a metastable intermediate (discussed in detail later) which decays to form quantitative yields of  $(\text{H}_2\text{O})_5\text{CrCN}^{2+}$ . The stoichiometry of the over-all reaction (eq 3) was verified by ion exchange and spectro-



photometric techniques as follows. The products of each reaction were passed through a 25-cm column of cation-exchange resin in the sodium ion form and subsequently eluted by sodium perchlorate. Sufficiently slow elution with the appropriate concentration of electrolyte resulted in a fairly good separation of  $\text{CrCN}^{2+}$  from  $\text{Co}^{2+}$ . Cyanochromium(III) ion was eluted first (with 0.01 *F* perchloric acid, 1 *F* sodium perchlorate) and, after ca. 40% of it had been recovered,  $\text{Co}^{2+}$  began to come off the column. A slightly higher electrolyte concentration efficiently moved  $\text{Co}^{2+}$  from the resin. No visual evidence for other chromium(III) species was noted; in particular, a band of the hexaquo ion was absent. The yield of  $\text{CrCN}^{2+}$  appeared to be quantitative regardless of which reactant was in excess, as judged by the visual absence of other substances on the resin column and by the constancy of the  $\text{CrCN}^{2+}$  spectrum from early and late elution fractions.

(16) The nonlinear least-squares programs are based on the report from Los Alamos Scientific Laboratory, LA2367 + addenda.

(17) G. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

(18) G. P. Rowland, Jr., *Ind. Eng. Chem., Anal. Ed.*, **11**, 442 (1939).

The indicated 1:1 stoichiometry for the reaction of chromium(II) and monocyanocobalt(III) was verified by spectrophotometric measurements. Addition of various amounts of chromium(II) to solutions containing excess cobalt(III) complex produced total absorbance changes directly proportional to the chromium(II) concentration. The absorbance change remained invariant, however, for solutions containing a given concentration of cobalt(III) complex and various excess concentrations of chromium(II). These observations are consistent only with the 1:1 stoichiometry given in eq 3.

Kinetic studies were carried out on the first stage of reaction which corresponds to an electron-transfer process (eq 4). In the interest of clarity, we shall represent the process in eq 4 by a reaction producing meta-



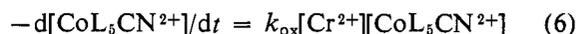
stable  $\text{CrNC}^{2+}$  although, as discussed later, this is not the only possible interpretation of the data; this representation is given in eq 5. The rate studies on these reactions were made by conventional spectrophotome-



tric measurements with a Cary Model 14 recording spectrophotometer (all complexes) and also by the stopped-flow technique (aquo complexes) utilizing spectrophotometric detection. These measurements were made both at maxima in the visible spectra of the cobalt(III) complexes and at wavelengths in the ultraviolet region where the molar absorptivities of the complexes are large ( $\epsilon \sim 2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 210 nm). The second-stage reaction did not interfere because either the first-stage reaction was much more rapid under all conditions (aquo complexes), or else studies at low concentration were confined to wave lengths where the second stage absorbance change was negligibly small. We were able to cover quite a large range of concentrations in the kinetic studies since the time scale available with a combination of stopped-flow and conventional measurements is very large and also because the molar absorptivities at the various wavelengths span a wide range. Rate studies were carried out at 5–35° and 0.150 *M* ionic strength (maintained with lithium perchlorate) over the following concentrations (*M*).

Co(III) complex	$10^6[\text{Co(III)}]_0$	$10^6[\text{Cr}^{2+}]_0$	[H <sup>+</sup> ]
$\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$	0.2–600	4.5–650	0.030–0.15
$\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CN}^{2+}$	0.2–60	3.7–1300	0.015–0.15
$\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{CN}^{2+}$	0.08–1300	1.5–1300	0.010–0.15

Rate constants were calculated for each run on the assumption that the oxidation reaction proceeded by a second-order rate law (eq 6). The linearity of the ap-



propriate graphical treatment of the kinetic data and the constancy of  $k_{\text{ox}}$  for a particular cobalt(III) complex over the range of concentrations cited above confirmed the assumed rate expression. Table I summarizes the observed average values of  $k_{\text{ox}}$  for each complex at the temperatures studied.

The temperature dependence of the rate constants was expressed in the form of the absolute rate theory expression, and values of the activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  (with  $\kappa = 1$ ) were calculated for each reaction. This computation was carried out with a nonlinear

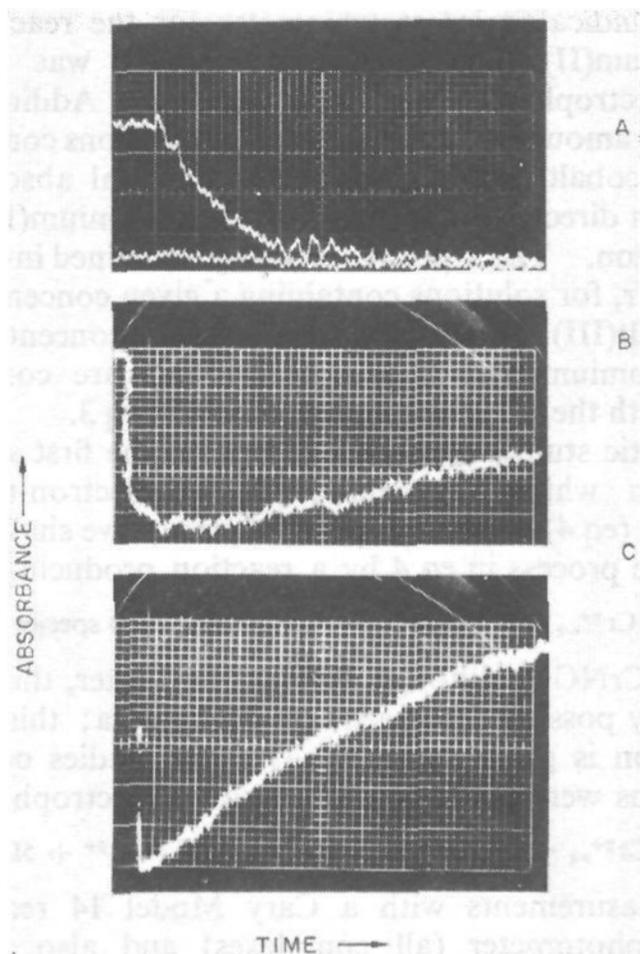


Figure 1. Stopped-flow oscillograms showing the presence of an intermediate in the reaction of  $\text{Cr}^{2+}$  with  $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CN}^{2+}$ . Conditions:  $5.25 \times 10^{-3} M \text{Cr}^{2+}$ ,  $9.65 \times 10^{-4} M \text{Co}(\text{III})$ ,  $0.995 M \text{H}^+$ ,  $I = 1.00 M$ ,  $25.0^\circ$ ,  $\lambda 520 \text{ nm}$ . The three photographs represent different sweep speeds: 50 msec/cm (top), 2.0 sec/cm (middle), and 16.4 sec/cm (lower). The vertical scale represents  $\sim 0.015$  absorbance unit full scale.

least-squares program for the IBM 360 computer;<sup>16</sup> the results are presented in Table II.

Table I. Rate Constants for Oxidation of Chromium(II) by Cyanocobalt(III) Complexes<sup>a</sup>

Complex	Temp, °C	$k_{\text{ox}}, M^{-1} \text{sec}^{-1}$	
		Exptl <sup>b</sup>	Calcd <sup>c</sup>
$\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$	5.1	$14.5 \pm 0.5$	14.4
	15.0	$22.8 \pm 2.0$	22.9
	25.0	$35.8 \pm 1.3$	35.5
<i>trans</i> - $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CN}^{2+}$	15.8	$1230 \pm 80$	1230
	25.0	$1450 \pm 130$	1420
	34.2	$1670 \pm 110$	1625
<i>trans</i> - $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{CN}^{2+}$	15.8	$770 \pm 120$	790
	25.0	$1120 \pm 90$	1090
	34.2	$1490 \pm 160$	1470

<sup>a</sup> Ionic strength 0.150 *M* with lithium perchlorate and perchloric acid. <sup>b</sup> The tabulated values of  $k_{\text{ox}}(\text{exptl})$  are weighted averages (weight =  $1/k_{\text{ox}}^2$ ) and uncertainties are mean weighted average deviations. <sup>c</sup> Calculated from the activation parameters in Table II.

Table II. Activation Parameters for Chromium(II)-Cobalt(III) Reactions

	$\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$	$\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CN}^{2+}$	$\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{CN}^{2+}$
$\Delta H^\ddagger$ , kcal mole <sup>-1</sup> <sup>a</sup>	$6.9 \pm 0.4$	$2.1 \pm 0.3$	$5.4 \pm 0.3$
$\Delta S^\ddagger$ , eu <sup>a</sup>	$-28.3 \pm 1.2$	$-37.2 \pm 0.9$	$-26.7 \pm 1.0$

<sup>a</sup> In the least-squares computation of the activation parameters, individual values of  $k_{\text{ox}}$  were weighted as  $1/k_{\text{ox}}^2$ . The uncertainties given for  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are standard deviations.

**Formation of  $\text{CrNC}^{2+}$  and Its Isomerization.** Spectrophotometric studies on the reaction of chromium(II) and  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$  gave clear evidence for the existence of an intermediate; some of these results were cited earlier.<sup>4</sup> Similar observations were made on the reactions of chromium(II) with the complexes *trans*- $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CN}^{2+}$  and *trans*- $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{CN}^{2+}$ . Since the aquo complexes have relatively high rate constants for the first (electron-transfer) stage, the effects can be illustrated quite dramatically. Figure 1 shows the absorbance behavior at 520 nm for a particular reaction of chromium(II) with  $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CN}^{2+}$ . The rapid decrease in absorbance at 520 nm corresponds to the first-stage electron-transfer reaction which, in this particular run, follows kinetics that are nearly pseudo-first order with a half-life of 44 msec at  $25.0^\circ$  and ionic strength 1.0 *M*. The subsequent absorbance increase is revealed quite distinctly in the slower sweeps at the same wavelength. This second-stage process follows pseudo-first-order kinetics and measures the rate of formation of cyanochromium(III) ion ( $\lambda_{\text{max}} 525 \text{ nm}$ ) from the reaction intermediate. Our interpretation of this step is that it corresponds to a reaction in which the relatively unstable isocyano complex reverts to the more stable C-bonded form (eq 7).



Detailed kinetic studies on the rate of reaction 7 were carried out for each cobalt(III) complex at ionic strength 1.00 *M* (maintained with lithium perchlorate) under the following conditions.

Temp, °C	[Co(III)], <i>M</i>	Excess [Cr <sup>2+</sup> ], <i>M</i>	[H <sup>+</sup> ], <i>M</i>
15.0	0.002–0.015	0–0.041	0.40
25.0	0.004	0.00081–0.041	0.05–0.91

These studies confirmed the first-order kinetics of the linkage isomerization reaction (eq 7), and the data in each run were fit to a first-order rate law (eq 8). Values

$$-d[\text{CrNC}^{2+}]/dt = k_i[\text{CrNC}^{2+}] \quad (8)$$

of  $k_i$  increase linearly with increasing chromium(II) concentration, consistent with a two-term rate expression (eq 9) in which one term involves catalysis by

$$k_i = k' + k_c'[\text{Cr}^{2+}] \quad (9)$$

chromium(II). Typical plots of  $k_i$  vs.  $[\text{Cr}^{2+}]$  at constant hydrogen ion concentration are shown in Figure 2, for experiments in which each of the three cobalt complexes was used as a starting material. The data depicted in Figure 2 prove that, within experimental error, the kinetics for reaction 7 are *independent of the cobalt(III) complex used as the source of intermediate in a particular experiment*. This feature of the kinetic behavior is important in our interpretation and will be referred to further in the discussion.

The data at  $15.0^\circ$  and 0.400 *M*  $\text{H}^+$  ( $I = 1.00 M$ ) were fit to eq 9 with a nonlinear least-squares computer program.<sup>16</sup> The parameters derived considering simultaneously data for all three cobalt(III) complexes are  $k' = 0.0100 \pm 0.0004 \text{ sec}^{-1}$  and  $k_c' = 0.569 \pm 0.029 M^{-1} \text{sec}^{-1}$ , from which one calculates that the average deviation of observed and calculated  $k_i$  is 8.2%. This fit can be compared to that obtained when the rate constants for each of the three cobalt(III) complexes were treated separately to arrive at individual sets of constants

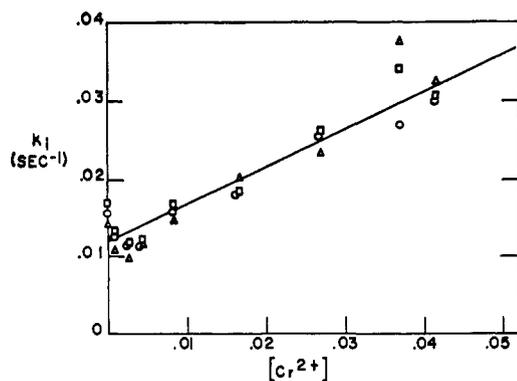


Figure 2. Plot of  $k_i$  vs.  $[\text{Cr}^{2+}]$  at constant  $[\text{H}^+]$  for the isomerization of  $\text{CrNC}^{2+}$  at  $15.0^\circ$ ,  $0.40\text{ M H}^+$ ,  $I = 1.00\text{ M}$ :  $\circ$ ,  $\text{Co}(\text{NH}_3)_6\text{CN}^{2+}$ ;  $\square$ ,  $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2\text{CN}^{2+}$ ;  $\triangle$ ,  $\text{Co}(\text{en})_2(\text{H}_2\text{O})_2\text{CN}^{2+}$ .

$k'$  and  $k_c'$ . The average deviation then was 6.7% for  $\text{Co}(\text{NH}_3)_6\text{CN}^{2+}$ , 8.3% for  $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2\text{CN}^{2+}$ , and 7.6% for  $\text{Co}(\text{en})_2(\text{H}_2\text{O})_2\text{CN}^{2+}$ . Since the fit was nearly as good for all complexes considered together as it was for each treated independently, we conclude that the second-stage kinetics are independent of the choice of cobalt(III) complexes, as stated above.

The concentration of hydrogen ion was varied over the range of  $0.05 < [\text{H}^+] < 0.91\text{ M}$  in the experiments at  $25.0^\circ$ . At low  $[\text{H}^+]$  ( $< ca. 0.2\text{ M}$ ), the rate remained approximately independent of  $[\text{H}^+]$  within experimental error, whereas the values of  $k_i$  decreased at higher  $[\text{H}^+]$ . This effect persisted both at low  $[\text{Cr}^{2+}]$  when the dominant reaction term was  $k'$  and at high  $[\text{Cr}^{2+}]$  when the  $k_c'$  term carried most of the reaction. The effect of  $[\text{H}^+]$  is depicted in the runs shown in Figure 3, which cover a range of  $[\text{Cr}^{2+}]$  such that 11.5, 34, and 50% of the reaction proceeds by the chromium(II)-catalyzed pathway. The rate measurements were not extremely precise, however, although all the data appeared consistent with an increasing order with respect to  $[\text{Cr}^{2+}]$  as its concentration increased, but a decreasing order in  $[\text{H}^+]$ . Since several free parameters are involved, these data are open to a possible reinterpretation; we have chosen to describe the behavior as simply as possible and with the minimum number of adjustable parameters. The plots shown in Figure 3 are of the form  $k_i$  (log scale) at constant  $[\text{Cr}^{2+}]$  vs.  $[\text{H}^+]$  (log scale). The decreasing order with respect to  $[\text{H}^+]$  as  $[\text{H}^+]$  increases suggests a rate equation involving a sum of terms in the denominator which can be written in a form suggesting a preequilibrium protonation step (eq 10). This equation requires that a plot of  $1/k_i$  vs.

$$k_i = (k + k_c[\text{Cr}^{2+}]) \frac{Q_a}{Q_a + [\text{H}^+]} \quad (10)$$

$[\text{H}^+]$  (at constant  $[\text{Cr}^{2+}]$ ) be linear, with intercept  $1/(k + k_c[\text{Cr}^{2+}])$  and slope = intercept/ $Q_a$ . Typical plots at two chromium(II) concentrations are shown in Figure 4. It should be noted that the data in Figures 3 and 4 illustrate that the hydrogen ion dependence is also independent of the cobalt(III) complex used as the source of intermediate. The data for all complexes at  $25.0^\circ$  were fit to eq 10 considering simultaneously the dependence on  $[\text{Cr}^{2+}]$  and  $[\text{H}^+]$ . This computation was carried out by means of a nonlinear least-squares procedure with three adjustable parameters. The values

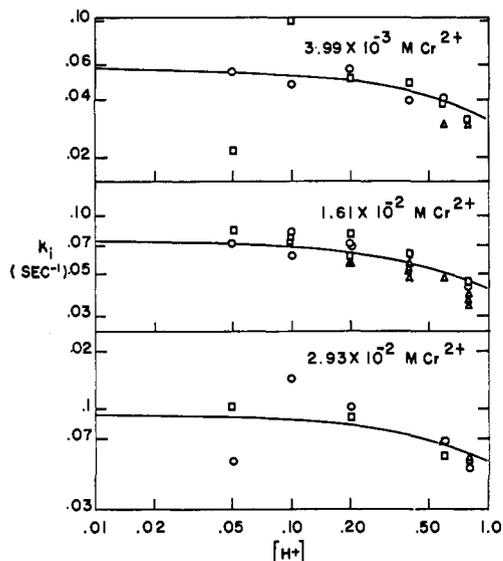


Figure 3. Logarithmic plot of  $k_i$  vs.  $[\text{H}^+]$  at constant  $[\text{Cr}^{2+}]$  for the isomerization of  $\text{CrNC}^{2+}$  at  $25.0^\circ$ ,  $I = 1.00\text{ M}$ . Lines were calculated from the best fit of the data to eq 10. For Co(III) legend, see Figure 2.

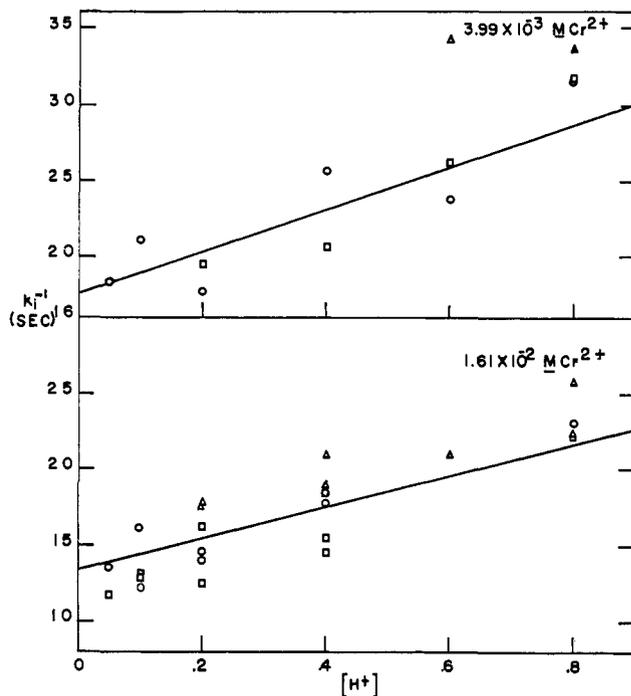


Figure 4. Plot of  $k_i^{-1}$  vs.  $[\text{H}^+]$  at constant  $[\text{Cr}^{2+}]$  for isomerization of  $\text{CrNC}^{2+}$  at  $25.0^\circ$ ,  $I = 1.00\text{ M}$ . Lines were calculated from the best fit of the data to eq 10. For Co(III) legend, see Figure 2. Two of the data points lay so far off the line that they could not be shown on this scale, although they appeared in Figure 3.

at  $25.0^\circ$  obtained for all sources of  $\text{CrNC}^{2+}$  considered simultaneously are  $k = 0.0493 \pm 0.0025\text{ sec}^{-1}$ ,  $k_c = 1.60 \pm 0.14\text{ M}^{-1}\text{ sec}^{-1}$ , and  $Q_a = 1.06 \pm 0.13\text{ M}$ .

**Tracer Experiments on the Isomerization Reaction.** Experiments were performed to decide whether one or both of the pathways for linkage isomerization were accompanied by chromium(II)-(III) electron exchange. On the basis of the specific activity of chromium(II) and of cyanochromium(III) ion at the end of the isomer-

Table III. Exchange of  $^{51}\text{Cr}^{2+}$  with the Intermediate<sup>a</sup>

$10^3[\text{CrNC}^{2+}]_0,^b$ <i>M</i>	$10^3[\text{CrCN}^{2+}]_0,^c$ <i>M</i>	$[^* \text{Cr}^{2+}]$ , <i>M</i>	$10^{-6} \times$ specific activity, counts/min mmole								Model <sup>d</sup> for calcn
			$\text{Cr}^{2+}$ fraction				$\text{CrCN}^{2+}$ fraction				
			Initial	Obsd	Cor <sup>d</sup>	Calcd	Obsd	Cor <sup>d</sup>	Calcd		
9.98	0	0.0111	9.91	5.46	8.06	7.76	4.78	2.04	2.34	I	
						5.15			5.29	II	
						4.03			6.54	III	
						9.91			0.0	IV	
0	9.98	0.0111	9.91	7.31 <sup>e</sup>	9.91	...	2.74 <sup>f</sup>	0.0	...	Blank <sup>g</sup>	
9.98	0	0.0204	10.70	7.57	9.44	8.77	6.74	3.08	3.96	I	
						8.29			5.55	II	
						6.56			8.46	III	
						10.7			0.0	IV	
0	9.98	0.0204	10.70	8.83	10.70	...	3.66	0.0	...	Blank	

<sup>a</sup>  $I = 1.00 M$  with  $\text{LiClO}_4$ ;  $0.400 M \text{H}^+$ ;  $15.0^\circ$ . <sup>b</sup> Intermediate was generated by the rapid reaction of  $\text{Cr}^{2+}$  with  $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CN}^{2+}$ . <sup>c</sup>  $\text{CrCN}^{2+}$  was generated by decay of the intermediate. <sup>d</sup> Corrected for subsequent exchange of  $\text{CrCN}^{2+}$  and  $\text{Cr}^{2+}$ . <sup>e</sup> See text. <sup>f</sup> Specific activities for this blank were normalized to the same total activity as in the tracer experiment; observed values were 6.84 for  $\text{Cr}^{2+}$  and 2.55 for  $\text{CrCN}^{2+}$ .

ization reaction, various exchange models can be tested and distinguished from one another.

The tracer experiments were carried out by the following procedure. A solution *ca.*  $0.01 M$  in the isocyano intermediate was generated by the reaction of  $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CN}^{2+}$  and a slight excess of unlabeled chromium(II). This reaction was essentially complete on mixing. A small volume of labeled chromium(II) was added immediately thereafter and the reaction allowed to proceed for a measured length of time corresponding to *ca.* four to five half-lives for isomerization at the particular chromium(II) concentration in question. The reaction was quenched in a stream of air, which oxidized chromium(II) to  $\text{Cr}_2(\text{OH})_2^{4+}$ , a dimer of chromium(III). The species  $\text{CrCN}^{2+}$  and  $\text{Cr}_2(\text{OH})_2^{4+}$  were separated by ion exchange, and the specific activity of each fraction was determined.

Exchange of chromium(II) with the C-bonded cyanochromium(III) ion, which is a subject of a separate publication,<sup>19</sup> complicates the interpretation of the tracer experiments on the isomerization of  $\text{CrNC}^{2+}$ . The exchange rate is not so low that it can be ignored in these experiments. A blank experiment was performed under identical conditions, except that the labeled chromium(II) was added after the isomerization reaction was complete. Exchange was allowed to proceed for the same length of time as in the corresponding tracer experiment, and the solution was then quenched by air oxidation of chromium(II). The fractions  $\text{CrCN}^{2+}$  and  $\text{Cr}_2(\text{OH})_2^{4+}$  were separated as before and the specific activity of each was determined. This blank represents only an approximation to the appropriate blank for the isomerization experiment. In the blank experiment,  $\text{CrCN}^{2+}$  and  $\text{Cr}^{2+}$  were in contact and  $\text{CrCN}^{2+}$  remained at fixed concentration for the entire length of time, whereas in the tracer experiment on isomerization the concentration of  $\text{CrCN}^{2+}$  only slowly built up to this value as a consequence of the slow isomerization of  $\text{CrNC}^{2+}$ . Direct application of this blank to the isomerization experiment will over-correct for the exchange of  $\text{CrCN}^{2+}$  and chromium(II), with the effect that the corrected specific activity of  $\text{CrCN}^{2+}$  will be too low and that of chromium(II) too high. The results of these experiments are summarized in Table III.

Consider the rate law for isomerization at a particular hydrogen ion concentration (eq 9). The interpretation

we have offered is that the chromium(III)-catalyzed term represents a pathway that accomplishes  $\text{CrNC}^{2+}$ - $\text{Cr}^{2+}$  electron exchange, whereas the term  $k'[\text{CrCN}^{2+}]$  implies a reaction which proceeds without  $\text{Cr}(\text{II})$ - $\text{Cr}(\text{III})$  interchange. This model (I) allows one to calculate the expected specific activities of  $\text{CrCN}^{2+}$  and of chromium(II) in the product solutions, assuming no subsequent exchange of  $\text{CrCN}^{2+}$  and chromium(II). The equations and their solution are presented in the Appendix. Other exchange-isomerization patterns must be considered, however, before we can conclude that agreement of model I predictions with experiment constitutes a confirmation of this pattern. Other models we have considered are these: II, chromium(II) exchange accompanies the  $k'$  term but *not* the  $k_c'$  term; III, chromium(II) exchange accompanies both terms; and IV, chromium(II) exchange accompanies neither term. The equations for each model are presented in the Appendix, and the predictions of each model are compared with the observed results in Table III. Only the predictions of model I, chromium(II) transfer for the  $k_c'$  term alone, come close to our results; the direction of the deviations of specific activities observed and those calculated from model I are consistent with the over-correction introduced in the blank.

It should be noted that these computations assumed that  $\text{CrNC}^{2+}$  was formed in the first stage in quantitative yield; *i.e.*, that no  $\text{CrCN}^{2+}$  was formed directly by a reaction involving adjacent attack. This assumption will be discussed in detail in a later section.

**Spectrum of  $\text{CrNC}^{2+}$ .** The visible absorption spectrum was obtained for the intermediate formed in the reaction of  $\text{CoL}_3\text{CN}^{2+}$  complexes with chromium(II). These measurements were carried out at  $2-5^\circ$  to minimize effects of isomerization occurring during the time of spectral measurements. This was not entirely successful since even at the low temperature the half-time for isomerization is *ca.* 200-500 sec (depending on  $[\text{H}^+]$ ), and it was necessary to record spectra as a function of time and extrapolate to the time of mixing. This procedure could be followed readily in dealing with the aquocyano complexes of cobalt(III), but for the pentaammine complex the electron-exchange step was sufficiently slow that substantial isomerization had occurred and a long extrapolation was necessary. The spectrum of the intermediate was essentially identical regardless of which of the three cobalt(III) complexes

(19) J. P. Birk and J. H. Espenson, to be published.

was used to generate it. The general form of the spectrum was that expected for a monosubstituted complex of  $\text{Cr}^{3+}_{\text{aq}}$ . In 0.90  $M$   $\text{H}^+$  absorption peaks of  $\text{CrNC}^{2+}$  appeared at 535 nm ( $\epsilon$  19.6  $M^{-1} \text{cm}^{-1}$ ) and at 396 nm (23), compared with 525 nm (25.2) and 393 nm (20.0) for  $\text{CrCN}^{2+}$ . There were noticeable shifts in the spectrum of  $\text{CrNC}^{2+}$  with  $[\text{H}^+]$ ; e.g., at 0.2  $M$   $\text{H}^+$ ,  $\lambda_{\text{max}}$  532 (22.7) and 393 (22). Such changes are consistent with the protonation equilibrium reaction which was found to be important in the isomerization kinetics (eq 10), but were not sufficiently great to allow us to obtain an accurate value of the equilibrium quotient for acid dissociation,  $Q_a$ .

**Reactions of Chromium(II) with a Dicyano Complex of Cobalt(III).** The electron-transfer reaction between  $\text{Cr}^{2+}$  and the complex  $\text{cis-Co(en)}_2(\text{CN})_2^+$  was examined, primarily to learn whether an isocyano intermediate was involved. The reaction eventually resulted in quantitative yields of  $(\text{H}_2\text{O})_5\text{CrCN}^{2+}$ , although the kinetic situation was considerably more complex than in the case of the monocyano reactions. The details of this reaction have not been completely resolved. The information we have obtained to date is summarized as follows.

Reduction of the dicyanocobalt(III) complex is rather slow compared to the monocyano reactions. The reaction was studied at 15°, 0.15  $M$  ionic strength,  $[\text{H}^+] \cong 0.15 M$ , over the concentration ranges  $2 \times 10^{-4} < [\text{Cr}^{2+}]_0 < 5 \times 10^{-3}$  and  $5 \times 10^{-6} < [\text{Co(III)}]_0 < 2.4 \times 10^{-4} M$  at wavelengths 210–250 nm. The reaction followed pseudo-first-order kinetics under these conditions, with a calculated second-order rate constant of  $4.5 \pm 1.2 M^{-1} \text{sec}^{-1}$ . On the other hand, in two runs at higher concentration,  $[\text{Cr}^{2+}]_0 = 0.02$ ,  $[\text{Co(III)}]_0 = 0.001 M$ , studied at 280 and 300 nm, the absorbance quickly rose to very high values and subsequently fell slowly with a half-time of ca. 400 sec. This behavior is consistent with formation and disappearance of an intermediate, but the rate of its disappearance is far too low for it to be  $\text{CrNC}^{2+}$  (for which, under these conditions,  $t_{1/2} \sim 35$  sec).

### Interpretation and Discussion

**Oxidation-Reduction Reactions.** The rate constants for chromium(II) reduction of the *trans* complexes  $\text{Co(en)}_2(\text{H}_2\text{O})\text{CN}^{2+}$  and  $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CN}^{2+}$  are both substantially larger than the values for reduction of the complex  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$  (Table I). Moreover, the rate constants for the two aquo complexes are rather similar, whereas the aquo complexes react 30–40 times more rapidly than does the pentaammine. The corresponding ratio for chromium(II) reduction of the *trans* complex  $\text{Co(en)}_2(\text{H}_2\text{O})\text{NCS}^{2+}$  relative to  $\text{Co(en)}_2(\text{NH}_3)\text{NCS}^{2+}$  is 370,<sup>7</sup> and for iron(II) reductions of the *trans* complex  $\text{Co(en)}_2(\text{H}_2\text{O})\text{Cl}^{2+}$  and of  $\text{Co(en)}_2(\text{NH}_3)\text{Cl}^{2+}$  it is  $3.6 \times 10^3$ .<sup>20</sup> This effect has been discussed<sup>21,22</sup> in terms of the higher ligand field strength of  $\text{NH}_3$  relative to  $\text{H}_2\text{O}$ ; the greater splitting caused by *trans*  $\text{NH}_3$  leads to a larger activation enthalpy and a lower rate. The studies we have made are consistent with these trends.

The similarity in the reactivity patterns for chromium(II) and iron(II) reactions has been cited<sup>23</sup> as indirect

(20) P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965).

(21) A. E. Ogard and H. Taube, *ibid.*, **80**, 1084 (1958).

(22) D. E. Pennington and A. Haim, *Inorg. Chem.*, **5**, 1887 (1966).

(23) (a) A. M. Zwickel and H. Taube, *Discussions Faraday Soc.*, **29**,

evidence that the latter proceed by inner-sphere transition states analogous to those that can be directly substantiated for the former. Comparable data do not appear to be available, however, for processes that are thought or known to proceed by outer-sphere mechanisms.<sup>24</sup> Studies are needed to examine the effect of such nonbridging ligands for reactions of analogous cobalt(III) complexes with such reducing agents as vanadium(II),  $\text{Cr}(\text{bipy})_3^{2+}$ , and  $\text{Ru}(\text{NH}_3)_6^{2+}$  which are thought or known to react by outer-sphere mechanisms.<sup>23,25</sup>

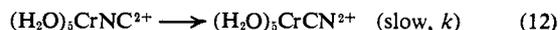
The values of  $\Delta S^\ddagger$  for the electron-transfer reactions of the monocyano ions studied here fall in the general range  $-30 \pm 6$  eu, which is quite typical of the values frequently found for reactions of chromium(II) with dipositive complexes of cobalt(III). Cyanide ion has frequently been cited as a particularly effective ligand in electron-transfer reactions. This is certainly true in outer-sphere reactions, e.g., electron exchange of ferro- and ferricyanide ions. The effectiveness of cyanide ion in inner-sphere reactions, however, is substantially lower than that of any of the halide ions or of azide ion. At least part of the relatively low electron-transfer rate constant for cyanide bridging may be due to the fact that the N-bonded isocyano intermediate constitutes a relatively unstable situation. The slowness of the reactions is not attributable to this factor exclusively, however, for the N-bonded configuration for cyanochromium(III) is less stable than the C-bonded<sup>19</sup> by ca. 2 kcal mole<sup>-1</sup>, whereas  $\Delta G^\ddagger$  is higher for cyano than halo by ca. 7 kcal mole<sup>-1</sup>.

**Isocyanochromium(III) Ion.** The reaction intermediate whose detailed kinetics, exchange, and spectral properties we have studied will be formulated in the following discussion as the isocyanochromium(III) complex,  $(\text{H}_2\text{O})_5\text{CrNC}^{2+}$ . This is not the only possible alternative although it appears to be the most reasonable. Other possible formulations will be discussed later.

The two-term rate equation for the isomerization of the intermediate (eq 9) is consistent with two parallel reaction pathways for isomerization. One of these pathways ( $k$ ) is a first-order decay, and the other ( $k_c$ ) is catalyzed by chromium(II). Moreover, the dependence of rate upon  $[\text{H}^+]$  equally affects both of the isomerization pathways, as described by the rate law given in eq 10. The kinetic observations suggest the following sequence of reactions. A very rapid acid-base equilibrium is involved (eq 11), followed by two independent



and parallel reactions of the basic form of the isocyano complex. The first of these (eq 12) is an intramolecular reaction. The chromium(II) catalysis term is viewed

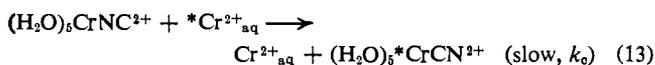


as the result of a Cr(II)–Cr(III) ligand-bridged electron-exchange reaction (eq 13) which, in transferring cyanide ion, causes its net isomerization. These three reactions

42 (1960); (b) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

(24) The rate constants for the reaction of  $\text{V}^{2+}$  with  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$  and  $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CN}^{2+}$  are 11.0 and 9.4  $M^{-1} \text{sec}^{-1}$ , respectively (J. H. Espenson and L. A. Berge, unpublished experiments). The relative values stand in sharp contrast to those found for  $\text{Cr}^{2+}$ .

(25) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964).



lead to the correct expression for the reaction rate, as given in eq 10, and the parameters in that equation are expressed in terms of the elementary reactions given here.

The kinetic behavior of the intermediate does not depend on which of the monocyano cobalt(III) ions is used for its preparation. As presented above, the rate expression and rate parameters for formation of  $CrCN^{2+}$  are independent, within experimental error, of the source of its immediate precursor. This is an important point of evidence in favor of the isocyano formulation, where an intermediate, the ion  $(H_2O)_5CrNC^{2+}$ , is common to all three reactions. As discussed below, the alternate formulations would involve a different intermediate for each reaction. Although such alternates do not necessarily require that the intermediate exhibit kinetic and other properties that are detectably different within experimental error, this interpretation appears the most likely.

The intramolecular pathway, independent of chromium(II) concentration (eq 12), is similar to that found<sup>7</sup> for the analogous isomerization of  $(H_2O)_5CrSCN^{2+}$  and may very well proceed by a similar mechanism. The most likely detailed sequence of reactions for the intramolecular pathway appears to be an ion-pair formulation analogous to that suggested by Haim and Sutin<sup>7</sup> for the related linkage isomerization of  $CrSCN^{2+}$ . According to this model, the reaction involves an intimate ion pair  $[(H_2O)_5Cr^{3+} \cdot NC^-]$  which undergoes "internal return," with accompanying ligand isomerization, at a higher rate than that at which it dissociates to the separated ions. The net effect is intramolecular isomerization, and this process is consistent with the observed first-order kinetics.

The second isomerization pathway involves chromium(II) catalysis, and the mechanism for ligand isomerization we have proposed is a ligand-bridged electron-transfer reaction (eq 13). This, too, finds its parallel in the isomerization of  $(H_2O)_5CrSCN^{2+}$ .<sup>7</sup> In the preliminary communication on the isocyano complex where the rate studies were restricted to relatively low chromium(II) concentrations, we reported that such catalysis played a negligible role in linkage isomerization.<sup>4</sup> Redox catalysis is a less important pathway here then it is for the thiocyanato complex. At 0.01 *M* chromium(II) 24.5% of the isomerization of  $CrNC^{2+}$  goes by the catalyzed pathway, and at 0.05 *M* chromium(II), 61.8%. In contrast, for  $CrSCN^{2+}$  the catalysis would account for >99.9% at either of these chromium(II) concentrations.

The Cr(II)-Cr(III) electron-exchange formulation for the chromium(II) catalysis term  $k_c$  can be tested by use of isotopic tracers. According to the model set forth, only this pathway, and not the first-order term, incorporates Cr(II)-Cr(III) isotopic exchange. As discussed in the section on results, only this particular exchange model agrees with the observed tracer results. This observation in itself cannot be viewed either as proof of the identity of the intermediate or as a sufficient criterion substantiating the electron-transfer mechanism for its isomerization. On the other hand, it is a necessary consequence of the electron-transfer model and provides strong support for the model.

A final point of information about the intermediate is provided by its absorption spectrum at visible wavelengths. The rather high rate at which the intermediate reacts precluded our obtaining very accurate spectral data. The observations on  $CrNC^{2+}$  lead to a long wavelength maximum of  $\sim 535$  nm. Shriver, *et al.*,<sup>26</sup> studied the spectroscopic properties of crystals containing cyanide ion in both C-bonded and N-bonded environments and concluded that the ligand field splitting energy of the N-bonded configuration is somewhat lower. Although our spectra hardly constitute compelling evidence for our assignments, the species  $CrNC^{2+}$  and  $CrCN^{2+}$  have spectra consistent with the ligand field parameters. Moreover, the slight shifts in the spectrum of the intermediate with hydrogen ion concentration over the range 0.2–1 *M*  $H^+$  are consistent with the existence of an equilibrium between two species,  $CrNC^{2+}$  and  $CrNCH^{3+}$ , that can be shifted appreciably by variation of  $[H^+]$  comparable over a range to a value of  $Q_a$  (eq 10). The shifts with  $[H^+]$  are small, which is reasonable for protonation at a site somewhat removed from the metal.<sup>27</sup>

The change in absorption intensity with  $[H^+]$  at a particular wavelength should enable one to calculate an independent value of the acid dissociation constant of  $CrNCH^{3+}$ , which would serve as a check for the value derived from the kinetic studies. The absorptivity changes are so small, however, that little accuracy can be claimed. Provided one considers only those wavelengths where the molar absorptivities of  $CrNC^{2+}$  and  $CrNCH^{3+}$  differ most, the changes with  $[H^+]$  are consistent with  $Q_a \sim 0.2$  *M* at 2–5°, which does not seem unreasonable in view of the value derived from kinetics,  $Q_a = 1.06$  *M* at 25°.

**Alternate Formulations for the Intermediate.** Consider other models, not involving the linkage isomer of cyanochromium(III) ion as the intermediate, that are consistent with the kinetics observed in this particular situation. One such alternate model identifies the reaction intermediate as a dimeric or binuclear species containing both chromium and cobalt, of unspecified oxidation number. The sequence of reactions leading to this intermediate and to its decay, in turn, to  $CrCN^{2+}$  is given as follows. The intermediate is formed from the reaction of the appropriate cyanocobalt(III) complex with chromium(II) (eq 14), and in a subsequent reaction (eq 15) the dimer decom-



poses to yield  $(H_2O)_5CrCN^{2+}$  and  $Co^{2+}$ . This sequence does not specify the detailed composition of the intermediate, especially the question of the number of non-bridging ammine ligands, if any, remaining bonded to cobalt in the dimer. Furthermore, for this model to be consistent with the kinetic pattern observed in these reactions, the second step must proceed by independent parallel paths including a path involving chromium(II) catalysis of the dimer decomposition. The tracer experiments described above demand that the catalyzed pathway results in Cr(II)-Cr(III) interchange, whereas the spontaneous path must not. A further provision must be noted: the intermediates produced from dif-

(26) D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, **4**, 725 (1965).

(27) C. A. Andrade and H. Taube, *ibid.*, **5**, 1087 (1966).

ferent monocyancobalt(III) complexes must either be identical (*i.e.*, they must have lost the ammine groups) or else the kinetic properties for dimer dissociation must be independent, within experimental error, of their compositions.

This formulation appears unlikely. Perhaps the strongest arguments against the binuclear intermediate are those based on its likely chemistry. The dissociation of such a dimer to form  $\text{CrCN}^{2+}$  involves substitution at cobalt(II); that this process would be as slow as observed for the decomposition of this intermediate seems improbable in view of the known rates of Co(II) substitutions. In addition, the role of a Cr(II) catalyst in such a decomposition is difficult to envisage, especially considering the requirements of Cr(II)–Cr(III) exchange accompanying this pathway. Arguments such as these are speculative and secondary, however, and they do not constitute a definitive proof against a mechanism that is otherwise acceptable with all the experimental observations.

In principle this formulation could be tested, relative to the  $\text{CrNC}^{2+}$  model, were a way found to test whether Co(II) is produced at its final concentration by the end of the main oxidation step or whether it builds up to this value during the second stage of reaction. Unfortunately, the media we have found in which one can monitor the Co(II) concentration are quite drastic changes from aqueous solution (*e.g.*, 9 *F* hydrochloric acid or 50 vol % acetone containing  $\text{SCN}^-$ ). A few attempts were made but hardly an exhaustive study; we were unable to detect intermediate formation. This is a question deserving further study.

**Remote and Adjacent Attack.** The question should be raised of whether any of the  $\text{CrCN}^{2+}$  that is produced in the reaction of  $\text{L}_5\text{CoCN}^{2+}$  and  $\text{Cr}^{2+}$  is formed directly rather than through the isocyano intermediate. Direct formation of  $\text{CrCN}^{2+}$  would constitute evidence for a mechanism that could be termed "adjacent attack" of chromium(II), in contrast to  $\text{CrNC}^{2+}$  formation, the result of "remote attack." In the case of  $\text{CrSCN}^{2+}$  and  $\text{CrNCS}^{2+}$ , the very much slower isomerization and the different chemical behavior toward certain reagents permitted a direct assay for the concentration of each isomer and showed that appreciable reaction proceeded by each mechanism.<sup>7</sup> No such distinguishing reactions were discovered despite a survey of some likely possibilities. Two of the studies we have made bear directly on this point although neither can provide a very accurate measure of the importance of the adjacent attack mechanism.

In the spectral studies on the intermediate, the molar absorptivity of  $\text{CrNC}^{2+}$  was calculated on the assumption that 100% of the reaction proceeds through the intermediate, *i.e.*, remote attack is the exclusive pathway. The agreement of the molar absorptivity calculated on this basis for each of the three sources of  $\text{CrNC}^{2+}$  was within the experimental error of the determination (which was unfortunately rather large;  $\epsilon = 24 \pm 1 \text{ M}^{-1} \text{ cm}^{-1}$ ). This observation is taken to mean either that all three sources produced  $\text{CrNC}^{2+}$  exclusively or all three fortuitously produced  $\text{CrCN}^{2+}$  and  $\text{CrNC}^{2+}$  in the same ratio.

The second observation relating to this point has to do with the tracer experiments on the isomerization reaction of  $\text{CrNC}^{2+}$ . An adjacent attack mechanism

produces  $\text{CrCN}^{2+}$  (unlabeled) which can exchange with  $^*\text{Cr}^{2+}$  but which will not incorporate  $^*\text{Cr}^{2+}$  at the rate of the Cr(II)-catalyzed pathway for isomerization. The fair agreement of the experimental values and those calculated on the basis of exclusive  $\text{CrNC}^{2+}$  formation constitutes evidence that direct  $\text{CrCN}^{2+}$  formation is not a major pathway. The correction for  $\text{CrCN}^{2+}$ – $^*\text{Cr}^{2+}$  exchange is large, however, and it cannot be made rigorously. The necessity of this sizable blank correction renders the absence of adjacent attack a rather tentative conclusion.

**Linkage Isomerism of Cyanide Ion.** The possibility of linkage isomerization for cyanide ion has been recognized for some time.<sup>2</sup> The structural question on the mode of cyanide attachment is rather difficult to answer on the basis of X-ray studies although for some materials, notably ferrocyanide ion and  $\text{KAg}(\text{CN})_2$ , very accurate studies have established that the metal atom is attached to carbon.<sup>2</sup> Neutron diffraction studies<sup>6</sup> have established that  $\text{Co}(\text{CN})_6^{3-}$  is carbon bonded. Similar work has not yet been done for  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$  or for any other monocyancobalt(III) complexes.

The kinetics and mechanisms of the reactions involved here have been formulated in terms of C-bonded cobalt(III). The visible spectrum is consistent with this formulation although the anticipated shifts are not likely to be so large as to make the structural assignment completely unambiguous. The similarity of the spectrum of  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$  to that of  $\text{Co}(\text{NH}_3)_5\text{NCCH}_3^{3+}$  has led Sargeson and Taube<sup>28</sup> to suggest that the original Co(III) complex could possibly have the N-bonded isocyano formulation  $\text{Co}(\text{NH}_3)_5\text{NC}^{2+}$ . Siebert<sup>11</sup> interpreted the infrared spectrum in terms of C-bonded cyanide, but again it is not clear that the alternate structure could not give a similar result.

Since Halpern and Nakamura<sup>5</sup> have shown that the reaction of  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$  and  $\text{Co}(\text{CN})_5^{3-}$  produces the metastable intermediate  $\text{Co}(\text{CN})_5\text{NC}^{3-}$ , the isocyano structure for the pentaammine complex appears rather unlikely.<sup>29</sup> The more recent synthesis<sup>9</sup> of a cobalt(III) complex containing an isocyano ligand established that the visible spectra would be shifted only slightly toward lower energies for  $-\text{NC}^-$  compared to  $-\text{CN}^-$ .

In the case of  $(\text{H}_2\text{O})_5\text{CrCN}^{2+}$  it seems somewhat clearer that cyanide is C-bonded in view of the alternate synthesis by the stepwise aquation of hexacyanochromate(III),<sup>30</sup> the latter showing attachment of cyanide through carbon. The nature of the factors leading to a reversal of stabilities does not seem to be well understood even in the case of thiocyanate ion where more documented examples of ligand isomerism are known.<sup>8</sup> A striking example is the stability of the isomer  $\text{Co}(\text{CN})_5\text{SCN}$ ,<sup>3-3c</sup> whereas the isothiocyanate form  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$  is the more stable of the pentaammines.

(28) A. M. Sargeson and H. Taube, *Inorg. Chem.*, **5**, 1094 (1966).

(29) In the cyanocobalt complexes considered here, were the discovery made that the isocyano structure was the form prepared and studied, these results could be most easily explained by invoking adjacent attack of  $\text{Cr}^{2+}$  on  $\text{Co}(\text{NH}_3)_5\text{NC}^{2+}$ , leading to  $\text{CrNC}^{2+}$ . A neutron diffraction study is presently in progress: R. A. Jacobson and W. Ozbirn, private communication.

(30) (a) R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967); (b) W. B. Schaap and R. Krishnamurthy, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 36-O.

The *cis*-dicyanocobalt(III) complex offers an opportunity for a double-bridged transition state. No  $(\text{H}_2\text{O})_4\text{Cr}(\text{CN})_2^+$  could be isolated by ion exchange from a quenched reaction. This is not necessarily proof of its unimportance, however, since it reacts<sup>19</sup> with  $\text{Cr}^{2+}$  at a rate not greatly different from that of  $\text{Cr}^{2+} + \text{Co}(\text{en})_2(\text{CN})_2^+$ . It is possible that this suspected intermediate never builds up to detectable levels.

**Acknowledgment.** We thank Dr. T. W. Newton and R. H. Moore for supplying the computer programs<sup>16</sup> and Professor A. F. Voigt for use of the scintillation counter.

## Appendix

Derivations will be presented for the equations used for calculations of specific activities in the tracer experiments on the  $\text{Cr}^{2+}$ -catalyzed isomerization of  $\text{CrNC}^{2+}$ . The expressions will be simplified by the abbreviations  $\text{A} = \text{CrNC}^{2+}$ ,  $\text{B} = \text{Cr}^{2+}$ , and  $\text{C} = \text{Cr-CN}^{2+}$  to designate the species, and  $A$ ,  $B$ , and  $C$  their concentrations, respectively.

A subscript indicates time and a superscript a tagged Cr atom. The value  $\Sigma B$  stands for  $[\text{Cr}^{2+}] + [^*\text{Cr}^{2+}]$ . Exchange of B and C is specifically excluded and, as discussed in the text, is treated as a correction to the final equation.

According to model I (eq 12, 13) the differential equations are

$$-dA/dt = (k' + k_c' \Sigma B)A \quad (16)$$

$$dC^*/dt = -dB^*/dt = k_c' AB^* \quad (17)$$

Solutions of (16) gives  $A$  as a function of time

$$A = A_0 \exp[-(k' + k_c' \Sigma B)t] \quad (18)$$

Substitution of this result into (17) and integration give

$$\ln(B^*/B_0^*) = [k_c' A_0 / (k' + k_c' \Sigma B)] \{ \exp[-(k' + k_c' \Sigma B)t] - 1 \} \quad (19)$$

At the end of a tracer experiment, the concentration of  $B^*$  is

$$B^*_{\infty} = B^*_0 \exp[-k_c' A_0 / (k' + k_c' \Sigma B)]$$

The final specific activity  $a$  of B in these experiments, where  $B^*_0 = \Sigma B$  is

$$a_B = B^*_{\infty} a_0 / \Sigma B = a_0 \exp[-k_c' A_0 / (k' + k_c' \Sigma B)] \quad (20)$$

Conservation of activity provides a relation from which  $a_c$  can be calculated

$$a_c = (a_0 - a_B) \Sigma B / A_0 \quad (21)$$

Similar expressions can be derived for the other three models.

## Reductions of Pentaamminecobalt(III) Complexes of Substituted Pyridines by Chromium(II)

Francis Nordmeyer and Henry Taube

*Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received June 30, 1967*

**Abstract:** Reactions of  $\text{Cr}^{2+}$  with the pentaamminecobalt(III) complexes of pyridine, nicotinamide, and isonicotinamide were studied. All the complexes are reduced at rates described by a rate law of the form  $k(\text{Co}^{\text{III}}) \cdot (\text{Cr}^{2+})$ . The pyridinepentaammine complex produces only  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  from  $\text{Cr}^{2+}$ , and  $k$  for the reaction at  $25^\circ$  is  $4.0 \pm 0.1 \times 10^{-3} M^{-1} \text{sec}^{-1}$  ( $\Delta H^\ddagger = 9 \pm 2$  kcal/mole,  $\Delta S^\ddagger = -39 \pm 7$  eu). The nicotinamidepentaammine complex yields two products by parallel reaction paths:  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  with  $k = 1.4 \pm 0.1 \times 10^{-2} M^{-1} \text{sec}^{-1}$  at  $25^\circ$  ( $\Delta H^\ddagger = 9 \pm 2$  kcal/mole,  $\Delta S^\ddagger = -36 \pm 7$  eu) and an amide-bound  $\text{Cr}^{\text{III}}$ -nicotinamide complex with  $k = 3.3 \pm 0.2 \times 10^{-2} M^{-1} \text{sec}^{-1}$  at  $25^\circ$  ( $\Delta H^\ddagger = 10 \pm 1$  kcal/mole,  $\Delta S^\ddagger = -31 \pm 3$  eu). The isonicotinamidepentaammine complex reacts to produce an amide-bound  $\text{Cr}^{\text{III}}$ -isonicotinamide complex with  $k = 17.4 \pm 0.5 M^{-1} \text{sec}^{-1}$  at  $25^\circ$  ( $\Delta H^\ddagger = 3.9 \pm 0.3$  kcal/mole and  $\Delta S^\ddagger = -40 \pm 1$  eu). The latter  $\text{Cr}^{\text{III}}$  complex reacts further under the influence of  $\text{Cr}^{2+}$  to produce a pyridinyl nitrogen-bound  $\text{Cr}$ -isonicotinamide complex according to a ( $\text{H}^+$ ) dependent equilibrium. Aquations of the  $\text{Cr}^{\text{III}}$  products were also studied. The structures of  $\text{Cr}^{\text{III}}$  products were assigned on the basis of their infrared spectra. These structures demonstrate that the  $\text{Cr}^{\text{III}}$  products are formed *via* activated complexes in which the oxidizing and reducing centers are coordinated to remote positions of the bridging ligand. Arguments based on rate comparisons indicate that complexes of isonicotinamide react with  $\text{Cr}^{2+}$  by a radical intermediate mechanism.

Pentaamminecobalt(III) complexes of a wide variety of organic molecules have been examined in reactions with reducing agents such as  $\text{Cr}^{2+}$ .<sup>1</sup> In these

(1) See, for example, (a) H. Taube, *Advances in Chemistry Series*, No. 49, American Chemical Society, Washington, D. C., 1965, p 107; (b) E. S. Gould, *J. Am. Chem. Soc.*, **87**, 4730 (1965); (c) *ibid.*, **88**, 2983 (1966).

investigations most interest has been placed on the rates and rate laws of these reactions. In only a few instances were the identity or yields of the  $\text{Cr}^{\text{III}}$  products examined. It appeared to us that, in addition to a rate study, such an examination might be worthwhile for the reactions of  $\text{Cr}^{2+}$  with pyridine-, nicotinamide-, and isonicotinamidepentaamminecobalt(III). In a pre-