

(~10%) and 2E (90%), of ${}^2T_{2g}$. This leads us to point out that, even when large spin-orbit interaction is present, arguments about the energy order of ${}^2T_{2g}$ descendants, i.e., whether ${}^2E[(xz, yz)^3(xy)^2]$ is higher or lower in energy than ${}^2B_2[(xy)^1(xz, yz)^4]$, are still applicable, and in this case are as predicted, ${}^2E < {}^2B_2$ (vide supra).

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Registry No. [Ru(NH₃)₅NCO]Br₂, 55101-90-1; [Ru(NH₃)₅Cl]Cl₂, 18532-87-1; [Ru(NH₃)₅Br]Br₂, 16446-65-4.

References and Notes

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Studies of Ammineaquocobalt(III) Chemistry. Kinetics and Mechanisms of Formation and Dissociation of Monochlorodiammineaquocobalt(III) Complexes and of the Reduction of *cis*-Diammineaquocobalt(III) Species by Br⁻ in Acid Perchlorate Solution¹

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The synthesis and characterization of nitrate and perchlorate salts of *cis*-Co(NH₃)₂(H₂O)₄³⁺ and *fac*-Co(NH₃)₃(H₂O)₃³⁺ is described. Reactivity studies indicate that diammineaquo species are moderately strong oxidizing agents in acid solution but are much more inert to substitution than is Co³⁺_{aq}. The rate law for the approach to equilibrium in the reaction between *cis*-Co(NH₃)₂³⁺_{aq} and Cl⁻ in the concentration ranges [H⁺] = 0.10–1.20 M and [Cl⁻] = 0.10–1.60 M at ionic strength 2.0 M (NaClO₄, HClO₄) over the temperature range 28.0–47.6° is given by $d \ln [\text{Co}(\text{NH}_3)_2\text{Cl}^{2+}_{\text{aq}}] / dt = A'[\text{Cl}^-] / [\text{H}^+] + B' / [\text{H}^+]$, where $A' = (1.50 \pm 0.03) \times 10^{-4} \text{ sec}^{-1}$ and $B' = (2.7 \pm 0.2) \times 10^{-5} \text{ sec}^{-1}$ at 28.0°. The inverse acidity dependence of the rate law is ascribed to the involvement of hydroxodiammineaquocobalt(III) species in the formation and dissociation of the monochlorodiammineaquocobalt(III) complex. The rate law for the *cis*-Co(NH₃)₂³⁺_{aq} oxidation of Br⁻ to Br₂ under similar experimental conditions follows the rate law $-d[\text{Co}^{\text{III}}] / dt = 2d[\text{Br}_2] / dt = (C + D / [\text{H}^+])[\text{Co}^{\text{III}}][\text{Br}^-]$, where $C = (6.0 \pm 0.2) \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ and $D = (1.7 \pm 0.2) \times 10^{-4} \text{ sec}^{-1}$ at 28.0°. Consideration of the rate laws and kinetic parameters obtained in these two reactions suggests that the rate-determining process in the oxidation of Br⁻ by Co(NH₃)₂OH²⁺_{aq} is substitution of the reductant at the metal center. The possible stereochemical directing influence of inner-sphere hydroxide ion is discussed; it appears that a trans-directing influence predominates in these aquo complexes.

Introduction

The Co³⁺_{aq} ion is much more labile to substitution than are typical ammineaquocobalt(III) complexes.³ This unusual property has prompted speculation concerning the decreasing availability of labile, high-spin electronic states of cobalt(III) in the series Co(NH₃)_{*n*}(H₂O)_{6-*n*}³⁺_{aq} as *n* increases from 0 to 5.^{4,5}

Although a wealth of data has been accumulated concerning the kinetic properties of ammineaquocobalt(III) complexes with *n* ≥ 4,⁶ comparatively little is known about aquocobalt(III) species which carry fewer ammonia molecules.⁷⁻⁹

This paper describes the synthesis and characterization of solid *cis*-diammineaquocobalt(III) and *fac*-triammineaquocobalt(III) nitrates and perchlorates, together with studies of the spectral, substitutional, and redox properties of diammineaquo species in acid perchlorate media. Kinetic and spectral data obtained from a detailed investigation of the kinetics of the base-catalyzed reactions of the diammineaquocobalt(III) species with chloride and bromide ions are reported.

Experimental Section

Reagents and Analytical Procedures. The water used throughout this work was doubly distilled from an all-glass apparatus. Sodium perchlorate stock solutions were prepared by neutralization of perchloric acid with sodium carbonate and contained no detectable chloride ion impurities. These solutions were standardized gravimetrically. Reagent grade sodium chloride and sodium bromide were dried at 110° for 8 hr prior to making up stock solutions. All other chemicals were of reagent grade and were used without further purification.

Concentrations of cobalt(II) were determined spectrophotometrically as the thiocyanato complex in 50% v/v aqueous acetone ($\epsilon_{623} = 1842 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁰ Cobalt(III) was determined by treatment of an aliquot with a measured excess of acidic iron(II) solution;⁷ the remaining iron(II) was titrated with standardized chromium(VI) using diphenylamine as the indicator. The stoichiometric cobalt concentrations of reagent solutions were conveniently and accurately measured by treatment of aliquots with 50% w/v aqueous NaOH to pH 13 and dropwise addition of concentrated HCl to bring the pH to 5. This treatment resulted in quantitative reduction to cobalt(II), which was analyzed by the thiocyanate-acetone procedure.¹¹

The stoichiometric ammonia content of reagent solutions was

determined by steam distillation of 5–20-ml aliquots from a large excess of 50% w/v aqueous sodium hydroxide in a closed-still system.¹² Ammonia from the distillation was absorbed in excess 2% aqueous boric acid and then titrated with standardized dilute hydrochloric acid using an indicator consisting of Bromocresol Green (0.1 g in 50 ml of 95% v/v aqueous ethanol) and Methyl Red (0.1 g in 100 ml of 95% v/v aqueous ethanol) mixed in a volume proportion of 5:1. The apparatus was standardized with ammonium chloride over the range of ammonia determined in the cobalt ammine studies and was found to be reproducible to better than $\pm 0.3\%$. Elemental analyses of solid samples were performed by Galbraith Laboratories, Knoxville, Tenn.

Apparatus. Spectrophotometric measurements were made on Cary 14 or Beckman DK-1 ratio recording instruments. The latter was equipped with a temperature-controlled cell housing so that kinetic runs could be made over a temperature range of 28.0–47.6°, with a maximum uncertainty of $\pm 0.2^\circ$ at each temperature. Infrared measurements were performed on a Beckman IR-10 spectrophotometer using Nujol mulls.

Synthetic Methods. The reaction of an aqueous mixture of a cobalt(II) salt and hydrogen peroxide with an aqueous slurry of potassium bicarbonate produces the well-known green "Field-Durrant" solution which is a convenient starting point for the preparation of cobalt ammine complexes.¹³ The product distribution obtained in the reaction of the green solution with ammonium salts was found to be influenced by variations of (i) the initial stoichiometric cobalt(II):ammonium ratio, (ii) the concentration of Cl^- , (iii) reaction temperature, and (iv) reaction time. Two procedures were investigated in some detail in the synthesis of diammineaquocobalt(III) salts. The first involved reaction of excess ammonium carbonate or ammonium chloride with the Field-Durrant solution in boiling aqueous ethanol; the product mixture was separated by cation exchange after addition to excess aqueous HClO_4 and gave good yields of monomeric amminecobalt(III) salts, with the *cis*-diammineaquocobalt(III) complex as the major product. In the second procedure, the reaction was carried out at lower temperatures and, depending on reaction conditions (vide supra), gave both monomeric and dimeric ammineaquocobalt(III) complexes which could be separated by cation-exchange techniques after acidification. In the following sections the synthesis and characterization of *cis*-diammineaquocobalt(III) and *fac*-triammineaquocobalt(III) perchlorates and nitrates are described.

(A) High-Temperature Synthesis. An ice-cold solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (20 g, 0.05 mol) and H_2O_2 (5 ml, 10 M, 0.05 mol) in 200 ml of water was added at the rate of 2 ml/min to a constantly stirred, ice-cold slurry of KHCO_3 (40 g, 0.25 mol) in 200 ml of water, in a 1-l. erlenmeyer flask which was covered with aluminum foil to protect the green product from light. Ethanol (200 ml) was added, and the mixture was heated to boiling. Ammonium chloride (15 g, 0.28 mol) was then added in small amounts with constant stirring over a period of 10 min and the resulting mixture was boiled for a further 10 min before it was cooled and added to a large excess of ice-cold acetone. The blue precipitate¹⁴ was collected on a sintered-glass filter, washed with ice-cold ethanol and peroxide-free ether, and dried in air. The solid was dissolved in an excess of ice-cold 1 M HClO_4 , filtered at 0° to remove KClO_4 , and then charged onto a Dowex 50W-X8 (50–100 mesh) or Dowex 50W-X2 (100–200 mesh) column in the H^+ form. Elution with 1.0 M HClO_4 was continued at room temperature until cobalt(II) could no longer be detected in the eluent. During the later stages of the elution with 1.0 M acid, a minor blue band moved down the column. Analysis showed it to contain cobalt(III) and coordinated ammonia and chlorine. This blue solution reverted to the violet color characteristic of the diammineaquocobalt(III) complex on standing; the same change could be rapidly effected by addition of mercury(II) perchlorate. These results are in agreement with earlier observations.⁷ Treatment of the column with 2.0 M HClO_4 resulted in the isolation of eluent fractions with an $[\text{ammonia}]/[\text{cobalt(III)}]$ ratio of 2.00 ± 0.03 (twenty-five 50-ml fractions). These fractions were combined and evaporated to half-volume at 40° in air, followed by freeze-drying (acetone, solid CO_2 trap) until no more water could be removed. The dark violet crystalline product was separated by filtration and immediately washed with anhydrous peroxide-free ether or hexane¹⁵ and dried in air. The typical yield was 6.1 g (26%) of a complex with the following characteristics: equiv wt calcd for $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4](\text{ClO}_4)_3$ 463.4 g-atom/Co(III), found 466 \pm 5 g-atom/Co(III) (three determinations); ammonia:cobalt(III) calcd 2.00, found (from three determinations) 1.97 ± 0.04 ; N analysis calcd 6.04%, found $5.93 \pm 0.07\%$

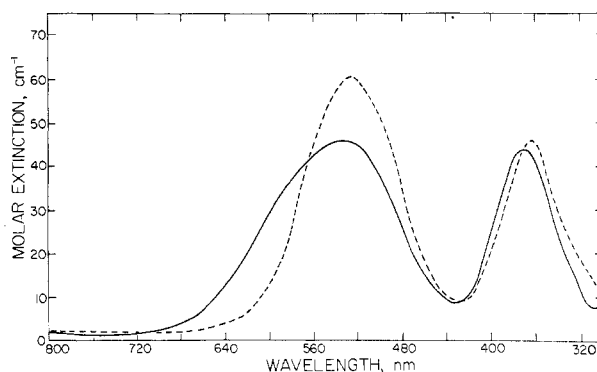


Figure 1. Visible spectra of *cis*- $\text{Co}(\text{NH}_3)_2^{3+}\text{aq}$ (full line) and *fac*- $\text{Co}(\text{NH}_3)_3^{3+}\text{aq}$ (dashed line) complexes in 1.0 M HClO_4 at 25.0°.

(three determinations); ir strong band at 1625 cm^{-1} , general broad absorption $1400\text{--}400\text{ cm}^{-1}$. The uv-visible spectrum (see Figure 1) exhibits maxima at 537 nm (molar absorptivity 48 ± 1) and 370 nm (46 ± 1) with no other maxima in the region 360–210 nm; minima were observed at 440 nm (9.0 ± 0.3) and 310 nm (7.0 ± 0.3).¹⁶

The anhydrous nitrate salt $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4](\text{NO}_3)_3$ was also isolated. This compound was obtained by repeating the above procedure with nitrate substituted for perchlorate throughout or by passing a solution of the perchlorate salt in 0.05 M HNO_3 through an anion-exchange column (Amberlite IRA-400, 20–50 mesh) in the NO_3^- form, followed by evaporation and washing as before. The dark violet, crystalline product was found to be somewhat less soluble than the perchlorate and was much easier to handle. Its ammonia:cobalt(III) ratio and near-uv-visible spectral characteristics were identical with those of the perchlorate salt.

The second major product on the ion-exchange column was eluted with 3 M HClO_4 and yielded chromatographic fractions which all had identical ammonia:cobalt(III) ratios and uv-visible spectra. The carmine red product isolated by evaporation as described above had a stoichiometric ammonia:cobalt(III) ratio of 3.03 ± 0.04 (ten determinations) and contained $9.02 \pm 0.03\%$ N (two determinations) (calcd for $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3](\text{ClO}_4)_3$ 9.07% N). Its uv-visible spectral characteristics (see Figure 1) were as follows: maxima at 526 nm (60 ± 1) and 361 nm (46 ± 1) with no other maxima in the region 210–360 nm; minima at 428 nm (8 ± 1) and 300 nm (12 ± 1). These data are in good agreement with previous measurements.¹⁷ The anhydrous nitrate salt was also prepared and had an identical uv-visible spectrum. Its equivalent weight was found to be 358 ± 4 g-atom/Co(III) (three determinations) (calcd for $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3](\text{NO}_3)_3$ 350.1 g-atom/Co(III)).

B. Low-Temperature Synthesis. Studies were made of the reaction of the Field-Durrant solution with ammonium carbonate and ammonium chloride at various initial ammonia:cobalt ratios under conditions ranging from reaction times of a few minutes at 0° to several days at room temperature.¹⁸ The products of these reactions were separated on a cation-exchange column after addition to excess acid. Fractions which contained identical ammonia:cobalt(III) ratios were segregated and treated as described above to obtain monomeric products with properties identical with those obtained in method A. Special chromatographic techniques developed to obtain fractions containing dimeric cobalt amines will be described in a later paper.

Stoichiometric Measurements. The uv-visible spectra of the final products of the reaction of known amounts of the *cis*-diammine with bromide were examined over the range of conditions used in the kinetic measurements (see below). These spectra were each compared to standard solutions of Br_2 under identical conditions (temperature, $[\text{H}^+]$, $[\text{Br}^-]$, $[\text{Co(II)}]$).

Kinetic Measurements. The reactions of *cis*-diammineaquocobalt(III) with chloride and bromide were monitored spectrophotometrically. In the reaction with chloride, the appearance of the monochloro complex was monitored in the wavelength range 275–315 nm over the following initial concentration ranges: $[\text{Co}^{III}] = (0.78\text{--}3.8) \times 10^{-3}\text{ M}$, $[\text{Cl}^-] = 0.05\text{--}1.60\text{ M}$, and $[\text{HClO}_4] = 0.1\text{--}1.20\text{ M}$. The experimental temperature range was 28.0–47.6°. In the reaction with bromide, spectrometric measurements were made of the disappearance of diammine (at 537 nm) and the appearance of Br_3^- (in the range 340–390 nm) over the concentration ranges $[\text{Co}^{III}]$

= $(0.78-8.0) \times 10^{-3} M$, $[Br^-] = 0.05-1.60 M$, and $[HClO_4] = 0.10-1.20 M$. In all cases the ionic strength of the reaction medium was maintained at $2.0 M$ by addition of sodium perchlorate, and reactant solutions were thermostated at the desired temperature and transferred to the thermostated cell within 60 sec of mixing. Absorbance changes were followed for at least 5 half-lives and final absorbances were obtained for each run.

Results and Treatment of Data

Preliminary Reactivity Studies. A stock solution of the diammine (ca. $5 \times 10^{-2} M$) in $3.0 M HClO_4$ was found to be stable to reduction by water, to dimerization, and to loss of ammonia at 50° for at least 5 days. However, slow titration with sodium hydroxide at 25° resulted in marked spectral changes above pH 2.5. A yellow solid precipitated above pH 3.5. Analysis of this solid showed that coordinated ammonia had been lost to the solution on addition of base. Dissolution of this solid in perchloric acid gave only cobalt(II) and ammonium ions. The marked spectral changes which occur in the region 300-400 nm on addition of base are consistent with acid dissociation of $Co(NH_3)_2^{3+}_{aq}$ followed by polymerization and ammonia loss.²⁰ These properties are very unusual for a cobalt ammine; for example, the first acid dissociation constant of the *fac*- $Co(NH_3)_3(H_2O)_3^{3+}_{aq}$ complex is $4.7 \times 10^{-6} M$ at ionic strength $0.1 M$ ($NaClO_4$) and 20° ,²¹ and ammonia loss is only observed in strongly basic solution.

In $1.0 M HClO_4$, the diammine is rapidly reduced to cobalt(II) by iron(II)⁷ and iodide at room temperature. Complex formation was observed with Cl^- , and the diammine was slowly reduced by $NaBr$ and $NaNCS$ ($5 \times 10^{-2} M$) under similar conditions. Addition of hydrazine resulted in slow gas evolution (presumably nitrogen). Slow reduction was observed with NaN_3 and hydroquinone at 50° .

Kinetics of Formation and Dissociation of Monochloro-aquodiamminecobalt(III) Complexes. In the presence of a large excess of chloride ion, first-order plots of $\log(A_\infty - A_t)$ vs. time, where A_t and A_∞ are the absorbances of the reacting solution at time t and at equilibrium, respectively, were linear for at least 5 half-lives. The results of replicate rate determinations agreed to within $\pm 5\%$.

The final absorbance at fixed wavelength in each run was stable and was used to obtain equilibrium data for the monochlorodiammineaquocobalt(III) complex (see below). At fixed chloride concentration, acidity, and temperature the pseudo-first-order complexation rate constant, k_{obsd} , was independent of the monitoring wavelength and initial cobalt(III) concentration, $[Co(III)]_0$. At fixed acidity and temperature k_{obsd} was, within experimental error, a linear function of $[Cl^-]$, where $[Cl^-]$ is the stoichiometric halide concentration and A and B are empirical constants, eq 1. This

$$k_{obsd} = A[Cl^-] + B \quad (1)$$

relationship is consistent with monochloro complex formation, eq 2.



Acid Concentration Dependence. The empirical parameters A and B in eq 1 were both found to be proportional to $1/[H^+]$ at constant temperature. Including the acid dependence, the observed rate constant is thus given by eq 3, where $A =$

$$k_{obsd} = A'[Cl^-]/[H^+] + B'/[H^+] \quad (3)$$

$A'/[H^+]$ and $B = B'/[H^+]$. According to eq 3, a plot of $k_{obsd}[H^+]$ vs. $[Cl^-]$ should be linear, as was found experimentally (Figure 2).

Complete kinetic data for the reaction with chloride are collected in Table I. Data at fixed temperature were fitted to eq 3 using a nonlinear least-squares program and the empirical parameters A' and B' and their corresponding ac-

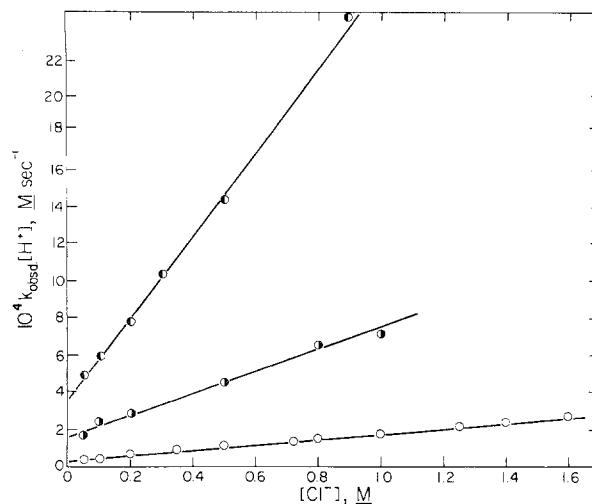


Figure 2. Plot of $10^4 k_{obsd}[H^+]$ vs. $[Cl^-]$ at ionic strength $2.0 M$ ($NaClO_4, HClO_4$) and the following temperatures: \circ , 28.0° , \bullet , 37.6° ; \circ , 47.6° . The experimental data are in Table I.

Table I. Kinetic Data for the Reaction of *cis*-Diammineaquocobalt(III) Species with Chloride at Ionic Strength $2.0 M$ (Na^+, H^+, ClO_4^-)

Temp, $^\circ C$	$[H^+]^a$	$[Cl^-]^a$	$10^3 k_{obsd}^b$	$10^3 k_{calcd}^{b,c}$	
28.0	0.20	0.10	0.35	0.37	
		0.20	0.32	0.42	
		0.35	0.48	0.50	
		0.50	0.50	0.58	
		0.72	0.65	0.70	
		1.25	1.1	1.0	
	0.40	0.10	0.12	0.17	
		1.00	0.42	0.43	
		1.44	0.58	0.55	
		1.20	0.20	0.057	0.067
		0.50	0.087	0.097	
		0.80	0.13	0.13	
37.6	0.10	0.10	2.5	2.2	
		0.20	3.0	2.7	
		1.00	7.0	7.2	
		0.20	0.05	0.87	0.93
		0.10	1.1	1.1	
		0.20	1.8	1.4	
	0.20	0.50	2.2	2.2	
		1.00	3.6	3.6	
		0.40	0.10	0.42	0.53
		0.20	0.62	0.67	
		0.50	1.1	1.1	
		0.60	0.05	0.23	0.30
47.6	0.10	0.10	0.43	0.37	
		0.50	0.83	0.73	
		0.80	1.3	1.0	
		1.20	0.05	0.15	0.15
		0.10	0.17	0.17	
		0.20	0.21	0.22	
	0.20	0.10	6.0	5.8	
		0.20	7.5	8.0	
		0.40	12	12	
		0.05	2.5	2.3	
		0.10	2.2	2.8	
		0.20	4.0	4.0	
0.30	0.30	5.0	5.0		
	0.50	7.3	7.3		
	0.60	4.7	4.8		
	0.10	1.0	0.95		
	0.20	1.3	1.3		
	0.50	2.5	2.5		
0.90	0.90	4.0	4.0		

^a Units are M . ^b Units are sec^{-1} . ^c Obtained from nonlinear least-squares fit of data (see text).

tivation parameters (see below for method of determination) are collected in Table II. The calculated values of the

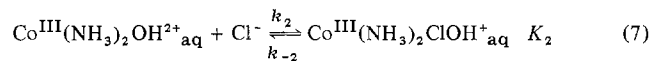
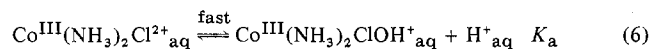
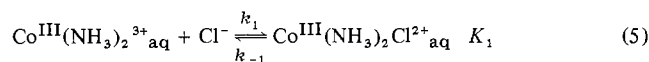
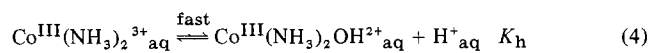
Table II. Empirical Kinetic Parameters for Reaction of *cis*-Diammineaquocobalt(III) Species with Chloride at Ionic Strength 2.0 *M*^a

Temp, °C	10 ⁴ <i>A'</i> ^b	10 ⁵ <i>B'</i> ^c	<i>A'/B'</i> ^d	Δ ⁻ <i>H</i> ⁺ _{<i>A</i>} ^e	Δ ⁻ <i>S</i> ⁺ _{<i>A</i>} ^f	Δ ⁻ <i>H</i> ⁺ _{<i>B</i>} ^e	Δ ⁻ <i>S</i> ⁺ _{<i>B</i>} ^f
28.0	1.50 ± 0.03	2.7 ± 0.2	5.6				
37.6	6.5 ± 0.7	13.8 ± 1.1	4.7	28 ± 1	22 ± 4	17 ± 2	-21 ± 6
47.6	22.5 ± 1.0	33.3 ± 0.2	6.7				

^a Parameters obtained from a nonlinear least-squares fit of data from Table I into eq 1 and 3. Errors quoted are 1 standard deviation. ^b Units are sec⁻¹. ^c Units are *M* sec⁻¹. ^d Units are *M*⁻¹. ^e Units are kcal mol⁻¹. ^f Units are cal deg⁻¹ mol⁻¹.

pseudo-first-order rate constant under a given set of conditions are included in Table I for comparison with *k*_{obsd}.

Mechanism. Consideration of the species likely to be present under the reaction conditions³ suggests the mechanism given by eq 4–7. Here, *K*_h and *K*_a are the acid dissociation constants



of $\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4^{3+}_{\text{aq}}$ and $\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_3\text{Cl}^{2+}_{\text{aq}}$, respectively, and steps 5 and 7 are rate determining. The rate law predicted by this mechanism is shown by eq 8.

$$\frac{d \ln [\text{product}]}{dt} = k_{\text{obsd}} = \frac{(k_1 + k_2 K_h / [\text{H}^+]) [\text{Cl}^-]}{1 + K_h / [\text{H}^+]} + \frac{k_{-1} + k_{-2} K_a / [\text{H}^+]}{1 + K_a / [\text{H}^+]} \quad (8)$$

Attempts to fit the data at fixed temperature in Table I to eq 8 gave a much worse fit than that provided by eq 3, indicating that *k*₁, *k*₋₁, *K*_h, and *K*_a are too small to be evaluated directly. Equation 8 reduces to empirical form (3) if the following limits hold under all experimental conditions: (1) *K*_h/[*H*⁺] ≪ 1 and *K*_a/[*H*⁺] ≪ 1; (2) *k*₁ ≪ *k*₂*K*_h/[*H*⁺] and *k*₋₁ ≪ *k*₋₂*K*_a/[*H*⁺]. If it is assumed that *K*_h/[*H*⁺] ≤ 0.1 at the lowest experimental acidity, then *K*_h ≤ 10⁻² *M* and the same upper limit applies to *K*_a. Likewise, if it is assumed that *k*₁ ≤ 0.1*k*₂*K*_h/[*H*⁺] and *k*₋₁ ≤ 0.1*k*₋₂*K*_a/[*H*⁺] at the highest experimental acidity, then *k*₁ ≤ 7 × 10⁻⁶ *M*⁻¹ sec⁻¹ and *k*₋₁ ≤ 1 × 10⁻⁶ sec⁻¹ for the reaction with chloride at 25°. Based on the above considerations, lower limits for *k*₂ and *k*₋₂ can be estimated from the products *A'* = *k*₂*K*_h and *B'* = *k*₋₂*K*_a using the upper limits for *K*_h and *K*_a. These estimates are *k*₂ ≥ 1 × 10⁻² *M*⁻¹ sec⁻¹ and *k*₋₂ ≥ 2 × 10⁻³ sec⁻¹.

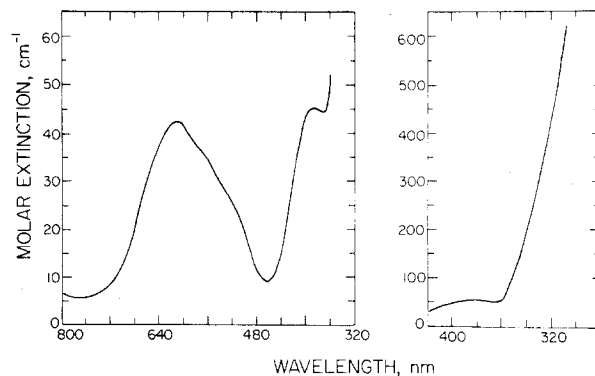
Empirical activation parameters for *A'* and *B'* were obtained by a nonlinear least-squares routine which replaces *A'* and *B'* by functions of the form of eq 9, where Δ*H*⁺_{*A*} and Δ*S*⁺_{*A*} are

$$A' = (kT/h) e^{-\Delta H^+_{A}/RT} e^{\Delta S^+_{A}/R} \quad (9)$$

parameters and the other symbols have their usual significance. These data are collected in Table II. According to the principle of microscopic reversibility, *K*₁, the equilibrium constant for complex formation, is given by eq 10. Independent estimates

$$K_1 = \frac{k_1}{k_{-1}} = A'/B' = \frac{k_2 K_h}{k_{-2} K_a} = \frac{[\text{Co}^{\text{III}}\text{Cl}]}{[\text{Co}^{\text{III}}][\text{Cl}^-]} \quad (10)$$

of the equilibrium constant in a particular experiment can be

**Figure 3.** Near-uv-visible spectrum of *fac*(?) $\text{Co}(\text{NH}_3)_2\text{Cl}^{2+}_{\text{aq}}$. (See text for method of derivation.)

obtained from the absorbance, *A*_∞, at equilibrium, as follows. It can be shown that eq 11 holds for equilibria 4–7, where *E*

$$E = \frac{A_{\infty}}{[\text{Co}(\text{III})]} = \frac{\epsilon_1 + \epsilon_2 K_h / [\text{H}^+] + \epsilon_3 K_1 [\text{Cl}^-] + \epsilon_4 K_2 K_h [\text{Cl}^-] / [\text{H}^+]}{1 + K_h / [\text{H}^+] + K_1 [\text{Cl}^-] + K_2 K_h [\text{Cl}^-] / [\text{H}^+]} \quad (11)$$

is the apparent molar absorptivity of the reacted solution at equilibrium and ϵ_1 , ϵ_2 , ϵ_3 , and ϵ_4 are the molar absorptivities of $\text{Co}(\text{NH}_3)_2^{3+}_{\text{aq}}$, $\text{Co}(\text{NH}_3)_2\text{OH}^{2+}_{\text{aq}}$, $\text{Co}(\text{NH}_3)_2\text{Cl}^{2+}_{\text{aq}}$, and $\text{Co}(\text{NH}_3)_2\text{ClOH}^+_{\text{aq}}$, respectively. This function was tested for the reaction with Cl^- at 315 nm, where $\epsilon_1 = 7.6 \text{ M}^{-1} \text{ cm}^{-1}$ and the change in absorbance on reaction with Cl^- is maximal. If ϵ_1 , $\epsilon_2 K_h / [\text{H}^+]$, and $K_h / [\text{H}^+]$ are much smaller than the other terms, then

$$E = \frac{\epsilon_3 K_1 [\text{Cl}^-] + \epsilon_4 K_2 K_h [\text{Cl}^-] / [\text{H}^+]}{1 + K_1 [\text{Cl}^-] + K_2 K_h [\text{Cl}^-] / [\text{H}^+]} \quad (12)$$

This assumption seems justified by the upper limit found for *K*_h (see above), with $\epsilon_1 \approx \epsilon_2$.³ *E* was found to increase with increasing [Cl^-] but was experimentally independent of [H^+] at fixed [Cl^-] and temperature, indicating that $\epsilon_4 K_2 K_h / [\text{H}^+] \ll \epsilon_3 K_1$ and $K_2 K_h [\text{Cl}^-] / [\text{H}^+] \ll 1 + K_1 [\text{Cl}^-]$ in eq 12 for the concentrations used in this study.

These observations allow eq 12 to be written as

$$E = \frac{\epsilon_3 K_1 [\text{Cl}^-]}{1 + K_1 [\text{Cl}^-]} \quad (13)$$

As expected from eq 13, plots of 1/*E* vs. 1/[Cl^-] were linear.

The parameter ϵ_3 obtained by a nonlinear least-squares treatment of the *A*_∞ readings for the experimental conditions shown in Table I was found to be 580 ± 50 *M*⁻¹ cm⁻¹ (1 standard deviation quoted) over the experimental temperature range and was statistically temperature independent, validating the above assumptions. The equilibrium constant *K*₁ had values of 4.7 ± 0.5, 5.0 ± 0.5, and 5.1 ± 0.5 *M*⁻¹ at 28.0, 37.6, and 47.6°, respectively. These data are in satisfactory agreement with the requirements of eq 10 (see Table II). The uv-visible spectrum of the monochloro complex (Figure 3) was derived from measured product spectra using *K*₁ = 5 *M*⁻¹ in eq 13.

Reduction of *cis*-Aquadiamminecobalt(III) by Bromide Ion. Stoichiometric Measurements. The kinetic and spectrophotometric data obtained for the reaction of the *cis*-diammine with bromide were not consistent with complex formation but showed that reaction 14 occurs. The formation of Br_2 was



qualitatively confirmed by extraction of product solutions with CCl_4 and by the observation of rapid removal of the characteristic yellow color on shaking product solutions with

Table III. Kinetic Data for the Reduction of *cis*-Diammineaquocobalt(III) Species by Bromide at Ionic Strength 2.0 M (Na⁺, H⁺, ClO₄⁻)

Temp, °C	[H ⁺] ^a	[Br ⁻] ^a	10 ³ · <i>k</i> _{obsd} ^b	10 ³ · <i>k</i> _{calcd} ^b
28.0	0.10	0.20	0.42	0.27
		1.00 ^c	1.2	1.4
		1.44	2.7	2.0
	0.20	0.20	0.20	0.18
		0.50	0.50	0.46
		0.72	0.57	0.65
		1.25	1.3	1.1
		1.60	1.4	1.4
	0.40	0.20	0.10	0.13
		1.00	0.45	0.68
		1.44	0.67	0.98
	1.20	1.10 ^c	0.038	0.053
0.50 ^c		0.017	0.026	
0.80 ^c		0.037	0.042	
37.6	0.10	0.20	1.2	1.0
		0.30	1.5	1.5
		0.50	2.3	2.5
	0.40	0.50 ^c	2.3	2.5
		0.10	0.25	0.18
		0.20	0.43	0.37
1.20	1.00	1.6	1.8	
	0.10	0.12	0.12	
	0.20 ^c	0.25	0.22	
47.6	0.10	0.80 ^c	0.73	0.87
		0.05	1.2	1.1
		0.10	2.1	2.1
	0.20	0.20	4.0	4.2
		0.20 ^c	4.0	4.2
		0.10	1.1	1.1
0.40	0.20	2.1	2.2	
	0.30	3.2	3.3	
	0.50 ^c	5.8	5.6	
1.20	0.40	0.50	6.2	5.6
		0.05	0.33	0.31
		0.10	0.70	0.62
	1.20	0.50	3.5	3.2
		0.10 ^c	0.37	0.28
		0.35 ^c	0.92	0.98
		0.50 ^c	1.3	1.4
		0.80 ^c	2.2	2.2

^a Units are M. Data refer to measurements at 340–390 nm unless noted otherwise. ^b Units are sec⁻¹. ^c Disappearance of *cis*-Co(NH₃)₂³⁺aq monitored at 537 nm (see eq 15).

cyclohexene. Under similar conditions, no reaction of cyclohexene with either the *cis*-diammine or its chloro complex was observed.

Kinetics. Preliminary stopped-flow experiments at constant ionic strength and acidity indicated that no fast spectral changes occur on mixing diammineaquocobalt(III) species with Br⁻; in addition, spectral scans during the course of the subsequent slow reaction gave no evidence for the formation of measurable concentrations of bromocobalt(III) species. Kinetic measurements confirmed these conclusions; thus, in the presence of a large excess of bromide ions, first-order plots for the appearance of Br₃⁻ or for the disappearance of Co^{III} were linear for at least 3 half-lives. The pseudo-first-order rate constant, *k*_{obsd}, values obtained by monitoring the disappearance of Co^{III} under fixed conditions were twice as large as those obtained by following the appearance of Br₃⁻, as required by eq 14. The kinetic data are collected in Table III.

At fixed acidity and temperature, *k*_{obsd} was proportional to [Br⁻] within experimental error. The rate law for the reaction is thus

$$\frac{d[\text{Co}^{\text{III}}]}{dt} = 2 \frac{d[\text{Br}_2]}{dt} = k_{\text{obsd}}[\text{Co}^{\text{III}}][\text{Br}^-] \quad (15)$$

The second-order rate constant *k*_{obsd} increased with decreasing acidity and plots of *k*_{obsd} vs. 1/[H⁺] at the three temperatures

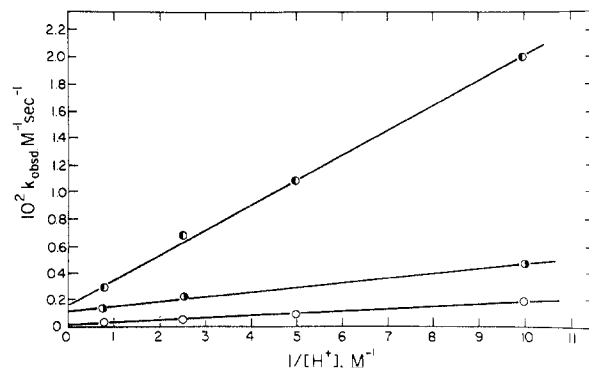


Figure 4. Plot of 10²*k*_{obsd} vs. 1/[H⁺] for the reaction with bromide at ionic strength 2.0 M (NaClO₄, HClO₄) and the following temperatures: ○, 28.0; □, 37.6; ◇, 47.6°. The experimental data are in Table III.

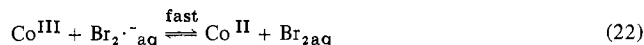
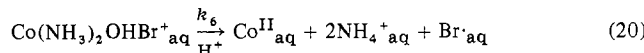
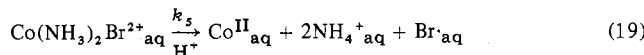
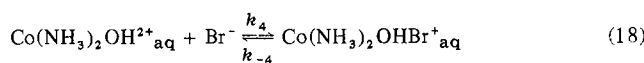
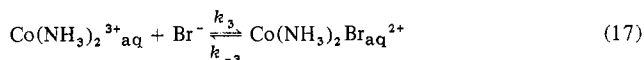
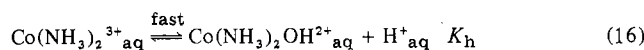
Table IV. Empirical Kinetic Parameters for the Reduction of *cis*-Diammineaquocobalt(III) by Bromide at Ionic Strength 2.0 M^a

Temp, °C	10 ⁴ <i>C</i> ^b	10 ⁴ <i>D</i> ^c	Δ <i>H</i> [‡] _{<i>C</i>} ^d	Δ <i>S</i> [‡] _{<i>C</i>} ^e	Δ <i>H</i> [‡] _{<i>D</i>} ^d	Δ <i>S</i> [‡] _{<i>D</i>} ^e
28.0	6.0 ± 0.2	1.7 ± 0.2				
37.6	7.5 ± 1.2	4.3 ± 0.5	8 ± 3	-46 ± 10	29 ± 1	21 ± 4
47.6	12.3 ± 0.2	19.8 ± 0.8				

^a Obtained from nonlinear least-squares fit of data from Table III to eq 15 (see text). Errors quoted are 1 standard deviation. ^b Units are M⁻¹ sec⁻¹. ^c Units are sec⁻¹. ^d Units are kcal mol⁻¹. ^e Units are cal deg⁻¹ mol⁻¹.

were found to be linear with a nonzero intercept at 1/[H⁺] = 0 (see Figure 4). The empirical rate law is thus given by eq 15 with *k*_{obsd} = *C* + *D*/[H⁺], where *C* and *D* are empirical parameters. Estimates for *C* and *D* at three temperatures and their corresponding activation parameters were obtained from a nonlinear least-squares fit of the kinetic data and are shown in Table IV.

Mechanism. The mechanism shown by eq 16–22 is con-



sistent with the empirical rate law. Although we have no direct experimental evidence for reactions 20–22, their involvement seems plausible in this system. If a steady state is assumed for Br[•] and Br₂⁻, then the observed second-order rate constant is given by eq 23. This relationship reduces to the empirical

$$k_{\text{obsd}} = \left(\frac{k_3 k_5}{k_{-3} + k_5} + \frac{k_4 k_6 K_{\text{h}} / [\text{H}^+]}{k_{-4} + k_6} \right) / \left(1 + \frac{K_{\text{h}}}{[\text{H}^+]} \right) \quad (23)$$

rate law (15) if *K*_h/[H⁺] ≪ 1 over the experimental acidity range, which is the same as that employed in the reaction with chloride (see above). Good agreement between parameters

A' and D at all temperatures suggests that similar rate-determining steps are involved in the complexation of diammineaquocobalt(III) species by chloride and its reduction by bromide. If $k_5 \gg k_{-3}$ and $k_6 \gg k_{-4}$ in eq 23, then $C = k_3$ and $D = k_4K_h$, corresponding to steps 17 (forward) and 18 (forward) being rate determining. This situation would correspond to substitution-controlled oxidation of Br^- by $\text{Co}(\text{NH}_3)_2\text{OH}^{2+}_{\text{aq}}$.²²

Discussion

There are strong similarities between the kinetic patterns of *cis*-diammineaquocobalt(III) and aquocobalt(III) reactions but vast differences in their substitutional labilities. Both complexes react with halide ions in second-order processes which are markedly base catalyzed. Specifically, a discrete mono complex is formed with Cl^- (although $\text{CoCl}^{2+}_{\text{aq}}$ is oxidatively unstable), Br^- apparently is oxidized via a substitution-controlled mechanism, and I^- is rapidly oxidized in the outer sphere. However, the measured rates of chloride and bromide substitution at $\text{Co}(\text{NH}_3)_2^{3+}_{\text{aq}}$ and $\text{Co}(\text{NH}_3)_2\text{OH}^{2+}_{\text{aq}}$ are still ca. 10^5 times slower than are those of $\text{Co}^{3+}_{\text{aq}}$ and $\text{CoOH}^{2+}_{\text{aq}}$. These observations indicate that while $\text{Co}(\text{NH}_3)_2^{3+}_{\text{aq}}$ is a moderately strong oxidizing agent, it is kinetically inert. Thermodynamically, this is in accord with an increasing oxidation potential for the $\text{Co}^{\text{III}}-\text{Co}^{\text{II}}_{\text{aq}}$ couple as n decreases in the series $\text{Co}(\text{NH}_3)_n(\text{H}_2\text{O})_{6-n}^{3+}_{\text{aq}}$.

The tendency of $\text{Co}(\text{NH}_3)_2^{3+}_{\text{aq}}$ toward dimerization is similar to that found for other aquocobalt amines^{17,21} but, like that of $\text{Co}^{3+}_{\text{aq}}$,³ occurs at relatively low pH. The estimate of $K_h \leq 10^{-2} M$ obtained from kinetic considerations (vide supra) and the observed spectral changes which occur at $\text{pH} \geq 3$ suggest that $\text{p}K_h \approx 3.5 \pm 1$, consistent with the previous estimate obtained by extrapolation of data for higher ammineaquocobalt(III) complexes.^{7a} The data for A' and D in Tables II and IV can be interpreted to indicate that $\text{Co}(\text{NH}_3)_2\text{OH}^{2+}_{\text{aq}}$ is 10^3-10^4 times more labile to substitution than is $\text{Co}(\text{NH}_3)_2^{3+}_{\text{aq}}$. A similar factor has been inferred in comparing the rates of $\text{Co}^{3+}_{\text{aq}}$ and $\text{CoOH}^{2+}_{\text{aq}}$ reactions.³

The equilibrium constant obtained for reaction 5 is reasonable for a first-row transition element in oxidation state III. However, there are insufficient data available to allow a direct comparison with the corresponding parameters for other aquocobalt amines.^{6,23} The dissociation of $\text{Co}(\text{NH}_3)_2\text{Cl}^{2+}_{\text{aq}}$ is evidently subject to marked base catalysis, which indicates that the $\text{Co}-\text{Cl}$ bond is labilized by the presence of inner-sphere OH^- . A knowledge of the geometry of the monochloro product(s) in this reaction would be of particular value in elucidating the detailed mechanism. For example, a *cis*-directing influence of inner-sphere hydroxide would lead to formation of a mixture of *fac* and *mer* isomers of $\text{Co}(\text{NH}_3)_2\text{Cl}^{2+}_{\text{aq}}$, whereas a *trans*-directing influence would produce only the *fac* isomer. The fact that we observe only a one-component dissociative process and consideration of microscopic reversibility arguments suggest either that a single product actually is formed or that rapid isomerization accompanies formation and dissociation of the complex. There is no compelling reason to expect particularly rapid *fac-mer* isomerization in this system; our observation that the spectrum of the monochloro product is invariant with experimental conditions (especially with respect to temperature, which might alter the position of any *fac-mer* equilibrium) suggests that only one product is formed, which, from the above considerations, would be the *fac*-monochlorodiammineaquocobalt(III) complex in this case.²⁴ One could then speculate that in cobalt(III) complexes which carry predominantly aquo ligands in the inner coordination sphere, the *trans*-directing influence of inner-sphere OH^- predominates over the *cis*-directing influence.²⁵ However, the very high solubility of the monochloro complex in the reaction medium prevents confirmation of the

product in this interesting reaction.

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Registry No. *cis*- $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4](\text{ClO}_4)_3$, 55177-48-5; *cis*- $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4](\text{NO}_3)_3$, 55177-49-6; *fac*- $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3](\text{ClO}_4)_3$, 36273-24-2; *fac*- $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3](\text{NO}_3)_3$, 20745-92-0; Br , 24959-67-9; Cl , 16887-00-6.

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- (12) Details of this apparatus are available from the authors on request.
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- (15) The crystalline product from evaporation is coated with concentrated perchloric acid and rapidly absorbs water.^{7a} Immediate washing with ether or hexane gives a dry microcrystalline solid.
- (16) The molar absorptivities and standard deviations quoted were obtained from ten determinations over the concentration ranges $[\text{Co}(\text{III})] = 1.0-22.3 \times 10^{-3} M$ and $[\text{H}^+] = 1.0-3.0 M$. These molar absorptivities are somewhat higher than those reported previously;⁷⁻⁹ however, they were determined from the spectra of solutions which were all analyzed for cobalt(II), cobalt(III), and stoichiometric cobalt, as well as from weighed quantities of the anhydrous perchlorate and nitrate salts in solution which were analyzed in the same fashion. We feel that these parameters are reliable since they represent many determinations and also include data at much higher concentrations than those previously reported.⁷⁻⁹
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- (18) Under similar experimental conditions (temperature, stoichiometric ammonium:cobalt ratio, and reaction time) the presence of chloride ion (from CoCl_2 or NH_4Cl starting materials) appears to promote the formation of higher cobalt amines, such as *cis*- $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}_{\text{aq}}$.¹⁹
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- (20) Spectral measurements directed at obtaining a value for the acid dissociation constant of the *cis*-diammine were vitiated by the marked affinity of the solid diammine for water even under very dry conditions. Thus, dissolution of stored product solids in 1 M HClO_4 showed an increase of absorbance in the 340-nm region which we associate with the formation of dimeric species^{19,21} due to hydrolysis in the solid state. Since solutions of the diammine cannot be directly titrated with base at $\text{pH} > 2$, it would be necessary to dissolve a small amount of solid in solutions preadjusted to a desired acidity. The above observations as to the hydrolytic properties of the solid suggest that the absorbances of such solutions would be irreproducible. Dimeric impurities in stock solutions of the diammine in 1 M HClO_4 may be removed by heating the solution to 50° for ca. 1 day.
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