Inorganic Chemistry, Vol. 13, No. 9, 1974 **2165**

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Characterization of the $Co(NH_3)_5{}^{3+}$ Intermediate and Induced Aquation of the $(H_3N)_5CoOHCo(NH_3)_5{}^{5+}$ Cation

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Received December 6, 1973

AIC30882*

The competition values for dimethyl sulfoxide and acetonitrile *vs.* water when capturing $(NH_3)_5Co^{3+}$ derived from the nitrosation of $(NH_3)_5CoN_3{}^{2+}$ and $(NH_3)_5CoO_2CNH_2{}^{2+}$ are the same under the same conditions. Another source of $(NH_3)_5Co^{3+}$ was sought in the cleavage of $(NH_3)_5CoOHCo(NH_3)_5{}^{5+}$ which follows a rate law of the form

$$k_{\mathrm{obsd}} = \frac{k_0 + k_{\mathrm{H}}K_{\mathrm{H}}[\mathrm{H}^+] + k_{\mathrm{HY}}K_{\mathrm{HY}}K_{\mathrm{Y}}[\mathrm{H}^+][\mathrm{Y}^-] + k_{\mathrm{HY}_2}K_{\mathrm{HY}_2}K_{\mathrm{HY}}K_{\mathrm{Y}}[\mathrm{H}^+][\mathrm{Y}^-]^2}{1 + K_{\mathrm{Y}}[\mathrm{Y}^-]}$$

for $Y^- = Cl^-$ or $CH_3SO_3{}^-$ and for $[H^+] \approx 10^{-4}$–1 *M*. K_{Y}, K_{H}, k_{H}, K_{HY}, k_{HY}, K_{HY_2}, and k_{HY_2} are interpreted as ion aggregate, proton association, and rate constants. At low $[H^+]$, acid-independent cleavage of the dinuclear cation occurs. At higher $[H^+]$ values rapid cleavage is induced by H^+ attributed to protonation of the OH bridge. This process is assisted by association with anions. The rate data and competition studies are consistent with dissociative chemistry but ion aggregates hinder further interpretations.

Introduction

In previous publications the competition properties of various anions for the supposed five-coordinate intermediate have been described. These experiments comprise rapid induced aquation processes arising from nitrosation of coordinated azide[1] and N-[2] and O-bonded[3] carbamate, oxidation of coordinated azide with Co^{3+},[4] Hg^{2+}-assisted removal of coordinated halide,[5] and photochemical means.[6] These studies have neglected the prospect of neutral competitors except for isotopes of water[5] and this paper now looks at this aspect as well as a potential new route to the intermediate.

Recently, Siebert and Feuerhake reported an ingenious synthetic route to the hitherto unknown monool cation $(H_3N)_5Co\text{-}OH\text{-}Co(NH_3)_5{}^{5+}$.[7] The present work was undertaken because of the possibility of generating $Co(NH_3)_5{}^{3+}$ through its cleavage. We report here kinetic results of this cleavage reaction in acidic media (pH 4–0) and the competition behavior of species in solution for the cleaved fragments.

Experimental Section

$[(H_3N)_5Co\text{-}OH\text{-}Co(NH_3)_5]Cl_5$ was prepared according to Siebert and Feuerhake.[7] The reddish violet solid was dissolved quickly in 1% acetic acid at 0°. The solution was filtered, and the complex was precipitated from the filtrate with a saturated aqueous solution of lithium chloride. The crystals were collected, washed with ethanol (to remove excess LiCl) and ether, and dried in a vacuum desiccator for 12 hr. The substance was stored in a refrigerator at 4°. Absence of the chloropentaammine ion was established as follows. The complex (~50 mg) was dissolved in 1 *M* H_2SO_4 (10 ml) and allowed to react for 2 min. The solution was diluted to 100 ml, sorbed on a column of Dowex 50W-X2, 200–400 mesh, H^+ form, 5 × 1 cm, and eluted with 1 *M* $HClO_4$. No $(H_3N)_5CoCl^{2+}$ appeared, while a blank experiment showed that less than 1% of $(H_3N)_5CoCl^{2+}$ can clearly be detected under these conditions. Since some chloropentaammine ion was found in aged samples (~2 months), this purity check was always performed before use. *Anal.* Calcd for $(H_3N)_{10}OHCl_5Co_2 \cdot H_2O$: Co, 23.55; Cl, 35.42. Found: Co, 23.4; Cl, 35.4.

$[(H_3N)_5CoOS(CH_3)_2](ClO_4)_3 \cdot (CH_3)_2SO$.[8] $[(H_3N)_5Co(OH_2)](ClO_4)_3$ (10 g) dissolved in dimethyl sulfoxide (DMSO, Mallinckrodt AR grade, (50 ml)) was heated on a steam bath for 90 min in a stoppered flask. The orange-red solution turned purple. The solution was added dropwise to ethanol (500 ml) whereby the compound precipitated as a fine flocculent solid. The suspension was digested at 40° on a steam bath for 10 min and filtered while still warm. The orange-red filtrate contained some unreacted aquo complex. The purplish red precipitate was washed three times with absolute ethanol (30 ml) and then twice with absolute ether (30 ml) and dried *in vacuo* for 12 hr (yield 9 g). A sample was dissolved in water, sorbed on a column of Dowex 50W-X2 ion-exchange resin, 200–400 mesh, H^+ form, 10 × 1 cm, and eluted with "Tris" buffer (pH 7.5, $\mu = 1$ ($NaClO_4$)). No hydroxopentaammine ion could be detected. *Anal.* Calcd for $C_4H_{27}N_5O_{14}S_2Cl_3Co$: C, 8.02; H, 4.55; N, 11.69; Co, 9.84. Found: C, 8.00; H, 4.5; N, 11.7; Co, 10.0. The pmr spectrum (Jeol Minimar, 100 MHz) showed peaks at 3.83 ppm (broad, 15 H), 2.72 ppm (6 H), and 2.58 ppm (6 H) in 2 *M* D_2SO_4–D_2O, relative to external TMS. The intensity of the last peak was enhanced on addition of DMSO; thus the peak at 2.72 ppm is due to coordinated DMSO. The visible spectrum showed ϵ_{517} 61 and ϵ_{345} 73 M^{-1} cm^{-1} (sh) in 1 *M* $NaClO_4$, pH 5.

Kinetics. All kinetic runs were measured on a Cary 16K spectrophotometer. Unless otherwise stated, the temperature was 25.0 ± 0.1° and the ionic strength was maintained at 1.0 ± 0.03 with $NaClO_4$, NaCl, or $NaCH_3SO_3$.

Cleavage of the Monool. (A) In Cl^-–$ClO_4{}^-$ and $CH_3SO_3{}^-$–$ClO_4{}^-$ Media in Strong Acid. Water (30 ml, pH 3.5–4 ($HClO_4$)) and the appropriate acid solution (30 ml, $\mu = 2$) were thermostated separately in the storage cylinders of a stopped-flow reactor,[2] equipped with a 1-cm quartz cell. The complex (40–60 mg) was dissolved quickly in the water immediately before mixing.

(B) In Weakly Acidic Cl^-–$ClO_4{}^-$ and $CH_3SO_3{}^-$–$ClO_4{}^-$ Media. The complex was dissolved in water (pH 3.5–4). To this, an equal volume of the appropriate electrolyte (pH 3–4) of twice the final ionic strength was added to give in some cases a supersaturated solution of the complex at 25° in the spectrophotometric cell.

(C) In Aqueous Solutions at Various Acidities Containing $ClO_4{}^-$. The complex (9.5–10 mg) was dissolved in water (8 ml). To this $AgClO_4$ solution (2 ml, ~5% excess Ag^+) was added to give a suspension of AgCl. Addition of 10 ml of 1 *M* $NaClO_4$ solution coagulated the silver chloride which was removed. An aliquot of this solution was diluted with a measured volume of 1 *M* $HClO_4$. The whole procedure was performed in <90 sec at 25°.

(D) In Mixed Aqueous–Organic Media at Various Acidities with $ClO_4{}^-$ as Anion. The complex (~10 mg) was dissolved in water (3 ml, pH 3.5–4) and treated with $AgClO_4$ solution (2 ml, 5% excess Ag^+). The resulting suspension was poured into a mixture of $HClO_4$–$NaClO_4$ (5 ml, $\mu = 2$) and acetonitrile (16 g, analytical

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(8) *Warning!* Safety precautions should be taken when heating cobalt(III) ammine perchlorates in organic solvents: W. R. Tomlinson, K. G. Ottoson, and L. F. Audrieth, *J. Amer. Chem. Soc.*, 71, 375 (1949).

reagent grade) or dimethyl sulfoxide (14.45 or 10.84 g, reagent grade), respectively. After filtering, thermostating to 25° required 3-5 min.

Aquation of $[(H_3N)_5Co(DMSO)]^{3+}$. Hydrolysis in 2 *M* H_2SO_4 and in Tris buffer (0.1 *M*)-$NaClO_4$ (1 *M*) was followed at 25° at 325 and 400 nm, respectively, for 2 half-lives. From a plot of $A(t)$ *vs.* $A(t + \tau)$ a straight line was obtained. The constant time interval τ was chosen such that a slope m of >1.2 resulted. From this, k was obtained as ln (m/τ).[9]

Competition Studies at 25°. (A) In Aqueous Solution. $[(H_3N)_5CoOHCo(NH_3)_5]Cl_5$ was dissolved in <30 sec in water (pH 3.5-4, $HClO_4$) and a solution of twice the final concentration in acid and electrolyte was added at once to the stirred solution. After reaction (>$10t_{1/2}$) the solutions were diluted to 0.2 *M* in electrolyte and sorbed on Dowex 50W-X2 resin (200-400 mesh, H^+ form, 10 × 1 cm column). $(H_3N)_5CoSO_4^+$ and $(H_3N)_5CoCl^{2+}$ were eluted with 1 *M* $HClO_4$ and $(H_3N)_5Co(H_2O)^{3+}$ with 2 *M* H_2SO_4. The aquo ion had ϵ_{492} 48 M^{-1} cm^{-1}; the extinction coefficients of the other ions were the same as those reported earlier.[3,10] The concentrations of the eluates as determined spectrophotometrically (Cary 14) agreed within the error with those determined by atomic absorption (Techtron AA-4, high-intensity Co lamp). The results are compiled in Tables IVA and B. Recovery was variable (>85%) and this was due partly to some decomposition of the starting material in the weakly acidic solvent (*vide supra*). This decomposition manifests itself as a dark immobile zone at the top of the resin.

(B) In Acetonitrile-Water Mixtures. For the nitrosations and mercury-catalyzed reactions, the complex was dissolved in a mixture of acetonitrile and water. The solutions were acidified with 70% $HClO_4$ to 0.2 mol/kg of solution. Solid $NaNO_2$ (4 × 10^{-2} mol/kg) or solid hydrated $Hg(ClO_4)_2$ (~300 mg) was added. For cleavage of the monool, the chloride salt was dissolved in water and treated with 5% excess $AgClO_4$. Then acetonitrile was added, followed by 70% $HClO_4$ to make up the concentrations given in Table V. The reaction mixtures (>$10t_{1/2}$) were diluted to 150 ml and sorbed on Sephadex SP (Na^+ form, 60 × 1.2 cm column). The mercury reactions were quenched with excess NaI before adsorption. $NaClO_4$ (0.7 *M*) eluted first $(H_3N)_5CoNCCH_3^{3+}$ (ϵ_{465} 63) and then $(H_3N)_5CoOH_2^{3+}$ (ϵ_{492} 47.7). Results are given in Table V.

(C) In Dimethyl Sulfoxide-Water Mixtures. For the nitrosations and Ag^+- and Hg^{2+}-catalyzed reactions, the complex was dissolved in a mixture of DMSO and 1 *M* $HClO_4$ at 25° and $NaNO_2$ (fivefold excess), $AgClO_4$ (20% excess), or solid hydrated $Hg(ClO_4)_2$ (3-4-fold excess) was added. For cleavage of the monool, the chloride salt was treated quickly with aqueous $AgClO_4$ (~5% excess, pH 4). DMSO was added, followed by 2 *M* $HClO_4$. To avoid most of the large enthalpy effect of mixing DMSO and acid, all solutions were precooled in ice to ~5°. After reaction, excess mercuric ion was quenched with NaI, or silver halide was filtered off and the washings of the residue were combined with the filtrate. The reaction solutions were diluted (100 ml), sorbed on Dowex 50W-X2 (200-400 mesh, H^+, 5 × 1 cm), and eluted with 0.1 *M* "Tris"-$HClO_4$, pH 7.2, and $NaClO_4$ (1 *M*). $[(H_3N)_5CoOH]^{2+}$ was eluted first and was acidified with $HClO_4$ to pH 3. $[(NH_3)_5Co(DMSO)]^{3+}$ was eluted with 2 *M* H_2SO_4 (ϵ_{517} 62). The concentrations of the species were determined spectrophotometrically and by atomic absorption with good agreement. The presence of the organic solvents results in slightly poorer recoveries in some instances (Table V).

Tracer Experiments. (A) Monool chloride (500 mg, 1 mmol) was suspended in ^{18}O-enriched water (10 ml) and HCl (1 ml, 35%) was immediately added. The resulting suspension was stirred for 25 min whereupon the reactant dissolved slowly and chloropentaammine chloride deposited. The suspension was filtered through a sintered-glass filter funnel (G4) and the ice-cooled filtrate was treated with ice-cold HBr (5 ml, 60%). The pentaammineaquo bromide (250 mg) was collected and washed with dry methanol and dried *in vacuo* at 25° (12 hr). It was then heated to 80° (12 hr) in a closed tube. The water evolved was collected in a break-seal tube and converted to CO_2[11] and a sample of solvent water was equilibrated with CO_2. The enrichment of the CO_2 samples was determined by mass spectrometry ($R_{monool} = 0.010019$, $R_{solvent} = 0.30761$, $R_{natural\ CO_2} = 0.003879$) where R is the mass ratio of 46/44.

In a completely analogous experiment on a smaller scale (30 mg of complex) using normal water, the reaction products were separated on cation-exchange resin as above.

(B) Monool chloride (500 mg, 1 mmol) was suspended in ^{18}O-enriched 1 *M* NaCl (20 ml) and stirred for 1 hr. The reaction mixture was treated as in A and mass spectrometry on the recovered CO_2 gave $R_{monool} = 0.012936$, $R_{solvent} = 0.032612$. A duplicate experiment on a 30 mg scale was carried out and the products separated chromatographically and analyzed by atomic absorption for Co.

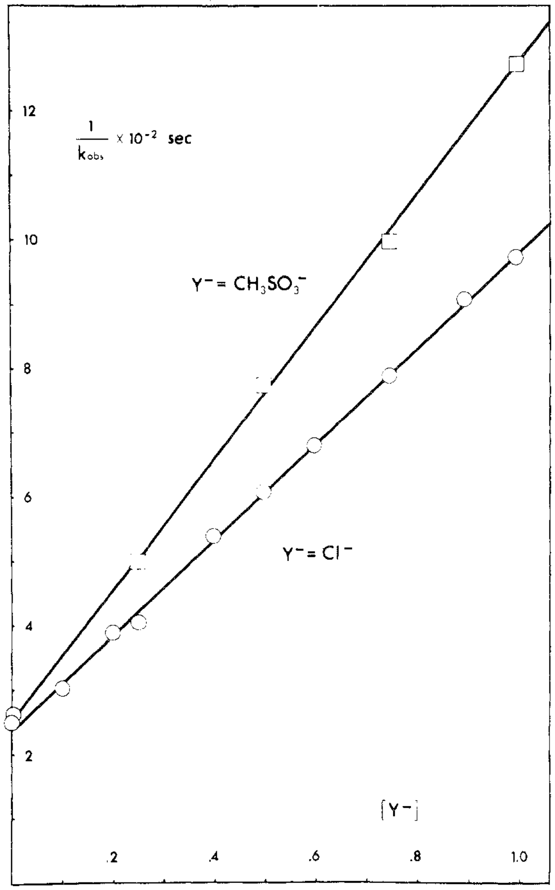

Figure 1. Second-order rate constants for the acid-catalyzed cleavage of $[(H_3N)_5CoOHCo(NH_3)_5]^{5+}$ ($\mu = 1.0$ $NaClO_4$, 25.0°).

Results

Kinetics. The cleavage of $(NH_3)_5CoOHCo(NH_3)_5^{5+}$ to $(NH_3)_5CoOH_2^{3+}$ was followed spectrophotometrically at 284 nm in perchlorate, chloride, and methanesulfonate media and in mixed ClO_4^--Cl^- and ClO_4^--$CH_3SO_3^-$ media at constant ionic strength ($\mu = 1.0$). The pseudo-first-order rate constants were determined from linear plots of log $(A_t - A_\infty)$ *vs.* time (A = absorbance) over at least $3t_{1/2}$.

The rate constants for the cleavage reaction at lower acidities (pH 3-4) were found to vary little with the acidity as observed previously.[7] In this pH range the observed rate constants in mixed ClO_4^--Cl^- and ClO_4^--$CH_3SO_3^-$ media decrease with increasing Cl^- or $CH_3SO_3^-$ concentrations, Figure 1. In 1 *M* $NaClO_4$, pH 3.5 isosbestic points at 422 and 470 nm were maintained for at least $6t_{1/2}$. Above pH 4.5 the dinuclear cation decomposed rapidly with deposition of dark brown "fusco" complexes[12] and the reactions were not pursued in this pH region.

In the region of pH 3.5 a limiting rate law of the form

$$k_{obsd} = \frac{k_0}{1 + K_Y[Y^-]}$$

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[10] D. A. Buckingham, I. I. Olsen, A. M. Sargeson, *J. Amer. Chem. Soc.*, 88, 5443 (1966).

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[12] E. Fremy, *Ann. Chim. Phys.*, [3], 35, 257 (1852).

Table I. Rate Constants for Cleavage of $(H_3N)_5CoOHCo(NH_3)_5^{5+}$ in Perchlorate–Chloride and Perchlorate–Methanesulfonate Media at 25°, $\mu = 1.0 \pm 0.03$ (Na Salts)

Medium	$[H^+]$, M	10^2k_{obsd}, sec^{-1}	10^2k_{calcd},[c] sec^{-1}
1 M ClO_4^-	$10^{-3.5}$	0.396 ± 0.014 (4)[a]	
	0.25	0.552 ± 0.002 (2)	0.56
	0.5	0.712 ± 0.002 (2)	0.72
0.005 M Cl^-–0.995 M ClO_4^-	10^{-4}	0.374 ± 0.012 (2)	
	10^{-3}	0.390 ± 0.009 (2)	
0.1 M Cl^-–0.9 M ClO_4^-	$10^{-3.5}$	0.33 (1)	0.31
	0.1	0.60 (1)	0.69
	0.6	2.22 ± 0.06 (2)	2.6
	1.0	3.82 ± 0.02 (4)	4.1
0.2 M Cl^-–0.8 M ClO_4^-	$10^{-3.5}$	0.257 (1)	0.25
0.25 M Cl^-–0.75 M ClO_4^-	$10^{-3.5}$	0.246 ± 0.005 (2)	0.23
	0.25	2.35 ± 0.05 (2)	2.37
	0.5	4.66 ± 0.02 (3)	4.51
	1.0	9.39 ± 0.05 (4)	8.8
0.4 M Cl^-–0.6 M ClO_4^-	$10^{-3.5}$	0.186 (1)	1.85
0.5 M Cl^-–0.5 M ClO_4^-	$10^{-3.5}$	0.165 ± 0.005 (2)	0.163
	0.2	3.25 ± 0.18 (4)	3.4
	0.5	7.80 ± 0.45 (3)	8.4
	1.0	16.2 ± 0.9 (4)	16.5
0.6 M Cl^-–0.4 M ClO_4^-	$10^{-3.5}$	0.146 (1)	0.146
	0.2	3.95 ± 0.03 (2)	4.05
	0.6	12.1 ± 0.1 (4)	11.8
	1.0	20.4 ± 0.9 (4)	19.6
0.75 M Cl^-–0.25 ClO_4^-	$10^{-3.5}$	0.127 ± 0.004 (2)	0.126
	0.25	6.24 ± 0.07 (2)	6.17
	0.5	12.3 ± 0.3 (4)	12.2
	1.0	24.9 ± 0.7 (4)	24.3
0.9 M Cl^-–0.1 M ClO_4^-	$10^{-3.5}$	0.109 ± 0.006 (2)	0.11
	0.25	6.94 ± 0.03 (3)	7.3
	0.5	14.4 ± 0.2 (4)	14.5
	0.9	26.0 ± 0.1 (4)	26.1
	1.0	28.9 ± 1.2 (3)	28.9
1 M Cl^-	$10^{-3.5}$	0.103 ± 0.006 (3)	0.102
	0.1	2.73 ± 0.03 (2)	3.3
	0.25	7.49 ± 0.11 (2)	8.1
	0.5	15.1 ± 0.3 (3)	16.1
	0.5	14.8 ± 0.3 (2)[b]	16.1
	0.75	22.6 ± 0.1 (2)	24.1
	1.00	29.1 ± 0.1 (3)	32.1
0.25 M $CH_3SO_3^-$–0.75 M ClO_4^-	10^{-4}	0.204 ± 0.008 (2)	0.198
	0.5	1.03 ± 0.07 (4)	1.11
	1.0	1.85 ± 0.04 (3)	2.02
0.5 M $CH_3SO_3^-$–0.5 $MClO_4^-$	10^{-4}	0.130 ± 0.003 (2)	0.133
	0.5	1.76 ± 0.06 (4)	1.80
	0.75	2.39 ± 0.08 (3)	2.63
	1.0	3.49 ± 0.05 (4)	3.47
0.75 M $CH_3SO_3^-$–0.25 M ClO_4^-	10^{-4}	0.102 (1)	0.098
	0.5	2.54 ± 0.05 (4)	2.55
	1.0	4.97 ± 0.31 (4)	5.01
1 M $CH_3SO_3^-$	10^{-4}	0.0078 ± 0.0001 (2)	0.0078
	0.2	1.33 ± 0.10 (3)	1.38
	0.5	3.23 ± 0.24 (5)	3.33
	1.0	6.60 ± 0.10 (5)	6.59

[a] Number of determinations; errors are maximum deviations from the mean values quoted. [b] 0.5 M LiCl–0.5 M HCl. [c] Calculated from rate law (1) using the constants $k_0 = 4.0 \times 10^{-3}$ sec^{-1}, $k_H = 6.2 \times 10^{-3}$ M^{-1} sec^{-1}, $K_{Cl} = 2.9$ M^{-1}, $k_{HCl} = 0.34$ M^{-1} sec^{-1}, $k_{HCl_2} = 0.90$ M^{-2} sec^{-1}, $K_{CH_3SO_3} = 4.1$ M^{-1}, $k_{H(SO_3CH_3)} = 0.056$ M^{-1} sec^{-1}, and $k_{H(SO_3CH_3)_2} = 0.27$ M^{-2} sec^{-1}. The reliability index (R) for k_{calcd} is less than 4% for both sets of values where $R = \Sigma|k_{obsd} - k_{calcd}|/\Sigma k_{obsd}$.

was obeyed. However in more acidic solutions a complex dependence on H^+ and anion concentration was observed. For a particular anion the rate law observed has the form

$$k_{obsd} = k_0 + k_H[H^+]$$

However the derived second-order rate constants k_H varied over a factor of 50 for 1 M solutions of ClO_4^-, $CH_3SO_3^-$, or Cl^- (Table I). For mixed ClO_4^-–Cl^- media ($\mu = 1$) at constant H^+ (1 M) an essentially linear dependence on chloride was found (Figure 2). In ClO_4^-–$CH_3SO_3^-$ media the same rate law essentially holds over 0.1–1.0 M $CH_3SO_3^-$. The extrapolated value for k_H at $[CH_3SO_3^-] = 0$ and $[Cl^-] = 0$ is the same for both media and agrees with the derived rate constant k_H from $HClO_4$–$NaClO_4$ media, Figure 2.

A general rate law which accommodates both acid-independent and acid-induced data has the form

$$k_{obsd} = \frac{k_0 + k_H[H^+] + k_{HY}[H^+][Y^-] + k_{HY_2}[H^+][Y^-]^2}{1 + K_Y[Y^-]} \quad (1)$$

At low H^+ values and $[Cl^-] = 0$ this reduces to the limiting form $k_{obsd} = k_0$. At higher H^+ values and over the anion range studied it reproduces the essentially linear plots in Figure 2 and the calculated values are compared with k_{obsd} in Table I for various conditions. The constants derived from this expression are $k_0 = 4.0 \times 10^{-3}$ sec^{-1}, $k_H = 6.2 \times 10^{-3}$ M^{-1} sec^{-1}, $K_{Cl} = 2.9$ M^{-1}, $k_{HCl} = 0.34$ M^{-1} sec^{-1}, and $k_{HCl_2} = 0.90$ M^{-2} sec^{-1} for chloride ion media and $K_{CH_3SO_3} = 4.1$ M^{-1}, $k_{H(SO_3CH_3)} = 0.056$ M^{-1} sec^{-1}, and $k_{H(SO_3CH_3)_2} =$

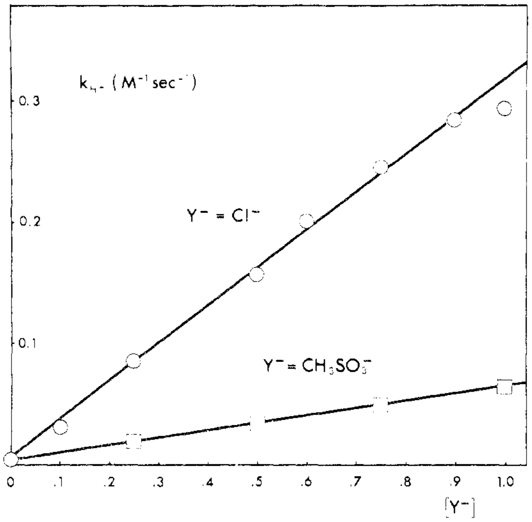

Figure 2. First-order rate constants for the spontaneous cleavage of $[(H_3N)_5CoOHCo(NH_3)_5]^{5+}$ in the pH range 3-4 ($\mu = 1.0$ NaClO$_4$, 25.0°).

$0.27\ M^{-2}$ sec^{-1} for methanesulfonate ion media. K_Y was obtained from the linear plot of $1/k_{obsd}$ (pH 3.5) *vs.* [Y$^-$] as the product of the slope and intercept (Figure 1).

The deviation observed in 1 *M* HCl is assigned to a specific ion activity effect in the electrolyte mixtures concerned. Some evidence for this can be inferred from the ClO_4^--$CH_3SO_3^-$ results where the ions are more closely matched in stereochemistry and size and no analogous effect was observed.

The temperature dependence of the HCl-catalyzed path was also investigated. Table II gives the second-order rate constants at various temperatures in 1 *M* chloride media at different acid concentrations but the reaction is so complex that these results could not be interpreted. The spontaneous cleavage in 1 *M* Cl$^-$ gave a curved Arrhenius plot.

In an acetonitrile-water mixture (mole fraction $X_{CH_3CN} = 0.5$) the observed rate constants show a smaller dependence on the acid concentration (HClO$_4$) and the rate law $k_{obsd} = k_0 + k_{H^+}[H^+]$ holds (Table III). In acetonitrile-water (1:1) the acid-catalyzed path for cleavage of monool contributed 17% to the total rate in 1 *M* HClO$_4$. This limited the study essentially to spontaneous aquation. In DMSO-water ($X_{DMSO} = 0.2, 0.25$), a strong acid dependence was found which can be represented by the same law (Table III). In all mixed-solvent systems, attempts to measure the rate constants at $[H^+] = 10^{-3}\ M$ gave poor reproducibility (±30%); the values of k_0 given were obtained by extrapolation of the data at the higher acidities.

Competition Experiments. The results of product analyses of the cleavage reaction in the presence of added HSO_4^- and SO_4^{2-} or Cl$^-$ are given in Table IVA and B. In the sulfate experiments, a roughly constant amount of sulfatopentaammine was formed irrespective of the sulfate concentration over the range 1-0.03 *M* $[SO_4]_{tot}$, Figure 3. The amounts of sulfatopentaammine formed were more than 3 times those arising from nitrosation of $(H_3N)_5CoN_3^{2+}$ in 1 *M* sulfuric acid.[3] In one experiment, the presence of 1 *M* Na$_2$SO$_4$ together with 0.05 *M* H$_2$SO$_4$ did not significantly increase the amount of sulfatopentaammine. Competition by chloride counterions present in the reactant monool chloride salt was found only when $[SO_4^{2-}]_{tot} < [Cl]$ and then much less $(H_3N)_5CoCl^{2+}$ than $(H_3N)_5CoSO_4^+$ was formed. In 0.1 *M* H$_2$SO$_4$-0.8 *M* HClO$_4$ only a little less $(H_3N)_5CoSO_4^+$ was formed than in 0.1 *M* H$_2$SO$_4$ alone.

Table II. Temperature Dependence of the Second-Order Rate Constants for Acid-Induced Cleavage of the Monool in 1 *M* HCl

T, °C (±0.1°)	[H$^+$], *M*	k_{obsd}, sec^{-1}	k_{H^+}, M^{-1} sec^{-1}
18.6	0.25	$(4.36 \pm 0.03) \times 10^{-3}$ (3)	
	0.5	$(8.44 \pm 0.34) \times 10^{-2}$ (3)	
	1.0	$(1.63 \pm 0.01) \times 10^{-1}$ (2)	$(1.69 \pm 0.06) \times 10^{-1}$
20.0	0.25	$(4.94 \pm 0.08) \times 10^{-2}$ (3)	
	0.5	$(9.97 \pm 0.16) \times 10^{-2}$ (3)	
	1.0	$(1.99 \pm 0.02) \times 10^{-1}$ (5)	$(1.98 \pm 0.06) \times 10^{-1}$
29.5	0.1	$(4.25 \pm 0.25) \times 10^{-2}$ (3)	
	0.25	$(1.03 \pm 0.06) \times 10^{-1}$ (3)	
	0.5	$(2.13 \pm 0.11) \times 10^{-1}$ (3)	$(4.16 \pm 0.08) \times 10^{-1}$

Table III. Rate Constants for Acid-Induced Cleavage of $[(H_3N)_5CoOHCO(NH_3)_5](ClO_4)_5$ in Acetonitrile-Water and in DMSO-Water at 25°, (λ 283.6 nm)

[H$^+$], mol kg^{-1}	k_{obsd}, sec^{-1}	k_0 (extrapolated), sec^{-1}	k_{H^+}, mol^{-1} kg sec^{-1}
A. Acetonitrile-Water ($X_{CH_3CN} = 0.5$), 0.25 mol kg^{-1} of ClO$_4^-$			
10^{-3}	2.15×10^{-3}	2.30×10^{-3}	
0.25	$(2.40 \pm 0.01) \times 10^{-3}$ (2)		
0.5	$(2.51 \pm 0.02) \times 10^{-3}$ (3)		4.05×10^{-4}
B. DMSO-Water ($X_{DMSO} = 0.25$), 0.70 mol kg^{-1} of ClO$_4^-$			
0.075	1.07×10^{-4}	$\leqslant 3 \times 10^{-5}$	
0.375	$(4.05 \pm 0.11) \times 10^{-4}$ (2)		
0.75	$(8.33 \pm 0.11) \times 10^{-4}$ (2)		1.11×10^{-4}
C. DMSO-Water ($X_{DMSO} = 0.20$), 0.80 mol kg^{-1} of ClO$_4^-$			
0.75	$(2.75 \pm 0.03) \times 10^{-4}$ (2)	1.80×10^{-4}	
0.45	7.7×10^{-4}		
0.75	$(1.20 \pm 0.01) \times 10^{-3}$ (2)		1.35×10^{-3}

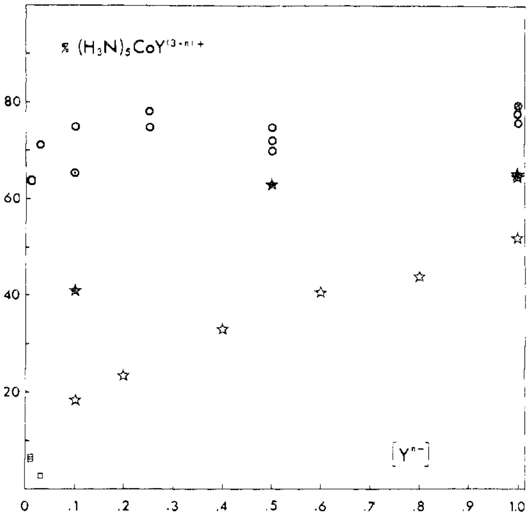

Figure 3. Competition products from the acid-catalyzed and spontaneous cleavage of $[(H_3N)_5CoOHCo(NH_3)_5]^{5+}$. ○, $Y^{n-} = SO_4^{2-}$, $[H^+] = 1\ M$; ⊙, $Y^{n-} = SO_4^{2-}$, 0.8 *M* HClO$_4$; ⊗, 0.05 *M* H$_2$SO$_4$, 1 *M* Na$_2$SO$_4$; □, $(H_3N)_5CoCl^{2+}$ arising at low $[SO_4^{2-}]$ from competition for Cl$^-$ of the monool chloride reactant; ★, $Y^{n-} = Cl^-$, $[H^+] = 1\ M$; ☆, $Y^{n-} = Cl^-$, $[H^+] = 10^{-3}$-$10^{-4}\ M$.

A constant amount of $(H_3N)_5CoCl^{2+}$ was formed on cleavage in 1 *M* HCl, 0.5 *M* HCl-0.5 *M* NaCl, or 0.5 *M* HCl-0.5 *M* HClO$_4$, again 3 times more than on nitrosation of $(H_3N)_5CoN_3^{2+}$. In 0.1 *M* HCl-0.9 *M* HClO$_4$, the spontaneous path makes a contribution of ~9% to the total rate. The observed amount of competition (41%) shows that the competition is reduced by about 17% in 0.1 *M* Cl$^-$; if it were constant, (0.09 × 7.5%) + (0.91 × 64%) = 58% would arise. Considerable competition also arose from spontaneous cleavage in chloride-perchlorate media (Table IV). A non-

Table IV. Product Analysis for Cleavage of the Monool Cation at 25° in Aqueous Solution

A. In Sulfuric Acid[a]

					% competition	
$[H_2SO_4]$, *M*	% recovery	% $(H_3N)_5$-$CoCl^{2+}$	% $(H_3N)_5$-$CoSO_4{}^{+}$ [f]	% $(H_3N)_5$-$CoOH_2{}^{3+}$ [f]	For Cl^-	For $HSO_4{}^-$–$SO_4{}^{2-}$
1	92.6		37.9	62.1		75.8
1	98.2		38.6	61.4		77.2
0.05 (1 *M* Na_2SO_4)	94.2		39.7	60.3		79.4
0.5	92.5		37.4	62.6		74.8
0.5	90.1		36.0	64.0		72.0
0.5	99.4		35.0	65.0		70.0
0.25	97.3		37.4	62.6		74.8
0.25[b]	96.0		39.1	60.9		78.2
0.1 (0.8 *M* $HClO_4$)	95.8		32.7	67.3		65.4
0.1	95.0		37.4	62.6		74.8
0.03[c]	96.5	1.3	35.6	63.1	2.6	71.2
0.01[d]	96.0	3.3	31.9	64.8	6.6	63.8
0.01[d]	97.8	3.2	31.9	64.9	6.4	63.8

B. In Chloride Media

Medium	[Complex], *M*	% recovery	% $(H_3N)_5$-$CoCl^{2+}$ [f]	% $(H_3N)_5$-$CoOH_2{}^{3+}$ [f]	% competition for Cl^-
1 *M* HCl	*a*	95.3	32.1	67.9	64.2
0.5 *M* HCl, 0.5 *M* NaCl	*a*	93.9	32.4	67.6	64.8
0.5 *M* HCl, 0.5 *M* $HClO_4$	3.4×10^{-3}	100.6	31.4	68.6	62.8
0.1 *M* HCl, 0.9 *M* $HClO_4$	*a*	91.8	20.3	79.7	40.6
1 *M* NaCl	*e*	92.3	26.0	74.0	52.0
	b, 1.4×10^{-3}	85.6	23.7	76.3	47.4
0.9 *M* NaCl, 0.1 *M* $NaClO_4$	*b*, 1.2×10^{-3}	85.8	24.5	75.5	49.0
0.8 *M* NaCl, 0.2 *M* $NaClO_4$	*e*	97.0	22.0	78.0	44.0
0.6 *M* NaCl, 0.4 *M* $NaClO_4$	*e*	96.4	20.3	79.7	40.6
0.4 *M* NaCl, 0.6 *M* $NaClO_4$	*e*	96.5	16.5	83.5	33.0
0.2 *M* NaCl, 0.8 *M* $NaClO_4$	*e*	100.3	11.7	88.6	23.4
0.1 *M* NaCl, 0.9 *M* $NaClO_4$	*e*	97.3	9.3	90.7	18.6

[a] [Monool] = (5–8) × 10^{-3} *M*. [b] Complex suspended in solvent; heterogeneous reaction. [c] $[SO_4]_{tot} \approx [Cl^-]$. [d] $[SO_4]_{tot} \approx [Co]_{tot}$. [e] [Monool] = (3–5) × 10^{-3} *M*. [f] Based on 100% recovery.

Table V. Product Analysis for Competition Experiments in Acetonitrile–Water at 25°

Mole fraction of CH_3CN	Reactant complex (~100 mg)	Reagent	% recovery	% $(H_3N)_5$-$Co(OH_2)^{3+}$ [f]	% $(H_3N)_5Co$-$NCCH_3{}^{3+}$ [f]	% $(H_3N)_5Co$-$NCCH_3{}^{3+}$ (adjusted)[e]
0.67	$[(H_3N)_5CoN_3](ClO_4)_2$	NO^+ [a]	99.0	51.0	49.0	49.0
0.5	$[(H_3N)_5CoN_3](ClO_4)_2$	NO^+ [a]	99.0	62.0	38.0	38.0
0.5	$[(H_3N)_5CoO_2CNH_2](ClO_4)_2$	NO^+ [a]	102.0	70.0	30.0	38.0
0.5	$[(H_3N)_5CoI](ClO_4)_2$	Hg^{2+} [b]	98.0	74.0	26.0	26.0
0.5	$[(H_3N)_5CoBr](ClO_4)_2$	Hg^{2+} [b]	100.0	72.0	28.0	28.0
0.5	$[(H_3N)_5CoOHCo(NH_3)_5](ClO_4)_5$	H^+ [c]	103.0	90.0	10.0	19.0
0.5	$[(H_3N)_5CoOHCo(NH_3)_5](ClO_4)_5$	H^+ [d]	97.0	89.0	11.0	21.0
0.33	$[(H_3N)_5CoN_3](ClO_4)_2$	NO^+ [a]	96.0	68.0	32.0	32.0
0.09	$[(H_3N)_5CoN_3](ClO_4)_2$	NO^+ [a]	97.0	80.0	20.0	20.0
0.09	$[(H_3N)_5CoO_2CNH_2](ClO_4)_2$	NO^+ [a]	100.0	83.0	17.0	21.0
0.09	$[(H_3N)_5CoOHCo(NH_3)_5](ClO_4)_5$	H^+ [c]	94.0	97.0	3.5	7.0

[a] $[HClO_4]$ = 0.2 mol/kg, $[NaNO_2]$ = 4 × 10^{-2} mol/kg. [b] Reacted with ~300 mg of $Hg(ClO_4)_2$. [c] $[HClO_4]$ = 0.2 mol/kg. [d] $[HClO_4]$ = 0.9 mol/kg. [e] Correction for amount of Co–O bond breaking. [f] Based on 100% recovery.

linear dependence on $[Cl^-]$ was found and a limiting value may occur at high $[Cl^-]$, Figure 3.

The cleavage reaction was also performed in ~1 *M* HCl using ^{18}O-enriched water as a solvent. The aquopentaammine product showed an enrichment of 0.305%; the solvent was enriched 1.316%. Thus, 23% of the water in the $(H_3N)_5CoOH_2{}^{3+}$ product originated from the solvent. In a separate experiment under the same conditions, 34% of $(H_3N)_5CoCl^{2+}$ and 66% of $(H_3N)_5CoOH_2{}^{3+}$ resulted. From the tracer results, 0.23 × 66% = 15% of the aquo species contain solvent label and 50% is unlabeled. Thus only one Co–O bond breaks during the HCl induced aquation. Similarly, spontaneous aquation at $[Cl^-]$ = 0.5 *M*, pH 2.8, gave enrichments of 0.449% (aquo complex) and 1.411% (solvent). Product analysis gave 39% of $(H_3N)_5CoCl^{2+}$ and 61% of $(H_3N)_5CoOH_2{}^{3+}$. Thus 12% of the latter is labeled and 51% is unlabeled. It follows that in spontaneous aquation only one Co–O bond is broken.

Qualitative experiments showed that competition also arises for CH_3SO_3H. The short half-life of the product in acidic solution precluded the determination of the competition value. However, no chloropentaammine was formed. For many other anions such as Br^-, I^-, and $NO_3{}^-$ insolubility of the resulting salts of the monool precluded homogeneous competition experiments.

The competition for neutral molecules during the cleavage reaction was investigated using aqueous acetonitrile and DMSO mixtures. Table V gives the results for acetonitrile–water mixtures. Considerable formation of $(H_3N)_5CoNCCH_3{}^{3+}$ occurred in solvents at X_{CH_3CN} = 0.091–0.67 on nitrosation of $(H_3N)_5CoN_3{}^{2+}$ and $(H_3N)_5CoOCONH_2{}^{2+}$ as well as for mercury-catalyzed removal of halide from

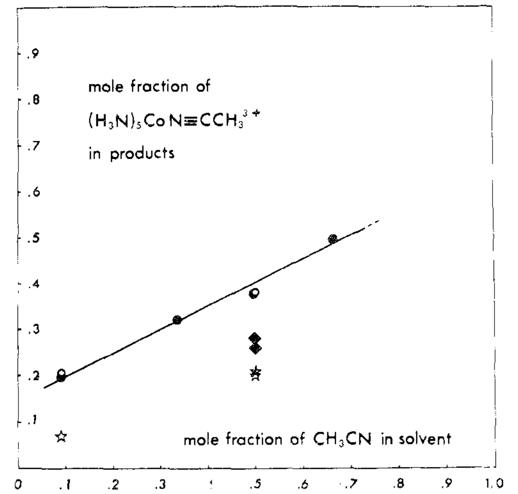

Figure 4. Competition of CH_3CN and H_2O for $(H_3N)_5Co^{3+}$ from different sources: nitrosation of $(H_3N)_5CoN_3^{2+}$ (●) and $(H_3N)_5CoO_2CNH_2^{2+}$ (○); mercury-catalyzed removal of halide from $(H_3N)_5CoX^{2+}$ with $X^- = Br^-, I^-$ (◆); cleavage of the monool cation (✩).

$(H_3N)_5CoX^{2+}$ ($X^- = I^-, Br^-$) and for the nearly acid-independent cleavage reaction of $(H_3N)_5CoOHCo(NH_3)_5^{5+}$. After correction for the path which leads to C-O bond cleavage (20%),[13] the values for the nitrosation of carbamatopentaammine agree with those for nitrosation of azidopentaammine at two different compositions of the solvent. Considerably less competition arose on cleavage of $(H_3N)_5CoOHCo(NH_3)_5^{5+}$ as well as for mercury-catalyzed removal of halide from $(H_3N)_5CoX^{2+}$ ($X^- = Br^-, I^-$). The values for $HgBr^+$ and HgI^+ as leaving groups essentially agree. $(H_3N)_5CoOH_2^{3+}$ treated with acetonitrile-water ($X_{CH_3CN} = 0.5$) under the conditions of the competition experiments gave no $(H_3N)_5CoNCCH_3^{3+}$.

The plot of the competition values for the nitrosation of $(H_3N)_5CoN_3^{2+}$ against the mole fraction of acetonitrile shows a linear dependence on the mole fraction of CH_3CN (Figure 4). However the slope is not unity (~0.5) and extrapolation at both ends requires discontinuities near $X_{CH_3CN} = 1$ and 0.

In DMSO-water mixtures $(H_3N)_5CoDMSO^{3+}$ resulted from nitrosation of azido- and carbamatopentaammines, and the corrected competition values agree, Table VI. Halide removal from $(H_3N)_5CoX^{2+}$ ($X^- = I^-, Br^-$) with Hg^{2+} and from $(H_3N)_5CoI^{2+}$ with Ag^+ gave somewhat higher values and the Hg^{2+}-catalyzed reaction products are the same for $X^- = I^-, Br^-$.

The acid-catalyzed path for cleavage of the monool in DMSO-H_2O ($X_{DMSO} = 0.2, 0.25$) is faster (8 and 30 times, respectively) than spontaneous cleavage, but considerably less competition for DMSO arose. Up to $X_{DMSO} = 0.25$, the competition for the nitrosation reactions and Hg^{2+}-assisted removal of halide and cleavage of $(H_3N)_5CoOHCo(NH_3)_5^{5+}$, respectively, increases linearly with X_{DMSO}, Figure 5. At higher mole fractions there is an increase in slope for the nitrosations and cleavage of the monool. Two points for the nitrosations at higher X_{DMSO} lie on the extrapolated curve for the mercury-induced aquations. For the latter reaction, a negative deviation from this line is found at $X_{DMSO} = 0.5$. On spontaneous aquation of the monool ($[H^+] \approx 10^{-2}$ *M*, $X_{DMSO} = 0.2$), 85% of the cobalt was recovered as aquopentaammine and little or no $(H_3N)_5CoDMSO^{3+}$ was formed.

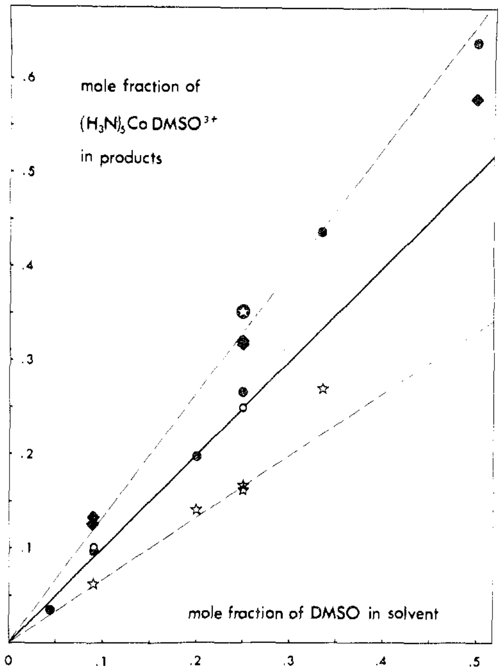

Figure 5. Competition of $(CH_3)_2SO$ and H_2O for $(H_3N)_5Co^{3+}$ from different sources: the symbols used have the same meaning as in Figure 4, except: Ag^+-catalyzed removal of I^- from $(H_3N)_5CoI^{2+}$ (⊙).

The $(H_3N)_5CoDMSO^{3+}$ Ion. To evaluate the competition experiments above, some knowledge of the properties of the DMSO competition product was required. The preparation and properties of several salts containing this ion have been reported recently.[14]

$[(H_3N)_5CoDMSO](ClO_4)_3{\cdot}DMSO$ was obtained by warming the aquopentaammine perchlorate in dry DMSO to 60-80°. Some unreacted aquo complex was removed by careful crystallization of the complex. It was characterized by elemental analysis, by its visible and pmr spectrum (the latter shows the presence of two nonequivalent molecules of DMSO and the presence of a pentaammine species), and by its elution characteristics as a 3+ cation on an ion-exchange column.

The rates of hydrolysis to $(NH_3)_5CoOH_2^{3+}$ were determined in both eluents used for its separation from hydroxopentaammine (Tris buffer, 0.1 *M*, pH 7.5, $k = 1.8 \times 10^{-5}$ sec^{-1}, 25°) and its recovery from the resin (2 *M* H_2SO_4, $k = 1.8 \times 10^{-5}$ sec^{-1}, 25°). Solvent exchange of $(H_3N)_5CoOH_2^{3+}$ with DMSO was found to be negligible under the conditions of the experiments.

Discussion

Cleavage of the monool cation obeys rate law (1) over the pH range 0-4. The three pathways will be discussed separately. In neutral or alkaline conditions the reaction is complicated by the formation of products other than $(H_3N)_5CoOH_2^{3+}$ or $(H_3N)_5CoOH^{2+}$ and these apparently result from rapid loss of ammonia in the monool species since the aquo or hydroxo products are relatively stable under these conditions.

Spontaneous Aquation. At low acidity (pH 3-4), the observed rate decreases (~4 times) on increasing $[Y^-]$ from 0 to 1 *M* (Y = Cl, CH_3SO_3) and is characterized by the first term in (1). These properties are accommodated by an ion-pair equilibrium preceding the cleavage reaction (Scheme I).

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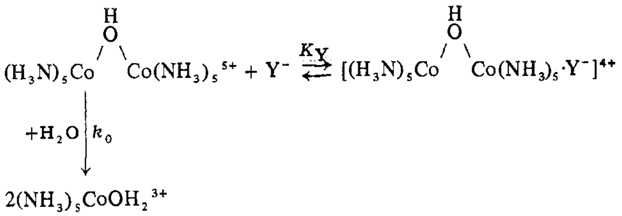
(13) A. M. Sargeson and H. Taube, *Inorg. Chem.*, 5, 1094 (1966).

(14) C. R. Piriz MacColl and L. Beyer, *Inorg. Chem.*, 12, 7 (1973).

Scheme I



The ion-pairing constants are relative to the perchlorate medium

$$K_Y = \frac{[(H_3N)_5CoOHCo(NH_3)_5{\cdot}Y^{4+}]}{[(NH_3N)_5CoOHCo(NH_3)_5^{5+}][Y^-]}$$

The overall linearity of the plots $1/k_{obsd}$ against $[Y^-] = 0$-1 *M*, Figure 2, requires the ion pair with Cl^- or $CH_3SO_3^-$ to be unreactive compared with the non-ion-paired species. This leads to a derived rate law

$$k_{calcd} = k_0/(1 + K_Y[Y^-]) \qquad (2)$$

relative to the perchlorate medium.

The expression gives a linear relationship $1/k_{calcd}$ against $[Y^-]$ with a slope K_Y/k_0 and an intercept $1/k_0$. It is not certain however that the ion-pairing deduced kinetically is the formation of the first ion pair. It could be the formation of an ion triplet or higher term which provides the kinetically inert species.

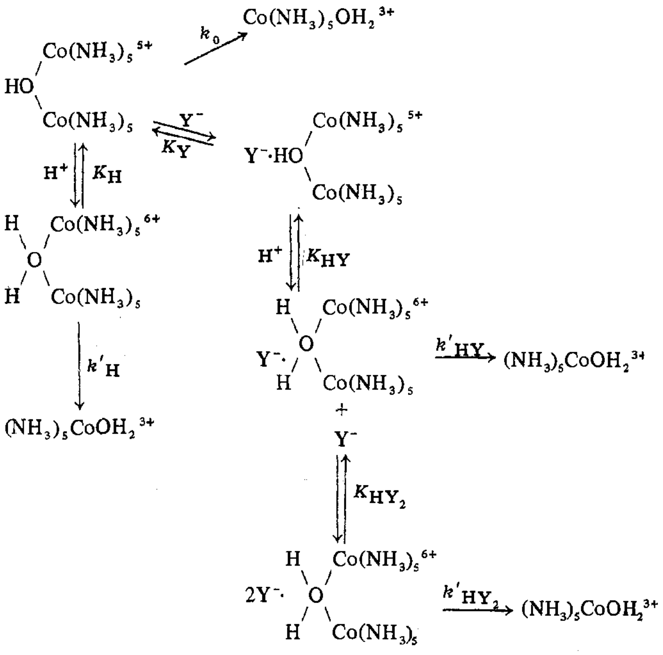
The product analyses in chloride and chloride-perchlorate media (Table IVB) show that the $(H_3N)_5CoCl^{2+}$ produced is not proportional to the Cl^- concentration. A limiting situation may exist at >1 *M* Cl^-, and since only one Co-O bond is broken in the spontaneous process, the value at $[Cl^-] = 1$ *M* is about 3 times that obtained for nitrosation of $(H_3N)_5CoN_3^{2+}$ under similar conditions.[3]

The kinetic and product analysis results diverge in the sense that as $[Cl^-]$ increases, the rate decreases while the formation of $(NH_3)_5CoCl^{2+}$ increases. Clearly Cl^- is not involved in a nucleophilic role in the rate-determining step. The results can be accommodated if the process is dissociative and yields $Co(NH_3)_5^{3+}$ in an atmosphere enhanced in Cl^- ions. This would be consistent with the high charge on the parent ion and with $Co(NH_3)_5^{3+}$ sampling that environment before relaxation of the atmosphere with bulk solvent. Other evidence indicates that $Co(NH_3)_5^{3+}$ is very reactive and probably captures its immediate atmosphere.[3] The rate-determining step here may be the abstraction of the nucleophile from the solvent sheath.[3]

The nonlinear plot of $(NH_3)_5CoCl^{2+}$ produced against $[Cl^-]$ suggests that ion pairing is involved. However these ion pairs must differ from the kinetically detectable species and it seems likely that they are involved after the rate-determining step. This could be a reflection of the approach to ion-pair saturation of the parent ion with Cl^- if the intermediate produced captures that atmosphere. Clearly the situation with the monool aquation is much more complex than for the other methods of generating $(NH_3)_5Co^{3+}$ and is not resolved.

Induced Aquation. At pH 0-1 the H^+-induced cleavage dominates the kinetics. This implies that protonation of the hydroxo bridge assists hydrolysis. The result has been reported previously for perchlorate media[15] and the same behavior was found here for Cl^- and $CH_3SO_3^-$ media. The apparent first-order dependence of the H^+-induced cleavage on $[Y^-]$ has to be considered in the context of the term $(1 + k_Y[Y^-])$ in the denominator of the general rate law. To reproduce the linearity over the conditions used at least two ion aggregates appear to be required and the data have been analyzed in terms of Scheme II. This scheme yields the derived rate law

Scheme II



$$k_{obsd} = \frac{k_0 + k_HK_H[H^+] + k_{HY}K_{HY}[H^+][Y^-] + k_{HY_2}K_{HY}K_Y[H^+][Y^-]^2}{1 + K_Y[Y^-] + K_H[H^+] + K_{HY}K_Y[Y^-][H^+] + K_{HY_2}K_{HY}K_Y[H^+][Y^-]^2}$$

which reduces to the observed rate law (1) if the last three terms in the denominator are small compared with 1 and $K_Y[Y^-]$. At low $[H^+]$ and $[Y^-]$ the expression approaches k_0 while at higher $[H^+]$ and $[Y^-]$ it simplifies to

$$k_{obsd} = \frac{k'_HK_H[H^+] + k'_{HY}K_{HY}K_Y[H^+][Y^-] + k'_{HY_2}K_{HY_2}K_{HY}K_Y[H^+][Y^-]^2}{1 + K_Y[Y^-]}$$

where $k'_HK_H = k_H$, $k'_{HY}K_{HY}K_Y = k_{HY}$, and $k'_{HY_2}K_{HY}K_Y = k_{HY_2}$ are equated to the rate law (1).

For zero $[Y^-]$ the rate law reduces to $k_{obsd} = k_0 + k'_HK_H[H^+]$, consistent with the observations. The complex dependence on anion concentration reproduces the observed rate constants over the anion range used but clearly the term in $[Y^-]^2$ should dominate the kinetics at higher concentrations. Unfortunately anion concentrations greater than 1 *M* were impractical with the present system. The two terms involving $[Y^-]$ are attributed to ion aggregates of the protonated monool cation, a 6+ ion. By inference Y^- association with the 6+ cation should be greater than K_Y but K_{HY_2} should equal or be less than K_Y. Also the limiting rate law at $[Y^-] = 0$ implies that $K_H \ll 1$ which is not unexpected since it should be difficult to protonate a 5+ cation. If the

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(15) J. D. Ellis, K. L. Scott, R. K. Wharton, and A. G. Sykes, *Inorg. Chem.*, 11, 2562 (1972); R. K. Wharton and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 439 (1973).

Table VI. Product Analysis for Competition Experiments in $(H_3C)_2SO-H_2O$ at 25°

Mole fraction of $(H_3C)_2SO$[a]	Reactant complex (~100 mg)	Reagent	% recovery[b]	% $(H_3N)_5$-$CoOH_2^{3+}$ [c]	% $(H_3N)_5$Co-$OS(CH_3)_2^{3+}$ [c]	% competition by $(H_3C)_2SO$[d]
0.50	$[(H_3N)_5CoN_3](ClO_4)_2$	NO^+	100.0	36.0	64.0	64.0
	$[(H_3N)_5CoBr](ClO_4)_2$	Hg^{2+}	95.0	42.0	58.0	58.0
0.33	$[(H_3N)_5CoN_3](ClO_4)_2$	NO^+	99.0	58.0	44.0	44.0
	$[(H_3N)_5CoOHCo(NH_3)_5](ClO_4)_5$	H^+	92.0	87.0	14.0	27.0
0.25	$[(H_3N)_5CoN_3](ClO_4)_2$	NO^+	95.0	74.0	27.0	27.0
	$[(H_3N)_5CoO_2CNH_2](ClO_4)_2$	NO^+	97.0	80.0	20.0	25.0[d]
	$[(H_3N)_5CoI](ClO_4)_2$	Hg^{2+}	97.0	68.0	32.0	32.0
	$[(H_3N)_5CoBr](ClO_4)_2$	Hg^{2+}	101.0	68.0	32.0	32.0
	$[(H_3N)_5CoI](ClO_4)_2$	Ag^+	92.0	65.0	35.0	35.0
	$[(H_3N)_5CoOHCo(NH_3)_5](ClO_4)_5$	H^+	91.0	92.0	8.0	16.0
			92.0	92.0	8.0	17.0
0.20	$[(H_3N)_5CoN_3](ClO_4)_2$	NO^+	94.0	80.0	20.0	20.0
	$[(H_3N)_5CoOHCo(NH_3)_5](ClO_4)_5$	H^+	94.0	93.0	7.0	14.0
0.09	$[(H_3N)_5CoN_3](ClO_4)_2$	NO^+	98.0	90.0	10.0	10.0
	$[(H_3N)_5CoO_2CNH_2](ClO_4)_2$	NO^+	100.0	92.0	8.0	10.0[d]
	$[(H_3N)_5CoI](ClO_4)_2$	Hg^{2+}	98.0	87.0	13.0	13.0
	$[(H_3N)_5CoBr](ClO_4)_2$	Hg^{2+}	90.0	88.0	13.0	13.0
	$[(H_3N)_5CoOHCo(NH_3)_5](ClO_4)_5$	H^+	94.0	97.0	3.0	6.0
0.045	$[(H_3N)_5CoN_3](ClO_4)_2$	NO^+	90.0	97.0	3.0	3.0

[a] 21–26 g of solvent. [b] Sum of the spectrophotometrically determined percentages; direct Co determinations by atomic absorption were in good agreement. [c] Corrected for aquation of $[(H_3N)_5CoOS(CH_3)_2]^{3+}$ during separation; based on 100% recovery. [d] Corrected for percentage of Co–O bond breaking.

influence of $(NH_3)_5Co^{3+}$ on the dissociation constant for H_2O is reproduced for the binuclear ion, then K_H could be in the vicinity of 10^{-2} M^{-1}. Both K_{HY} and K_{HY_2} therefore could be substantially less than 1 and the terms involving these constants in the denominator could be small relative to 1 or K_Y $[H^-]$. It follows also that k_{HY} and k_{HY_2} need to be large since the terms involving them dominate the rates at medium to high Y^- concentrations. All these observations of course are relative to perchlorate as counterions, and ion aggregates with ClO_4^- could also be expected but we have no way of assessing that problem.

Further strong evidence for the importance of ion pairing on HY-induced cleavage comes from analysis of the reaction products. In 1 M H_2SO_4 and 1 M HCl cleavage of the monool produces (based on the one $(H_3N)_5Co^{3+}$ moiety generated) about 3 times as much $(H_3N)_5CoSO_4^+$ and $(H_3N)_5CoCl^{2+}$ as on nitrosation of $(H_3N)_5CoN_3^{2+}$ and $(H_3N)_5CoO_2CNH_2^{2+}$ in the same media.[3] In sulfuric acid, cleavage of the monool gives rise to a constant amount of $(H_3N)_5CoSO_4^+$ over a wide range of concentrations. The amount does not vary appreciably in the presence of a large concentration of $HClO_4$ or Na_2SO_4. This is consistent with the proposal that ion aggregates with SO_4^{2-} (or HSO_4^-) accelerate the rate very substantially and form much more stable ion pairs than other anions in the system. In 1 M HCl, 25% more $(H_3N)_5CoCl^{2+}$ is formed than by the spontaneous process in NaCl, pH 3.5–4. In HCl media, the amount of $(H_3N)_5CoCl^{2+}$ formed is independent of the acidity over a range where the contribution from the acid-induced path is dominant; moreover, it is independent of $[Cl^-]$ when varied over a factor of 2 at constant ionic strength. In this respect, these competition results differ from other systems studied including spontaneous aquation of the monool. Previously, the amount of competition was proportional to the competitor concentration between 0.35 and 1 M, except for the spontaneous aquation of the monool where a nonlinear increase was found.

These features along with the kinetics results point to ion-aggregate equilibria prior to the cleavage step. Due to the high charge of the reactant, ion aggregation displays a dominant influence on the acid-induced cleavage pathway, which does not generally manifest itself with the rate- and product-determining steps in the lower charged (2+, 3+) Co(III) complexes.[1,2,3,5]

Although the rate of acid-induced cleavage increases with anion concentration in contrast to the spontaneous process, it seems likely that the process is largely dissociative especially since the leaving group is now improved. Some evidence for a dissociative process can also be seen in the lack of discrimination of $(H_3N)_5Co^{3+}$ for different nucleophiles. However, the ion atmospheres around both reactant and possible intermediate complicates the issue, and in an attempt to avoid this problem, some kinetics and competition studies were carried out in the presence of neutral competitors.

The results described for the monool cleavage on the whole support and complement those reported by Sykes, *et al.*,[15] except for a few features. We find it surprising for example that NCS^- competes completely for exactly half the cobalt. Even 1 M SO_4^{2-} ion captures only 40%. Also the lack of a NO_3^--dependent path for cleavage is unusual when $CH_3SO_3^-$ shows such a dependence. Finally the report that no S-bonded $(NH_3)_5CoSCN^{2+}$ is formed in the acid-induced cleavage reactions is at variance with our observations. In two experiments at 25° using fresh 1 M HSCN ($Ba(SCN)_2$ + H_2SO_4) to cleave the monool, a purple 2+ species was observed when the reaction mixture was eluted on the cation-exchange column with 1 M $NaClO_4$. The purple species converted to the red N-bonded isomer in a few minutes on the column.

Competition for Neutral Molecules. Acetonitrile–water and DMSO–water mixtures were chosen since the resulting pentaammine complexes are kinetically stable in acid solution. The common competition results obtained for the nitrosations of $(H_3N)_5CoN_3^{2+}$ and $(H_3N)_5CoO_2CNH_2^{2+}$ in these solvents suggest a common intermediate for the two reactions, consistent with competition studies using anionic competitors.[1,11] A lower competition value was observed for the mercury-induced reactions on $(H_3N)_5CoX^{2+}$ (X^- = I^-, Br^-) although it was essentially the same for the different leaving groups HgX^+. This is also consistent with the results for competition by anions in Hg^{2+}-catalyzed aquation of $(H_3N)_5CoX^{2+}$ (X^- = Cl^-, Br^-, I^-).[3,5] Although the competition values in both sets of experiments differ from the corresponding nitrosation reactions, the stereochemical studies in aqueous solution imply a common intermediate for nitrosation of *cis*-$[Co(en)_2ClN_3]^+$ and Hg^{2+}-catalyzed aquation of *cis*-$[Co(en)_2Cl_2]^+$ to $[Co(en)_2ClH_2O]^{2+}$.[16] It may be argued therefore that the competition differences arise from different ionic atmospheres for anion competition and selective solvation in the competition by neutral species. Clearly the charges in the transition states leading to the supposed intermediate are different, *e.g.*, $(H_3N)_5CoNNNNO^{3+}$ and $(H_3N)_5CoI{\cdot}Hg^{4+}$. However these problems are not involved for the stereochemical studies where common agreement is found. Additional evidence for selective solvation might be deduced from the slope of the competition plot for the NO^+ reactions in the CH_3CN-H_2O mixtures (Figure 4). Since this extrapolates to a nonzero intercept $[X_{CH_3CN}] = 0$, the competition pattern must alter sharply at low CH_3CN concentrations. The monool also competes less effectively than the other reactions discussed. While these are not especially discriminating results, the competition is consistent with a predominantly dissociative path.

In the competition experiments in DMSO-water common results were also obtained for the nitrosations suggesting a common intermediate. Similarly, Hg^{2+}-catalyzed aquation of the halide complexes ($X^- = I^-, Br^-$) also gave a common result but now significantly more DMSO is incorporated than in the nitrosation experiments. Finally, the monool cleavage which now occurs by the acid-induced path gave results which are different from the others. Unlike the results in CH_3CN-H_2O solutions, the competition for DMSO appears to extrapolate in all cases to zero at [DMSO] = 0 although the apparently linear plot of mole fraction of DMSO in the solvent *vs.* mole fraction of competition product deviates at $X_{DMSO} > 0.25$ (Figure 5) in the nitrosation and monool cases. This discontinuity correlates with discontinuities in other physical properties of DMSO-H_2O mixtures which imply specific solution aggregates.[17,18] Probably selective solvation of the intermediates is again involved although the results are insufficient at this time to substantiate this argument fully.

In short, no simple answer is obtained except that the competition by the neutral competitors in the nitrosation reactions is consistent with a common intermediate. On the whole the remaining results are consistent with the dissociative chemistry generally observed for substitution cobalt(III)-ammine complexes without giving strong support to this thesis. There is an additional implication that competition for $(H_3N)_5Co^{3+}$ and related species will be dependent on the charge of the immediate source of the intermediate and this aspect is being examined further.

Acknowledgment. We wish to thank A. J. Herlt for his assistance in the preparations and one of the referees for detecting a major error in the original manuscript.

Registry No. $Co(NH_3)_5{}^{3+}$, 44236-77-3; $(NH_3)_5CoOHCo(NH_3)_5{}^{5+}$, 38467-75-3; $[(H_3N)_5CoOS(CH_3)_2](ClO_4)_3$, 51667-94-8; $[(H_3N)_5Co(OH_2)](ClO_4)_3$, 13820-81-0; DMSO, 67-68-5.

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Isomers of the Bis(diethylenetriamine)cobalt(III) Cation. Dependence of Equilibrium Isomer Proportions on Environmental Parameters

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Received December 18, 1973 AIC30900N

The equilibrium distribution of the three geometric isomers of $[Co(dien)_2]^{3+}$ depends considerably on the environmental parameters solvation, ion association, and temperature. Addition of a basic oxy anion such as phosphate, selenite, or sulfate profoundly modifies the isomer distribution through the differential specific associations between the anion and the three isomers. The relative magnitudes of the specific interactions with phosphate as deduced from isomer proportions measurements are correlated with the measured association constants of the three isomers with that anion, and they are rationalized in terms of the detailed molecular structures of the isomers. The equilibrium isomer distribution measurements carried out at different temperatures lead to quantitative assessment of the enthalpy and entropy differences between the isomers. These thermodynamic data allow the first comparison of experimental equilibrium results with the predictions from energy-minimized conformational analysis calculations for different topological forms of a multidentate ligand complex and indicate the limitations of the present calculative methods.

Introduction

It has been appreciated for many years that a number of factors may determine the relative stabilities of the various isomeric forms of a metal complex, where these forms differ in relative geometry, *i.e.*, geometric isomers, internal diastereoisomers, or conformational isomers.[1] These factors include ion association, solvation, temperature, intramolecular nonbonded atomic interactions, and statistical weighting factors. The quantitative evaluation of all these factors, either on an experimental or on a theoretical basis, has not been possible however since it is recognized that they are not all independent. Even the relative importance of intramolecular and intermolecular factors is not generally known.

Experimentally, the reliable quantitative data for equilibrium distributions of isomers are essentially confined to some cobalt(III) complexes, with equilibrium frequently

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