772 *Inorg. Chem.* **1988**, *27*, 772-776

Contribution from the Institut de Chimie Physique,
Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

Base Hydrolysis of Pentaammine Complexes of Cobalt(III): Structure, Reactivity, and Lifetime of the Intermediates[†]

François P. Rotzinger

Received July 22, 1987

Base hydrolysis of $Co(NH_3)_5NO_3^{2+}$ and $Co(NH_3)_5OS(CH_3)_2^{3+}$ has been studied in 0.01 M NaOH and 0.02–0.40 M NaN_3 at 25 °C. The products $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5OH^{2+}$ are formed. The ionic strength dependence of the competition ratio $R = [Co(NH_3)_5N_3^{2+}]_\infty/([Co(NH_3)_5OH^{2+}]_\infty[N_3^-])$ is described by the charge of the intermediate, z_I, and the competition ratio at zero ionic strength, R_0. For NO_3^- and $(CH_3)_2SO$ as leaving groups, the parameters $z_I = 1.02 \pm 0.04$, $R_0 = 0.304 \pm 0.005$ M^{-1} and $z_I = 2.04 \pm 0.02$, $R_0 = 0.980 \pm 0.013$ M^{-1}, respectively, were found. Base hydrolysis of $Co(NH_3)_5SO_4^+$, studied in 0.04 and 0.20 M NaOH, 0.05–0.40 M NaN_3, and 0.1 M NH_3 at 25 °C, leads to an uncharged intermediate, since the competition ratio $R = 0.078 \pm 0.002$ M^{-1} is independent of the ionic strength. The experimental results are rationalized by postulating two hexacoordinated intermediates, namely $[Co(NH_3)_4(NH_2)\cdots X]^{n-1}$ and $[Co(NH_3)_4(NH_2)\cdots X,N_3]^{n-2}$, which equilibrate rapidly with each other during their lifetime. The free intermediate $[Co(NH_3)_4(NH_2)\cdots X]^{n-1}$ forms exclusively hydroxopentaamminecobalt(III) by water scavenging whereas the ion-paired intermediate $[Co(NH_3)_4(NH_2)\cdots X,N_3]^{n-2}$ forms exclusively azidopentaamminecobalt(III) by collapsing. The lifetimes of the intermediates generated by base hydrolysis of $Co(NH_3)_5SO_4^+$, $Co(NH_3)_5NO_3^{2+}$, and $Co(NH_3)_5OS(CH_3)_2^{3+}$ were determined to be >1600, >190, and 190, ps, respectively.

Introduction

Base hydrolysis of amine complexes of cobalt(III) has been and still is studied extensively,[1] because a great deal of detailed information about substitution mechanisms can be obtained. One of the most challenging topics in this field is the characterization of the short-lived pentacoordinated intermediates, if they exist at all.

At the present time, very little is known about the structure, reactivity, and lifetime of the postulated intermediates.[1] Furthermore, no work analyzing the stage of back-protonation has been published.[2] The charge of the leaving group affects[1,3] the competition ratio R to some extent, but this effect is small at unit ionic strength and is not quantitatively understood. Interestingly, the relative amount of azidopentaamminecobalt(III) formed by base hydrolysis of $Co(NH_3)_5X^{2+}$ complexes in the presence of 1 M NaN_3 (at 25 °C) depends slightly on the nature of the leaving group. It increases[3] in the order Cl^-, $Br^- < FSO_3^-$, $CF_3SO_3^- <$ SCN^-, $CH_3SO_3^-$, $I^- < NO_3^-$, ClO_4^-. This indicates that the leaving group influences the product formation. This observation argues against the existence of a discrete pentacoordinated intermediate.

Alkaline hydrolysis is currently believed[1] to proceed via a limiting dissociative conjugate-base mechanism (D_{cb}). From recent work[4,5] further evidence for the dissociative character of this reaction has been obtained: (i) ammonia loss of $(NH_3)_5CoNH_2Co(NH_3)_5^{5+}$ is retarded[4] in the presence of ammonia, which is only possible if an intermediate reacts with ammonia to restore the (deprotonated) reactant, and (ii) the ion-paired conjugate bases with a poor competing anion, perchlorate, and an excellent one, azide, in the second coordination sphere exhibit identical reactivities.[5] These arguments confirm the dissociative nature of the substitution process but by no means prove the existence of genuine pentacoordinated intermediates.

The rate-determining steps in base hydrolysis of pentaammine complexes of cobalt(III), illustrated for the thoroughly studied $Co(NH_3)_5NO_3^{2+}$ ion, are summarized in Scheme I.[5] The ion pair of the reactant with hydroxide $[Co(NH_3)_5NO_3,OH]^+$, and the ion triplet of the reactant with hydroxide and an anion from the solution (Y^-) $[Co(NH_3)_5NO_3,(OH)(Y)]$ are in equilibrium with the corresponding conjugate bases, which are present at unknown and low concentrations. The free as well as the ion-paired conjugate bases are expected to generate the corresponding free and ion-paired intermediates, whose structure, reactivity and lifetime have been investigated in this work by analyzing the ionic strength dependence of the competition ratio.

Experimental Section

Physical Measurements. The UV-vis spectra were recorded on a HP 8450 A spectrophotometer thermostated to 25 °C.

Scheme I

$$\begin{tikzcd}
Co(NH_3)_5NO_3^{2+} \arrow[r, shift left, "\pm Y^-{,}\ K_Y"] \arrow[d, shift right, "\pm OH^-{,}\ K_{OH}"'] & {[Co(NH_3)_5NO_3,\ Y]^+} \arrow[l, shift left, "fast"] \arrow[d, shift right] \\
{[Co(NH_3)_5NO_3,\ OH]^+} \arrow[u, shift right, "fast"'] \arrow[r, shift left, "\pm Y^-"] \arrow[d, shift right, "\mp H_2O"'] & {[Co(NH_3)_5NO_3,\ (OH)(Y)]} \arrow[u, shift right, "\pm OH^-{,}\ K'_{OH}\ fast"'] \arrow[l, shift left, "fast"] \arrow[d, shift right, "\mp H_2O"'] \\
Co(NH_3)_4(NH_2)NO_3^+ \arrow[u, shift right] \arrow[r, shift left] \arrow[d, "slow"] & {[Co(NH_3)_4(NH_2)NO_3,\ Y]} \arrow[u, shift right] \arrow[l, shift left] \arrow[d, "slow"] \\
intermediate(s) & intermediate(s)
\end{tikzcd}$$

Preparations. $[Co(NH_3)_5SO_4]ClO_4$, $[Co(NH_3)_5NO_3](ClO_4)_2$, $[Co(NH_3)_5OS(CH_3)_2](ClO_4)_3{\cdot}H_2O$, $[Co(NH_3)_5OH_2](ClO_4)_3$, and $[Co(NH_3)_5N_3]Cl_2$ were prepared according to the literature.[3,6-11] $Co(NH_3)_5N_3^{2+}$ was handled under strict exclusion of light.

Competition Experiments. The UV-vis spectra of $Co(NH_3)_5OH^{2+}$ (prepared by dissolving $[Co(NH_3)_5OH_2](ClO_4)_3$, 5.06×10^{-3} M, in 0.01 M NH_3) and $Co(NH_3)_5N_3^{2+}$ (prepared by dissolving $[Co(NH_3)_5N_3]Cl_2$, 2.008×10^{-3} and 8.03×10^{-5} M in H_2O) were recorded immediately after the preparation, since even under mild conditions (ammonia buffer) $Co(NH_3)_5OH^{2+}$ hydrolyzes slowly and $Co(NH_3)_5N_3^{2+}$ is extremely light-sensitive. The UV-vis spectrum ($\lambda > 300$ nm) of $Co(NH_3)_5N_3^{2+}$ was not altered upon addition of 0.4 M NaN_3, and therefore, the product analysis was not affected by the competing anion (the hydroxide concentration was too low to perturb the spectra).

The competition experiments were carried out by placing ~3 mL of the solvent, a solution containing 0.01 M NaOH and 0.02–0.40 M NaN_3, in a 1-cm quartz cell and storing its spectrum as the base line at 25 °C. Then, solid $[Co(NH_3)_5NO_3](ClO_4)_2$ or $[Co(NH_3)_5OS(CH_3)_2](ClO_4)_3{\cdot}H_2O$ was added and the cell shaken for about 2–10 s and placed into the spectrophotometer. The reactant concentrations were typically $(1-5) \times 10^{-3}$ M. The spectrum of the products was recorded after ~4–6 min. Under these conditions, base hydrolysis of $Co(NH_3)_5NO_3^{2+}$ and Co-

---

[†] In memory of the late professor Dr. Werner Marty.

(1) Tobe, M. L. *Advances in Inorganic and Bioinorganic Mechanisms*; Sykes, A. G., Ed.; Plenum: New York, 1983; Vol. 2, p 1.
(2) Studies on the base hydrolysis of Co(dien)(dapo)X^{n+} complexes show that back-protonation occurs *after* nucleophile scavenging (Comba, P.; Marty, W.; Zipper, L., work in progress).
(3) Dixon, N. E.; Jackson, W. G.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1982**, *21*, 688.
(4) Rotzinger, F. P.; Müller, E.; Marty, W. *Inorg. Chem.* **1987**, *26*, 3704.
(5) Rotzinger, F. P. *Inorg. Chem.*, preceding article in this issue.
(6) Jörgensen, S. M. *J. Prakt. Chem.* **1885**, *31*, 268.
(7) Po, L. L.; Jordan, R. B. *Inorg. Chem.* **1968**, *7*, 526.
(8) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1966**, *88*, 5443.
(9) Buckingham, D. A.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1974**, *13*, 2165.
(10) Lamb, A. B.; Mysels, K. J. *J. Am. Chem. Soc.* **1945**, *67*, 468.
(11) Linhard, M.; Flygare, H. *Z. Anorg. Chem.* **1950**, *262*, 329.

0020-1669/88/1327-0772$01.50/0

Table I. Extinction Coefficients of $Co(NH_3)_5OH^{2+}$ (**1**) and $Co(NH_3)_5N_3^{2+}$ (**2**)

	ϵ, M^{-1} cm^{-1}			ϵ, M^{-1} cm^{-1}	
λ, nm	**1**	**2**	λ, nm	**1**	**2**
302	39.0	8629 (max)	442	23.9	56.2 (min)
315	25.0 (min)	7240	504	67.6 (max)	250
370	64.9 (max)	638	516	64.5	269 (max)
426	19.0 (min)	89			

Table II. Analysis of the Products Formed by Base Hydrolysis of $Co(NH_3)_5X^{n+}$ Complexes in 0.01 M NaOH and 0.02–0.40 M NaN_3 at 25 °C

$[N_3^-]$, M	$[Co(NH_3)_5OH^{2+}]_\infty$, mM[a]	$[Co(NH_3)_5N_3^{2+}]_\infty$, μM[a]	$[Co]_{tot}$, mM[a]
		(a) X = NO_3	
0.02	3.09 (2)	12.7 (2)	3.11 (2)
	4.37 (1)	18.4 (2)	4.39 (1)
0.05	3.56 (4)	35.3 (6)	3.59 (4)
	3.83 (4)	37.6 (6)	3.87 (4)
0.10	2.88 (5)	52.7 (10)	2.94 (5)
	2.44 (4)	44.5 (7)	2.49 (4)
0.20	1.18 (3)	37.9 (6)	1.22 (3)
	3.46 (4)	111 (2)	3.57 (4)
	2.66 (5)	83.9 (17)	2.75 (5)
	2.00 (6)	62.8 (16)	2.06 (6)
0.30	2.79 (5)	124 (3)	2.91 (5)
	1.59 (4)	71.9 (13)	1.66 (4)
0.40	1.66 (4)	91.6 (18)	1.75 (4)
	2.88 (5)	164 (6)	3.05 (5)
	0.990 (36)	55.7 (9)	1.05 (4)
		(b) X = $(CH_3)_2SO$	
0.02	1.20 (1)	11.3 (2)	1.21 (1)
	3.69 (3)	34.2 (4)	3.72 (3)
	2.12 (2)	20.1 (2)	2.14 (2)
	2.19 (2)	20.5 (2)	2.21 (2)
0.05	2.41 (1)	48.4 (3)	2.46 (1)
	1.43 (1)	29.2 (1)	1.46 (1)
	1.69 (1)	34.6 (2)	1.72 (1)
0.10	1.84 (2)	63.1 (5)	1.90 (2)
	1.97 (1)	67.4 (4)	2.04 (1)
	1.78 (2)	58.0 (6)	1.78 (2)
0.20	1.86 (2)	103 (1)	1.96 (2)
	0.928 (16)	52.4 (4)	0.980 (16)
	1.83 (1)	106 (1)	1.94 (1)
0.30	1.24 (2)	94.5 (8)	1.33 (2)
	0.992 (21)	74.2 (7)	1.07 (2)
	1.63 (2)	121 (1)	1.75 (2)
0.30[b]	2.74 (2)	152 (2)	2.89 (2)
	1.61 (1)	90.0 (5)	1.70 (1)
	1.53 (1)	86.5 (6)	1.62 (1)
0.40	1.47 (1)	129 (1)	1.60 (1)
	1.92 (2)	165 (2)	2.08 (2)
	1.99 (2)	172 (2)	2.16 (2)
	2.13 (2)	181 (3)	2.31 (2)
0.40[c]	1.44 (1)	96.9 (6)	1.53 (1)
	1.57 (1)	107 (7)	1.68 (1)
	1.96 (1)	131 (1)	2.09 (1)

[a] The standard deviation of the last digit(s) is given in parentheses. [b] 0.30 M $NaClO_4$ added. [c] 0.40 M $NaClO_4$ added.

$(NH_3)_5OS(CH_3)_2^{3+}$ is sufficiently fast that the reactions were completed within less than 4–6 min ($10t_{1/2}$). During this time, decomposition of the products did not interfere significantly. Afterwards, decomposition of the reaction products started to perturb the spectrum. Hydroxide concentrations higher than 0.01 M were not investigated, because formation of cobalt hydroxide is accelerated, and an unperturbed UV–vis spectrum is more difficult to obtain.

Base hydrolysis of $Co(NH_3)_5SO_4^+$, however, is slow, and decomposition of the products is relatively fast compared to their formation. For this reason, it is impossible to obtain the products of interest in the absence of secondary products. The reaction was studied in 0.04–0.2 M NaOH with 0.1 M NH_3 added in order to retard ammonia loss of the pentaammines and to prevent formation of "cobalt(III) hydroxide". Accurate results were only obtained in 0.2 M NaOH and 0.10–0.40 M NaN_3. The experimental procedure was the same as described above, but the spectra were recorded after 10 or 50 min for solutions containing 0.2 or 0.04 M NaOH, respectively.

The concentration of $Co(NH_3)_5OH^{2+}$ (**1**) and $Co(NH_3)_5N_3^{2+}$ (**2**) was determined as follows: the extinction coefficients of **1** and **2** were measured at the extremas (Table I). The optical density vector **d** (containing the optical densities d_i at the wavelengths given in Table I) may then be expressed as $\mathbf{d} = \mathbf{E}\cdot\mathbf{c}$. The matrix **E** contains the extinction coefficients of **1** and **2** as columns (Table I), and **c** is a column vector with the elements $c_1 = [\mathbf{1}]$ and $c_2 = [\mathbf{2}]$. At high $[N_3^-]$, large amounts of **2** were formed and its absorbance dominated the spectrum, especially at $\lambda < 400$ nm. The concentration vector **c** was determined by weighted least-squares fits using the relation $\mathbf{c} = (\mathbf{E}^T\mathbf{W}\mathbf{E})^{-1}\mathbf{E}^T\mathbf{W}\mathbf{d}$. **W** is a diagonal-weight matrix with the elements $w_{ii} = 10^{-2d_i}$ and $w_{ij} = 0$. This method allowed us to determine the concentration of **1** and **2** very accurately (Tables II and III).

General Considerations

Currently, it is accepted[1] that the products formed by base hydrolysis of (acidato)pentaamminecobalt(III) complexes arise from scavenging of nucleophiles and water by intermediate(s). In the present study, azide was used as a nucleophile. The competition ratio R, defined by eq 1, is constant at constant ionic strength.

$$R = \frac{[Co(NH_3)_5N_3^{2+}]_\infty}{[Co(NH_3)_5OH^{2+}]_\infty[N_3^-]} \qquad (1)$$

The step of product formation involves the reaction of the intermediate with water, a neutral molecule, and the reaction with azide, an anion. For a charged intermediate the rate for water scavenging is independent of the ionic strength, but the overall rate constant for azide scavenging (k'_{N_3}) is expected to depend on the ionic strength. On the basis of the Debye–Hückel equation for the activity coefficients $-\log f_i = z_i^2 A I^{1/2}/(1 + BI^{1/2})$ the ionic strength dependence of k'_{N_3} is given by eq 2. The parameter z_I

$$k'_{N_3}(I) = k'_{N_3,0}10^{-2z_I A I^{1/2}/(1+BI^{1/2})} \qquad (2)$$

represents the charge of the intermediate, $A = 0.509$ $M^{-1/2}$ and $B = \beta r$ with $\beta = 0.329$ $M^{-1/2}$ Å^{-1} at 25 °C are physical constants, r is the distance of closest approach of the reactants in Å, and I is the ionic strength. In the Discussion it will be shown why the competition ratio R exhibits the same ionic strength dependence as k'_{N_3} (eq 3).

$$R(I) = R_0 10^{-2z_I A I^{1/2}/(1+BI^{1/2})} \qquad (3)$$

Results

In order to obtain the ionic strength dependence of R, a large number of product analyses were required. The concentrations of the reaction products were determined directly (in the mixture) by spectrophotometry (Tables II and III), in contrast to the classical way, which required separation of the products by ion-exchange chromatography. This assured highly accurate results and prevented losses of the very light-sensitive azido complex.

The very accurately determined R values for base hydrolysis of $Co(NH_3)_5NO_3^{2+}$ and $Co(NH_3)_5OS(CH_3)_2^{3+}$ (the O═S bond is not cleaved[3]) were measured in 0.01 M NaOH, 0.02–0.40 M NaN_3 at 25 °C (Table IV). The competition ratios are strongly ionic strength dependent and depend further on the charge of the reactant or, more precisely (see Discussion), on the charge of the intermediate. Interestingly, addition of $NaClO_4$ does not affect the ionic strength dependence of R.

In azide-containing alkaline solutions, the intermediates may in principle react with H_2O, OH^-, and N_3^-. Green and Taube[12,13] showed with ^{18}O-labeling experiments that OH^- is not scavenged by the intermediates. Under the present experimental conditions, competition by hydroxide would affect R by less than 1%, if it is assumed that azide and hydroxide are comparable competing anions.[14] If nevertheless hydroxide would compete for the in-

---

(12) Green, M.; Taube, H. *Inorg. Chem.* **1963**, *2*, 948.
(13) Green, M.; Taube, H. *J. Phys. Chem.* **1963**, *67*, 1565.

Table III. Analysis of the Products Formed by Base Hydrolysis of $Co(NH_3)_5SO_4^+$ in 0.2 M NaOH, 0.05–0.40 M NaN_3, and 0.1 M NH_3 at 25 °C: Ionic Strength Dependence of *R*

$[N_3^-]$, M	$[Co(NH_3)_5OH^{2+}]_\infty$, mM[a]	$[Co(NH_3)_5N_3^{2+}]_\infty$, μM[a]	$[Co]_{tot}$, mM[a]	I_{av}[b]	*R*, M^{-1}[a]
0.05	3.04 (3)	10.0 (3)	3.05 (3)	0.258	0.066 (2)[c]
	5.02 (6)	16.4 (7)	5.03 (6)	0.263	0.066 (3)[c]
	5.44 (7)	17.9 (8)	5.46 (7)	0.264	0.066 (3)[c]
	6.50 (8)	21.4 (9)	6.52 (8)	0.266	0.066 (3)[c]
0.10[d]	3.33 (6)	28.9 (9)	3.36 (6)	0.148	0.087 (3)[c,d]
	4.61 (8)	39.7 (13)	4.65 (8)	0.152	0.086 (3)[c,d]
0.10	2.28 (3)	17.6 (4)	2.29 (3)	0.306	0.077 (2)
	3.74 (6)	28.6 (8)	3.76 (6)	0.309	0.076 (2)
	5.12 (8)	39.0 (12)	5.15 (8)	0.313	0.076 (3)
	6.27 (4)	48.1 (18)	6.31 (4)	0.316	0.077 (3)
0.20	2.32 (5)	37.1 (9)	2.36 (5)	0.406	0.080 (3)
	2.78 (6)	44.3 (12)	2.82 (6)	0.407	0.080 (3)
	2.86 (6)	45.5 (12)	2.90 (6)	0.407	0.080 (3)
	2.86 (6)	45.5 (12)	2.91 (6)	0.407	0.079 (3)
	5.92 (10)	92.7 (34)	6.01 (10)	0.415	0.078 (3)
0.40	1.27 (5)	40.5 (9)	1.31 (5)	0.603	0.080 (3)
	1.55 (5)	48.8 (11)	1.60 (5)	0.604	0.079 (3)
	3.17 (7)	98.3 (31)	3.26 (7)	0.608	0.078 (3)
	4.62 (9)	141 (7)	4.77 (9)	0.612	0.076 (4)
					0.078 (2) (av)

[a] The standard deviation of the last digit(s) is given in parentheses. [b] $I_{av} = [OH^-]_0 + [N_3^-]_0 + 2.5[Co(NH_3)_5SO_4^+]_0$. [c] Not considered for the calculation of the average of *R*. [d] 0.04 M NaOH.

Table IV. Ionic Strength Dependence of the Competition Ratio *R*

(a) Base Hydrolysis of $Co(NH_3)_5NO_3^{2+}$

I	R_{obsd}, M^{-1}	R_{calcd}, M^{-1}[a]	*I*	R_{obsd}, M^{-1}	R_{calcd}, M^{-1}[a]
0.0393	0.205 ± 0.003	0.212	0.216	0.157 ± 0.006	0.160
0.0432	0.210 ± 0.002	0.209	0.221	0.161 ± 0.004	0.160
0.0708	0.198 ± 0.004	0.194	0.315	0.151 ± 0.005	0.150
0.0716	0.196 ± 0.004	0.194	0.319	0.148 ± 0.004	0.149
0.117	0.182 ± 0.004	0.179	0.413	0.141 ± 0.006	0.142
0.119	0.183 ± 0.004	0.178	0.415	0.138 ± 0.004	0.142
0.214	0.160 ± 0.005	0.161	0.419	0.142 ± 0.006	0.142
0.218	0.158 ± 0.004	0.160			

(b) Base Hydrolysis of $Co(NH_3)_5OS(CH_3)_2^{3+}$

I	R_{obsd}, M^{-1}	R_{calcd}, M^{-1}[b]	*I*	R_{obsd}, M^{-1}	R_{calcd}, M^{-1}[b]
0.0355	0.469 ± 0.008	0.492	0.315	0.249 ± 0.006	0.241
0.0396	0.474 ± 0.006	0.478	0.316	0.254 ± 0.004	0.241
0.0399	0.469 ± 0.006	0.477	0.318	0.246 ± 0.004	0.240
0.0467	0.464 ± 0.006	0.456	0.417	0.219 ± 0.003	0.218
0.0666	0.407 ± 0.003	0.411	0.419	0.215 ± 0.004	0.217
0.0677	0.410 ± 0.004	0.409	0.420	0.217 ± 0.003	0.217
0.0711	0.402 ± 0.003	0.403	0.420	0.212 ± 0.004	0.217
0.118	0.336 ± 0.006	0.342	0.623[c]	0.185 ± 0.002	0.188
0.119	0.343 ± 0.005	0.341	0.618[c]	0.187 ± 0.002	0.189
0.119	0.342 ± 0.003	0.341	0.617[c]	0.188 ± 0.002	0.189
0.214	0.282 ± 0.005	0.278	0.817[d]	0.169 ± 0.002	0.171
0.219	0.278 ± 0.004	0.275	0.818[d]	0.169 ± 0.002	0.171
0.219	0.290 ± 0.003	0.275	0.819[d]	0.167 ± 0.002	0.170

[a] Calculated according to eq 4 with $z_I = 1.02 \pm 0.04$, $B = 1.60$ $M^{-1/2}$, and $R_0 = 0.304 \pm 0.005$ M^{-1}. [b] Calculated according to eq 4 with $z_I = 2.04 \pm 0.02$, $B = 1.63$ $M^{-1/2}$, and $R_0 = 0.980 \pm 0.013$ M^{-1}. [c] 0.30 M $NaClO_4$ added. [d] 0.40 M $NaClO_4$ added.

termediate instead of water, the *R* values would be independent of the ionic strength and the charge of the intermediate, since hydroxide and azide are both singly charged anions. The ionic strength dependence of *R* establishes that $Co(NH_3)_5OH^{2+}$ is formed by water scavenging as already known.[12,13]

Equation 3 contains three parameters, namely R_0, z_I, and *B*. Weighted nonlinear least-squares fits of the experimental data (Table IV) to this expression showed that z_I and *B* are strongly correlated with coefficients >0.98. The same observation was made when kinetic data from the literature were fitted to expressions analogous to that of eq 3. Therefore, *B* was estimated as βr with $r = r_+ + r_-$; r_+ is the mean radius of the cation calculated[15] as 3.60 and 3.71 Å for $Co(NH_3)_5NO_3^{2+}$ and $Co(NH_3)_5OS(CH_3)_2^{3+}$, respectively, and r_- represents the mean radius of the anion, estimated as $(d_xd_yd_z)^{1/3}/2 = 1.26$, 1.93, and 1.14 Å for azide, perchlorate, and hydroxide, respectively.

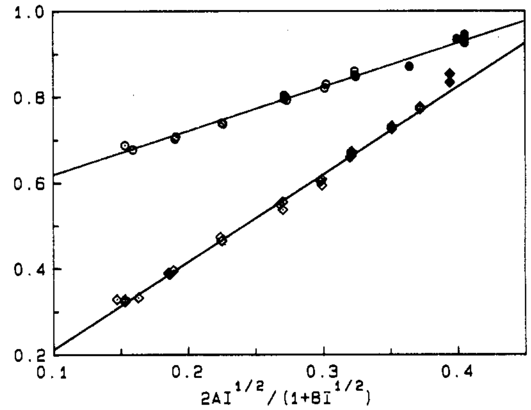


Figure 1. Plots of $-\log R$ vs $2AI^{1/2}/(1 + BI^{1/2})$: circles, $Co(NH_3)_5NO_3^{2+}$; diamonds, $Co(NH_3)_5OS(CH_3)_2^{3+}$; open symbols, data determined in this work; filled symbols, literature values;[3,8,17,18] solid lines, weighted least-squares fits to eq 4 based on the data determined in this work.

The charge of the intermediate, z_I, and the competition ratio at $I \to 0$, R_0, were obtained by eq 4, the logarithmic form of eq

$$\log R(I) = \log R_0 - 2z_IAI^{1/2}/(1 + BI^{1/2}) \qquad (4)$$

3 using the estimated B values.[16] Plots of $-\log R$ vs $2AI^{1/2}/(1 + BI^{1/2})$ are linear (Figure 1). The parameters z_I and $\log R_0$, the slopes and the intercepts, were determined by weighted

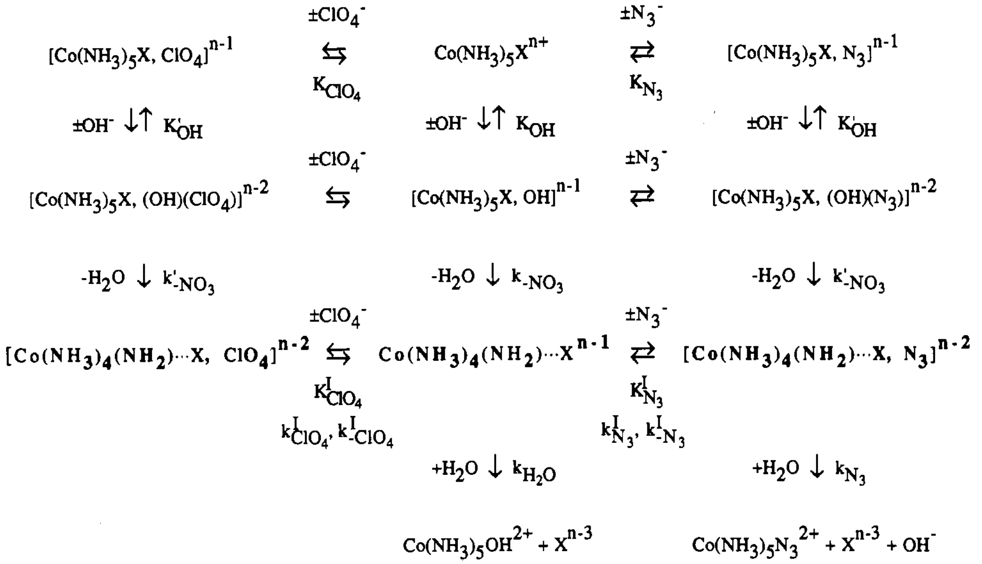
---

(14) If both azide and hydroxide would react at the same rate with the intermediate, $R' = [Co(NH_3)_5N_3^{2+}]_\infty/([Co(NH_3)_5OH^{2+}]_\infty[N_3^-]) = \{R^{-1} + [OH^-]\}^{-1} \cong R$ would result, since $R^{-1} > 1$ M and $[OH^-] < 0.01$ M holds.

(15) For a variety of X-ray crystal structures of cobalt(III) complexes we found that one electron occupies 1.85 Å³. If spherical ions are assumed, the radius is given by the expression $r_+ = \{3 \times (\text{number of electrons of the cation}) \times 1.85/(4\pi)\}^{1/3}$.

(16) The parameters z_I and R_0 do not depend critically on the choice of *B*, since a 10% change of *B* affects R_0 and z_I by only ~3 and ~6%, respectively.

Scheme II



least-squares fits. The minimized function was $\sum_i w_i(\log R_{i,\text{calcd}} - \log R_{i,\text{obsd}})^2$ with $w_i = \{\sigma_{i,R}(\log e)/R_{i,\text{obsd}}\}^{-2}$. The results are summarized in Table IV. The agreement between observed and calculated values is excellent. Less precise competition ratios R were obtained for base hydrolysis of $Co(NH_3)_5SO_4^+$, which was studied in 0.04–0.2 M NaOH, 0.05–0.40 M NaN_3, and 0.1 M NH_3 at 25 °C (see Experimental Section and Table III). In 0.04 M NaOH the reaction of $Co(NH_3)_5SO_4^+$ is slow ($10t_{1/2} \approx 50$ min), and the amount of decomposed pentaammines is large compared to the amount of $Co(NH_3)_5N_3^{2+}$ formed. The same observation was also made when $[N_3^-]$ was low (0.05 M) at 0.2 M NaOH. Nevertheless, accurate R values were obtained in 0.2 M NaOH, 0.10–0.40 M NaN_3, and 0.1 M NH_3 (Table III). Clearly, $R = 0.078 \pm 0.002$ M^{-1} is independent of the ionic strength.

Literature values for azide competition are known[3,8,17,18] for all the investigated three reactants (25 °C). They are included in Figure 1 as filled symbols, and they are in perfect agreement with the solid lines calculated by least-squares fits based on the data given in Table IV (the literature data were excluded from the calculations). Since Dixon et al.[3] studied the slow base hydrolysis of $Co(NH_3)_5SO_4^+$ in the absence of ammonia, decomposition of both $Co(NH_3)_5OH^{2+}$ and $Co(NH_3)_5N_3^{2+}$ occurred. This is probably the origin of the difference between their (5.5–6.1%) and our (7.2%) amounts of azido complex found.

Discussion

The ionic strength dependence of the competition ratio for base hydrolysis of $Co(NH_3)_5SO_4^+$, $Co(NH_3)_5NO_3^{2+}$, and $Co(NH_3)_5OS(CH_3)_2^{3+}$, reactants representing three different charge types, has been analyzed. The respective competition ratios R(independent of I) = 0.078 ± 0.002 M^{-1}, $R_0 = 0.304 \pm 0.005$ and 0.980 ± 0.013 M^{-1} have been found at 25 °C. They depend strongly on the charge of the reactant. The literature values[3,8,17,18] obtained at unit ionic strength show the same trend, which is, however, less pronounced.

For the reactants above the respective z_I parameters of 0, 1.02 ± 0.04, and 2.04 ± 0.02 have been found. They are integers and correspond exactly to the charges of the corresponding free reactants diminished by 1.

The present results, together with data from the literature, suggest that base hydrolysis of (acidato)pentaamminecobalt(III) complexes, $Co(NH_3)_5X^{n+}$, proceeds as shown in Scheme II. The ion-pairing equilibria of the reactant with perchlorate (a poor competing anion) and azide (a good competing anion) are shown in the first row of this scheme. The free reactant as well as the ion pairs form the corresponding ion pair and ion triplets with hydroxide presented in the second row. The ion aggregates with hydroxide are in equilibrium with the corresponding conjugate bases, the reactive species, which, however, are present at low, not precisely known concentrations. They were omitted for the sake of clarity[5] and because of their unknown stability constants. The ion aggregates with hydroxide subsequently are transformed via the conjugate bases into the intermediates shown in the third row. These steps are rate-determining, and this part of the scheme is based on the detailed kinetic analysis[5] of the base hydrolysis of $Co(NH_3)_5NO_3^{2+}$.

It will be shown that the equilibration of the three intermediates is much faster than water and azide scavenging. The free intermediate $[Co(NH_3)_4(NH_2)\cdots X]^{n-1}$ reacts exclusively with water to form $Co(NH_3)_5OH^{2+}$ whereas the intermediate associated with azide forms exclusively $Co(NH_3)_5N_3^{2+}$. The intermediate associated with perchlorate reacts neither with water nor with perchlorate (or azide) in competition to loss of perchlorate from the second coordination sphere.

On the basis of Scheme II the ionic strength dependence of the competition ratio is given by eq 5, where $z_I = n - 1$ represents the charge of the free intermediate $[Co(NH_3)_4(NH_2)\cdots X]^{n-1}$. The

$$R(I) = \frac{k_{N_3}K_{N_3}{}^{1}}{k_{H_2O}} = \frac{k_{N_3}K_{N_3,0}{}^{I}}{k_{H_2O}} 10^{-2z_I A I^{1/2}/(1+BI^{1/2})} \quad (5)$$

experimental ionic strength dependence of R determined in this work agrees with eq 5, which is identical with eq 3, if $R_0 = k_{N_3}K_{N_3,0}{}^{1}/k_{H_2O}$. In the following discussion I shall show that the features shown in Scheme II are consistent with the present results and the literature data.

The trivial and wrong model[5] in which the ion-paired conjugate base $[Co(NH_3)_4(NH_2)NO_3,N_3]$ forms directly $Co(NH_3)_5N_3^{2+}$ and the free conjugate base $Co(NH_3)_4(NH_2)NO_3^+$ forms directly $Co(NH_3)_5OH^{2+}$ already has been ruled out in the preceding[5] kinetic study. The ionic strength dependence of R would also follow eq 3, but $R_0 = k'_{-NO_3}K'_{OH,0}K_{N_3,0}/(k_{-NO_3}K'_{OH,0})$ would result. On the basis of the kinetic data[5] $R_0 = 2.28$ M^{-1} is calculated, which by no means compares to the experimental value of 0.304 ± 0.005 M^{-1}. In order to explain this discrepancy, one might argue that the ion-paired conjugate base reacts also with water to form $Co(NH_3)_5OH^{2+}$. In this case, however, the competition ratio would depend not only on the ionic strength but also on $[N_3^-]$, which was not observed, and, furthermore, z_I would be a noninteger.

From the kinetics it is known[5] that in 1 M azide about 50% of the base hydrolysis of $Co(NH_3)_5NO_3^{2+}$ proceeds via the ion-pair pathway but that only about 10% of $Co(NH_3)_5N_3^{2+}$ is formed.[8,17] Only one possible explanation, consistent with the observed ionic

---

(17) Reynolds, W. L.; Hafezi, S. *Inorg. Chem.* **1978**, *17*, 1819.
(18) Birus, M.; Reynolds, W. L.; Pribanic, M.; Asperger, S. *Croat. Chem. Acta* **1975**, *47*, 561.

strength dependence of R (eq 3 or 5) and integer z_I values, remains: the ion-paired intermediate equilibrates rapidly with its free form as shown in Scheme II. This model is in perfect agreement with the present experiments.

In most of the work reported in the literature[1] the intermediates are believed to be pentacoordinated. The competition experiments[3] mentioned in the Introduction show that the leaving groups participate in the product formation. Complete dissociation of the leaving group would give rise to an ion pair of the leaving group with the pentacoordinated intermediate. If this would happen, the effect due to the different sizes of the leaving groups would be predictable by eq 3, since the parameter $B = \beta r$ depends on the size of the leaving group. Also, R_0 would increase with increasing size. Thus, for the reported[3] leaving groups an increase of the competition ratios with increasing size would be expected. The observed[3] variation, however, does not reflect the predicted size dependence. This argues against the existence of intermediates with the leaving group released into the second coordination sphere.

Further evidence against a true pentacoordinated intermediate is obtained from the ionic strength dependence of the competition ratios: any loss of a charged leaving group into the bulk solution in competition to the equilibration of the free and the ion-paired intermediate or to nucleophile addition would lead to higher and noninteger z_I values. If e.g. the ion-paired intermediate $[Co(NH_3)_4(NH_2)\cdots ONO_2,N_3]$ were an ion triplet with both N_3^- and NO_3^- in the second coordination sphere, loss of NO_3^- would also be expected to occur and, then, $z_I > 1$ would be observed. The present experiments are in agreement with a model where azide dissociation from the second coordination sphere occurs in a rapid equilibrium, but not nitrate loss. Hence, nitrate is more tightly bound than azide and is not located in the second coordination sphere. The intermediate is still hexacoordinated.

Protonation of the intermediates does not take place either, because the experimentally determined charge of the free intermediates z_I is identical with $n - 1$, namely the charge of the free reactant diminished by 1. Any protonation in competition to the other reactions would give rise to noninteger and larger z_I values; i.e., $n > z_I > n - 1$ would be observed. Quantitative protonation of the intermediates would lead to $z_I = n$, which was not observed.

The present experiments show also that the intermediate $[Co(NH_3)_4(NH_2)\cdots OS(CH_3)_2,ClO_4]^+$ does not react with any nucleophile, neither with ClO_4^- nor with H_2O, but it equilibrates rapidly as shown in Scheme II. In order to prove this assertion, base hydrolysis of $Co(NH_3)_5OS(CH_3)_2^{3+}$ has also been carried out in ClO_4^-/N_3^- mixtures (parts b of Tables II and IV). Any reaction of $[Co(NH_3)_4(NH_2)\cdots OS(CH_3)_2,ClO_4]^+$ with perchlorate or water would lower the competition ratio: perchlorate scavenging would produce $Co(NH_3)_5ClO_4^{2+}$, which would react subsequently with azide and water at a lower competition ratio than for $Co(NH_3)_5OS(CH_3)_2^{3+}$; water scavenging by the intermediate $[Co(NH_3)_4(NH_2)\cdots OS(CH_3)_2,ClO_4]^+$ anyway would give rise to a lower competition ratio. The present experiments show that addition of perchlorate has no effect on the competition ratio (Figure 1). Obviously, perchlorate is too weak a nucleophile to displace the $(CH_3)_2SO$ ligand. If the process were purely dissociative, the intermediate $[Co(NH_3)_4(NH_2)\cdots OS(CH_3)_2,ClO_4]^+$ would scavenge perchlorate (or possibly water), and lowering of the competition ratio in the presence of perchlorate would have been observed. Since this is not the case, this experiment favors the $I_{d,cb}$ mechanism.

Substitution of the leaving group is much slower than equilibration of the intermediate with anions from the bulk solution, and it is controlled by the stability of the deprotonated product, because the poorly competing anion perchlorate is unable to displace the $(CH_3)_2SO$ ligand. Hydration and dehydration processes are certainly much faster and therefore do not control the product formation. The selectivity of the intermediates for various competitors[3,8] and preferential formation of the thermodynamically unstable isomers when SCN^-, $S_2O_3^{2-}$, and NO_2^- are used as competing anions[19-21] are in agreement with a thermodynamically controlled substitution. In contrast to the case for base hydrolysis, spontaneous or induced substitution leads preferentially to the thermodynamically stable isomers where the "hard" end of the competing anion forms the bond to the cobalt(III) center. I believe that the "soft" end is preferred in base hydrolysis, because the cobalt center with a coordinated amido ligand exhibits "soft" character as well. According to extended-Hückel MO calculations[22] the electronic ground state of the intermediates is a triplet, which indeed could be "soft". The constant ratio of the isomer mixture obtained by base hydrolysis of various (acidato)pentaamminecobalt(III) complexes in the presence of ambidentate competitors (NCS^-, S/N = 2.0 ± 0.1;[19] NO_2^-, O/N = 2.0 ± 0.2;[21] SO_3^{2-}, S/O = 2.3 ± 0.3[20]) reflects the constant difference of the energies of activation for the two product-forming steps, namely the reactions of the intermediate with the "soft" and "hard" ends of the competitor.

The hexacoordinated intermediates are formed by dissociative activation, and subsequently, they equilibrate with the anions present in solution. The observed ionic strength dependence can only be explained on the basis of this fast equilibrium occurring *after* the rate-determining steps. Since the intermediates live sufficiently long to equilibrate with anions in solution, they are in fact intermediates and not transition states. The parameters $k_{N_3}{}^1$ and $K_{N_3}{}^I$ (Scheme II) were calculated by using the equations of Debye[23] and Fuoss,[24] respectively ($D = 2.5 \times 10^{-5}$ cm^2 s^{-1}). The time (τ) that the intermediate requires to equilibrate is given as $\tau = (k_{N_3}{}^I[N_3^-] + k_{-N_3}{}^I)^{-1} = (k_{N_3}{}^I[N_3^-] + k_{N_3}{}^I/K_{N_3}{}^I)^{-1} \approx 72$ and 190 ps for the intermediates $[Co(NH_3)_4(NH_2)\cdots ONO_2]^+$ and $[Co(NH_3)_4(NH_2)\cdots OS(CH_3)_2]^{2+}$, respectively. These values represent lower limits for the lifetime. Another way to obtain lower limits is based on the fact that the intermediates are hexacoordinated. Release of an, indeed weakly bound, charged leaving group into the bulk solution requires more energy than loss of the same leaving group from the second coordination sphere. The lifetime of a charged leaving group in the second sphere thus also serves as a lower limit for the lifetime of the intermediate. For the intermediates $[Co(NH_3)_4(NH_2)\cdots OSO_3]$ and $[Co(NH_3)_4(NH_2)\cdots ONO_2]^+$ τ = 1600 and 190 ps, respectively, are calculated as described above.

Acknowledgment. Dr. P. Comba and Dr. E. Müller contributed helpful criticism and suggestions. This work was supported by the National Energy Research Foundation.

Registry No. $Co(NH_3)_5NO_3^{2+}$, 15077-47-1; $Co(NH_3)_5OS(CH_3)_2^{3+}$, 44915-85-7; $Co(NH_3)_2SO_4^+$, 18661-07-9; N_3^-, 14343-69-2.

---

(19) Jackson, W. G.; Hookey, C. N. *Inorg. Chem.* **1984**, *23*, 668, 2728.

(20) Jackson, W. G.; Fairlie, D. P.; Randall, M. L. *Inorg. Chim. Acta* **1983**, *70*, 197.

(21) Jackson, W. G.; Randall, M. L.; Sargeson, A. M.; Marty, W. *Inorg. Chem.* **1983**, *22*, 1013.

(22) Rotzinger, F. P., work in progress.

(23) Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265.

(24) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.