continue to consider the relatively large $\Delta V^{*}_{NH_3} - \Delta V^{*}_{Cl}$ differences as evidence for a predominantly dissociative mechanism.

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Volume Profiles for the Base Hydrolysis of a Series of Pentaamminecobalt(III) Complex Ions in Aqueous Solution[1]

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Volumes of activation (ΔV^{*}_{exptl}) for the base hydrolysis reactions of the complexes $Co(NH_3)_5X^{(3-n)+}$, where X^{n-} = F^-, Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, and Me_2SO, were determined from the pressure dependencies of the hydrolysis rate constants and have values between 22 and 40 cm^3 mol^{-1}. Partial molar volume measurements on all the reactant species, as well as overall reaction volume ($\Delta \bar{V}_0$) determinations by a dilatometric technique, enable the construction of reaction volume profiles for the base hydrolysis reactions. These clearly demonstrate that $\Delta V^{*}_{exptl} - \Delta \bar{V}_0$ is fairly constant for almost all the studied systems. Furthermore, these data enable the estimation of the partial molar volume of the five-coordinate species $Co(NH_3)_4NH_2^{2+}$, which turns out to be independent of the nature of X^{n-}. These results underline the validity of the S_N1CB mechanism and demonstrate the general applicability of volume equation calculations in obtaining information on the partial molar volumes of intermediate and/or transition-state species.

Introduction

Our general interest in the application of high-pressure kinetic techniques in the elucidation of chemical reaction mechanisms has led us to the study of typical aquation reactions of ammine complexes of cobalt(III), rhodium(III), and chromium(III).[3-9] Volume equation calculations were adopted to demonstrate that the aquation reactions of pentaamminecobalt(III) complexes proceed according to a dissociative reaction mode.[3] In these it was assumed that the partial molar volume of the five-coordinate transition state, $Co(NH_3)_5^{3+}$, equals that of the hexaammine species on the basis of predictions presented by Stranks.[10] In a later study Swaddle and a co-worker[11] criticized this assumption and presented arguments against a common five-coordinate intermediate and in favor of an I_d mechanism. Furthermore, they also ascribed the earlier found consistency in the partial molar volume of the five-coordinate intermediate to errors in the partial molar volumes of some of the studied complexes.

Very recently, Lawrance[12] studied the pressure dependence of the aquation reactions of a series of pentaamminecobalt(III) complexes, all with neutral leaving groups. He finds a good correlation between the partial molar volume of the complex and that of the neutral sixth ligand. Furthermore, he demonstrates very clearly that the calculated volume of the five-coordinate intermediate in the case of a dissociative mechanism strongly depends on the charge of the complex, i.e. the charge of the sixth ligand—the leaving group during aquation. These and recent theoretical predictions by Swaddle[13] clearly demonstrate that Stranks' postulate is indeed in error and another approach must be sought.

Along these lines we have studied the volume profiles for a series of base hydrolysis reactions of pentaamminecobalt(III) complexes. These are generally accepted[14-19] to proceed according to a S_N1CB mechanism in which a five-coordinate intermediate, $Co(NH_3)_4NH_2^{2+}$, is formed, which rapidly reacts with water or any other competing nucleophile to produce the reaction products. If this is really the case, it should be possible to estimate the volume of this common intermediate from reaction volume and volume of activation measurements. This will add not only to the validity of the suggested mechanism but also to the general understanding of the applicability of volume equation calculations and the construction of reaction volume profiles.[20-22]

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Experimental Section

The following complexes were prepared as described in the literature; their chemical analyses[23] were in excellent agreement with the theoretically expected values, and their UV-visible absorption spectra were in good agreement with those reported in the quoted references: $[Co(NH_3)_5Cl](ClO_4)_2$;[25,26] $[Co(NH_3)_5Br](ClO_4)_2$;[26,27] $[Co(NH_3)_5I](ClO_4)_2$;[26,28] $[Co(NH_3)_5NO_3](ClO_4)_2$;[26,29] $[Co(NH_3)_5SO_4]ClO_4{\cdot}H_2O$;[19,30] $[Co(NH_3)_5OH_2](ClO_4)_3$;[4,24,31] $[Co(NH_3)_5Me_2SO](ClO_4)_3{\cdot}H_2O$;[19,32] $[Co(NH_3)_5F](ClO_4)_2$[24] ($\lambda_{max} = 513$ ($\epsilon = 44.8$) and 353 ($\epsilon = 38.8$) nm). Chemicals of analytical reagent grade and doubly distilled water were used throughout this study. UV-visible spectra were recorded on a Perkin-Elmer 555 spectrophotometer. pH measurements were performed with a Radiometer pHM 64 instrument using a combination glass-reference electrode, of which the latter was filled with a saturated NaCl solution. Special care was taken to avoid the presence of CO_2 in the test solutions. For this reason the distilled water was boiled for several minutes and cooled under the exclusion of CO_2.

In the dilatometric studies a Carlsberg dilatometer was used and the procedures have been outlined elsewhere.[33] The CO_2-free distilled water was evacuated for a while before use. The commercially obtained kerosene was purified by passing through a silica gel and an aluminum oxide column. The dilatometer was thermostated at 25.0 °C within an accuracy of ±0.002 °C. Approximately 25 min was allowed for temperature equilibration before the complex solution was mixed with the base (1:1). The extent of spontaneous aquation during this period was negligible. The percentage conversion was determined spectrophotometrically and was found to be 100% for $X^{n-} = Cl^-, Br^-, I^-, NO_3^-$, and Me_2SO.

Kinetic measurements were performed on a Zeiss PMQ II spectrophotometer equipped with a thermostated (±0.1 °C) high-pressure cell[34,35] and on a high-pressure stopped-flow instrument.[36] The hydrolysis reactions were studied under pseudo-first-order conditions, and the observed rate constants, k_{obsd}, were calculated in the usual way. The corresponding first-order plots were linear for at least 3 half-lives of the reaction when the experimentally obtained infinity absorbance was employed. Only in the case of the $Co(NH_3)_5F^{2+}$ species was the Guggenheim method adopted over the first half-life, since decomposition of the complex occurred during the later stage of the base hydrolysis process.

The apparent molar volumes of the investigated complexes were measured with a digital densimeter, Anton Paar DMA 02, which was thermostated at 25.000 ± 0.002 °C. A range of concentrations (5-15 mM) was studied for each complex, and the apparent molar volumes were averaged since they showed no significant concentration dependence.

Results and Discussion

The aquation reactions of complexes of the type $Co(NH_3)_5X^{(3-n)+}$ are in general catalyzed by base, such that

$$k_{obsd} = k_1 + k_2[OH^-] \qquad (1)$$

where k_1 is the rate constant for spontaneous aquation and k_2 is that for the base-catalyzed path. At higher $[OH^-]$ the k_2 path overrules the spontaneous aquation process[30,37] and eq 1 simplifies to $k_{obsd} = k_2[OH^-]$. The linear dependence of k_{obsd} on $[OH^-]$ is a general characteristic of base-hydrolysis processes for such complexes and has been ascribed to the well-known and generally accepted S_N1CB mechanism:[14-19]

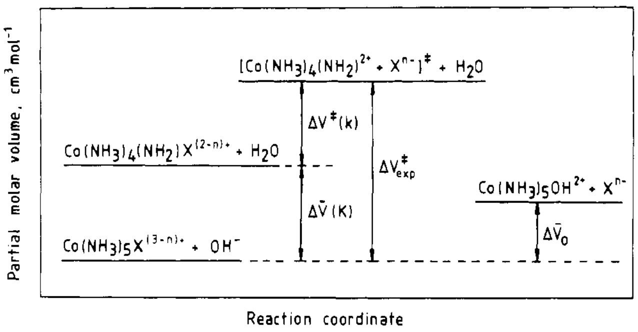

Figure 1. Volume profile for the overall reaction $Co(NH_3)_5X^{(3-n)+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + X^{n-}$.

$$Co(NH_3)_5X^{(3-n)+} + OH^- \overset{K}{\rightleftharpoons} Co(NH_3)_4(NH_2)X^{(2-n)+} + H_2O$$

$$Co(NH_3)_4(NH_2)X^{(2-n)+} \xrightarrow{k} Co(NH_3)_4NH_2^{2+} + X^{n-}$$

$$Co(NH_3)_4NH_2^{2+} + H_2O \xrightarrow{\text{fast}} Co(NH_3)_5OH^{2+} \qquad (2)$$

Under pseudo-first-order conditions, i.e. at least a 10-fold excess of OH^-

$$k_{obsd} = kK[OH^-]/(1 + K[OH^-]) \qquad (3)$$

which in general simplifies to $k_{obsd} = kK[OH^-]$, since $1 + K[OH^-] \approx 1$ due to the magnitude of K.[38] It follows that the observed second-order rate constant k_2 is a composite quantity, viz. $k_2 = kK$, where K is the equilibrium constant for the deprotonation of the amine and k the rate constant for the formation of the five-coordinate intermediate.

The base hydrolysis reactions investigated in this study are such that $k_2[OH^-] \gg k_1$. This tendency can clearly be seen from a comparison of the rate data in Table I with those published elsewhere for the spontaneous aquation processes.[30,37,39] The values of k_2 at ambient pressure are in good agreement with literature data especially when the difference in ionic strength is taken into account.[19,39,40]

The base hydrolysis of $Co(NH_3)_5Cl^{2+}$ was studied at different ionic strengths (see Table I) and under similar conditions (μ = 10 mM) at two different occasions to determine the reproducibility of the measurements. Plots of $\ln k_{obsd}$ vs. pressure are linear within the experimental error limits for all the studied systems up to 1 kbar. The volumes of activation are obtained from eq 4, where γ_A, γ_B, and $\gamma_\ddagger$ are the activity

$$\Delta V^{\ddagger}_{\text{exptl}} = -RT\left(\frac{d \ln k_2}{dp}\right)_T + RT\frac{d}{dp}\left(\ln \frac{\gamma_A\gamma_B}{\gamma_\ddagger}\right)_T \qquad (4)$$

coefficients for the $Co(NH_3)_5X^{(3-n)+}$ species, the hydroxy ion, and the activated complex, respectively. The first term in eq 4 was determined from the slope of the $\ln k_2$ (or $\ln k_{obsd}$) vs. pressure plot, for which it was assumed that $[OH^-]$ is independent of pressure.[41] The second term ($\Delta V^{\ddagger}_{\gamma}$) was estimated by using the Debye-Hückel limiting law for the activity

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Table I. Values of k_{obsd} for the Base Hydrolysis of a Series of Pentaamminecobalt(III) Complexes as a Function of Pressure at 25 °C

complex	[complex], mM	[OH$^-$], mM	wavelength, nm	ionic strength, mM	pressure, bar	$10^x k_{obsd}$, s^{-1}			x
$Co(NH_3)_5F^{2+}$	0.36	10	244	11	8	12.0	12.7		5
					253	9.20	10.0	9.22	
					507	7.12	6.57		
					760	5.89	5.46		
					1013	4.18	4.45		
					1266	3.24	3.64		
					1520	2.78	2.63		
$Co(NH_3)_5Cl^{2+}$	0.07	1	240	1	8	11.3	10.9		4
					253	8.00	8.64		
					507	5.69	5.83		
					760	4.05	4.06		
					1013	2.90	2.94		
					1266	2.33	2.16		
					1520	1.77	1.76		
	0.07	1	240	10[a]	8	8.45	8.30		4
					253	5.59	5.68		
					507	3.92	3.73		
					760	2.84	2.84		
					1013	2.24	2.30		
					1266	1.62	1.79		
					1520	1.49	1.43		
	0.07	1	240	10[a]	8	8.90	8.51		4
					253	6.03	6.15		
					507	4.49	4.30		
					760	3.18	2.96		
					1013	2.36	2.36		
					1266	1.83	1.76		
					1520	1.38	1.40		
	0.07	1	240	100[a]	8	4.62	4.60		4
					253	3.05	3.21		
					507	2.27	2.23		
					760	1.62	1.61		
					1013	1.23	1.30		
					1266	0.96	1.01		
					1520	0.81	0.84		
$Co(NH_3)_5Br^{2+}$	1	10	290	13	20	3.39	3.27	3.53	2
						3.70	3.84	3.58	
					250	3.02	3.00	3.05	
						3.05	2.93	2.89	
					500	1.68	1.60	1.64	
						1.69	1.69	1.69	
					750	1.25	1.30	1.24	
						1.28	1.35	1.39	
					1000	1.17	1.10	1.09	
						1.06	1.09	1.08	
$Co(NH_3)_5I^{2+}$	0.2	10	310	11	20	7.60	7.63	7.63	2
						8.09	8.22	8.16	
					250	7.06	6.92	7.00	
						6.87	6.83	6.81	
					500	4.52	4.62	4.53	
						4.35	4.35	4.21	
					750	2.96	2.88	2.97	
						2.92	2.98	3.00	
					1000	2.39	2.51	2.42	
						2.27	2.32	2.24	
$Co(NH_3)_5NO_3^{2+}$	1	10	290	13	20	2.55	2.45	2.41	1
						2.42	2.35	2.42	
					250	1.82	1.87	1.89	
						1.93	2.00	2.05	
					500	1.61	1.57	1.53	
						1.56	1.48	1.47	
					750	1.09	1.11	1.11	
						1.07	1.07	1.03	
					1000	0.705	0.733	0.722	
						0.725	0.715	0.710	
$Co(NH_3)_5SO_4^{+}$	0.36	10	260	10	8	10.4	10.3		4
					253	8.20	8.67	7.90	
					507	6.35	6.55		
					760	5.22	5.14		
					1013	4.27	4.35		
					1266	3.25	3.38		
					1520	2.85	2.76		

Table I (*Continued*)

complex	[complex], mM	$[OH^-]$, mM	wavelength, nm	ionic strength, mM	pressure, bar	$10^x k_{obsd}$, s^{-1}				x
$Co(NH_3)_5Me_2SO^{3+}$	1	10	400	16	20	3.48	3.51	3.55	3.55	1
						3.76	3.75	3.83		
					250	2.69	2.66	2.68		
						2.65	2.61	2.61		
					500	1.87	1.88	1.86		
						1.86	1.84	1.85		
					750	1.17	1.18	1.22		
						1.21	1.20	1.16		
					1000	0.801	0.792	0.782	0.781	
						0.763	0.770	0.767		

[a] By addition of $NaClO_4$.

coefficients and taking the pressure dependence of the water density and its dielectric constant into account.[42,43] The magnitude of ΔV^{*}_{γ} ($cm^3\ mol^{-1}$) turns out to be as follows: 0.6 ($X^{n-} = F^-, Cl^-, Br^-, NO_3^-, I^-$ at ionic strength 10–13 mM); 0.2 ($X^{n-} = Cl^-$ at ionic strength 1 mM); 0.3 ($X^{n-} = SO_4^{2-}$ at ionic strength 10 mM); 1.8 $X^{n-} = Cl^-$ at ionic strength 100 mM); 1.1 ($X^{n-} = Me_2SO$ at ionic strength 16 mM). The resulting values of ΔV^{*}_{exptl} are summarized in Table II.

The values of ΔV^{*}_{exptl} are large and positive in all cases and a composite of the contributions of the effect of pressure on k and K according to eq 5. This is illustrated in the general

$$\Delta V^{*}_{exptl} = \Delta\bar{V}(K) + \Delta V^{*}(k) \qquad (5)$$

volume profile for such base hydrolysis reactions in Figure 1. The values of ΔV^{*}_{exptl} for the chloro and bromo complexes are in close agreement with the respective values 33.4 and 32 $cm^3\ mol^{-1}$ reported before.[6,44] Furthermore, it is important to note that these values in Table II are subjected to relatively small error limits and do not show any appreciable ionic strength dependence. According to the volume profile in Figure 1, it is expected that ΔV^{*}_{exptl} and $\Delta\bar{V}_0$ (the overall reaction volume) should depend on the nature of X^{n-}, i.e. especially on the charge and size of the leaving group. This is clearly seen in the values of ΔV^{*}_{exptl} for $X^{n-} = Me_2SO$, Cl^-, and SO_4^{2-}. The difference $\Delta V^{*}_{exptl} - \Delta\bar{V}_0$, however, should be independent of the nature of X^{n-} since it only involves the recombination of $Co(NH_3)_4NH_2^{2+}$ and H_2O to produce $Co(NH_3)_5OH^{2+}$. In order to investigate the validity of this statement, $\Delta\bar{V}$ for the overall base hydrolysis process was (a) measured dilatometrically and (b) calculated from partial molar volume measurements.

The $\Delta\bar{V}_0$ values in Table II were determined with a Carlsberg dilatometer, except for the fluoro complex, where unreproducible results were obtained due to the subsequent decomposition of the complex. The quoted results are the average of two or more determinations and were corrected for changes in ionic strength during the mixing of the reactant solutions.[23,45] The ionic strength dependence of the apparent molar volume (ϕ_i) of an ionic species is approximated by eq 6, where ϕ_{i0} is the apparent molar volume at infinite dilution

$$\phi_i = \phi_{i0} + 0.93 z_i^2 \mu^{1/2} \qquad (6)$$

and z_i the charge on the ion. The reaction volume at infinite dilution was obtained from eq 7, where $\Delta\bar{V}_{cor}$ has the values

$$\Delta\bar{V}_0 = \Delta\bar{V}_{exptl} - \Delta\bar{V}_{cor} \qquad (7)$$

0 ($X^{n-} = F^-, Cl^-, Br^-, I^-, NO_3^-$), 1.3 ($X^{n-} = SO_4^{2-}$), and −1.8 $cm^3\ mol^{-1}$ ($X^{n-} = Me_2SO$). The values of $\Delta\bar{V}_0$ (Table II) show a strong dependence on the nature of X^{n-}; the largest value is for the leaving of a neutral molecule (Me_2SO) and the smallest value (even negative!) for the leaving of a highly charged species (SO_4^{2-}). These tendencies emphasize the important role played by electrostriction in base hydrolysis reactions.

The $\Delta\bar{V}_0$ values in Table II are in good agreement with those estimated from partial molar volume data for educt and product species as shown in Tables III and IV, which were either obtained from density measurements or taken from the literature. The adopted partial molar volumes call for some comments since significant discrepancies have been reported.[3,11] Our value for $[Co(NH_3)_5Cl](ClO_4)_2$ is in close agreement with other values[3,12] but differs significantly from the value reported by Sisley and Swaddle.[11] We do not understand this discrepancy since their compound gave in our laboratory[11] a value of 180 ± 2 $cm^3\ mol^{-1}$, which is in close agreement with the present results. We cannot go along with the explanation that the difference may be due to a difference in humidity.[11] The $\Delta\bar{V}_{calcd}$ value for the hydrolysis of the sulfato complex is in excellent agreement with the $\Delta\bar{V}_0$ value and further underlines the large collapse in volume due to significant charge creation during the release of SO_4^{2-}. Spiro et al.[23] reported a value of +1.4 $cm^3\ mol^{-1}$ for this reaction at 30 °C. However, they made a trivial error in the calculation of $\Delta\bar{V}_{cor}$, such that a value of −1.5 $cm^3\ mol^{-1}$ in fact arises from their data, which is fairly close to ours. Their[23] results for the chloro, bromo, and nitrato complexes are close to those found in this study.

A remarkable observation in Table II is the fact that $\Delta V_{exptl} - \Delta\bar{V}_0$ is indeed fairly constant for all the complexes, except the sulfato species, which has a significantly larger value. The remainder of the complexes show an average vlaue of 19.7 ± 2.1 $cm^3\ mol^{-1}$. This volume decrease (see Figure 1) almost equals the partial molar volume of water, demonstrating that a water molecule is completely absorbed during the final step of the base hydrolysis process. Alternatively, this volume decrease is very close to that found for the ionization of water at 25 °C, viz. −22.1 $cm^3\ mol^{-1}$,[47,48] suggesting that the addition of water to the five-coordinate intermediate proceeds via the protonation of the amide ligand and subsequent addition of hydroxide or vice versa. In addition, as will be seen later, the partial molar volumes of $Co(NH_3)_4NH_2^{2+}$ and $Co(NH_3)_5OH^{2+}$ are indeed very similar, from which is follows that a water molecule is inserted into the coordination sphere of $Co(NH_3)_4NH_2^{2+}$ without a remarkable increase in volume of the latter species. Although the most of the data in Table II are for 2+ charged complexes, the value of $\Delta V^{*}_{exptl} - \Delta\bar{V}_0$ for the Me_2SO complex falls well within the range of values

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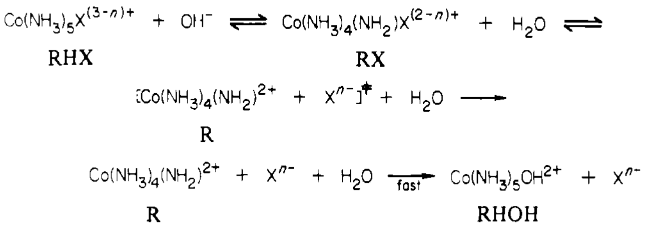
Table II. Activation and Reaction Volumes for a Series of Base Hydrolysis Reactions of the Type[a] $Co(NH_3)_5X^{(3-n)+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + X^{n-}$

X^{n-}	ionic strength, mM	$\Delta V^{\ddagger}_{\text{exptl}}$[b]	$\Delta\bar{V}_0$[c]	$\Delta V^{\ddagger}_{\text{exptl}} - \Delta\bar{V}_0$
F^-	11	26.4 ± 1.0	7.4 ± 1.0[d]	19.0 ± 2.0
Cl^-	1	33.6 ± 0.6		
	10	33.0 ± 0.8	9.9 ± 0.2	23.1 ± 1.0
	10	33.0 ± 1.4		
	100	33.8 ± 1.0		
Br^-	13	32.5 ± 1.4	11.1 ± 0.2	21.4 ± 1.6
I^-	11	33.6 ± 1.0	15.5 ± 0.3	18.1 ± 1.3
NO_3^-	13	31.0 ± 0.8	13.2 ± 0.4	17.8 ± 1.2
SO_4^{2-}	10	22.2 ± 0.7	−3.9 ± 0.4	26.1 ± 1.1
Me_2SO	16	40.2 ± 0.5	21.2 ± 0.3	19.0 ± 0.8

[a] Temperature = 25 °C; all volume quantities in $cm^3\ mol^{-1}$. [b] Calculated from the data in Table I with use of eq 4. [c] Measured with a Carlsberg dilatometer—see Results and Discussion. [d] Estimated from molar volume measurements—see Table IV.

Scheme I



$$Co(NH_3)_5X^{(3-n)+} + OH^- \rightleftharpoons Co(NH_3)_4(NH_2)X^{(2-n)+} + H_2O \rightleftharpoons$$

RHX RX

$$[Co(NH_3)_4(NH_2)^{2+} + X^{n-}]^{\ddagger} + H_2O \longrightarrow$$

R

$$Co(NH_3)_4(NH_2)^{2+} + X^{n-} + H_2O \xrightarrow[\text{fast}]{} Co(NH_3)_5OH^{2+} + X^{n-}$$

R RHOH

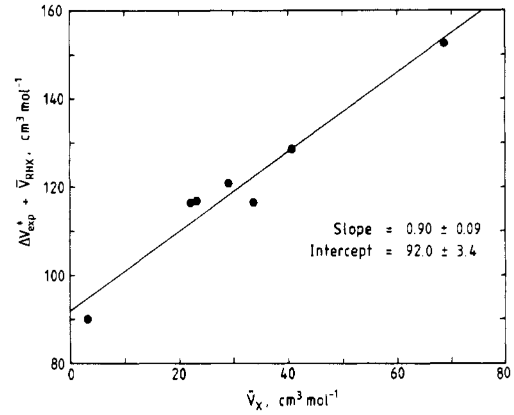


Figure 2. Plot of $\Delta V^{\ddagger}_{\text{exptl}} + \bar{V}_{RHX}$ vs. $\bar{V}_X$ from the data in Tables II and IV.

found for the 2+ species. The deviation in the case of the sulfato complex can probably be ascribed to the occurrence of ion-pair formation between $Co(NH_3)_4NH_2^{2+}$ and SO_4^{2-} in the transition state. This would mean that $\Delta V^{\ddagger}_{\text{exptl}} - \Delta\bar{V}_0$ does represent not only the entrance of a water molecule but also the dissociation of the ion pair if it is assumed that the final product species exist as individual ions in solution. This effect should be significantly smaller for singly charged and neutral leaving groups.

Another aim of this study was to obtain more information on the partial molar volume of the $Co(NH_3)_4NH_2^{2+}$ intermediate species. If we rewrite the overall reaction system in the way indicated in Scheme I, i.e. a combination of the reactions in (2) and Figure 1, eq 8 and 9 can be formulated. In

$$\begin{aligned}\Delta V^{\ddagger}_{\text{exptl}} &= \bar{V}_{\ddagger} + \bar{V}_{H_2O} - \bar{V}_{RHX} - \bar{V}_{OH} \\ &\approx \bar{V}_R + \bar{V}_X + \bar{V}_{H_2O} - \bar{V}_{RHX} - \bar{V}_{OH} \qquad (8)\end{aligned}$$

$$\Delta\bar{V}_0 = \bar{V}_{RHOH} + \bar{V}_X - \bar{V}_{RHX} - \bar{V}_{OH} \qquad (9)$$

eq 8 it is assumed that the dissociative reaction of the conjugate base species RX has a late ("productlike") transition state, such that $\bar{V}_{\ddagger} \approx \bar{V}_R + \bar{V}_X$. The only unknown in eq 8 is $\bar{V}_R$, and its values are summarized in Table IV. It is seen that $\bar{V}_R$ is remarkably constant, especially when the various approximations and error limits are taken into account. Furthermore, no significant dependence on the nature of X^{n-} exists, underlining the principle of a common intermediate in all cases.

Alternatively, eq 8 can be rewritten in the form given by eq 10, from which it follows that a plot of $\Delta V^{\ddagger}_{\text{exptl}} + \bar{V}_{RHX}$

$$\Delta V^{\ddagger} + \bar{V}_{RHX} = \bar{V}_R + \bar{V}_{H_2O} - \bar{V}_{OH} + \bar{V}_X \qquad (10)$$

vs. $\bar{V}_X$ should be linear with a slope of unity and an intercept $\bar{V}_R + \bar{V}_{H_2O} - \bar{V}_{OH}$, i.e. $\bar{V}_R$ + 17.6.[46,49] Such a plot is given

Table III. Apparent Molar Volumes ($cm^3\ mol^{-1}$) of Some Co(III) Ammine Complexes at 25 °C

complex	ref 3	ref 11	ref 12	this work
$[Co(NH_3)_5F](ClO_4)_2$	159.3 ± 0.4			160.8 ± 1.0
$[Co(NH_3)_5Cl](ClO_4)_2$	187.2 ± 0.4	168.8	179.0	180.7 ± 0.2
$[Co(NH_3)_5Br](ClO_4)_2$	196.4 ± 1.1	184.6		185.7 ± 2.1
$[Co(NH_3)_5I](ClO_4)_2$				192.0 ± 0.8
$[Co(NH_3)_5NO_3](ClO_4)_2$	161.1 ± 1.1[a]			182.6 ± 0.8
$[Co(NH_3)_5SO_4]ClO_4$	147.2 ± 0.6	137.7		143.2 ± 1.1[b]
$[Co(NH_3)_5Me_2SO](ClO_4)_3$	277.3 ± 1.4		253.8	258.0 ± 0.9[b]

[a] Value for $[Co(NH_3)_5NO_3](NO_3)_2$. [b] Corrected for 1 mol of water of crystallization.

Table IV. Molar Volume Data and Volume Equation Calculations for the Series of Base Hydrolysis Reactions[a] $Co(NH_3)_5X^{(3-n)+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + X^{n-}$

complex	ϕ[b]	$\bar{V}_{RHX}$[c]	$\bar{V}_X$[d]	$\Delta\bar{V}_{\text{calcd}}$[e]	$\Delta\bar{V}_0$[f]	$\bar{V}_R$[g]
$[Co(NH_3)_5F](ClO_4)_2$	160.8 ± 1.0	63.6 ± 1.0	3.3	7.4 ± 1.0		69.1 ± 2.0
$[Co(NH_3)_5Cl](ClO_4)_2$	180.7 ± 0.2	83.5 ± 0.2	22.3	6.5 ± 0.2	9.9 ± 0.2	76.6 ± 1.0
$[Co(NH_3)_5Br](ClO_4)_2$	185.7 ± 2.1	88.5 ± 2.1	29.2	8.4 ± 2.1	11.1 ± 0.2	74.2 ± 3.5
$[Co(NH_3)_5I](ClO_4)_2$	192.0 ± 0.8	94.8 ± 0.8	40.7	13.6 ± 0.8	15.5 ± 0.3	70.1 ± 1.8
$[Co(NH_3)_5NO_3](ClO_4)_2$	182.6 ± 0.8	85.4 ± 0.8	33.5	15.8 ± 0.8	13.2 ± 0.4	65.3 ± 1.6
$[Co(NH_3)_5SO_4]ClO_4$	143.2 ± 1.1	94.6 ± 1.1	23.0	−3.9 ± 1.1	−3.9 ± 0.4	76.2 ± 1.8
$[Co(NH_3)_5Me_2SO](ClO_4)_3$	258.0 ± 0.9	112.2 ± 0.9	68.8[h]	24.3 ± 0.9	21.2 ± 0.3	66.0 ± 1.4
						av 71.1 ± 3.9

[a] Temperature = 25 °C; all volume quantities in $cm^3\ mol^{-1}$. [b] Apparent molar volume, from density measurements—see Table III. [c] Estimated by using $\bar{V}(ClO_4^-)$ = 48.6 (see footnote *d*). [d] Taken from ref 46 on the assumption that $\bar{V}(H^+)$ = −4.5. [e] Calculated by using eq 9, and $\bar{V}_{OH}$ = 0.5 (see footnote *d*) and $\bar{V}_{RHOH}$ = 68.2 (volume of neutralization of $Co(NH_3)_5OH_2^{3+}$ is 25.5[47] and $\bar{V}(Co(NH_3)_5OH_2^{3+})$ = 60.3 (footnote *c* and ref 3)). [f] Data reported in Table II. [g] Calculated by using eq 8, and $\bar{V}_{OH}$ = 0.5 (see footnote *d*) and $\bar{V}_{H_2O}$ = 18.1. [h] Taken from ref 3.

Table V. Values of $\Delta\bar{V}(K)$ and $\Delta V^{\ddagger}(k)$ for the Series of Base Hydrolysis Reactions at 25 °C[a]

$$\begin{tikzcd} Co(NH_3)_5X^{(3-n)+} + OH^- \arrow[r, "K", harpoon, shift left] & Co(NH_3)_4(NH_2)X^{(2-n)+} + H_2O \arrow[l, harpoon, shift left] \arrow[d, "k"] \\ & Co(NH_3)_4NH_2^{2+} + X^{n-} \end{tikzcd}$$

X^{n-}	$\Delta V^{\ddagger}_{\text{exptl}}$[b]	Δz^2	$\Delta\bar{V}(K)$[c]	$\Delta V^{\ddagger}(k)$[d]
F^-	26.4	−3	22.0	4.4
Cl^-	33.0	−3	22.0	11.0
Br^-	32.5	−3	22.0	10.5
I^-	33.6	−3	22.0	11.6
NO_3^-	31.0	−3	22.0	9.0
SO_4^{2-}	22.2	−1	17.0	5.2
Me_2SO	40.2	−5	27.0	13.2

[a] All volume data in $cm^3\ mol^{-1}$. [b] From Table II. [c] Estimated by using eq 11. [d] Estimated by using eq 5.

in Figure 2, which demonstrates that the data satisfy eq 10. The value of $\bar{V}_R$, viz. 74.4 ± 3.4 $cm^3\ mol^{-1}$, is in good agreement with that calculated above (see Table IV). The magnitude of $\bar{V}_R$ in Table IV is close to the value of 68.2 $cm^3\ mol^{-1}$ estimated[45] for the $Co(NH_3)_5OH^{2+}$ species, from which the conclusion could be drawn that these five- and six-coordinated Co(III) complexes have approximately the same volume.[3,10] It is, however, important to note that this agreement is probably only due to the fact that the partial molar volume of OH^- is almost zero. It has been shown that $\bar{V}$ for such Co(III) complexes depends linearly on the volume of the sixth ligand coordinated to the $Co(NH_3)_5^{3+}$ moiety.[12] Furthermore, the value of $\bar{V}_R$ is significantly larger than $\bar{V}$ for $Co(NH_3)_5OH_2^{3+}$ (60.3 $cm^3\ mol^{-1}$)[12] and $Co(NH_3)_6^{3+}$ (61.3 $cm^3\ mol^{-1}$).[3,11] This difference can be explained to result from differences in electrostriction, since our recent measurements[47] demonstrated that 3+ complex ions can be ca. 12.5 $cm^3\ mol^{-1}$ smaller than 2+ complex ions of similar nature.

To sum up, the volume equation calculations performed above do not only underline the general validity of the suggested mechanism but also provide direct information regarding the volume of a five-coordinate species. The fact that $\bar{V}_R$ differs significantly from that for closely related 3+ charged complexes but that it agrees well with the value for $Co(NH_3)_5OH^{2+}$ is an important conclusion and should simplify the handling of such species in future investigations.

We now turn to a discussion of the values of $\Delta V^{\ddagger}_{\text{exptl}}$ reported in Table II. The composite nature of this quantity has been referred to above (Figure 1 and eq 5). We are interested in obtaining values for $\Delta V^{\ddagger}(k)$ since that should provide more information on the nature of the dissociative process. A reasonable estimate of $\Delta\bar{V}(K)$ is needed, since this cannot be determined experimentally in the usual way due to the magnitude of K. We, therefore, measured the volumes of neutralization for a series of aquo and ammine complexes that have pK_a values in the range 2.7–10.9.[47] These complexes were considered to be model systems to deduce the influence of charge on the magnitude of $\Delta\bar{V}(K)$. The results demonstrated the close similarity between aquo and ammine complexes, and the volumes of neutralization could be expressed as shown in eq 11, where Δz^2 is the difference in the squares of the charges

$$\Delta\bar{V}(K) = (14.5 \pm 0.8) - (2.5 \pm 0.2)\Delta z^2 \qquad (11)$$

on the deprotonated and protonated complex species, respectively. With the aid of this relationship, $\Delta\bar{V}(K)$ was estimated for the formation of the various conjugate base species and $\Delta V^{\ddagger}(k)$ could be calculated as shown in Table V. The values of $\Delta V^{\ddagger}(k)$ are almost similar for the chloro, bromo, iodo, and nitrato complexes. This is reasonable since these reactions involve the dissociation of ions of similar charge and approximately the same volume (see Table IV). The values for the fluoro and sulfato complexes are significantly smaller, illustrating the effect of electrostriction during this reaction especially in the case of the sulfate species. The partial molar volume of fluoride is indeed very small (Table IV) and indicates that the fluoride ion is a dense charge point. This, through electrostriction or the absolute size of the fluoride ion, can account for the small $\Delta V^{\ddagger}(k)$ value for the fluoro complex. Finally, the largest value of $\Delta V^{\ddagger}(k)$ is for the Me_2SO complex, in line with bond breakage and no significant changes in electrostriction. It follows that $\Delta V^{\ddagger}(k)$ strongly depends on the nature of the leaving group as expected for a dissociative reaction process.

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Registry No. $Co(NH_3)_4NH_2^{2+}$, 90219-23-1; $Co(NH_3)_5F^{2+}$, 15392-06-0; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(NH_3)_5Br^{2+}$, 14970-15-1; $Co(NH_3)_5I^{2+}$, 15392-08-2; $Co(NH_3)_5(NO_3)^{2+}$, 15077-47-1; $Co(NH_3)_5(SO_4)^+$, 18661-07-9; $Co(NH_3)_5(Me_2SO)^{3+}$, 44915-85-7.

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