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Determination of the Mechanism for the Aquation of Cobalt(III) and Chromium(III) Pentaammine Complexes by the Use of a Volume Profile Diagram

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The rate of aquation of $Co(NH_3)_5Me_2SO^{3+}$ was measured as a function of pressure up to 1.5 kbar at 25 °C and at an ionic strength of 0.1 M. The volume of activation was found to be -1.7 ± 0.7 cm^3 mol^{-1}. The partial molar volumes of a series of $Co(NH_3)_5X^{(3-n)+}$ complexes were determined at 25 °C, where $X^{n-} = F^-, Cl^-, I^-, SO_4^{2-}, NO_3^-, NCS^-, N_3^-, Me_2SO, OH_2$, and NH_3. These values were combined to formulate a volume equation from which the volume of a hypothetical transition state, formed according to a dissociative mechanism, could be calculated. The partial molar volume of the appropriate hexaammine complex was then used to test the validity of the proposed mechanism. This treatment confirmed the assignment of an I_d or D mechanism to the cobalt system and an I_a mechanism to the chromium system.

Introduction

The spontaneous reactions of pentaamminecobalt(III) complexes have been extensively investigated[1] using a wide variety of approaches[2–6] to establish the underlying mechanism. The mechanism is now commonly accepted to be dissociative in character with the bulk of recent evidence[2–5] pointing to the I_d type. Consequently these reactions represent a model system for testing the reliability of a different approach. Despite the almost equally abundant kinetic data[1] on the hydrolysis of the analogous chromium(III) complexes, and to a lesser extent the rhodium(III) analogues, the nature of the mechanisms involved remains controversial.[7,8] Indeed, detailed high-pressure studies[9] have not been able to unambiguously solve this dilemma.

Therefore we undertook to look in detail at the total volume changes incurred in such reactions in the form of a volume profile diagram. This method has been used in only a limited number of cases in organic chemistry,[10] either to simply rationalize the volumes of activation found in more complicated reactions or to attempt to quantitatively establish the reaction mechanism. This requires both precision measurements of the partial molar volumes of the reactants and, if possible, the products and accurate measurements of the pressure dependence of the rate constants themselves. Such a diagram has the advantage over the more commonly used energy profile diagram in that it involves absolute measurements, thereby allowing direct, quantitative comparisons to be made between reactions of different substrates. In addition, one can assign an absolute volume to the transition state itself.

Experimental Section

Materials. The complexes were prepared, recrystallized, and converted, in the majority of cases, to perchlorate salts by established methods: $[Co(NH_3)_6](ClO_4)_3$,[11] $[Co(NH_3)_5OH_2](ClO_4)_3$,[12] $[Co(NH_3)_5Cl](ClO_4)_2$,[13] $[Co(NH_3)_5Br](ClO_4)_2$,[14] $[Co(NH_3)_5F](ClO_4)_2$,[15] $[Co(NH_3)_5NCS](ClO_4)_2$,[2] $[Co(NH_3)_5SO_4]ClO_4$,[2] $[Co(NH_3)_5N_3]Cl_2$,[16] $[Co(NH_3)_5NO_3](NO_3)_2$,[17] $[Co(NH_3)_5Me_2SO](ClO_4)_3\cdot 2H_2O$,[18] $[Cr(NH_3)_6]I_3$,[19] $[Cr(NH_3)_5OH_2](NO_3)_3$,[20] $[Cr(NH_3)_5Cl](ClO_4)_2\cdot H_2O$,[21] $[Cr(NH_3)_5Br]Br_2$,[20] $[Cr(NH_3)_5NCS](ClO_4)_2$,[22] $[Cr(NH_3)_5I](ClO_4)_2$.[23] The latter complex was converted to the perchlorate salt by stirring small amounts of the corresponding iodide salt in 70% $HClO_4$ for 1 h, during which time the iodide ions were oxidized to iodine. The mixture was filtered and washed with small amounts of ice-cold water, followed by acetone. This procedure was repeated three times.

The purity of the complexes was checked by microanalysis (Hoechst AG, Analytical Laboratory, Frankfurt, West Germany) and by comparison of their visible and/or UV spectra with literature values. The solvent water was first passed through a commercial ion-exchange column and then doubly distilled. It showed an average density at 25 °C of 0.997 065 g cm^{-3} (cf. 0.997 075 g cm^{-3} [24]).

Density Measurements. These measurements were carried out using a digital density apparatus, DMA 02 (Anton Paar KG, Austria) thermostated at 25.000 ± 0.002 °C. In general, densities were measured at a minimum of six different complex concentrations over

Table I. Temperature Dependence of the Rate Constant for the Aquation of $Co(NH_3)_5Me_2SO^{3+}$

T, °C	10^5k_{obsd}, s^{-1}	T, °C	10^5k_{obsd}, s^{-1}
25.0	1.83 ± 0.07[a]	46.3	32.3 ± 0.9
30.2	3.96 ± 0.04	55.3	95.8 ± 1.5
36.2	10.6 ± 0.1		

[a] Cf. $k_{\mathrm{obsd}} = 2.0 \times 10^{-5}$ s^{-1} at 25 °C (ref 27).

Table II. Pressure Dependence of the Rate of Aquation of $Co(NH_3)_5Me_2SO^{3+}$ at 25 °C

P, bar	10^5k_{obsd}, s^{-1}	P, bar	10^5k_{obsd}, s^{-1}
1	1.83 ± 0.07	1000	2.15 ± 0.15
250	1.92 ± 0.10	1250	1.99 ± 0.02
500	2.02 ± 0.08	1500	2.14 ± 0.03
750	2.07 ± 0.03		

the range 3.0–17.0 × 10^{-3} M. These limits were enforced by the poor solubility of the complexes in water on the one hand and by the small differences between the densities of the solution and solvent at lower concentrations on the other hand. The former limitation accounts for the somewhat larger errors in $\bar{V}$ reported here as compared to those generally found in the literature.[25] The apparent molar volume of dimethyl sulfoxide in water was determined over the concentration range 3.1–23.7 × 10^{-2} M.

Kinetic Measurements. The rate of aquation of $Co(NH_3)_5Me_2SO^{3+}$ was followed "in situ" at 290 nm using a Cary 15 spectrophotometer equipped with a thermostated (±0.05 °C) high-pressure cell.[26] The reaction solutions were maintained at an ionic strength of 0.1 M and a hydrogen ion concentration of 0.005 M using $LiClO_4$ and $HClO_4$, respectively. Rate constants were calculated using the Guggenheim method fitted by a least-squares program (Computer Center, University of Frankfurt).

Results

The results of the temperature dependence of the rate of aquation of $Co(NH_3)_5Me_2SO^{3+}$ are given in Table I and yield the values $\Delta H^\ddagger = 24.6 \pm 0.6$ kcal mol^{-1} and $\Delta S^\ddagger = 2.3 \pm 1.8$ eu which compare favorably with the values since published of 24.7 kcal mol^{-1} and 4.5 eu, respectively.[27] The results of the corresponding pressure-dependence study are shown in Table II. The plot of ln k vs. pressure was assumed to be linear with $\Delta V^\ddagger = -1.7 \pm 0.7$ cm^3 mol^{-1} at 25 °C. The rate constants given in Tables I and II represent the mean of two independent runs. Apparent molar volumes, Φ_i, of the complexes in aqueous solution were evaluated according to the equation

$$\Phi_i = M/d_0 - [1000(d_i - d_0)]/c_i d_0 \qquad (1)$$

where d_0 and d_i are the densities of the solvent and solution, respectively, c_i is the molar concentration, and M is the molecular weight of the complex. Within experimental errors, no concentration dependence of Φ_i was observed, which is not surprising in view of the relatively low concentrations employed. Therefore we assume that the mean value of Φ_i is equal to the partial molar volume, $\bar{V}$, at infinite dilution. From a detailed discussion by Millero[25] we have calculated the molar volumes of the individual complex ions based on the assumption that $\bar{V} = -4.5$ cm^3 mol^{-1} for the hydrogen ion. These values are given in Table III together with the values taken from the literature for the corresponding anions.[28] The relatively high instabilities of $Co(NH_3)_5NO_3^{2+}$ and $Cr(NH_3)_5I^{2+}$ in aqueous solution made it necessary to extrapolate the density readings at each concentration to zero time (i.e., time of dissolution) to obtain the absolute d_i values.

Discussion

A concept often used in organic chemistry[29] is to divide $\Delta V^\ddagger_{\mathrm{exp}}$ into two components: $\Delta V^\ddagger_{\mathrm{intr}}$ for the intrinsic contribution resulting from nuclear movements at the reaction center during the formation of the transition state; $\Delta V^\ddagger_{\mathrm{solv}}$ which results from the rearrangement of solvent molecules around the reacting species. For charged or polar species $\Delta V^\ddagger_{\mathrm{solv}}$ mainly consists of volume changes resulting from changes in electrostriction. Consequently, $\Delta V^\ddagger_{\mathrm{solv}}$ is approximately equivalent to $\Delta V^\ddagger_{\mathrm{el}}$. This simplified approach to $\Delta V^\ddagger_{\mathrm{intr}}$ predicts that for reactions of type 2 a dissociative

$$M(NH_3)_5X^{(3-n)+} + H_2O \rightarrow M(NH_3)_5OH_2^{3+} + X^{n-} \qquad (2)$$

mechanism will result in a positive $\Delta V^\ddagger_{\mathrm{intr}}$ value due to stretching of the M–X bond, while for an associative mechanism the formation of a $M{-}OH_2$ bond should give rise to a negative value.

A consideration of the $\Delta V^\ddagger_{\mathrm{exp}}$ values in Table IV shows them all to be negative with the exception of the water exchange with $Co(NH_3)_5OH_2^{3+}$ and the hydrolysis of $Co(NH_3)_5N_3^{2+}$. However, the latter reaction is known to be acid catalyzed[2] and will be treated individually later in the discussion.

The high positive charges on the substrates studied here, and the charge separation during the reaction, demand that $\Delta V^\ddagger_{\mathrm{el}}$ be strongly negative and be the dominant term for a dissociative process involving anionic leaving groups, possible examples of this being $Co(NH_3)_5SO_4^{+}$, $Co(NH_3)_5Cl^{2+}$, and $Co(NH_3)_5Me_2SO^{3+}$ for which the $\Delta V^\ddagger_{\mathrm{exp}}$ values are −18.5, −10.6, and −1.7 cm^3 mol^{-1}, respectively. In such a concept the

Table III. Partial Molar Volumes of Salts and Their Ions in Aqueous Solution at 25 °C

Complex	$\bar{V}$, cm^3 mol^{-1}	Ion	$\bar{V}$, cm^3 mol^{-1}
$[Co(NH_3)_5Cl](ClO_4)_2$	187.2 ± 0.4	$Co(NH_3)_5Cl^{2+}$	85.8
$[Co(NH_3)_5Br](ClO_4)_2$	196.4 ± 1.1	$Co(NH_3)_5Br^{2+}$	95.0
$[Co(NH_3)_5SO_4]ClO_4$	147.2 ± 0.6	$Co(NH_3)_5SO_4^{+}$	96.5
$[Co(NH_3)_5F](ClO_4)_2$	159.3 ± 0.4	$Co(NH_3)_5F^{2+}$	57.9
$[Co(NH_3)_5NO_3](NO_3)_2$	161.1 ± 1.1	$Co(NH_3)_5NO_3^{2+}$	94.5
$[Co(NH_3)_5NCS](ClO_4)_2$	195.2 ± 0.7	$Co(NH_3)_5NCS^{2+}$	93.8
$[Co(NH_3)_5N_3]Cl_2$	128.8 ± 0.5	$Co(NH_3)_5N_3^{2+}$	85.3
$[Co(NH_3)_5Me_2SO](ClO_4)_3$	277.3 ± 1.4	$Co(NH_3)_5Me_2SO^{3+}$	125.2
$[Co(NH_3)_5OH_2](ClO_4)_3$	206.1 ± 0.7	$Co(NH_3)_5OH_2^{3+}$	54.0
$[Co(NH_3)_6](ClO_4)_3$	207.1 ± 1.1	$Co(NH_3)_6^{3+}$	55.0
$[Cr(NH_3)_5Cl](ClO_4)_2$	184.7 ± 1.0	$Cr(NH_3)_5Cl^{2+}$	83.2
$[Cr(NH_3)_5Br]Br_2$	150.7 ± 1.0	$Cr(NH_3)_5Br^{2+}$	91.9
$[Cr(NH_3)_5I](ClO_4)_2$	198.5 ± 1.7	$Cr(NH_3)_5I^{2+}$	97.1
$[Cr(NH_3)_5NCS](ClO_4)_2$	204.0 ± 0.9	$Cr(NH_3)_5NCS^{2+}$	102.6
$[Cr(NH_3)_5OH_2](ClO_4)_3$	170.4 ± 0.5	$Cr(NH_3)_5OH_2^{3+}$	70.6
$[Cr(NH_3)_6]I_3$	191.6 ± 0.7	$Cr(NH_3)_6^{3+}$	68.6
Me_2SO	68.8 ± 0.2		
$KClO_4$	55.2	ClO_4^-	50.7 (28)
KNO_3	37.8	NO_3^-	33.3 (28)
KCl	26.25	Cl^-	21.75 (28)
KBr	33.9	Br^-	29.4 (28)
KI	45.5	I^-	41.0 (28)

Table IV. Volume Changes for the Aquation Reactions of $M(NH_3)_5X^{(3-n)+}$ Complexes (25 °C; $\mu = 0.1$ M)

M	X	$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$	$\Delta\bar{V}$, $cm^3\ mol^{-1}$	Ref
Co	Cl^-	-10.6 ± 0.4	-11.6	2
	Br^-	-9.2 ± 0.2	-10.8	2
	SO_4^{2-}	-18.5 ± 0.7	-19.2	2
	NO_3^-	-6.3 ± 0.4	-7.2	2
	Me_2SO	-1.7 ± 0.7		This work
	H_2O	$+1.2 \pm 0.1$	0	31
	NCS^- [a]	-4.0 ± 1.0		2
	N_3^- [b]	$+16.8 \pm 0.5$		2
Cr	Cl^-	-10.8 ± 0.3	-8.4	30
	Br^-	-10.2 ± 0.3	-7.2	30
	I^-	-9.4 ± 0.2	-6.0	30
	NCS^-	-8.6 ± 1.0		32
	H_2O	-5.8 ± 0.2	0	33

[a] Measured at 88 °C. [b] Measured at 75 °C.

Table V. Partial Molar Volumes and Volume Changes Involved in the Aquation of $Co(NH_3)_5X^{(3-n)+}$ ($cm^3\ mol^{-1}$)

X	$\bar{V}_X$	$\bar{V}_R$ [a]	$\Delta\bar{V}_{calcd}$
Cl^-	21.75	53.5 ± 0.8	-10.1
Br^-	29.4	56.4 ± 1.3	-11.6
SO_4^{2-}	23.4	54.6 ± 1.3	-19.6
NO_3^-	33.3	54.9 ± 1.5	-7.2
Me_2SO	68.8	54.7 ± 2.1	-2.4
H_2O	0	55.2 ± 0.8	
NCS^-	40.2	49.6 ± 1.7	$+0.4$

[a] Calculated using eq 5 and the values listed in Tables III and IV.

role of electrostriction in an associative mechanism is not clear, although it would be expected to have secondary importance. Indeed, in the absence of any steric hindrance, constant $\Delta V^{\ddagger}_{exp}$ values could be anticipated. However, this approach does not take into account specific, nonelectrostatic solute–solvent interactions.

Swaddle et al.[2,30] put this concept on a semiquantitative basis by establishing that a linear relationship exists between $\Delta V^{\ddagger}_{exp}$ and $\Delta\bar{V}$ for both the Co(III) and Cr(III) complexes. For the Co(III) case the slope is unity indicating a strong similarity between the transition state and products. In other words, bond breaking is well established in the transition state. On the other hand, Cr(III) complexes show a slope of ca. 0.6 consistent with a partially dissociated leaving group complemented by the synchronous partial formation of a $Cr–OH_2$ bond during the activation process.

Although this argument is quite convincing, the superficial similarity between the $\Delta V^{\ddagger}_{exp}$ values for the corresponding chloro and bromo complexes of cobalt(III) and chromium(III) tends to obscure the explanation, particularly in the light of the above mentioned anticipated contributions of $\Delta V^{\ddagger}_{intr}$ and $\Delta V^{\ddagger}_{el}$ for the different mechanisms.

Kinetic studies on Co(III) complex systems have firmly established that a dissociative mechanism prevails, and more recent work has refined this to mean an I_d mechanism.[2-5] For the somewhat less intensively studied Cr(III) systems the mechanism is still controversial, with both I_a[30] and I_d[7] mechanisms being proposed for the cationic complexes. Therefore, consideration should first be given to the volume profile of the Co(III) system. It is presented as follows in terms of a limiting dissociative mechanism

$$Co(NH_3)_5X^{(3-n)+} + H_2O \rightleftarrows \{Co(NH_3)_5^{3+} + X^{n-}\}^{\ddagger} \rightleftarrows Co(NH_3)_5OH_2^{3+} + X^{n-} \tag{3}$$

which gives rise to the following equation, assuming that both species making up the transition state, $Co(NH_3)_5^{3+}$ and X^{n-}, are in thermodynamic equilibrium with the solvent. In other words, both species may be assigned partial molar volumes as if the cobalt pentaammine ion were a stable species. Thus the total partial molar volume of the transition state, $\bar{V}^{\ddagger}$, is given by

$$\bar{V}^{\ddagger} = \bar{V}_R + \bar{V}_X = \bar{V}_{RX} + \Delta V^{\ddagger}_{exp} = \bar{V}_{ROH_2} + \Delta V^{\ddagger}_{-exp} \tag{4}$$

where $\bar{V}_{RX}$, $\bar{V}_{ROH_2}$, $\bar{V}_R$, and $\bar{V}_X$ are the partial molar volumes of $Co(NH_3)_5X^{(3-n)+}$, $Co(NH_3)_5OH_2^{3+}$, $Co(NH_3)_5^{3+}$, and X^{n-}, respectively, and $\Delta V^{\ddagger}_{-exp}$ is the volume of activation for the reverse or anation reaction in which case $\bar{V}_X = \bar{V}_{H_2O}$, the partial molar volume of water. Equation 4 can be rearranged to the form

$$\bar{V}_R = \bar{V}_{RX} + \Delta V^{\ddagger}_{exp} - \bar{V}_X \tag{5}$$

Obviously the boundary condition for this scheme is that $\bar{V}_R$ be independent of X. The results, listed in Table V, clearly show that $\bar{V}_R$ is constant for X = Cl^-, Br^-, SO_4^{2-}, NO_3^-, Me_2SO, and H_2O and has a mean value of 54.9 ± 0.9 $cm^3\ mol^{-1}$. Considering the experimental errors involved, the consistency is very good. Surprisingly however, $\bar{V}_{H_2O}$ for the water exchange reaction must be taken as zero in order to fit the series. Stranks[11] determined that the intrinsic volume of the $Ni(NH_3)_6^{2+}$ cation should be virtually equal to that of a hypothetical $Ni(NH_3)_5^{2+}$ species to within 0.1 $cm^3\ mol^{-1}$. For an even less compressible cation such as $Co(NH_3)_6^{3+}$ the volume difference must be smaller and certainly well inside the experimental errors found in $\Delta V^{\ddagger}_{exp}$ and $\bar{V}$. In terms of its size, therefore, *$Co(NH_3)_6^{3+}$ may be used as a "model" for the transition state species, $Co(NH_3)_5^{3+}$*. As shown in Table III, $\bar{V}_R$ for the hexaammine complex cation is 55.1 ± 1.1 $cm^3\ mol^{-1}$ which is in excellent agreement with the calculated value for the pentacoordinated species.

The overall volume change of a reaction, $\Delta\bar{V}$, can also be calculated from the partial molar volumes of the educts and products according to the relationship

$$\Delta\bar{V}_{calcd} = \bar{V}_{ROH_2} + \bar{V}_X - \bar{V}_{RX} - \bar{V}_{H_2O} \tag{6}$$

and as shown in Table V they compare satisfactorily with the experimental values given in Table IV which were obtained by dilatometry. However, here again $\Delta\bar{V}_{calcd}$ values were calculated on the assumption that $\bar{V}_{H_2O} = 0$ which substantiates the kinetic result for water exchange. Swaddle et al.[2,34] interpreted the independence of $\Delta V^{\ddagger}_{exp}$ on pressure for X = H_2O as indicating that there is no change in the number of solvent molecules solvating the complex during the formation of the transition state. In accordance with a dissociative mechanism of the I_d type a water molecule is merely transferred from the first to the second coordination sphere in which the molar volume of water is estimated to be 14.9 $cm^3\ mol^{-1}$ as compared to 14.0 $cm^{-3}\ mol^{-1}$ for the former. Conversely, for a D mechanism $\Delta V^{\ddagger}_{exp}$ can be expected to be pressure dependent and to have a more distinctly positive value.

It is of interest to note that $\Delta V^{\ddagger}_{exp}$ for the aquation of $Co(NH_3)_5Me_2SO^{3+}$ is also not detectably pressure dependent, whereas the remaining charged leaving groups all showed a pressure dependence. The latter is fully consistent with charge separation during the dissociative process, whether D or I_d. Thus the pressure dependence of $\Delta V^{\ddagger}_{exp}$ stems from $\Delta V^{\ddagger}_{solv}$. Equation 5 can also be expressed in graphical form whereby $\bar{V}_{RX}$ is plotted against $\bar{V}_X$ so that ($\bar{V}_{RX} + \Delta V^{\ddagger}_{exp}$) lies on a straight line with unit slope and intercept $\bar{V}_R$. As shown in Figure 1 for X^- = NCS^- and N_3^-, $\Delta V^{\ddagger}_{exp}$ values of +1.4 and +1.5 $cm^3\ mol^{-1}$ are expected instead of those listed in Table

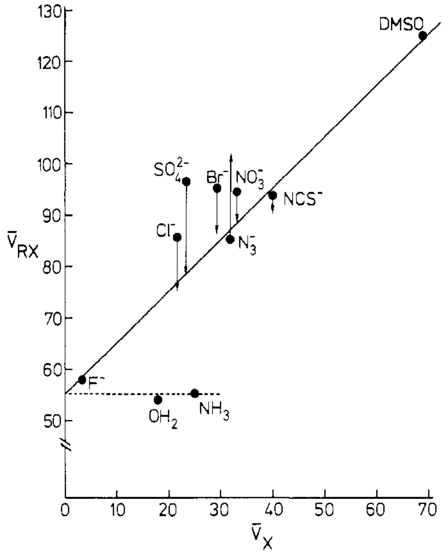

Figure 1. A plot of $\bar{V}_{RX}$ vs. $\bar{V}_X$ for the aquation reactions of $Co(NH_3)_5X^{(3-n)+}$. The arrows represent $\Delta V^{\ddagger}_{exp}$.

IV, assuming the mechanism remains dissociative. For NCS^-, $\Delta V^{\ddagger}_{exp}$ was measured at 88 °C and at a limited number of pressures.[1] Although partial molar volumes are generally not very sensitive to temperature variations[28] it is reasonable that a discrepancy of 5.4 ± 2.4 $cm^3\ mol^{-1}$ between the measured and calculated values of $\Delta V^{\ddagger}_{exp}$ may occur. For X = N_3^- the following reaction scheme is proposed

$$\underset{A}{Co(NH_3)_5N_3^{2+}} + \underset{H}{H^+} \overset{\Delta\bar{V}_1}{\rightleftharpoons} \underset{B}{Co(NH_3)_5N_3H^{3+}} \xrightarrow{\Delta V^{\ddagger}_2} [\underset{R}{Co(NH_3)_5^{3+}} + \underset{HN_3}{HN_3}]^{\ddagger} \rightarrow \tag{7}$$

Thus the observed $\Delta V^{\ddagger}_{exp}$ consists of the two contributions

$$\Delta V^{\ddagger}_{exp} = \Delta\bar{V}_1 + \Delta V^{\ddagger}_2 \tag{8}$$

or

$$\Delta V^{\ddagger}_{exp} = \bar{V}_B - \bar{V}_H - \bar{V}_A + \bar{V}_R + \bar{V}_{HN_3} - \bar{V}_B \tag{9}$$

The protonation of azide ion can be expressed by

$$H^+ + N_3^- \rightleftharpoons HN_3 \tag{10}$$

for which

$$\Delta\bar{V}_{HN_3} = \bar{V}_{HN_3} - \bar{V}_H - \bar{V}_{N_3} \tag{11}$$

Combining eq 9 and 11 one obtains

$$\Delta\bar{V}_{HN_3} = \Delta V^{\ddagger}_{exp} + \bar{V}_A - \bar{V}_R - \bar{V}_{N_3} \tag{12}$$

Substituting the values $\Delta V^{\ddagger}_{exp}$ = +16.8, $\bar{V}_A$ = 85.3, $\bar{V}_R$ = 54.9, and $\bar{V}_{N_3}$ = 31.8 $cm^3\ mol^{-1}$ in eq 12 results in $\Delta\bar{V}_{HN_3}$ = +15 ± 2 $cm^3\ mol^{-1}$. An additional error is likely to be introduced as $\Delta V^{\ddagger}_{exp}$ was determined at 75 °C while the remaining $\bar{V}$ values were taken at 25 °C. Nevertheless, the order of magnitude of $\Delta\bar{V}_{HN_3}$ is consistent with volume changes involved in the association of weak acids, e.g., for acetic acid at 25 °C, $\Delta\bar{V}$ = +11.7 $cm^3\ mol^{-1}$.[29] Thus the large positive value of $\Delta V^{\ddagger}_{exp}$ is mainly determined by the positive volume change accompanying the protonation of the azide ligand. This "volume equation" treatment provides quantitative evidence for a dissociative mechanism for the entire pentaamminecobalt(III) series of complexes investigated here. However, we are unable to distinguish between a D and an I_d mechanism as the "equation" adequately describes the D type. As an I_d mechanism is generally accepted, we must conclude that the contribution to $\Delta V^{\ddagger}_{exp}$ resulting from the diffusion of the leaving group $X^{(3-n)-}$ from the first solvation sphere to the bulk solvent is small, i.e., less than the overall experimental error of ca. ±2 $cm^3\ mol^{-1}$, and that the mechanism is of the I_d type or that in the absence of a high concentration of potential ion pairing counterions, as is here the case, a D mechanism holds.

Table VI. Calculated Partial Molar Volumes and Volume Changes Involved in the Aquation of $Cr(NH_3)_5X^{(3-n)+}$ ($cm^3\ mol^{-1}$)

X	$\bar{V}_R$	$\Delta\bar{V}_{calcd}$	$\Delta V^{\ddagger}_D$	$0.5\cdot\Delta V^{\ddagger}_D$	$\Delta\bar{V}^{\ddagger}_A$
Cl^-	50.7 ± 1.3	−8.9 ± 1.5	7.2	3.6	−14.4 ± 2.0
Br^-	52.3 ± 1.3	−9.9 ± 1.5	6.1	3.1	−13.3 ± 2.0
I^-	46.7 ± 1.9	−3.5 ± 2.2	12.5	6.3	−15.7 ± 2.6
NCS^-	53.8 ± 1.9	−9.8 ± 1.4	11.7	5.9	−14.5 ± 2.6
H_2O	64.8 ± 0.7[a]	0			
	46.8 ± 0.7[b]	0	16.0	8.0	−13.8 ± 1.4

[a] $\bar{V}_{H_2O} = 0$. [b] $\bar{V}_{H_2O} = 18.0$.

The chromium(III) pentaammines may be identically treated with a dissociative mechanism as a preconception. The values of $\bar{V}_R$, calculated according to eq 5, are shown in the first column of Table VI. They vary considerably more than in the cobalt case with the mean value being 50.1 ± 3.2 $cm^3\ mol^{-1}$ which, in view of the large error, alone does not substantiate the mechanism. Furthermore, when compared to the partial molar volume of $Cr(NH_3)_6^{3+}$ of 68.6 $cm^3\ mol^{-1}$, it clearly demonstrates that the mechanism is not purely dissociative in character. Two extreme values for $\bar{V}_{H_2O}$ were used in the calculation of $\bar{V}_R$ for the water exchange reaction. Significantly however, $\bar{V}_{H_2O}$ = 18 $cm^3\ mol^{-1}$ leads to $\Delta\bar{V}_{calcd}$ values, shown in column 2 of Table VI, which are in reasonable agreement with the limited number of experimentally derived values shown in Table IV.

The dependence of k_{obsd} on the nature of X strongly indicates that some lengthening of the Cr–X bond occurs during the activation process. Swaddle et al.[30] proposed that this bond is 50% dissociated in the transition state which would result in a contribution to $\Delta V^{\ddagger}_{exp}$ which can be approximated from eq 5. These values are shown in Table VI, column 3, calculated on the assumption that $\bar{V}_R = \bar{V}(Cr(NH_3)_6^{3+})$ = 68.6 $cm^3\ mol^{-1}$ for the complete dissociation of X^{n-}. The "half-dissociated" Cr–X bond is simply equated to $0.5\Delta V^{\ddagger}_D$, column 4 in Table VI. $\Delta V^{\ddagger}_A$ values listed in column 5 are then the associative contributions necessary to arrive at the experimental $\Delta V^{\ddagger}_{exp}$ values. The $\Delta V^{\ddagger}_A$ values are relatively constant with an average value of 14.3 ± 0.8 $cm^3\ mol^{-1}$ which is consistent with the molar volume of a water molecule in the first solvation sphere of a 2+ complex. In other words, the mechanism is typically I_a in character.

In general our results comply with the interpretation of Swaddle. Although the rate constants for aquation of the pentaamminechromium(III) complexes are more dependent on the nature of the leaving groups than for the analogous Co(III) complexes, it is the stronger solvation of these groups for the latter complexes that more effectively compensates for the underlying differences in bond energies.

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Registry No. $[Co(NH_3)_5Cl](ClO_4)_2$, 15156-18-0; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $[Co(NH_3)_5Br](ClO_4)_2$, 14591-65-2; $Co(NH_3)_5Br^{2+}$, 14970-15-1; $[Co(NH_3)_5SO_4]ClO_4$, 15156-23-7; $Co(NH_3)_5SO_4^+$, 18661-07-9; $[Co(NH_3)_5F](ClO_4)_2$, 15156-21-5; $Co(NH_3)_5F^{2+}$, 15392-06-0; $[Co(NH_3)_5NO_3](NO_3)_2$, 14404-36-5; $Co(NH_3)_5NO_3^{2+}$, 15077-47-1; $[Co(NH_3)_5NCS](ClO_4)_2$, 15663-42-0; $Co(NH_3)_5NCS^{2+}$, 14970-18-4; $[Co(NH_3)_5N_3]Cl_2$, 14916-48-4; $Co(NH_3)_5N_3^{2+}$, 14403-83-9; $[Co(NH_3)_5Me_2SO](ClO_4)_3$, 51667-94-8; $Co(NH_3)_5Me_2SO^{3+}$, 44915-85-7; $[Co(NH_3)_5OH_2](ClO_4)_3$, 13820-81-0;

$Co(NH_3)_5OH_2^{3+}$, 14403-82-8; $[Co(NH_3)_6](ClO_4)_3$, 13820-83-2; $Co(NH_3)_6^{3+}$, 14695-95-5; $[Cr(NH_3)_5Cl](ClO_4)_2$, 22478-30-4; $Cr(NH_3)_5Cl^{2+}$, 14482-76-9; $[Cr(NH_3)_5Br]Br_2$, 13601-60-0; $Cr(NH_3)_5Br^{2+}$, 22289-65-2; $[Cr(NH_3)_5I](ClO_4)_2$, 64146-51-6; $Cr(NH_3)_5I^{2+}$, 17979-08-7; $[Cr(NH_3)_5NCS](ClO_4)_2$, 22478-28-0; $Cr(NH_3)_5NCS^{2+}$, 16884-60-9; $[Cr(NH_3)_5OH_2](ClO_4)_3$, 32700-25-7; $Cr(NH_3)_5OH_2^{3+}$, 15975-47-0; $[Cr(NH_3)_6]I_3$, 31656-04-9; $Cr(NH_3)_6^{3+}$, 14695-96-6; Me_2SO, 67-68-5; $KClO_4$, 7778-74-7; KNO_3, 7757-79-1; KCl, 7447-40-7; KBr, 7758-02-3; KI, 7681-11-0.

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Kinetics of Rupture of Chromium–Ethylenediamine Bonds in Trans-Disubstituted Bis(ethylenediamine)chromium(III) Complexes

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The rate of aquation of several Cr(III) complexes of general type *trans*-$Cr(en)_2AX^{n+}$ are reported. Two types of aquation occur: loss of X (k_{-x}) or loss of one end of the chelated ethylenediamine (k_{-n}). The values of these rate constants and their corresponding activation parameters are (leaving halide italicized; rate constants in s, $\Delta H^\ddagger$ in kcal mol^{-1}, and $\Delta S^\ddagger$ in gibbs mol^{-1}): *trans*-$Cr(en)_2F\mathit{Br}^+$, $k_{-x} = 5.0 \times 10^{-4}$, 21.0, −3; *trans*-$Cr(en)_2F\mathit{Cl}^+$, $k_{-x} = 4.85 \times 10^{-5}$, 24.6, 4; $k_{-n} = 1.2 \times 10^{-5}$, 24.6, 2; *trans*-$Cr(en)_2FH_2O^{2+}$, $k_{-n} = 2.56 \times 10^{-5}$, 24.2, 2; *trans*-$Cr(en)_2NCS(\mathit{Br})^+$, $k_{-x} = 3.2 \times 10^{-5}$, 25, 5; $k_{-n} = 3.6 \times 10^{-6}$, 25, 1; *trans*-$Cr(en)_2NCS(H_2O)^{2+}$, $k_{-n} = 9.3 \times 10^{-6}$, 24.4, 0.7. Examination of these data and information in the literature indicate that a trans directing labilization is present but that this effect is not efficiently felt by the *cis*-ethylenediamine ligands. The great lability of ethylenediamine in *trans*-$Cr(en)_2AX^{n+}$ complexes but not in the corresponding cis isomers or in mono-en complexes is established.

The effect of nonlabile ligands on the rate of loss of a group from a six-coordinate transition metal–ion complex is, even after a great deal of experimentation, still a poorly understood phenomenon. From some of the earliest experiments on Co(III) complexes, it has been recognized that the effect of the so-called "directing group" in $Co(en)_2ACl^{n+}$ can be striking,[1] but the explanation of this phenomena in terms of a mechanistic change from dissociative to associative has not been verified and has been challenged.[2,3] Although certain ligands such as SO_3^{2-} enhance "trans" lability,[4,5] within the scope of ligands containing π saturated orbitals (amines, H_2O, halides), attempts to determine special directional labilizing phenomena have had little success.[6]

In the chemistry of Cr(III)–amine complexes, especially ethylenediamine complexes, as opposed to the corresponding Co(III) systems, an added factor is involved: the striking lability of the Cr(III)–amine bond.[7] This means that in a study of the "directing group" effect on rate of aquation of, say, Cl^- from complexes of the type $Cr(en)_2ACl^{n+}$, concern for loss of Cl^- and breakage of the Cr(III)–en bond must be manifest. Some time ago it was demonstrated that monodentate ethylenediamine persisted in the coordination shell of Cr(III) long enough for ion-exchange isolation of $Cr(enH)(H_2O)_5^{4+}$.[8] Since then, numerous other "one-ended" ethylenediamine complexes have been isolated even with anionic groups present: $Cr(en)(enH)(H_2O)F_2^{2+}$,[9] $Cr(en)(enH)H_2O(NCS)_2^{2+}$.[10] Indeed it was suggested in a study[9] of the aquation of *trans*-$Cr(en)_2F_2^+$ that breakage of the Cr(III)–en bond in complexes of trans geometry might be rather independent of the nature of the ligands along the axis, in somewhat of a contrast to the behavior of anionic leaving groups from Co(III) centers. In this paper that concept is tested by presentation of data on the aquation of *trans*-$Cr(en)_2(F)Cl^+$, *trans*-$Cr(en)_2(F)Br^+$, *trans*-$Cr(en)_2(F)H_2O^{2+}$, *trans*-$Cr(en)_2(NCS)Br^+$, and *trans*-$Cr(en)_2(H_2O)NCS^{2+}$. These systems, coupled with some data already in the literature, allow some conclusions to be drawn concerning factors important in Cr(III)–en bond rupture in *trans*-$Cr(en)_2AX^{n+}$ complexes.

Experimental Section

Materials. The complexes used in this study were prepared by procedures given in the literature and purity was checked by determining percentage Cr, spectral analysis, and ion-exchange chromatography. The pertinent references are: *trans*-$[Cr(en)_2(F)Br]ClO_4$ and *trans*-$[Cr(en)_2(F)Cl]ClO_4$;[11] *trans*-$[Cr(en)_2(F)H_2O](ClO_4)_2$.[12] *trans*-$[Cr(en)_2(NCS)Br]ClO_4$ was prepared by slight modification of the procedure of Fee, MacHarrowfield, and Jackson.[13]