redox changes are reported in Table III. It is seen that the $E_{1/2}$ value associated to the first oxidation step of the dimetallic complex is slightly less positive than that for the single-ring reference [13]dioxocyclam complex (consider that for the statistical effects the dimetallic species should be in any case favored by 18 mV). The oxidation of the second metal center occurs at a potential 100 mV more positive than for the first one. This difference is larger than that expected on statistical bases (36 mV) and is indicative of a small but detectable mutual influence of the two redox centers of electrostatic nature. A quite similar behavior is observed with the single and double 14-membered ring systems. For the [14-14]bis-dioxocyclam system a slightly large $E_{1/2}$ value has been found (110 mV), but the difference with respect to [13-13]bisdi-oxocyclam is too small to justify any speculation. It should be noted that, in the case of 14-membered rings, the oxidation of the first metal center of the dinuclear complex occurs at a potential considerably less positive than for the single-ring

system (by 70 mV, well beyond the statistical term of 18 mV). This has been ascribed[5] to the possible decrease of the intensity of the O-O repulsions due to an increased withdrawing of electrical charge by the tripositive cation. The same does not occur with the dimetallic complex of [13-13]dioxocyclam, for which the first oxidation process is advantaged on the single-ring complex only by a quantity corresponding to the statistical effect. It has been pointed out that the Cu^{II}/Cu^{III} change causes a drastic rearrangement of the 13-membered ring complex, which can affect in some way the intensity of the O-O ring-to-ring repulsion. This further effect may contribute to the overall energy term involved in the $Cu^{II}Cu^{II}/Cu^{III}Cu^{II}$ redox change in the 13-membered bima-crocycle complex, but a full explanation seems not possible, at present.

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Aquation of Chloropentaammine and Chloropentakis(methylamine) Complexes of Cobalt(III) and Chromium(III): Comparative Activation Volumes and Mechanistic Implications

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Volumes of activation for the aquation of $Co(NH_2CH_3)_5Cl^{2+}$ (-2.3 cm³ mol⁻¹), *trans*-$Co(NH_3)_4(NH_2CH_3)Cl^{2+}$ (-4.6 cm³ mol⁻¹), and $Cr(NH_2CH_3)_5Cl^{2+}$ (+0.5 cm³ mol⁻¹) have been determined and differ markedly from those for $Co(NH_3)_5Cl^{2+}$ (-9.9 cm³ mol⁻¹) and $Cr(NH_3)_5Cl^{2+}$ (-10.6 cm³ mol⁻¹). The activation volumes for the cobalt(III) series become more positive with increasing experimentally determined molar volume of the cation, and the activation entropy varies in a similar way. The behavior is consistent with a dissociative-interchange mechanism operating in all cases. The behavior of the chromium(III) complexes is similar to, but not identical with, that of the cobalt(III) complexes, since variation in $\Delta V^{\ddagger}$ is greater, but in $\Delta S^{\ddagger}$ smaller. The data are not fully consistent with a persistent associative-interchange process, and variation in the importance of bond-making and bond-breaking processes from the pentaammine to the pentakis(methylamine) complex is suggested.

Introduction

Volumes of activation ($\Delta V^{\ddagger}$) have been employed successfully in the elucidation of both organic and inorganic reaction mechanisms.[2-5] It has been recognized that the experimentally determined activation volume ($\Delta V^{\ddagger}_{exptl}$) can be considered as a composite of contributions originating from the displacement of atoms at the activation site (the intrinsic component, $\Delta V^{\ddagger}_{int}$) and from changes in electrostriction in forming the activated state ($\Delta V^{\ddagger}_{el}$). The latter term is principally related to changes in solvation of the precursor and activated states. In coordination chemistry, reactions often involve displacement of charged groups; hence, $\Delta V^{\ddagger}_{exptl}$ involves a substantial contribution from $\Delta V^{\ddagger}_{el}$, which may mask the mechanistically important $\Delta V^{\ddagger}_{int}$ component. Reactions involving neutral leaving groups such as solvent-exchange reactions[6] are more readily interpreted, and mechanistic differentiation can be quite clear from $\Delta V^{\ddagger}_{exptl}$ data.

Aquation reactions of octahedral halo amine complexes of cobalt(III) and chromium(III) have been subjected to extensive

and detailed investigation over recent decades.[7-9] The mechanisms for reactions of cobalt(III) are generally accepted to be dominated by bond-breaking (dissociative) processes, while those of chromium(III) are apparently characterized by bond-making (associative) processes. Comparative studies of pentaammine and pentakis(methylamine) complexes have defined the difference.[10,11] An increase in the rate of aquation when the five ammine ligand in $Co(NH_3)_5Cl^{2+}$ are replaced by bulkier alkylamine ligands is consistent with steric relief in a dissociated activated state; by contrast, the analogous chromium(III) system exhibits retardation, in accord with steric congestion of an associated state. Similar behavior is observed with $CF_3SO_3^-$ as leaving group.[12]

Despite this apparent mechanistic variation for cobalt(III) and chromium(III), it is notable that $\Delta V^{\ddagger}_{exptl}$ for aquation of $Co(NH_3)_5Cl^{2+}$ (-9.9 cm³ mol⁻¹)[13] and $Cr(NH_3)_5Cl^{2+}$ (-10.8

(1) (a) University of Newcastle. (b) University of Frankfurt.
(2) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978,** *78,* 407.
(3) Palmer, D. A.; Kelm, H. *Coord. Chem. Rev.* **1981,** *36,* 89.
(4) Lawrance, G. A.; Stranks, D. R. *Acc. Chem. Res.* **1979,** *12,* 403. Stanks, D. R. *Pure Appl. Chem.* **1974,** *38,* 303.
(5) le Noble, W. J.; Kelm, H. *Angew. Chem.* **1980,** *92,* 887.
(6) Merbach, A. E. *Pure Appl. Chem.* **1982,** *54,* 1479.

(7) *Inorg. React. Mech.* **1971-1980,** *1-7.*
(8) Edwards, J. O.; Monacelli, F.; Ortaggi, G. *Inorg. Chim. Acta* **1974,** *11,* 47.
(9) Wilkins, R. G. "The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, 1974.
(10) Parris, M.; Wallace, W. J. *Can. J. Chem.* **1969,** *47,* 2257.
(11) Swaddle, T. W. *Can. J. Chem.* **1977,** *55,* 3166.
(12) Curtis, N. J.; Lawrance, G. A.; Sargeson, A. M., to be submitted for publication.
(13) Jones, W. E.; Carey, L. R.; Swaddle, T. W. *Can. J. Chem.* **1972,** *50,* 2739.

cm^3 mol^{-1})^{14} is essentially identical, and differences in ΔV^*_{el} were suggested to account for this apparent discrepancy. On the other hand, however, solvent exchange in the aquo complexes, with ΔV^*_{exptl} = +1.2 cm^3 mol^{-1} for Co(NH$_3$)$_5$(OH$_2$)$^{3+}$ ^{15} and ΔV^*_{exptl} = -5.8 cm^3 mol^{-1} for Cr(NH$_3$)$_5$(OH$_2$)$^{3+}$,^{16} is more revealing, highlighting the complications that can occur with charged leaving groups. The problem with charged groups is exacerbated by reports of ΔV^*_{exptl} for chloro(amine)cobalt(III) complexes with multidentate amines ranging as high as +11 cm^3 mol^{-1}.^{17,18}

In dealing with ionic species with charged leaving groups, it is apparent that electrostrictive components can dominate intrinsic components of ΔV^*_{exptl}. While there are sufficient data to define the problems, no systematic approach to the role of the nonleaving groups has been adopted previously. Here, we report and compare activation volumes and molar volumes for the simple unidentate complexes Cr(NH$_2$CH$_3$)$_5$Cl^{2+}, Co-(NH$_2$CH$_3$)$_5$Cl^{2+}, and trans-Co(NH$_3$)$_4$(NH$_2$CH$_3$)Cl^{2+} with those for Cr(NH$_3$)$_5$Cl^{2+} and Co(NH$_3$)$_5$Cl^{2+}.

Experimental Section

Synthesis. [Co(NH$_2$CH$_3$)$_5$Cl]Cl$_2$ and [Cr(NH$_2$CH$_3$)$_5$Cl]Cl$_2$ were prepared by using previously described methods.^{19,20} trans-[Co-(NH$_3$)$_4$(NH$_2$CH$_3$)Cl](ClO$_4$)$_2$ was prepared by the literature method,^{21} which yields exclusively the trans isomer. The complexes were microanalytically pure (C, H, N, Cl analysis), and their electronic absorption spectra were consistent with literature values.

Kinetic Studies. The rates of acid aquation of the complexes were determined in 0.1 M HClO$_4$ or 0.05 M HClO$_4$ (I = 0.1 M (NaClO$_4$)) spectrophotometrically at 540 nm (Co) or 380 nm (Cr). Reactions at elevated pressures and one temperature were followed for at least 3 half-lives in a thermostated ($\pm$0.1 °C) high-pressure spectrophotometer cell with sapphire windows^{22} incorporated in a Varian 625 or a Zeiss PMQ II spectrophotometer. Samples were subjected to pressures of up to 1725 bar. Rate constants were determined by standard least squares using the Guggenheim method and/or exponential curve-fitting techniques. Activation volumes (ΔV^*_{exptl}) and activation compressibility coefficients ($\Delta \beta^*$) were determined by least-squares analysis of rate and pressure data using the expression

$$\ln k_p = \ln k_0 + bP + cP^2 \qquad (1)$$

where $\Delta V^* = -bRT$ and $\Delta \beta^* = 2cRT$.

Reactions at various temperatures for the (pentaamine)cobalt complexes were followed on a Gilford spectrophotometer in which the cell block temperature was regulated ($\pm$0.1 °C) by thermostated water circulation. Rate constants were determined as above, and activation enthalpy and entropy were determined in the usual way from plots of $\ln (k/T)$ vs. $1/T$.

Density Measurements. An Anton Paar DMA02 digital density meter, thermostated at 25 ($\pm$0.003) °C, was used. Triply distilled water and specially cleaned glassware were employed; the experimental methods and calculation of apparent molar volume (Φ_i) employed have been described previously.^{23}

Results

Aquation of Co(NH$_2$CH$_3$)$_5$Cl^{2+} and trans-Co(NH$_3$)$_4$-(NH$_2$CH$_3$)Cl^{2+} is accelerated by pressure, while aquation of Cr(NH$_2$CH$_3$)$_5$Cl^{2+} shows no significant effect with elevated pressure. Rate constants recorded at various pressures appear in Table I. Variations of rate constants with temperature for

Table I. Pressure Dependence of the Rate Constant for Aquation of Chloro Amine Complexes^a

complex	P, bar	$10^4 k$,^{b} s^{-1}
trans-Co(NH$_3$)$_4$(NH$_2$CH$_3$)Cl^{2+} ^{c}	1	2.15 ± 0.03 (3)
	345	2.30 ± 0.05 (2)
	690	2.43 ± 0.06 (3)
	1035	2.53 ± 0.06 (2)
	1380	2.72 ± 0.07 (3)
	1725	2.84 ± 0.05 (2)
Co(NH$_2$CH$_3$)$_5$Cl^{2+} ^{d}	1	2.26 ± 0.02 (3)
	345	2.32 ± 0.04 (2)
	690	2.37 ± 0.03 (3)
	1035	2.48 ± 0.05 (2)
	1380	2.59 ± 0.02 (3)
	1725	2.66 ± 0.03 (3)
Cr(NH$_2$CH$_3$)$_5$Cl^{2+} ^{e}	20	1.87 ± 0.13 (3)
	500	1.76 ± 0.07 (5)
	1000	1.77 ± 0.07 (5)
	1500	1.78 ± 0.10 (4)

^{a} Ionic strength 0.1 M (ClO$_4^-$); [H$^+$] = 0.05 or 0.10 M; [complex] = (2–8) × 10^{-3} M. ^{b} Standard deviation plus number of independent determinations (in parentheses) included. ^{c} T = 49.0 °C. ^{d} T = 39.0 °C. ^{e} T = 70.0 °C.

Table II. Temperature Dependences of the Rate Constant for Aquation of Chloro(amine)cobalt(III) Complexes^a

complex	T, °C	$10^4 k$,^{b} s^{-1}
trans-Co(NH$_3$)$_4$(NH$_2$CH$_3$)Cl^{2+}	33.5	0.35 ± 0.01 (2)
	41.9	0.94 ± 0.03 (3)
	49.0	2.15 ± 0.03 (3)
	55.7	4.21 ± 0.06 (3)
	60.2	8.04 ± 0.07 (3)
Co(NH$_2$CH$_3$)$_5$Cl^{2+}	21.5	0.25 ± 0.015 (3)
	30.0	0.82 ± 0.02 (2)
	39.0	2.26 ± 0.03 (3)
	46.9	6.20 ± 0.08 (3)
	53.1	11.9 ± 0.2 (3)

^{a} 0.05 M HClO$_4$ (I = 0.1 M (NaClO$_4$)). ^{b} Standard deviation plus number of independent determinations (in parentheses) included.

Co(NH$_2$CH$_3$)$_5$Cl^{2+} and trans-Co(NH$_3$)$_4$(NH$_2$CH$_3$)Cl^{2+} appear in Table II; the temperature dependence of the aquation of Cr(NH$_2$CH$_3$)$_5$Cl^{2+} under similar conditions has been reported previously.^{10} Activation parameters for the complexes studied, and for Co(NH$_3$)$_5$Cl^{2+} ^{24,13} and Cr(NH$_3$)$_5$Cl^{2+} ^{10,14} are collected in Table III.

For both cobalt(III) and chromium(III) there is a marked positive increase in ΔV^* for aquation of M(NH$_2$R)$_5$Cl^{2+} when R is varied from H to CH$_3$. The value for trans-Co(NH$_3$)$_4$-(NH$_2$CH$_3$)Cl^{2+} is intermediate between those of the pentaammine and pentakis(methylamine) complexes. The trend in ΔV^* is paralleled by a like change in ΔS^*, while the $\Delta \beta^*$ term also diminishes. The variation in ΔV^* may also be related to the size of the complex cation. The apparent molar volumes (Φ_v) of trans-[Co(NH$_3$)$_4$(NH$_2$CH$_3$)Cl](ClO$_4$)$_2$, [Co(NH$_2$C-H$_3$)$_5$Cl]Cl$_2$, and [Cr(NH$_2$CH$_3$)$_5$Cl]Cl$_2$ were determined and found to be 195.7, 201.8, 212.7 cm^3 mol^{-1}, respectively. Since $\bar{V}$(ClO$_4^-$) = 48.6 cm^3 mol^{-1} and $\bar{V}$(Cl$^-$) = 22.3 cm^3 mol^{-1},^{25} then $\bar{V}$(Cr(NH$_2$CH$_3$)$_5$Cl^{2+}) = 168.1 cm^3 mol^{-1}, $\bar{V}$(Co-(NH$_2$CH$_3$)$_5$Cl^{2+}) = 157.2 cm^3 mol^{-1}, and $\bar{V}$(trans-Co-(NH$_3$)$_4$(NH$_2$CH$_3$)Cl^{2+}) = 98.5 cm^3 mol^{-1}, while $\bar{V}$(Cr-(NH$_3$)$_5$Cl^{2+}) = 87.5 cm^3 mol^{-1} and $\bar{V}$(Co(NH$_3$)$_5$Cl^{2+}) = 82.8 cm^3 mol^{-1}. The increase in molar volume of the methyl-substituted ammine complexes is associated with an increase of about 16 cm^3 mol^{-1} per methyl group, similar to observations for a range of organic molecules.^{25} ΔV^*_{exptl} becomes more positive as $\bar{V}$(MN$_5$Cl^{2+}) becomes larger.

(14) Guastalla, G.; Swaddle, T. W. *Can. J. Chem.* **1973**, *51*, 821.
(15) Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 2642.
(16) Swaddle, T. W.; Stranks, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 8357.
(17) Lentz, H.; Oh, S. O. *High Temp.—High Pressures* **1975**, *7*, 91.
(18) Lawrance, G. A. *Inorg. Chim. Acta* **1980**, *45*, L275.
(19) Mithner, R.; Blankenburg, P.; Depkat, W. *Z. Chem.* **1969**, *9*, 68.
(20) Rogers, A.; Staples, P. J. *J. Chem. Soc.* **1965**, 6834.
(21) Buckingham, D. A.; Foxman, B. M.; Sargeson, A. M. *Inorg. Chem.* **1970**, *9*, 1790.
(22) Fleischmann, F. K.; Conze, E. G.; Stranks, D. R.; Kelm, H. *Rev. Sci. Instrum.* **1974**, *45*, 1427.
(23) Lawrance, G. A. *Inorg. Chem.* **1982**, *21*, 3687.

(24) Chan, S.C. *J. Chem. Soc. A* **1967**, 291.
(25) Millero, F. J. *Chem. Rev.* **1971**, *71*, 147.

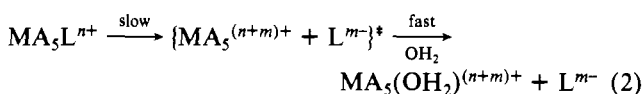**Table III.** Rate Constants at 25 °C, Activation Parameters, and Molar Volumes of $M(NH_2R)_5Cl^{2+}$ Complexes

complex	k^{25}, s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$exptl, cm^3 mol^{-1}	$\Delta \beta^{\ddagger}$, cm^3 kbar^{-1} mol^{-1}	$\bar{V}$, cm^3 mol^{-1}
$Co(NH_3)_5Cl^{2+}$ [a]	1.72×10^{-6}	93 (1)	−44 (3)	−9.9 (0.5)	−2.1 (0.2)	82.8
trans-$Co(NH_3)_4(NH_2CH_3)Cl^{2+}$	1.16×10^{-5}	95 (2)	−19 (6)	−4.6 (0.5)	−0.5 (0.2)	98.5
$Co(NH_2CH_3)_5Cl^{2+}$	3.96×10^{-5}	95 (1.5)	−10 (4)	−2.3 (0.4)	~0	157.2
$Cr(NH_3)_5Cl^{2+}$ [b]	8.70×10^{-6}	93 (0.5)	−29 (1.5)	−10.6 (0.3)	−1.0 (0.2)	87.5
$Cr(NH_2CH_3)_5Cl^{2+}$ [c]	2.61×10^{-7}	110 (0.5)	−2 (1.5)	+0.5 (0.6)	~0	168.8

[a] Data from ref 13 and 24. [b] Data from ref 10 and 14. [c] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ data, ref 10; other data, this work.

Discussion

Aquation reactions of series of $Co(NH_3)_5X^{n+}$ and $Cr(NH_3)_5X^{n+}$ with anionic leaving groups form two of the first systematic studies of activation volumes for metal complexes.[13,14] (Amine)cobalt(III) complexes are generally accepted to aquate by a dissociative process, usually characterized as the dissociative-interchange (I_d) mechanism.[7] (Amine)chromium(III) complexes apparently aquate by an associative process, characterized as the associative-interchange (I_a) mechanism. These are not limiting mechanisms but imply the importance of bond-making and bond-breaking processes in the transition state for chromium(III) and cobalt(III), respectively. An isolated $\Delta V^{\ddagger}$exptl value for any $M(NH_3)_5X^{n+}$ complex does not necessarily yield definitive mechanistic information. However, analysis of $\Delta V^{\ddagger}$exptl and ΔV° (reaction volume) data for the series of chromium(III) and cobalt(III) complexes is indicative of some mechanistic difference.[13,14,23,26,27] It is in reactions where displacement of neutral ligands is involved that the mechanistic constrast is more obvious. The $\Delta V^{\ddagger}$exptl for solvent exchange in the aqua complexes $Co(NH_3)_5(OH_2)^{3+}$ (+1.2 cm^3 mol^{-1})[15] and *cis*-Co(en)$_2$(OH$_2$)$_2$$^{3+}$ (+5.9 cm^3 mol^{-1})[28] differs from those for $Cr(NH_3)_5(OH_2)^{3+}$ (−5.8 cm^3 mol^{-1})[16] and $Cr(OH_2)_6^{3+}$ (−9.3 cm^3 mol^{-1}).[29] Since release of a neutral ligand is anticipated to produce small volume changes of an electrostrictive nature, a positive $\Delta V^{\ddagger}$exptl is diagnostic of a dissociative mechanism in the above water-exchange processes. Similarly, a negative $\Delta V^{\ddagger}$exptl is indicative of an associative mechanism. Activation volumes for solvent-exchange processes have been reported extensively for a range of transition-metal ions and different solvents,[6] and this basic concept appears to be well understood. However, the situation with changed leaving groups is not well resolved at all.
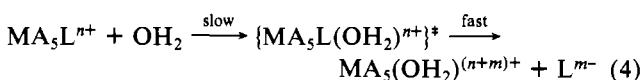
For the limiting dissociative mechanism

$$MA_5L^{n+} \xrightarrow{slow} \{MA_5^{(n+m)+} + L^{m-}\}^{\ddagger} \xrightarrow[OH_2]{fast}$$
$$MA_5(OH_2)^{(n+m)+} + L^{m-} \quad (2)$$

the molar volume change in forming the transition state, $\Delta V^{\ddagger}$, can be written as

$$\Delta V^{\ddagger} = \bar{V}(MA_5^{(n+m)+}) - \bar{V}(MA_5L^{n+}) + \bar{V}(L^{m-}) \quad (3)$$

while for the limiting associative mechanism

$$MA_5L^{n+} + OH_2 \xrightarrow{slow} \{MA_5L(OH_2)^{n+}\}^{\ddagger} \xrightarrow{fast}$$
$$MA_5(OH_2)^{(n+m)+} + L^{m-} \quad (4)$$

the molar volume change can be written as

$$\Delta V^{\ddagger} = \bar{V}(MA_5L(OH_2)^{n+}) - \bar{V}(MA_5L^{n+}) - \bar{V}(OH_2) \quad (5)$$

For these limiting mechanisms, the molar volume of the in-

accessible penta- or heptacoordinate intermediate is involved. Equating the molar volumes of precursor and transition-state intermediate implies a positive $\Delta V^{\ddagger}$ for a dissociative process and a negative $\Delta V^{\ddagger}$ for an associative process. However, this equality has now been challenged successfully,[27] and recent studies have indicated that the volume of the supposed pentacoordinate intermediate is not independent of the charge of the leaving group for simple aquation.[23] The implication is that eq 3 and eq 5 are not strictly correct, i.e. spontaneous aquation reactions do not involve limiting dissociative or associative mechanisms, which is the generally accepted view.

Where bond-breaking dominates, an intermediate

$$A_5ML^{n+} \rightarrow \{A_5M^{(n+m)+}...L^{m-}\}^{\ddagger}$$

where substantial bond-stretching occurs in the transition state can be envisaged. With a neutral leaving group, an expanded activated state and hence a positive $\Delta V^{\ddagger}$ is readily visualized. However, with an anionic leaving group the situation is less clear. Extension of the M–L bond will certainly involve solvent-rearrangement processes as part of the activation process, and not subsequent to it, associated with significant charge displacement. It is likely that these contributions to $\Delta V^{\ddagger}$el will be affected by the initial charge on the complex, the formal charge on the leaving group, and the type and size of the nonleaving groups. The steric interactions of the latter with the leaving group and with each other, and their motions during activation, will play a role in determining the change in solvation occurring.

Where bond-making dominates, an intermediate

$$MA_5L^{n+} + OH_2 \rightarrow \{MA_5L^{n+}...OH_2\}^{\ddagger}$$

where bond-making occurs in the activated state applies, and the concept of a negative $\Delta V^{\ddagger}$ for association of a neutral ligand can be visualized. While the roles of the complex charge, leaving group charge, and nonleaving groups should be somewhat similar to the bond-breaking case, it could be argued that their effects may be less substantial, since this case always deals with entry of a unique and neutral ligand. However, if substantial displacement of the charged leaving group L^{m-} occurs concomitant with aqua–metal bond making, then this may not be the case.

At least for cobalt(III) amine complexes with chloride as the leaving group, determined $\Delta V^{\ddagger}$exptl range from −9.9 cm^3 mol^{-1} for $Co(NH_3)_5Cl^{2+}$ [13] to +11 cm^3 mol^{-1} for *trans*-Co(en)$_2$Cl$_2^+$,[17] with large positive values also reported for *trans*-Co(dtcd)(N$_3$)Cl$^+$ (+8.7 cm^3 mol^{-1}; dtcd = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)[30] and Co(tren)Cl$_2^+$ (+7.5 cm^3 mol^{-1}; tren = tris(2-aminoethyl)-amine).[18] Although there is no apparent mechanistic change occurring, there is a trend toward positive $\Delta V^{\ddagger}$exptl with the larger cations, although the role of the multidentate ligands and their motions are not readily assessed. On the other hand, the positive $\Delta V^{\ddagger}$ values quoted are all for 1+-charged species where the negative contribution from $\Delta V^{\ddagger}$el (due to charge creation during a dissociative process) will be significantly

(26) Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1977**, *16*, 3139.
(27) Sisley, M. J.; Swaddle, T. W. *Inorg. Chem.* **1981**, *20*, 2799.
(28) Tong, S. B.; Krouse, H. R.; Swaddle, T. W. *Inorg. Chem.* **1976**, *15*, 2643.
(29) Stranks, D. R.; Swaddle, T. W. *J. Am. Chem. Soc.* **1971**, *93*, 2783.

(30) Lawrance, G. A.; Suvachittanont, S. *Aust. J. Chem.* **1980**, *33*, 273.

smaller than for the same process involving a 2+-charged species. This tendency was also recently observed for the photoaquation reactions of a series of closely related Rh(III) complexes.[31,32] It follows that these substantial changes in $\Delta V^{\ddagger}_{exptl}$ are not inconsistent with expectations for a dissociative-interchange type of mechanism, while the trend toward positive $\Delta V^{\ddagger}$ with larger complex cations is not unreasonable for the limiting dissociative mechanism and eq 3 when molar volumes of intermediate and precursor become more comparable. That the variations are closely tied to $\Delta V^{\ddagger}_{el}$ variations is clear from comparisons of $\Delta(\Delta V^{\ddagger}_{exptl})$ for aqua exchange of $Co(NH_3)_5(OH_2)^{3+}$ and cis-$Co(en)_2(OH_2)_2^{3+}$ (4.7 cm^3 mol^{-1}) and $\Delta(\Delta V^{\ddagger}_{exptl})$ for chloride anion aquation of $Co(NH_3)_5Cl^{2+}$ and $trans$-$Co(en)_2Cl_2^+$ (20.9 cm^3 mol^{-}); variation with the charged leaving group is far more substantial than with the neutral leaving group.

The system $M(NH_2R)_5Cl^{2+}$ (M = Co, Cr; R = H, CH_3) represents the simplest example of increased cation size with constant charge and leaving group. It involves only unidentate ligands, so that motions and rearrangements of chelate rings are not occurring. The crystal structures of $M(NH_2CH_3)_5Cl^{2+}$ (M = Co, Cr) have been reported,[31] and both exhibit substantial steric crowding, although this is greater for cobalt(III) than for chromium(III), due to shorter Co–N (1.99 Å) than Cr–N (2.10 Å) bonds. The intermediate cation $trans$-Co-$(NH_3)_4(NH_2CH_3)Cl^{2+}$ has not been characterized structurally, but the single methyl group remote to the leaving group should not involve substantial steric effects at that site. The molar volumes of the cations increase by about 16 cm^3 mol^{-1} per methyl group. Likewise, the $\Delta V^{\ddagger}_{exptl}$ becomes more positive with increasing molar volume: for cobalt(III), from −9.9 ((NH_3)$_5$) to −4.6 ((NH_3)$_4$(NH_2CH_3)) to −2.3 cm^3 mol^{-1} ((NH_2CH_3)$_5$). There is a related decrease in the compressibility coefficient of activation (Table III), and a parallel increase in the activation entropy, while the activation enthalpy remains essentially constant. Bond extension in the activated state to generate a new charge center should be associated with increased solvent electrostriction and a negative contribution to $\Delta V^{\ddagger}_{exptl}$; the reverse process of charge neutralization is associated with a positive contribution to $\Delta V^{\ddagger}_{exptl}$, as exemplified by the conjugate base preequilibrium in base-hydrolysis reaction.[2,34,35] The steady positive trend of $\Delta V^{\ddagger}_{exptl}$ for this series may imply that the activated state involves less M–L bond stretching in the larger ions, when $\Delta V^{\ddagger}_{el}$ will be less substantial. There is no obvious bond lengthening in the precursor M–Cl bonds, since at least for $Co(NH_2CH_3)_5Cl^{2+}$ the Co–Cl bond (2.283 Å) is identical within standard deviations with that of $Co(NH_3)_5Cl^{2+}$ (2.286 Å).[33,36] Further, $\Delta H^{\ddagger}$ is constant for all cases, so that it may be incorrect to assert that any M–Cl is easier to break. Assuming alternatively a constant M–Cl length in the activated state, the trend in $\Delta V^{\ddagger}_{exptl}$ and $\Delta S^{\ddagger}$ may merely reflect an appreciable decrease in electrostricted solvent reorganization in the larger ions, where the solvation sheath may be less organized.

It is notable that the change in $\Delta V^{\ddagger}_{exptl}$ from $Cr(NH_3)_5Cl^{2+}$ (−10.6 cm^3 mol^{-1}) to $Cr(NH_2CH_3)_5Cl^{2+}$ (+0.5 cm^3 mol^{-1}) is larger than that observed for the cobalt(III) analogues, although the molar volumes of the cations alter similarly. In terms of our arguments for association of a water molecule with limited displacement of Cl−, this is not the expected result. Either association of water occurs with substantial rearrangement of coordinated chloride geometry in the activation step, or else some mechanistic change may occur. The rate diminution from pentaammine to pentakis(methylamine) is certainly consistent with associative character for both cations, although the result could be accidental since only monoanionic leaving groups have been studied.[10–12] The pentakis(methylamine) complexes are sterically crowded,[33] which does not favor association and could account for the less negative $\Delta V^{\ddagger}$ values. It is likely that water entry would require some concomitant Cr–Cl stretching, and the approach of the water group in the transition state may be less for the pentakis(methylamine) than for the pentaammine complex, which would be consistent with the trend in $\Delta V^{\ddagger}_{exptl}$, but not with the size of the change.

The constancy of $\Delta H^{\ddagger}$ observed for the cobalt(III) complexes is not seen with chromium(III). Further, while $\Delta S^{\ddagger}$ varies in the same sense with $\Delta V^{\ddagger}_{exptl}$ for both metal ions, the slope of the linear $\Delta V^{\ddagger}/\Delta S^{\ddagger}$ relationship for the cobalt(III) complexes of 0.22 is not the same as that of the chromium(III) complexes (0.42); the linearity of the relationship for chromium(III) is also not tested in this study.

Evidently, then, the behavior of the chromium(III) and cobalt(III) complexes is not mechanistically indentical. The data for the cobalt(III) system support a common and evidently dissociative mechanism, with both $\Delta V^{\ddagger}_{exptl}$ and $\Delta S^{\ddagger}$ reflecting varying solvation differences between activated and precursor states along the series rather than any large mechanistic differences. The data for the chromium(III) system suggest that the gradual trend observed with cobalt(III) does not apply. Rather, the importance of bond-making and bond-breaking processes may change significantly from the pentaammine to pentakis(methylamine) complex, a change that is perhaps sterically enforced and a change that is absent in the dominantly bond-breaking cobalt(III) system.

The effect of the nonleaving groups on the value of $\Delta V^{\ddagger}_{exptl}$ which has led to some controversy in the literature,[37–39] is obviously significant when a charged leaving group is involved but is not greatly significant when neutral leaving groups occur. Nevertheless, investigations of related series of complexes would appear to offer an understanding of the way in which these effects operate with charged leaving groups, and further studies will be pursued.

Registry No. $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $trans$-$Co(NH_3)_4$-$(NH_2CH_3)Cl^{2+}$, 36527-86-3; $Co(NH_2CH_3)_5Cl^{2+}$, 30051-70-8; Cr-$(NH_3)_5Cl^{2+}$, 14482-76-9; $Cr(NH_2CH_3)_5Cl^{2+}$, 19418-71-4.

(31) Weber, W.; van Eldik, R.; Kelm, H.; DiBenedetto, J.; Ducommun, Y.; Offen, H.; Ford, P. C. *Inorg. Chem.* **1983**, *22*, 623.
(32) Skibsted, L. H.; Weber, W.; van Eldik, R.; Kelm, H.; Ford, P. C. *Inorg. Chem.* **1983**, *22*, 541.
(33) Foxman, B. M. *Inorg. Chem.* **1978**, *17*, 1932.
(34) Kitamura, Y.; van Eldik, R. *Ber. Bunsenges. Phys. Chem.*, in press.
(35) Kitamura, Y.; van Eldik, R.; Kelm, H. *Inorg. Chem.* **1984**, *23*, 2038.
(36) Messmer, G. G.; Amma, E. L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *B24*, 417.

(37) Langford, C. H. *Inorg. Chem.* **1979**, *18*, 3288.
(38) Swaddle, T. W. *Inorg. Chem.* **1980**, *19*, 3205.
(39) Newman, K. E.; Merbach, A. E. *Inorg. Chem.* **1980**, *19*, 2481.