s^{-1}), a best-fitting procedure (Figure 5b) leads to $k = 1.4 \times 10^{10}$ M^{-1} s^{-1} for the reaction between Br_2^- and $Co(sep)^{2+}$. It follows that more than 80% of the Br_2^- disappears via $Co(sep)^{2+}$ oxidation. This, together with the less accessible Br_3^- absorption, precluded an investigation of the reaction between Br_3^- and $Co(sep)^{2+}$.

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Registry No. $Co(sep)^{3+}$, 72496-77-6; I^-, 20461-54-5; Br^-, 24959-67-9; I_2^-, 12190-71-5; I_3^-, 14900-04-0; Br_2^-, 12595-70-9.

Contribution from the Institute for Physical and Theoretical Chemistry,
University of Frankfurt, 6000 Frankfurt/Main, FRG

Volume Profiles for the Base Hydrolysis of a Series of Monoalkyl-Substituted Chloropentaamminecobalt(III) Complexes in Aqueous Solution

Rudi van Eldik,* Yoichi Kitamura,[1a] and Carlos P. Piriz Mac-Coll[1b]

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Volumes of activation ($\Delta V^{*}_{\text{exptl}}$) for the base hydrolysis reactions of a series of complexes of the type $Co(NH_3)_4(NH_2X)Cl^{2+}$ (X: cis, CH_3; trans, CH_3; trans, C_2H_5; cis, n-C_3H_7; trans, n-C_3H_7; trans, n-C_4H_9; trans, i-C_4H_9) were determined from the pressure dependencies of the hydrolysis rate constants and have values between 26.4 and 29.9 cm^3 mol^{-1} at 25 °C. These data combined with dilatometrically determined overall reaction volumes ($\Delta \bar{V}_{BH}$) enable the construction of reaction volume profiles for the base hydrolysis process. Volume equation calculations reveal that the partial molar volume of the five-coordinate species $Co(NH_3)_3(NH_2)(NH_2X)^{2+}$ increases linearly with the partial molar volume of NH_2X and almost equals the partial molar volume of the $Co(NH_3)_4(NH_2X)OH^{2+}$ species. These results underline the validity of the S_N1CB mechanism and demonstrate the additivity properties of the partial molar volumes of five- and six-coordinate species of similar charge.

Introduction

Base hydrolysis reactions of pentaamminecobalt(III) complexes are generally accepted to proceed according to a S_N1CB mechanism in which a five-coordinate intermediate, $Co(NH_3)_4NH_2^{2+}$, is formed from the conjugate base species, which rapidly reacts with water or any other competing nucleophile to produce the hydrolysis products.[2-7] Such reactions are orders of magnitude faster than the corresponding aquation or ligand substitution processes and are, therefore, of general interest. However, there is still controversy over the question of a discrete reduced coordination number intermediate and the nature of the hydrolysis mechanism.[7,8] It has been proposed that an E2 mechanism is operative in which abstraction of an amine proton and loss of the leaving group are concerted processes; i.e., no six-coordinate conjugate base species are formed[9,10] (see Discussion). Subsequently, Sargeson and co-workers[11,12] have in detailed studies once again confirmed the applicability of the S_N1CB mechanism.

We have studied the base hydrolysis reactions of pentaamminecobalt(III) complexes in a different way by constructing reaction volume profiles from partial molar volume and volume of activation data.[13] This has enabled us to estimate the partial molar volume of the suggested five-coordinate intermediate and to demonstrate that its value is independent of the nature (size and charge) of the leaving group. Furthermore, the difference between the overall reaction volume for base hydrolysis and the volume of activation represents the volume change for the final step in this mechanism in which $Co(NH_3)_4NH_2^{2+}$ reacts with water to produce $Co(NH_3)_5OH^{2+}$ and was also found to be independent of the nature of the leaving group.[13] These observations further supported the operation of the S_N1CB mechanism.

Our ability to estimate the partial molar volume of a five-coordinate intermediate[13] has contributed to solving the longstanding discrepancy concerning the partial molar volume of such species.[14-19] In the present study we have investigated the base hydrolysis reactions of a series of monoalkyl-substituted chloropentaamminecobalt(III) complexes[20] to determine the effect of ligand size on the partial molar volume of the five-coordinate intermediate. The reported volume profiles enable interesting comparisons with similar data for related base hydrolysis and aquation reactions.

Experimental Section

The following complexes were prepared by Piriz Mac-Coll[1b] and supplied by Prof. S. Balt (Free University of Amsterdam, The Netherlands), originating from their earlier investigation:[20] *cis*-$[Co(NH_3)_4(CH_3NH_2)Cl](ClO_4)_2$; *trans*-$[Co(NH_3)_4(CH_3NH_2)Cl](ClO_4)_2$; *trans*-$[Co(NH_3)_4(C_2H_5NH_2)Cl](ClO_4)_2$; *cis*-$[Co(NH_3)_4(n\text{-}C_3H_7NH_2)Cl](ClO_4)_2$; *trans*-$[Co(NH_3)_4(n\text{-}C_3H_7NH_2)Cl](ClO_4)_2$; *trans*-$[Co(NH_3)_4(n\text{-}C_4H_9NH_2)Cl](ClO_4)_2$; *trans*-$[Co(NH_3)_4(i\text{-}C_4H_9NH_2)Cl](ClO_4)_2$. UV–vis, IR, and ^1H NMR spectral data have been reported before.[20]

In the dilatometric studies (base hydrolysis and subsequent neutralization) a Carlsberg dilatometer was used and the procedures have been

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(1) (a) On leave from the Department of Chemistry, Ehime University, Matsuyama, Ehime 790, Japan. (b) On leave from the Facultad de Quimica, Universidad de la Republica, Montevideo, Uruguay, at the Free University of Amsterdam, The Netherlands.

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

complex	pressure, MPa	10^2k_{obsd},[b] s^{-1}	$\Delta V^{\ddagger}_{exptl}$, $cm^3\ mol^{-1}$
cis-$Co(NH_3)_4(CH_3NH_2)Cl^{2+}$	5	16.7 ± 0.4	29.4 ± 0.4
	25	13.3 ± 0.7	
	50	10.0 ± 0.4	
	75	7.2 ± 0.5	
	100	5.3 ± 0.2	
trans-$Co(NH_3)_4(CH_3NH_2)Cl^{2+}$	5	6.3 ± 0.4	28.6 ± 1.3
	25	5.4 ± 0.2	
	50	4.0 ± 0.3	
	75	2.8 ± 0.1	
	100	2.2 ± 0.1	
trans-$Co(NH_3)_4(C_2H_5NH_2)Cl^{2+}$	5	6.1 ± 0.2	28.3 ± 1.4
	25	5.1 ± 0.2	
	50	3.6 ± 0.2	
	75	2.7 ± 0.2	
	100	2.1 ± 0.1	
cis-$Co(NH_3)_4(n\text{-}C_3H_7NH_2)Cl^{2+}$	5	11.2 ± 0.4	26.4 ± 1.5
	25	8.6 ± 0.4	
	50	6.4 ± 0.4	
	75	4.9 ± 0.3	
	100	4.0 ± 0.1	
trans-$Co(NH_3)_4(n\text{-}C_3H_7NH_2)Cl^{2+}$	5	4.0 ± 0.2	29.9 ± 1.2
	25	3.3 ± 0.3	
	50	2.3 ± 0.1	
	75	1.66 ± 0.06	
	100	1.30 ± 0.04	
trans-$Co(NH_3)_4(n\text{-}C_4H_9NH_2)Cl^{2+}$	5	5.8 ± 0.2	28.7 ± 0.7
	25	4.5 ± 0.4	
	50	3.3 ± 0.1	
	75	2.5 ± 0.1	
	100	1.92 ± 0.04	
trans-$Co(NH_3)_4(i\text{-}C_4H_9NH_2)Cl^{2+}$	5	7.4 ± 0.2	28.5 ± 1.2
	25	6.1 ± 0.2	
	50	4.8 ± 0.4	
	75	3.4 ± 0.3	
	100	2.5 ± 0.1	

[a] $[Co(III)] = 1 \times 10^{-3}$ M; $[OH^-] = 1 \times 10^{-2}$ M; ionic strength = 0.013 M; wavelength = 290 nm. [b] Mean value of at least six kinetic runs.

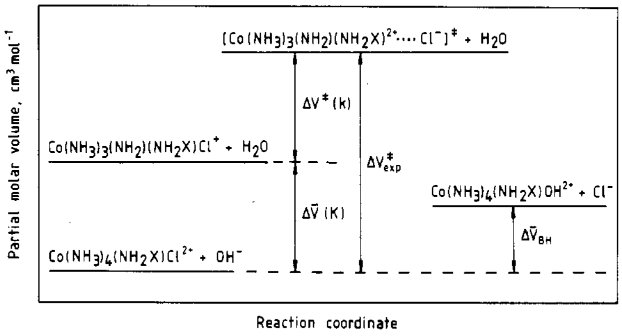

Figure 1. Volume profile for the overall reaction (see Scheme I) $Co(NH_3)_4(NH_2X)Cl^{2+} + OH^- \rightarrow Co(NH_3)_4(NH_2X)OH^{2+} + Cl^-$.

outlined elsewhere.[13,21] Kinetic measurements were performed on a thermostated (±0.1 °C) high-pressure stopped-flow instrument.[22] The hydrolysis reactions were studied under pseudo-first-order conditions, and the observed rate constants, k_{obsd}, were calculated in the usual way by plotting $\ln(A_t - A_\infty)$ vs. time, where A_t and A_∞ are the absorbances at time t and infinity, respectively. The first-order plots were linear for at least 3 half-lives of the reaction when the experimentally obtained infinity absorbance value was employed. These calculations were performed with the aid of an on-line microprocessor, through which at least 100 data points were used for each kinetic run. Chemicals of analytical reagent grade and doubly distilled water were used throughout this study.

Results and Discussion

A detailed kinetic and spectroscopic study[20] of the aquation and base hydrolysis reactions of the series of complexes of the type $Co(NH_3)_4(NH_2X)Cl^{2+}$ at ambient pressure revealed some important trends. The aquation reaction is 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. The rate data are such[20] that at $[OH^-] = 0.01$ M the k_2 path overrules the spontaneous aquation reaction completely and eq 1 simplifies to $k_{obsd} = k_2[OH^-]$. Throughout the series of complexes the cis species are stereoretentive, whereas the trans complexes produce up to 10% of the cis hydroxo product during base hydrolysis.[20] Competition experiments[20] once again underlined the validity of the S_N1CB mechanism, which can be summarized as in (2). At this point

$$Co(NH_3)_4(NH_2X)Cl^{2+} + OH^- \underset{}{\overset{K}{\rightleftharpoons}} Co(NH_3)_3(NH_2)(NH_2X)Cl^+ + H_2O$$

$$Co(NH_3)_3(NH_2)(NH_2X)Cl^+ \xrightarrow{k} Co(NH_3)_3(NH_2)(NH_2X)^{2+} + Cl^-$$

$$Co(NH_3)_3(NH_2)(NH_2X)^{2+} + H_2O \xrightarrow{\text{fast}} Co(NH_3)_4(NH_2X)OH^{2+} \qquad (2)$$

X: cis, CH_3; trans, CH_3; trans, C_2H_5; cis, n-C_3H_7; trans, n-C_3H_7; trans, n-C_4H_9; trans, i-C_4H_9

it is important to note that the results of the present investigation will first be treated in terms of the accepted S_N1CB mechanism, before other possible mechanisms will be considered.

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 simplifies to $k_{obsd} = kK[OH^-]$ since no significant curvature

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Table II. Partial Molar, Reaction, and Activation Volumes for a Series of Base Hydrolysis Reactions of the Type[a] $Co(NH_3)_4(NH_2X)Cl^{2+} + OH^- \rightarrow Co(NH_3)_4(NH_2X)OH^{2+} + Cl^-$

X	$\bar{V}_{NH_2X}$[b]	$\bar{V}_{RHCl}$[c]	ΔV^{*}_{exptl}[d]	$\Delta \bar{V}_{BH}$[e]	$\Delta V^{*}_{exptl} - \Delta \bar{V}_{BH}$	$\bar{V}_R$[f]	$\bar{V}_{RHOH}$[g]	$\Delta \bar{V}_N$[h]	$\bar{V}_{RHOH_2}$[i]
H[j]	24.8	83.5	33.0	9.9	23.1	76.6	71.6	−3.4[l]	63.7
cis, CH_3	41.7	96.8	29.4	9.8	19.6	86.3	84.8	−1.7	78.6
trans, CH_3	41.7	93.8	28.6	10.4	18.2	82.5	82.4	−3.8	74.1
trans, C_2H_5	58.4	114.8	28.3	10.1	18.2	103.2	103.1	−3.2	95.4
cis, *n*-C_3H_7	74.1	129.8	26.4	11.4	15.0	116.3	119.4	−3.0	111.9
trans, *n*-C_3H_7	74.1	124.8	29.9	(11.4)[k]	18.5	114.8	114.4	(−3.0)[k]	106.9
trans, *n*-C_4H_9	89.8	141.8	28.7	11.9	16.8	130.6	131.9	−1.4	126.0
trans, *i*-C_4H_9	89.5	143.8	28.5	12.0	16.5	132.4	134.0	−0.9	128.6

[a] Temp = 25 °C, all volume quantities in $cm^3\ mol^{-1}$; abbreviation RH = $Co(NH_3)_4(NH_2X)^{3+}$. [b] Data taken from ref 20. [c] Estimated from the reported molar volume[20] by using $\bar{V}(ClO_4^-) = 48.6$ on the assumption that $\bar{V}(H^+) = -4.5$.[23] [d] Data taken from Table I. [e] Base hydrolysis reaction volume determined dilatometrically—see Discussion. [f] Calculated by using eq 6, R = $Co(NH_3)_4(NH_2)(NH_2X)^{2+}$. [g] Calculated by using eq 7. [h] Neutralization reaction volume determined dilatometrically—see Discussion. [i] Calculated by using eq 8. [j] Data taken from ref 13 at ionic strength 0.01 M. [k] Not measured due to scarcity of complex, assumed to be equal to that for the cis complex. [l] Data taken from ref 24.

in plots of k_{obsd} vs. $[OH^-]$ was observed, indicating that $1 + K[OH^-] \sim 1$. It follows that $k_2 = kK$, 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.

Values of k_2 at ambient pressure found in this study are in close agreement with those reported before,[20] especially when the difference in ionic strength is taken into account. The pressure dependence of k_{obsd} ($=k_2[OH^-]$) is summarized in Table I. Plots of ln k_{obsd} vs. pressure are linear within the experimental error limits for all the studied systems up to 100 MPa. The volumes of activation were obtained from eq 4, and no correction for the

$$\Delta V^{*}_{exptl} = -RT\,(\partial \ln k_{obsd}/\partial P)_T \qquad (4)$$

pressure dependence of the activity coefficients was introduced since this amounts to 0.6 $cm^3\ mol^{-1}$ under the present conditions.[13] The values of ΔV^{*}_{exptl}, included in Table I, are all large and positive and remarkably constant. Since $k_{obsd} = kK[OH^-]$ under the present conditions, it follows that ΔV^{*}_{exptl} is a composite of the contributions of the effect of pressure on k and K according to eq 5. This is illustrated in the schematic volume profile for such

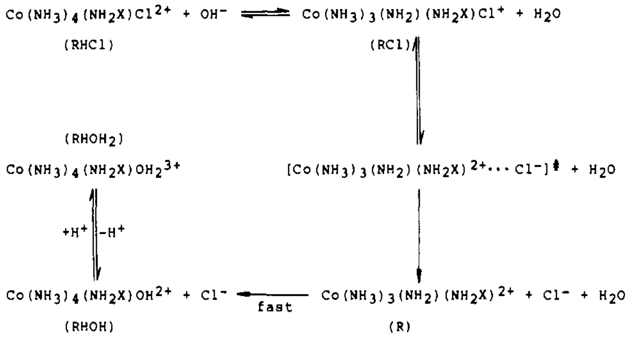
$$\Delta V^{*}_{exptl} = \Delta \bar{V}(K) + \Delta V^{*}(k) \qquad (5)$$

base hydrolysis reactions given in Figure 1. The transition state is written in such a way as to indicate that Cl^- is the leaving group, for which the degree of bond breakage will depend on the location of the transition state (early or late) along the reaction coordinate.

The overall reaction volume for base hydrolysis, $\Delta \bar{V}_{BH}$, was determined dilatometrically by mixing the $Co(NH_3)_4(NH_2X)Cl^{2+}$ species with equimolar OH^- and allowing 1 h for the reaction to go to completion at 25 °C. The values of $\Delta \bar{V}_{BH}$ were corrected for changes in ionic strength during the mixing of the reactant solutions as described before.[13] The data in Table II demonstrate that $\Delta \bar{V}_{BH}$ is approximately one-third of the value of ΔV^{*}_{exptl} and almost constant for all the complexes. It was pointed out before[13] that ΔV^{*}_{exptl} and $\Delta \bar{V}_{BH}$ should depend significantly on the nature of the leaving group, i.e. especially its charge and size. This was indeed shown to be the case for a series of leaving groups, viz. F^-, Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, and Me_2SO.[13] However, in the present case chloride is the leaving group in all the investigated systems, and the almost constant values observed for ΔV^{*}_{exptl} and $\Delta \bar{V}_{BH}$ therefore fit in with the expected tendency. The ΔV^{*}_{exptl} value for the base hydrolysis of $Co(NH_3)_5Cl^{2+}$, the first entry in Table II, i.e. where X = H, was taken from our earlier study[13] and seems to be slightly larger than values for the rest of the series (see further discussion).

A further consequence of the suggested mechanism and the associated volume profile is that $\Delta V^{*}_{exptl} - \Delta \bar{V}_{BH}$ should be independent of the substituent X since it presents the volume change associated with the reaction of the five-coordinate intermediate with water (last step in (2)). The data in Table II support this expected trend, especially when the experimental error limits on both ΔV^{*}_{exptl} and $\Delta \bar{V}_{BH}$ (of ca. 1-2 $cm^3\ mol^{-1}$) are taken into account. The values found in the present study are slightly lower than that reported for the $Co(NH_3)_5Cl^{2+}$ species before.[13] Nevertheless, the average value of 18.2 ± 2.4 for all the $\Delta V^{*}_{exptl} - \Delta \bar{V}_{BH}$ entries in Table II is in close agreement with the value of 20.6 ± 3.1 $cm^3\ mol^{-1}$ found in our study for a series of different leaving groups.[13] This volume decrease (Figure 1) almost equals the partial molar volume of water, demonstrating that a water molecule is completely absorbed on a volume basis during the final step of the base hydrolysis process (see further discussion).

Scheme I



The data in Table II enable us to calculate the partial molar volume of the five-coordinate intermediate, $Co(NH_3)_3(NH_2)(NH_2X)^{2+}$, abbreviated by R in Scheme I. In this treatment it is assumed that the dissociative reaction of the conjugate base species RCl has a late ("productlike") transition state such that $\bar{V}_{*} \approx \bar{V}_R + \bar{V}_{Cl}$. Equation 6 can then be formulated, and the calculated values of $\bar{V}_R$ are included in Table II.

$$\begin{aligned}\Delta V^{*}_{exptl} &= \bar{V}_{*} + \bar{V}_{H_2O} - \bar{V}_{RHCl} - \bar{V}_{OH}\\ &\approx \bar{V}_R + \bar{V}_{Cl} + \bar{V}_{H_2O} - \bar{V}_{RHCl} - \bar{V}_{OH}\end{aligned}$$

Thus

$$\begin{aligned}\bar{V}_R &= \Delta V^{*}_{exptl} + \bar{V}_{RHCl} + \bar{V}_{OH} - \bar{V}_{Cl} - \bar{V}_{H_2O}\\ &= \Delta V^{*}_{exptl} + \bar{V}_{RHCl} - 39.9 \qquad (6)\end{aligned}$$

The partial molar volumes substituted in eq 6 have the values $\bar{V}_{OH} = 0.5$, $\bar{V}_{Cl} = 22.3$, and $\bar{V}_{H_2O} = 18.1$; all are based on $\bar{V}(H^+) = -4.5\ cm^3\ mol^{-1}$.[23] The values of $\bar{V}_R$ in Table II show a systematic increase with increasing size of X as reflected by the values of $\bar{V}_{NH_2X}$. In fact a good linear correlation between $\bar{V}_R$ and $\bar{V}_{NH_2X}$ is found (Figure 2) with a slope of 0.90 ± 0.05. The $\bar{V}_R$ value for the $Co(NH_3)_5Cl^{2+}$ species seems to be on the high side since a significantly better correlation with a slope of 0.97 is found when this data point is omitted. An average value of 71 ± 4 $cm^3\ mol^{-1}$ was reported before[13] for a series of complexes in which X = H in the five-coordinate intermediate, thus indicating that the quoted value for the chloro complex may be too high. On the other hand, the introduction of a substituent on the amine ligand may influence

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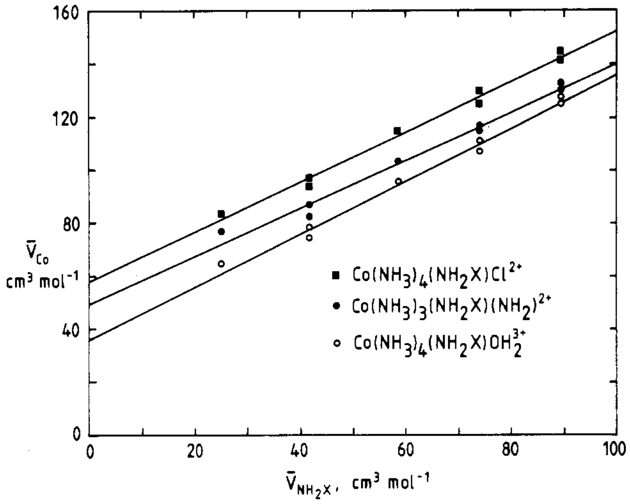

Figure 2. Plots of $\bar{V}_R$, $\bar{V}_{RHCl}$, and $\bar{V}_{RHOH_2}$ vs. $\bar{V}_{NH_2X}$ for the data in Table II.

the geometry of the five-coordinate intermediate in such a way that the unsubstituted species (X = H) does not fit the simple linear correlation. Lawrance[18] reported similar partial molar volume correlations for complexes of the type $Co(NH_3)_5X^{(3-n)+}$ as a function of X^{n-}.

With the aid of the values for $\Delta\bar{V}_{BH}$ the partial molar volume of the hydroxo products, $Co(NH_3)_4(NH_2X)OH^{2+}$, could be estimated by using eq 7. Surprising is the excellent correlation

$$\begin{aligned}\bar{V}_{RHOH} &= \Delta\bar{V}_{BH} + \bar{V}_{OH} + \bar{V}_{RHCl} - \bar{V}_{Cl} \\ &= \Delta\bar{V}_{BH} + \bar{V}_{RHCl} - 21.8 \qquad (7)\end{aligned}$$

between $\bar{V}_{RHOH}$ and $\bar{V}_R$ in Table II. Only in the case of the $Co(NH_3)_5Cl^{2+}$ species is $\bar{V}_R$ slightly larger, as referred to before. This correlation clearly demonstrates that the $Co(NH_3)_3(NH_2)(NH_2X)^{2+}$ and $Co(NH_3)_4(NH_2X)OH^{2+}$ species have approximately the same volume, in agreement with our earlier conclusion for the unsubstituted species (X = H).[13] This finding is in good agreement with arguments in favor of $\bar{V}(Co(NH_3)_5^{3+}) = \bar{V}(Co(NH_3)_6^{3+})$.[16,19] However, it is generally known that the additivity rule applies to the partial molar volume of octahedral complexes (see further discussion),[18] which means that the volume of the six-coordinate species will vary linearly with the volume of the sixth ligand. It follows that the above equality only holds for those cases where the sixth ligand is small enough like water and NH_3 to enter the sphere of the five-coordinate species without increasing its size significantly. This equality will therefore not hold for larger ligands.[18] Furthermore, the excellent agreement between the partial molar volumes of $Co(NH_3)_3(NH_2)(NH_2X)^{2+}$ and $Co(NH_3)_4(NH_2X)OH^{2+}$ clearly demonstrates how the solvent molecule completely disappears on a volume basis during the final step of the base hydrolysis process. In this respect it must be kept in mind that the water molecule coordinates as H^+ and OH^-, for which the partial molar volumes are −4.5 and 0.5 cm³ mol⁻¹, respectively,[23] i.e. close to zero, and account for the observed equality. It follows that $\Delta V^{\ddagger} - \Delta\bar{V}_{BH}$ approximately equals the partial molar volume of water. This volume collapse is therefore due to strong electrostriction effects during the ionization of the solvent molecule to coordinate as H^+ and OH^- during the final step, since the corresponding volume of ionization is −22.1 cm³ mol⁻¹.[13]

Additional dilatometric experiments were performed on the neutralization of $Co(NH_3)_4(NH_2X)OH^{2+}$ to produce $Co(NH_3)_4(NH_2X)OH_2^{3+}$. The corresponding volumes of neutralization, $\Delta\bar{V}_N$, recorded in Table II, are once again almost constant and enable the calculation of $\bar{V}_{RHOH_2}$ with the aid of eq 8. These

$$\begin{aligned}\bar{V}_{RHOH_2} &= \Delta\bar{V}_N + \Delta\bar{V}_{BH} + \bar{V}_{RHCl} + \bar{V}_{OH} + \bar{V}_H - \bar{V}_{Cl} \\ &= \Delta\bar{V}_N + \Delta\bar{V}_{BH} + \bar{V}_{RHCl} - 26.3 \qquad (8)\end{aligned}$$

values are on the average 7.0 ± 1.1 cm³ mol⁻¹ smaller than the partial molar volumes of the corresponding hydroxo complexes, which can be explained in terms of an increase in electrostriction in going from a 2+ to a 3+ complex ion. Both $\bar{V}_{RHCl}$ and $\bar{V}_{RHOH_2}$ exhibit excellent correlations with $\bar{V}_{NH_2X}$ (Figure 2), for which the slopes are 0.94 and 1.00, respectively. The plot of $\bar{V}_{RHOH}$ vs. $\bar{V}_{NH_2X}$ is very similar to that for $\bar{V}_R$ in Figure 2, since $\bar{V}_{RHOH}$ and $\bar{V}_R$ are almost equal. It follows from the above volume equation calculations and correlations that partial molar volumes indeed underline the additivity rule referred to before,[18-20] not only for stable six-coordinate species but also for five-coordinate intermediates. Furthermore, they also underline the general validity of the suggested S_N1CB mechanism and the corresponding volume profile (Figure 1).

The almost constant value of $\Delta V^{\ddagger}_{exptl}$ in Table I results in a constant value for $\Delta V^{\ddagger}(k)$, since $\Delta\bar{V}(K)$ can be estimated to be 22 cm³ mol⁻¹ on the basis of a series of neutralization volume data.[13,24] The average value of 6.5 ± 1.1 cm³ mol⁻¹ for $\Delta V^{\ddagger}(k)$ is the sum of an intrinsic volume increase due to Co–Cl bond rupture and a solvational volume decrease due to charge creation, viz. from 1+ to 2+ and 1− species. Since chloride is the leaving group in all cases, the constancy of $\Delta V^{\ddagger}_{exptl}$, and therefore of $\Delta V^{\ddagger}(k)$, is not suprising. The average value of $\Delta V^{\ddagger}(k)$ is significantly smaller than the value of 11.0 cm³ mol⁻¹ found for the unsubstituted chloro complex.[13] The decrease in $\Delta V^{\ddagger}(k)$, and consequently in $\Delta V^{\ddagger}_{exptl}$ as mentioned above, is in line with a limiting D mechanism in which the nonlabile ligand bonds are expected to shrink slightly, the effect depending on the size of the ligands. Although $\Delta V^{\ddagger}(k)$ exhibits no specific trend with the size of X, the introduction of a substituent on one amine ligand may be the overruling effect. An opposite trend was reported for the aquation of $Co(NH_2CH_3)_5Cl^{2+}$, *trans*-$Co(NH_3)_4(NH_2CH_3)Cl^{2+}$ and $Co(NH_3)_5Cl^{2+}$, for which $\Delta V^{\ddagger}$ = −2.3 ± 0.4, −4.6 ± 0.5, and −9.9 ± 0.5 cm³ mol⁻¹, respectively.[25] Introducing one methyl substituent increases the volume of activation substantially, which can be interpreted in terms of expansion of the nonlabile ligand bonds during the dissociation of chloride and the intrusion of a water molecule in the suggested I_d mechanism. However, the role of electrostriction, and its dependence on the size of the nonlabile ligands, cannot be ruled out completely and should always be considered in these cases where we are dealing with the creation of charges.[25]

Finally, it is instructive to predict $\Delta V^{\ddagger}$ values for alternative possible base hydrolysis mechanisms. For a limiting associative mechanism (S_N2), bond formation between CoN_5Cl^{2+} and OH^- will result in a negative intrinsic contribution accompanied by a positive contribution due to a decrease in electrostriction resulting from charge neutralization. The overall $\Delta V^{\ddagger}$ value is, therefore, expected to be small with a maximum value of ca. +10 cm³ mol⁻¹ expected for charge neutralization (see further discussion). In the case of a S_N2CB mechanism, $\Delta V^{\ddagger}_{exptl}$ will also be given by the expression in (5), where $\Delta V^{\ddagger}(k)$ will represent the contribution for the associative attack of a water molecule onto the conjugate base species. The latter contribution is expected to be approximately −10 cm³ mol⁻¹,[26-28] such that $\Delta V^{\ddagger}_{exptl} \sim +12$ cm³ mol⁻¹, which is significantly smaller than found in this and our earlier study.[13] Alternatively, one could consider an interchange mechanism as summarized in (9), for which $k_{obsd} = k_iQ[OH^-]/(1 + Q[OH^-])$, simplifying to $k_{obsd} = k_iQ[OH^-]$ under the present experimental conditions. It follows that $\Delta V^{\ddagger}_{exptl} = \Delta\bar{V}(Q) + \Delta V^{\ddagger}(k_i)$: $\Delta\bar{V}(Q)$ should be very similar to $\Delta\bar{V}$ recently measured[29]

$$CoN_5Cl^{2+} + OH^- \overset{Q}{\rightleftharpoons} \{CoN_5Cl^{2+}\cdot OH^-\} \xrightarrow{k_i} CoN_5OH^{2+} + Cl^- \qquad (9)$$

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for the addition of OH^- to the hexafluoroacetylacetonato (hfac) ligand in $Co(en)_2(hfac)^{2+}$ to produce $Co(en)_2(hfac{\cdot}OH)^+$; viz., $\Delta\bar{V} = +10.7$ cm^3 mol^{-1}. $\Delta V^*(k_i)$ is usually small for an interchange step (I_a or I_d).[30] The overall $\Delta V^*_{\mathrm{exptl}}$ value can again not be as large as found in this study. A final possibility is the recently suggested E2 mechanism,[9,10] which consists of a concerted process for the formation of the five-coordinate intermediate, thus basically S_N1, in which deprotonation immediately leads to loss of Cl^- as indicated in (10). It is realistic to expect $\Delta V^*_{\mathrm{exptl}}$ for this process

$$Co(NH_3)_4(NH_2X)Cl^{2+} + OH^- \rightarrow Co(NH_3)_3(NH_2)(NH_2X)^{2+} + Cl^- + H_2O \quad (10)$$

to be smaller than $\Delta\bar{V}(K)$, since the latter quantity also contains a positive contribution resulting from the recombination of water with the conjugate base species (see (2)). Thus we conclude that the significantly higher $\Delta V^*_{\mathrm{exptl}}$ value found in this study can only be interpreted in terms of the suggested S_N1CB mechanism.

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Registry No. *cis*-$Co(NH_3)_4(CH_3NH_2)Cl^{2+}$, 91383-91-4; *trans*-$Co(NH_3)_4(CH_3NH_2)Cl^{2+}$, 36527-86-3; *trans*-$Co(NH_3)_4(C_2H_5NH_2)Cl^{2+}$, 91321-37-8; *cis*-$Co(NH_3)_4$(*n*-$C_3H_7NH_2)Cl^{2+}$, 91321-39-0; *trans*-$Co(NH_3)_4$(*n*-$C_3H_7NH_2)Cl^{2+}$, 91384-21-3; *trans*-$Co(NH_3)_4$(*n*-$C_4H_9NH_2)Cl^{2+}$, 91321-41-4; *trans*-$Co(NH_3)_4$(*i*-$C_4H_9NH_2)Cl^{2+}$, 91321-43-6.

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Contribution from the Dipartimento di Chimica Generale,
Università di Pavia, 27100 Pavia, Italy

Thermodynamic Aspects of the Nickel(III/II) Redox Change in Polyaza Macrocyclic Complexes

Luigi Fabbrizzi,* Angelo Perotti, Antonella Profumo, and Teresa Soldi

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The reaction entropies $\Delta S°_{rc}$ of the Ni^{III}/Ni^{II} redox couple for some polyaza macrocyclic complexes in aqueous solution have been determined by measuring $E_{1/2}(Ni^{III}/Ni^{II})$ values through voltammetry experiments at varying temperatures using a nonisothermal cell. $\Delta S°_{rc}$ values are in any case positive, and their magnitudes decrease with the increasing number of nitrogen atoms of the coordinating system (from four to six): this is ascribed to the release of water molecules from the coordination sphere and/or the hydration sphere during the Ni^{III}/Ni^{II} redox change. The presence of negative charges on the coordinating system (deprotonated amido or carboxylate groups) makes the $\Delta S°_{rc}(Ni^{III}/Ni^{II})$ values substantially less positive. Redox equilibria of the type $M^{III}L_1 + M^{II}L_2 \rightleftharpoons M^{II}L_1 + M^{III}L_2$ have been considered and the corresponding values of the enthalpy term ($\Delta H°$) evaluated for chosen pairs of ligating systems L_1 and L_2. Inspection of the above values indicates that the enthalpy contribution (which includes bond energy terms) favors the attainment of trivalent nickel along the sequence N(amine) > N(deprotonated amido groups) $\simeq$ $-COO^-$ and that a square arrangement of four nitrogen atoms (cyclam) is the very most favorable coordinative situation (from the enthalpic point of view).

Introduction

Transition-metal complexes very often display one-electron or multielectron redox activity to give species that are stable in solution at least on the time scale of electrochemical perturbation techniques such as cyclic voltammetry. As a consequence, a lot of $E_{1/2}$ values, associated to redox changes of metal complexes, have been determined by conventional voltammetric methods. It should be noted that in the case of electrochemical reversibility the $E_{1/2}$ value approaches the standard electrode potential value, $E°$; thus, it has a thermodynamic significance. In general, for a given class of coordination compounds displaying redox reactivity, the trend of $E_{1/2}$ values has been interpreted in terms of bonding quantities, such as ligand field stabilization effects, intensity of the coordinative interactions, etc. However, one could argue that above quantities are all enthalpy terms, whereas the electrode potential $E°$ is proportional to the $\Delta G°$ value associated to the redox change and therefore it should be more correctly considered as "made" by two distinct contributions, enthalpic and entropic in nature. Whereas the $\Delta H°$ term is expected to include bonding quantities, i.e. the energies of the metal-donor atom interactions in the oxidized and in the reduced species, the $\Delta S°$ term should be mainly related to the solute–solvent interactions and to the order/disorder variations associated to the redox change.

In 1979 Weaver[1] pioneered the use of the voltammetric investigation at varying temperatures using a nonisothermal cell for the determination of $\Delta S°_{rc}$, the difference of the standard entropies of the reduced and oxidized forms, $S°_{red} - S°_{ox}$, for simple metal complexes in aqueous solution. Since then, a lot of papers reporting entropy data on coordination compounds of varying nature and complexity have appeared.[2]

We report here a temperature-dependent electrochemical study using a nonisothermal cell on the Ni^{III}/Ni^{II} redox change for metal complexes with polyaza macrocycles, a topic to which we have devoted some interest in past years.[3]

Trapping of the metal center by a cyclic coordinating framework permits the attainment of the usually unstable Ni^{III} oxidation state. The solution stability of the trivalent complex, relative to the divalent one, is expressed by the value of the $E_{1/2}(Ni^{III}/Ni^{II})$, a quantity that can be modulated over a substantial range of potentials through structural modifications on the ligand (nature and number of the donor atoms,[4] size of the macrocyclic cavity,[5] degree of unsaturation,[6] presence of substituents on the nitrogen atoms[7] or on the carbon backbone).[8]

We wish to report here a temperature-dependent electrochemical investigation on the Ni^{III}/Ni^{II} redox couple in aqueous solution for some fully saturated polyaza systems of varying denticity: the

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