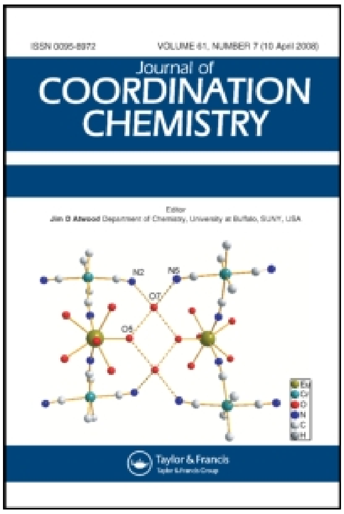

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A KINETIC STUDY OF ACID DISSOCIATION AND SOLVOLYSIS III. The second coordination sphere in liquid ammonia

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A KINETIC STUDY OF ACID DISSOCIATION AND SOLVOLYSIS

III. The second coordination sphere in liquid ammonia

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Key words: Cobalt(III); Ammonia, liquid; Conjugate base mechanism; Base hydrolysis; Outer sphere; Second coordination sphere; Chloropentaamminecobalt(III) perchlorate; Cis-chloroamminebis-(ethylenediamine)cobalt(III) perchlorate.

The base-catalyzed ammonolysis of $Co(NH_3)_5Cl \cdot (ClO_4)_2$ has been studied under circumstances that both $Co(NH_3)_4NH_2Cl^+$ and $Co(NH_3)_4NH_2Cl \cdot ClO_4$, the outer sphere complexes of the conjugate base derived from the pentaammine, are present in comparable quantities. The outer sphere complexes have nearly the same reactivity. Cis-$Co(en)_2NH_3Cl^{2+}$ in liquid ammonia forms the $Co(en)_2(NH_3)_2{}^{3+}$ via the conjugate base mechanism under retention of configuration. The activation parameters, in connection with rearrangements in the first and the second coordination sphere, are discussed.

INTRODUCTION

In the previous paper of this series[1] evidence has been presented to show that the complexes $[Co(NH_3)_5X](ClO_4)_2$, with $X = Cl$, Br, I, dissolved in liquid ammonia, react to form the hexaammine by way of the S_N1CB mechanism.[2] The reaction rates were found to be much larger than those reported for the corresponding base hydrolysis reactions in water; a detailed comparison between the two solvents indicated the difference in protonation enthalpy of the two solvents to be the determining factor in favouring the rates in ammonia over those in aqueous solution. Rather unexpectedly the high reactivity of the conjugate base compared to the undissociated pentaammine was found to be mainly due to an entropy factor, so that, at least in the cases studied, a labilization of the bond to the leaving group in the conjugate base is not the decisive factor, contrary to what is generally assumed.[2,3]

The second coordination sphere plays an important part in base hydrolysis generally.[3] It has also been shown to be an important factor in the reaction of cobalt(III) complexes with ammonia in aqueous solution.[4] Therefore we have tried to shed light on the mechanism of solvolysis in liquid ammonia and on general base hydrolysis by studying the role of the second coordination sphere in two independent studies:

1. The difference in rate between differently charged outer sphere complexes. For this experiment the $Co(NH_3)_5Cl^{2+}$ ion has been chosen, because within the experimental error this complex has the same value for the acid dissociation constant as the hexaammine,[1,5] so the kinetic analysis is not complicated by a change in acidity during the reaction.
2. The kinetics of solvolysis of a complex, reacting with retention of configuration in the first sphere. Cis-$Co(en)_2NH_3Cl^{2+}$ was found to fit this demand.

EXPERIMENTAL PART

General

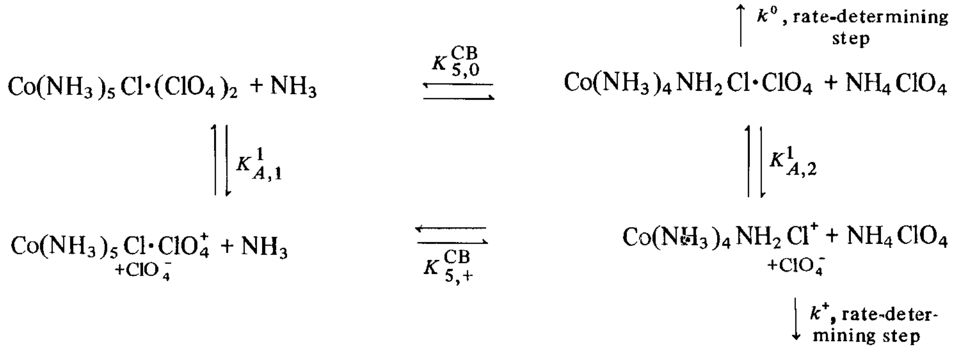
Chloropentaammine perchlorate has been prepared according to Linhard and Weigel.[6] Cis-chloroamminebis(ethylenediamine)cobalt(III) chloride was prepared by a slight modification of Werner's method:[7] it was found that keeping the temperature below 0°C in the conversion of trans-dichlorobis(ethylenediamine)-cobalt(III) chloride to the cis-chloroammine complex reduced the concentration of acidic impurities interfering with the kinetic experiments. As neither $Co(en)_2NH_3Cl(ClO_4)_2$ nor the nitrate[8] could be obtained sufficiently pure for the kinetic experiments, in the kinetic runs the chloride was used instead under addition of an excess of potassium perchlorate.

The complexes were obtained acid free by performing the final recrystallization from a borax containing solution. The purification of the other chemicals used and the experimental set-up for following the reactions photometrically and for measuring the conductivity of the solutions have already been described.[1,9,10]

RESULTS

1. Reactivity of Differently Charged Outer Sphere Complexes of the $Co(NH_3)_5Cl^{2+}$ Cation

The solvolysis reaction has been shown to proceed via the conjugate base. In the complex concentrations used ($>3 \times 10^{-3}$ m) only univalent ionic dissociation has to be considered.[9] This means that the rate-determining reactive species may be either a neutral or a positively charged complex. Consequently the following reaction scheme comes up:



$$\begin{tikzcd}
 & {} \\
Co(NH_3)_5Cl\cdot(ClO_4)_2 + NH_3 \arrow[r, shift left, "K^{CB}_{5,0}"] \arrow[d, shift left, "K^1_{A,1}"] & Co(NH_3)_4NH_2Cl\cdot ClO_4 + NH_4ClO_4 \arrow[l, shift left] \arrow[u, "k^0\text{, rate-determining step}"'] \arrow[d, shift left, "K^1_{A,2}"] \\
Co(NH_3)_5Cl\cdot ClO_4^+ + NH_3 + ClO_4^- \arrow[u, shift left] \arrow[r, shift left] & Co(NH_3)_4NH_2Cl^+ + NH_4ClO_4 + ClO_4^- \arrow[l, shift left, "K^{CB}_{5,+}"] \arrow[u, shift left] \arrow[d, "k^+\text{, rate-determining step}"] \\
 & {}
\end{tikzcd}$$

Kinetic Runs

1. The experiments designed to reveal a difference in rate between differently charged outer sphere complexes have been performed with chloropentaammine-cobalt(III) perchlorate without the addition of acid, but at varying ionic strength, realized by varying either the concentration of the cobalt complex without adding a neutral electrolyte, or by adding potassium perchlorate as neutral electrolyte at a constant concentration of the complex. Kinetic runs were performed at four different temperatures (accuracy 0.1°C). In all runs the measured absorbance (at 18,800 cm^{-1}) was found to obey a first order rate law, with a fitting error of less than 2%.

2. For the chloroamminebis(ethylenediamine) cobalt(III) complex kinetic runs were performed at constant ionic medium (0.2 m = 0.2 mol. (kg solvent)$^{-1}$), according to common use further denoted as ionic strength, and either at constant cobalt concentration (0.01 m) and varying acid concentration (ammonium perchlorate, (1-5) $\times 10^{-3}$ m) or without the addition of acid at varying cobalt concentration: at each of 4 temperatures cobalt concentrations of (5,7,10 and 14) $\times 10^{-3}$ m were used.

Only when acid was added, did the absorbance (measured at 19,000 cm^{-1}) obey a first order rate law, within 2%.

The constants $K^{CB}_{5,0}$ and $K^{CB}_{5,+}$ are defined as thermodynamic (activity) constants of the pentaammine complexes. The constants K^1_A are the first association constants for the outer sphere associations. It has been shown[9] that the values of the association constants for univalent association of cobalt(III) complexes in liquid ammonia are roughly independent of the character and charge of the cation. Therefore for the present case it may be assumed that $K^1_{A,2}$ equals $K^1_{A,1}$ the value of which is known from conductivity data. This means that also $K^{CB}_{5,0} = K^{CB}_{5,+}$. The value of these constants may be calculated by applying a correction for ionic dissociation of ammonium perchlorate to the gross constant K^{CB}_5 previously determined[1] at an excess of electrolyte (0.2 m). To do this the association constant of ammonium perchlorate has been calculated from published[11] values of the molar conductivity as a function of the concentration of this electrolyte, in the way described before.[9] Then the concentrations of $Co(NH_3)_4NH_2Cl \cdot ClO_4$ (denoted by c^0) and $Co(NH_3)_4NH_2Cl^+$ (denoted by c^+) can be calculated as a function of cobalt concentration and ionic strength. To do this we have used the Debye-Hückel formula for the activity coefficient, that can be used for univalent association in liquid ammonia up to 0.1 m.[12] The values obtained, together with the observed values for the first order rate constant *k*(obsd) are listed in Table I. The fact that a first order rate has been found supports the earlier reported[1] equality of the acid dissociation constants of the starting and the end product.

For the analysis of the rate constants we may split up the photometrically determined rate constant into the contributions from the two differently charged conjugate bases, as follows:

$$k(\text{obsd}) = \frac{c^+}{c} \cdot k^+ + \frac{c^0}{c} \cdot k^0 \qquad (1)$$

TABLE I

Reaction rates for the chloropentaaminecobalt(III) complex at varying ionic strength.

$10^3.c$ (m)	$10^3.(KClO_4)^a$ (m)	$10^5.c^+$ (m)	$10^5.c^0$ (m)	$10^3.k(obsd)$ (sec^{-1})	$\frac{k(obsd).c}{c^+ + c^0}$ (sec^{-1})
			t = -30.2 °C		
5	6.8	.22	.11	15.5	2.35
5	10	.20	.11	10.5	1.69
5	30.7	.13	.13	9.4	1.81
3	0	.32	.06	30.	2.37
5	0	.33	.09	25.2	3.00
10	0	.35	.15	12.0	2.40
			t = -33.9 °C		
5	10	.21	.12	4.7	.71
5	30.7	.14	.13	4.4	.81
3	0	.33	.06	14.0	1.08
5	0	.34	.09	13.0	1.51
10	0	.36	.15	6.3	1.24
			t = -37.2 °C		
5	10	.21	.12	3.2	.48
5	30.7	.14	.13	2.3	.43
3	0	.34	.06	9.0	.68
5	0	.35	.09	6.8	.77
10	0	.37	.16	3.7	.70
			t = -46.6 °C		
5	10	.32	.18	.45	.05
5	30.7	.22	.20	.22	.03
3	0	.51	.09	1.5	.08
5	0	.53	.14	1.3	.10
10	0	.56	.23	.7	.09

[a] Concentration of added potassium perchlorate.

in which c is the total concentration of pentaammine, as c^+ and c^0 are small compared to c.

It was found that the most satisfactory solution to Eq. (1) was to set $k^+ = k^0$, for the following reasons: It is seen from Table I that the quotient $k(\text{obsd}) \cdot c/(c^+ + c^0)$ is fairly constant for a given temperature, or at least does not show a significant trend, as the assumed equality implies. It is also implied that $k^+ = k^0 = k_1$, where k_1 is the gross rate constant for the rate determining step obtained[1] at excess (0.2 m) electrolyte concentration. Indeed the averaged values for the quotient defined above agree very well with the k_1 values (Table II).

TABLE II
Comparison of calculated values for the rate constant of the $Co(NH_3)_4NH_2Cl^+$ ion.

temp. ^0C	$k^+ = k^0$ (a) (sec^{-1})	$k^+ = k^0$ (b) (sec^{-1})	k_1 (c) (sec^{-1})
-30.2	2.27	2.32	2.13
-33.9	1.07	1.11	-
-37.2	.61	.56	.58
-46.6	.07	.07	.07

(a) : calculated average of k(obsd) . $c/(c^+ + c^0)$ from Table I.
(b) : calculated from the activation parameters of Table V.
(c) : gross constant at constant ionic strength (0.2 m).

Especially the equality of k_1 and the averaged quotient $k(\text{obsd}) \cdot c/(c^+ + c^0)$ is a strong indication that $k^+ = k^0$, as the present experiments were done under conditions where the positive ion is largely present, whereas at the excess electrolyte the neutral species dominates.

Evidently the activation parameters obtained from a least-squares fit[13] for k^+ equal those for k_1 within the experimental error (Table V).

2. *The cis-Co(en)$_2$NH$_3$Cl^{2+} Complex*

In the literature there is some disagreement whether the cis-$Co(en)_2NH_3Cl^{2+}$ ion in liquid ammonia forms the $Co(en)_2(NH_3)_2{}^{3+}$ ion with[14] or without[15] retention of configuration.

Under the experimental circumstances used in this study in all cases the spectrum of the end product of the reaction between cis-$Co(en)_2NH_3Cl^{2+}$ and liquid ammonia was identical to that of the cis diammine.[16] Also an aqueous solution of the end product, left over after boiling off the ammonia, did not give a precipitate with a solution of sodium dithionate. The formation of this precipitate is used as identification of the trans diammine.[17] During the reaction the spectrum in the visible region showed two isosbestic points, at 20,400 and 23,800 cm^{-1}.

All this means that we may conclude that no cis-trans configuration change has occurred during the reaction.

The reaction rate has been determined with and without the addition of acid at constant ionic strength (0.2 m). For the experiments with added acid the absorbance as a function of time was found to obey a first order rate law. Table III contains the observed first order rate constants obtained by applying a least-squares fit. For any fixed temperature k(obsd) was found to fit the relation previously[1] found for the pentaammines:

$$k(\text{obsd}) = A^{-1} \cdot k_1 \cdot K_5^{CB} \qquad (2)$$

A is the concentration of acid added (ammonium perchlorate) and k_1 is the rate constant for the rate-determining dissociation of the conjugate base;[1] we have kept the symbol K_5^{CB} for the acid-dissociation constant of the CoN_5Cl chromophore.

TABLE III

Reaction rate of the cis-$Co(en)_2NH_3Cl^{2+}$ complex as a function of added acid and temperature.

10^3.A (m)	10^3.k (sec^{-1}) obsd	10^3.k (sec^{-1}) calc[a]
	t = -17.7 °C	
5.13	2.21	2.33
2.33	5.50	5.13
1.56	7.76	7.67
1.18	10.0	10.2
	t = -21.0 °C	
5.13	1.33	1.23
2.25	2.91	2.83
1.56	4.08	4.07
1.18	5.33	5.40
	t = -25.5 °C	
5.13	0.67	0.60
2.33	1.35	1.31
2.25	1.42	1.36
1.56	2.00	1.95
1.18	2.50	2.58
	t = -30.1 °C	
5.13	0.33	0.34
2.25	0.67	0.77
1.56	1.18	1.11

[a] Calculated from equation (2) and the parameter values of Table IV.

No acid independent contribution to k(obsd) was found. Values of the parameter combination $k_1 \cdot K_S^{CB}$ as a function of the temperature, obtained by applying a least-squares fit of Eq. 2 to the k(obsd) values of Table III are in Table IV. Table III contains a comparison between observed k values and the ones calculated with the parameters from Table IV. A least-squares activation analysis[13] gave the parameters in Table V. We may then conclude that, as for the pentaammine studied earlier,[1] also the present ethylenediamine complex reacts with ammonia via the conjugate base mechanism. As outlined in Ref. 1, the constants k_1 and K_S^{CB} were then separately obtained by an analysis of the reaction rates at varying complex concentrations and constant ionic strength. For some of these experiments extrapolated values of $k_1 \cdot K_S^{CB}$ have been used, because the much larger reaction rates in the case that no acid was added made it impossible to use the same temperature range in both cases.

TABLE IV
Parameters for cis-chloroamminebis(ethylenediamine)cobalt(III) perchlorate[a].

temp.	$10^6.k_1.K_5^{CB}$	$10^8.\frac{(k_1.K_5^{CB})^2}{K_6^{CB}}$[c]	$\frac{K_5^{CB}}{K_6^{CB}}$[c]	k_1[d]	$10^7.K_5^{CB}$[d]	$10^7.K_6^{CB}$
(°C)	(m.sec^{-1})	(m.sec^{-2})		(sec^{-1})	(m)	(m)
-17.7	12.0					
-21.0	6.36					
-25.5	3.06	6720	2.1	10.5(7.0)	2.9(4.4)	1.4
-29.7	1.72[b]	1390	2.2	3.7(3.2)	4.6(5.4)	2.1
-30.1	1.74					
-34.7	0.77[b]	250	2.2	1.5(2.1)	5.3(3.6)	2.4
-41.0	0.27[b]	43	2.0	0.8(1.1)	3.3(2.5)	1.7

[a] at constant ionic strength (0.2m)
[b] extrapolated values, calculated from the activation parameters
[c] from the experiments at varying cobalt concentration
[d] in parentheses the values obtained by applying equation (3)

TABLE V
(Pseudo) Activation Parameters[a].

		$k_1.K_5^{CB}$		k_1	
Complex		$\Delta H^{\neq}$ (kcal.mol^{-1})	$\Delta S^{\neq}$ (cal.degree^{-1})	$\Delta H^{\neq}$ (kcal.mol^{-1})	$\Delta S^{\neq}$ (cal.degree^{-1})
$Co(NH_3)_5Cl.(ClO_4)_2$	k_1	20.9 ± 1	-3 ± 2	22.8 ± 2	38 ± 4
	$k^o=k^+$			22.6 ± 2	37 ± 4
$Co(NH_3)_5Br.(ClO_4)_2$	k_1	17.3 ± 1	-7 ± 2	17.5 ± 1	23 ± 2
cis-$Co(en)_2NH_3Cl.(ClO_4)_2$	k_1	18.0 ± 1	-10 ± 2	18.3 ± 1	20 ± 2

[a] at ionic strength 0.2 m

In the first place, because the observed absorbance did not obey a first order rate law, an extraplanation to zero time ($t = 0$) was applied. If the complex is acid free, the $k(\text{obsd})_{t=0}$ values should obey relation (9) of Ref. 1:

$$k(\text{obsd})_{t=0} = k_1 \cdot (K_5^{\text{CB}})^{\frac{1}{2}} \cdot c^{-\frac{1}{2}} \qquad (3)$$

c is the concentration of the starting product.

Indeed for all temperatures a plot of $k(\text{obsd})_{t=0}$ as a function of $c^{-\frac{1}{2}}$ resulted in straight lines passing through the origin. From these with the help of a least-squares fit the parameter combination $k_1 \cdot (K_5^{\text{CB}})^{\frac{1}{2}}$ was obtained, which, together with the $k_1 \cdot K_5^{\text{CB}}$ discussed above, gave approximate values for the parameters k_1 and K_5^{CB}. The results are given in Table IV in parentheses.

Then the complete kinetic curves of complex concentration versus time were analyzed numerically to give the parameter combinations in column 3 and column 4 of Table IV. From these and the entries in column 2 of Table IV new values of k_1 and K_5^{CB} were calculated, together with values for K_6^{CB}, the acid dissociation constant for the end product (the CoN_6 chromophore). The values for k_1 and K_5^{CB} are seen to agree closely with the approximate values in parentheses, obtained from the extrapolation procedure.

The errors in the parameter values are, for $k_1 \cdot K_5^{\text{CB}}$ 5%, for k_1 10%, and for K_5^{CB} and K_6^{CB} 25%.

Also the values of the parameters in Table IV have been subjected to a least-squares analysis to give the activation parameters. Results are in Table V, together with the values obtained earlier[1] for the bromo and chloro pentaammine complexes.

Separately, from conductivity measurements in the way described before,[9] the value of the association constant K_A^1 for the ethylenediamine complex was found to be nearly equal to the corresponding value for the pentaammines.[9] This means that under the present circumstances the neutral associate dominates ($K_A^1 > 200$ m).

DISCUSSION

The results obtained in the kinetic analysis of ammonolysis of the cis-chloroamminebis(ethylenediamine)cobalt(III) ion compel us to modify the conclusion reached in an earlier paper[1] on the cause of the reactivity of the conjugate base. From a comparison between aquation and ammonolysis parameters for the pentaammine cobalt complexes it was concluded that the high reactivity of the conjugate base is not primarily due to a weakening of the bond to the leaving group, but that the very favourable and positive entropy of activation is the rate-enhancing factor. This high value of the entropy was taken as evidence for extensive rearrangement on going from the ground state to the activated complex. Now the present ethylenediamine complex reacts under retention of configuration, so a rearrangement in the first coordination sphere seems to be excluded. However, from Table V it is clear that, compared to the chloropentaammine complex, for which a rearrangement has been observed in aqueous solution,[18,19] but cannot be proved for the present case, the entropy of activation for the ethylenediamine complex indeed shows the expected decrease (assuming that the chloropentaammine rearranges), but is still high and positive and nearly equal to the value for the bromopentaammine. We propose to describe this entropy to a rearrangement of solvent molecules in the second sphere, this being the most likely explanation of the effect that can be given at the moment. It seems that in this connection the charge of the second sphere is less important, as the apparent equality of the rate constants for the differently charged chloropentaammine complexes seems to imply.

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