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Kinetics of Water-Ammonia Exchange in the Series of Aquaamminecobalt(III) Complexes. I. Mechanism of the Reaction of the Diaquatetraamminecobalt(III) Ion with Ammonia

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Kinetic studies at a single temperature and varying ammonia concentration and ionic strength have provided a mechanism for the formation reaction of the hydroxopentaamminecobalt(III) ion from tetraamminecobalt(III) complexes. The principal rate determining step can be interpreted as a dissociative interchange reaction of the $Co(NH_3)_4(OH)(H_2O)^{2+}$ ion: coordinated water leaves the first coordination sphere, while an ammonia molecule comes in from the second sphere.

Introduction

The mechanism of substitution reactions of cobalt (III) ammine complexes in acidic[1,2] and alkaline[1,3] aqueous solutions is now firmly established. The main body of kinetic studies on both acid and base hydrolysis deals with ammine and ethylenediamine complexes, in which the "skeleton" of the complex is kinetically inert, that is, no Co-N bonds are broken. It seemed therefore of interest to gather more information on the kinetics of the Co-N bond. For such a kinetic study, when performed in aqueous solution, a class of compounds automatically presents itself, namely the group of aquaammine and hydroxoamminecobalt(III) complexes, that shows a gradually increasing lability when the number of aqua and hydroxo ligands is increased.[4,5]

This paper reports kinetic spectrophotometry on the reaction of diaquatetraamminecobalt(III) with ammonia: In ammoniacal solutions the complex splits off one or two protons in an instantaneous[5] acid-base reaction and then undergoes a *cis-trans* isomerization reaction.[6] This reaction is followed by a relatively slow uptake of ammonia,[6] as elaborated for the dihydroxo complex:

$$Co(NH_3)_4(OH)_2^+ + NH_3 \rightarrow Co(NH_3)_5(OH)^{2+} + OH^- \qquad (1)$$

This uptake of ammonia will be the subject of the present study. The reason for selecting this reaction is that it may be followed easily by conventional spectrophotometry at moderate temperatures; under mild alkaline conditions it proceeds completely to the pentaammine.

Experimental Section

General. Preparative details of the compounds used and the experimental procedure including pH measurement and calibrations have been outlined extensively in an earlier paper.[6] The purity of the diaquatetraamminecobalt(III) perchlorate used has been checked by comparing it in kinetic behaviour with the same compound after three recrystallizations. No difference in the rate constants was observed. The spectrophotometric procedure followed[5] has as a consequence that the solutions spend part of the reaction time in the spectrophotometer beam. However, the absorbance spectra of solutions kept in the dark showed no differences with those of the solutions kept in the spectrophotometer. So the reaction rate obtained is not appreciably influenced by the technique used. On the other hand irradiation of the solutions with much larger quantities of light was found to give photochemical reactions. These were not studied further.

Kinetic runs. All solutions were made up from ammonia-ammonium perchlorate buffers. The ionic strength was fixed by adding sodium perchlorate. Unless otherwise stated the ionic strength(I) is 0.20 ± 0.01 *M*. In preparing the solutions care was taken to exclude carbon dioxide by working under nitrogen atmosphere. The kinetic runs were started by dissolving a weighted amount of diaquatetraamminecobalt(III) perchlorate into a known volume of the buffer solution brought previously to the desired temperature. The reaction was then monitored spectrophotometrically. Temperature constancy (± 0.1°C) was attained by circulating thermostatted water around the optical cells. The total concentration of cobalt complex—shortened as (Co)—was varied between 10^{-2} and 10^{-3} *M*. It was observed to have no effect on the rate constants found.

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(1) F. Basolo and R.G. Pearson, « Mechanisms of Inorganic Reactions », sec. ed., New York, 1967.
(2) C.K. Poon, *Inorg. Chim. Acta Reviews*, *4*, 123 (1970).
(3) M.L. Tobe, *Accounts of Chem. Research*, *3*, 377 (1970).
(4) J.H. Takemoto and M.M. Jones, *J. Inorg. Nucl. Chem.*, *32*, 175 (1970).
(5) G. Schwarzenbach, J. Boesch, and H. Egli, *J. Inorg. Nucl. Chem.*, *33*, 2141 (1971).
(6) S. Balt, *Rec. Trav. Chim.*, *91*, 1026 (1972).

Results and Discussion

Figure 1 shows the change of absorbance spectrum during reaction (1) for a characteristic case. The starting product is the equilibrium mixture[6] of *cis*- and *trans*-$Co(NH_3)_4(OH)_2^+$, the end product is identical with $Co(NH_3)_5OH^{2+}$. The presence of isosbestic points guarantees that no additional compounds are present. At any wavenumber in the region covered by Figure 1 the measured absorbance as a function of time was found to obey a first order rate law.

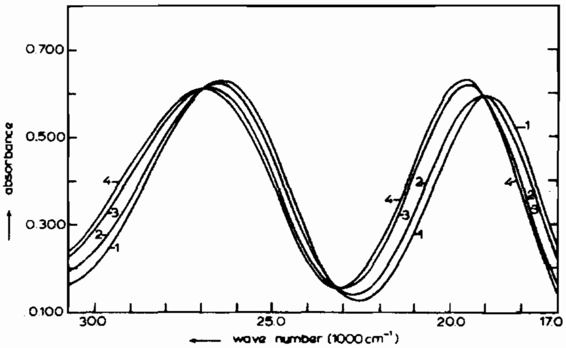

Figure 1. Absorption spectra of a solution of dihydroxotetraamminecobalt(III) perchlorate in 1.00*M* ammonia at different time intervals, showing the formation of the hydroxopentaammine ion. I = 0.20*M*; pH = 11.35; = 25.2±0.1°C. The spectra have been recorded: 1) after 13.2×10^3 sec (17% reaction). 2) after 27.0×10^3 sec (33% reaction). 3) after 108×10^3 sec (80% reaction). 4) after 186×10^3 sec (93% reaction).

The pseudo first order rate constants (k) were obtained from a least squares analysis, as described in previous papers.[6,7] The observed rate constant is independent of wavenumber; a restrinction has to be made for reactions at very low ammonia concentration, where the tetramerization reaction[8] has not completely been stopped. In this case the UV part of the spectrum can no longer be used because even when only an extremely small fraction of the total amount of cobalt complex present has been tetramerized, the enhancement in UV absorbance is considerable.[9]

Henceforth the results will be given at a single wavenumber: 20,750 cm^{-1}, for which the most accurate rate constant could be obtained. The reason is that the difference in molar absorbance between the *cis-trans* tetraammine equilibrium mixture and the pentaammine is at its maximum at this wavenumber.

The observed pseudo first order rate constants are a function of ammonia concentration and pH. The two factors will be treated separately.

pH-dependence. At a fixed ammonia concentration—shortened as (NH_3)—the rate constant k is proportional to the hydrogen ion activity $[H^+]$ as obtained from electrometric pH measurements (Figure 2). An important point is that the lines in Figure 2 have a non-zero intercept with the k axis; this means that k has a (small) pH independent contribution. At higher pH the observed k seems to be larger than the value extrapolated from lower pH.

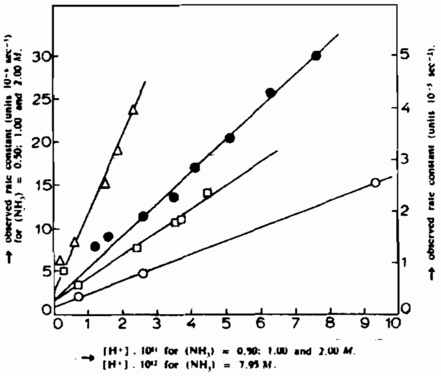

Figure 2. Observed rate constant as a function of the hydrogen ion activity at constant ammonia concentrations and constant ionic strength (0.20*M*). ○ = 0.50*M* (25.5°C); □ = 1.00*M* (25.5°C); △ = 2.00*M* (25.5°C); ● = 7.95*M* (25.2°C).

This enhancement in k cannot result from a contribution of the reverse of reaction (1), as for high pH the end spectra were still identical with that of the pentaammine. Another source of error, namely an appreciable alkaline error[10] in the measured pH, seems unlikely in the pH region chosen and with the glass electrode used and moreover would produce a k value lower than the extrapolated one. The enhancement mentioned must consequently have a kinetic explanation.

The most simple interpretation of the observed pH dependence is that the main part of the reaction rate is due to the aquahydroxo complex $Co(NH_3)_4(OH)(H_2O)^{2+}$, obtained by adding a proton to the compound $Co(NH_3)_4(OH)_2^+$. As the latter ion is predominantly present in the solutions studied,[6] this proposition predicts a rate proportional to $[H^+]$. Only a small fraction of reaction (1) will take the route via the $Co(NH_3)_4(OH)_2^+$ ion. The increase of the observed rate constant at high pH may be attributed to an additional reaction course via a compound, of which the concentration is inversely proportional to $[H^+]$, e.g. a conjugate base of the dihydroxo complex. This base cannot be expected to be present in measurable quantities.[3] The extraordinary reactivity of the aquahydroxo ion is parallelled in the isomerization rates.[6]

The observed k values of Figure 2 (except the deviating ones at high pH) have been subjected to a least squares analysis for the formula:

$$k = a_0 + a_1 \, . \, [H^+] \qquad (2)$$

Results are presented in Table I. The drawn lines in Figure 2 have been calculated from equation (2) and the parameters of Table I.

Influence of Ammonia Concentration. The influence of the ammonia concentration on the observed

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[7] S. Balt and P.M. Kwantes, *J. Inorg. Nucl. Chem.*, 35, 2407 (1973).
[8] S. Balt and W. de Kleviet, *Inorg. Chem.*, 9, 2251 (1972).
[9] A.B. Hoffman and H. Taube, *Inorg. Chem.*, 7, 903 (1968).
[10] R.G. Bates, Determination of pH, New York, 1964.

Table I. Kinetic parameters for the reaction of dihydroxotetraamminecobalt(III) with ammonia at constant ammonia concentration [a].

(NH_3) M	$10^6 . a_0$ sec^{-1}	$10^{-5} . a_1$ $M^{-1} . sec^{-1}$	$10^{-5} . a_1 . (NH_3)^{-1}$ $M^{-2} . sec^{-1}$
0.50	0.9±0.2	1.5±0.1	3.0
1.00	1.5±0.5	2.7±0.2	2.7
2.00	2.0±0.5	9.2±0.3	4.6
7.95	2.3±0.7	6.3±2	8.0

[a] $I = 0.20M$; $t = 25.5°C$; $(Co) = 10^{-3} - 10^{-2}M$.

rate constants can be deduced from the results presented in Table 1. We shall in the first place consider the most accurately determined parameter a_1. The term $a_1 . (NH_3)^{-1}$ has the same value for $(NH_3) = 0.50\,M$ and $1.00\,M$, but increases on raising the ammonia concentration over $1\,M$ (sec Table 1). This suggests that for $(NH_3) < 1\,M$ the rate of the principal reaction is proportional to (NH_3). This proposition has been tested at low pH, where the pH independent part of the rate constant can be neglected, so that, combined with the results obtained in the preceding section, the main reaction course is described by equation (3):

$$k = b . (NH_3) . [H^+] = c . (NH_4^+) . \qquad (3)$$

in which b and c are constants and $a_1 = b . (NH_3)$.

Equation (3) is only valid when the acid dissociation constant of the aquahydroxo ion is considerably larger than the hydrogen ion activity. The extrapolated[6] value for this constant under the present conditions (25°C; $I = 0.20\,M$) is *circa* 3×10^{-8}, so that equation (3) can be used down to approximately pH = 8.5.

Table II. Rate constant for the reaction of dihydroxotetraamminecobalt(III) with ammonia at constant ammonium perchlorate concentration [a].

pH	(NH_3) M	$10^5 . k$ sec^{-1}	$10^{-5} . k . (NH_3)^{-1} . [H^+]^{-1} .$ $M^{-2} . sec^{-1}$
8.84	0.03	1.40	3.2
8.92	0.04	1.62	3.4
9.71	0.30	1.55	2.7
10.03	0.54	1.52	3.0

[a] $(Co) = 3.10^{-3}M$; $(NH_4ClO_4) = 0.20M$; $t = 25.5°C$.

Table II shows that for the low ammonia concentrations employed the observed rate constant k is indeed independent of the ammonia concentration (the ammonium perchlorate concentration is kept constant). A still better evaluation gives the first part of equation (3), that predicts a constancy of $k . (NH_3)^{-1} . [H^+]^{-1} = b$, which is constant at an average of $3.1 \times 10^5\,M^{-2}\,sec^{-1}$. If the proposed relation is correct, this figure must equal the term $a_1 . (NH_3)^{-1}$ for $(NH_3) = 0.50\,M$ and $1.00\,M$, as indeed it does. The second parameter of equation (2), a_0, also seems to be proportional to (NH_3) at low ammonia concentrations, although the large standard deviation of this parameter makes this conclusion less secure, Proceding to higher ammonia concentrations than $1\,M$, the picture becomes more involved; $a_1 . (NH_3)^{-1}$ is seen to increase on increasing the ammonia concentration, while a_0 tends to go to a constant value.

To get a better view on the (NH_3) dependence, the reaction rate has been studied at constant pH and varying (NH_3) up to $8\,M$. This was realized experimentally by keeping the ratio between the ammonia and the ammonium perchlorate concentrations constant; it has been checked by measuring the pH (but see also later on). The observed k values (Figure 3) could be fitted rather well with the equation:

$$k = d_1 . (NH_3) + d_2 . (NH_3)^2 . \qquad (4)$$

A least squares analysis gives the parameters d_1 and d_2 and from these the calculated k values as the drawn lines in Figure 3. Neglecting the small pH independent part of k, the equations (3) and (4) may be combined to give: $a_1 . (NH_3)^{-1} = d_1[H^+]^{-1}$. The value of $a_1\ (NH_3)^{-1}$ is approximately $3 \times 10^5\,M^{-2}\,sec^{-1}$. The analysis cited gives for $d_1 . [H^+]^{-1}$ the values $3.3 \times 10^5\,M^{-2} . sec^{-1}$ (pH = 11.19) and $2.5 \times 10^5\,M^{-2} . sec^{-1}$ (pH = 10.88), which is in good agreement.

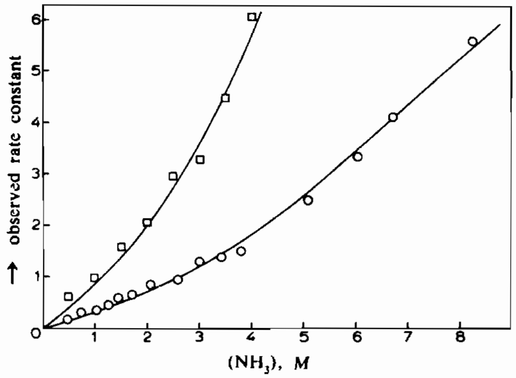

Figure 3. Observed rate constant as a function of ammonia concentration at fixed pH and ionic strength (0.20*M*). ○ pH = 11.19±0,02, rate constant in units $10^{-5}\,sec^{-1}$ (25.5°C). □ pH = 10.88±0,02, rate constant in units $0.5 . 10^{-5}\,sec^{-1}$ (25.2°C).

Mechanism of the Reaction. The results obtained so far may be compared to the picture generally accepted[1,2,11] for the anation reaction of cobalt(III) complexes, that is, the reaction is dissociative,[11] while the entering group must be present in the second coordination sphere (outer sphere) to be able to compete with water for the coordination site of the leaving group.[11,12,13] The present case can easily be adapted to this mechanism: The complex ion $Co(NH_3)_4(OH)(H_2O)^{2+}$ combining[1,5] the OH^- ion as a labilizing group and H_2O as a good leaving group compared

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[11] C.H. Langford and H.B. Gray, « Ligand Substitution Processes », New York, 1966.

[12] M.L. Tobe, *Adv. Chem. Series*, *49*, 7 (1965).

[13] C.H. Langford and W.R. Muir, *J. Am. Chem. Soc.*, *89*, 3141 (1967).

to OH^-, in a dissociative reaction splits off H_2O. At the same time NH_3 and H_2O from the second coordination sphere compete for the coordination place of the leaving water ligand. A similar mechanism will operate for the $Co(NH_3)_4(OH)_2^+$ ion, but at a much lower rate. We may now develop equations for the observed rate constants. To avoid confusion the numbering of the four tetraammine ions involved will follow previous publications:[6,7]

$$\begin{tikzcd}
③ & & ④ \\
cis\text{-}T(OH)(H_2O)^{2+} \arrow[rr, shift left] \arrow[d, shift left, "K_{13}"'] & & trans\text{-}T(OH)(H_2O)^{2+} \arrow[ll, shift left] \arrow[d, shift left, "K_{24}"] \\
cis\text{-}T(OH)_2^+ \arrow[u, shift left] \arrow[rr, shift left] & & trans\text{-}T(OH)_2^+ \arrow[u, shift left] \arrow[ll, shift left] \\
① & & ②
\end{tikzcd}$$

where T = $Co(NH_3)_4$; the acid dissociation constants have been defined as:

$$K_{rs}=\frac{A_r\,.\,[H^+]}{A_s} \text{ and } K_{rs,pq}=\frac{A_r+A_p}{A_s+A_q}\,.\,[H^+]$$

A_r is the concentration of complex ⓡ. $K_{rs,pq}$ is a gross constant. We assume stepwise outer sphere complex formation,[14] governed by the constants:

$$\beta_n{}^m=\frac{(ⓝ\,...mNH_3)}{A_n\,.\,(NH_3)^m}$$

$k_n{}^m$ is defined as the rate constant for the reaction route via the mth outer sphere complex of the complex ion ⓝ, symbolized as ⓝ. . . mNH_3. Outer sphere complex formation generally[15] has very little influence on the ligand field bands of transition metal complexes. As the reaction under study has been monitored at the ligand field bands, the pseudo first order rate constants obtained refer to the total concentration of the outer sphere complexes involved. In the pH regions studied, where the concentration of the aquahydroxo ions can be neglected compared to the total tetraammine concentration, the observed rate constant is then given by:

$$k=\frac{1}{1+\beta'_{1,2}\,.\,(NH_3)}\,.\,[k_1{}^1{}_{,2}\beta'_{1,2}\,.\,(NH_3)+ \\ +\frac{[H^+]}{K_{13,24}}\,.\,\sum_{m=1} k^m{}_{3,4}\beta^m{}_{3,4}\,.\,(NH_3)^m] \tag{5}$$

Because equation (5) of necessity uses gross constants for the equilibrium mixtures of *cis* and *trans* complexes, the individual products $k^m\,.\,\beta^m$ had to be replaced by the gross products $k_{n,p}{}^m\,.\,\beta_{n,p}{}^m$ (note that in the product $k\,.\,\beta$ the constants k and β cannot be separated). As the constant $\beta_{1,2}{}^1$ may be expected[16,17] to be significantly smaller than 1, equation (5) predicts that both the pH dependent and the pH independent part of the observed rate constant are proportional to (NH_3) for low (NH_3). The saturation effect in the pH independent part of k (a_0 of equation (2)) can be explained by assuming (as it has been done in equation (5)) that the dihydroxo complexes, having the lowest formal charge, will only form the first outer sphere complex. The presence of higher powers of (NH_3) in the observed rate constant, as exemplified by the empirical relation (4), could signify that for the higher charged aquahydroxo complexes also higher outer sphere complexes take part in the reaction. This statement must however be approached with caution. This caution is dictated by the fact that at high ammonia concentrations no distinction can be made between outer sphere complex formation and the effect on the observed rate constant caused by the drastic change in the dielectric constant of the medium, brought about by the large amounts of ammonia present. This change in the medium will not only influence the rate and equilibrium constants and activity constants, but also the liquid junction potentials[10] between the reference electrode and the tetraammine solutions in the pH measurements. As a result the picture becomes extremely involved. The conclusion must be that no definite proof for higher outer sphere complexes of equation (5) has been obtained. For this reason no further elaboration of the equations (4) and (5) has been undertaken.

Direct Measurement of the Rate Determining Step. In the proposed mechanism the concentration of the equilibrium mixture of *cis*- and *trans*-$Co(NH_3)_4(OH)(H_2O)^{2+}$ ions is the rate controlling factor, even though under the conditions employed as described in the previous sections, the tetraammine complex is almost completely present as the $Co(NH_3)_4(OH)_2^+$ ion. The mechanism can be tested by performing kinetic runs in the pH region, where a non-negligent fraction of the tetraammine consists in the form of the $Co(NH_3)_4(OH)(H_2O)^{2+}$ species. The necessary low pH cannot be obtained by only lowering the ammonia concentration, as the ammonia is needed as a buffer against tetramerization.[6,7] Therefore this experiment has been performed in a nearly saturated ammonium perchlorate solution. The ammonium perchlorate concentration was kept constant (1.70 *M*) to assure constant ionic strength.

Under these conditions equation (5) is no longer valid and must be extended to equation (6) that describes the pH dependent part of the rate constant as:

$$k(pH)=\frac{k'_{3,4}\beta'_{3,4}(NH_3)\,.\,[H^+]}{K_{13,24}+[H^+]} \tag{6}$$

The higher terms in (NH_3) have been dropped, as the ammonia concentration is lower than 1 *M*. Table III contains the experimental values. These values have been fitted with equation (6) using a least squares criterium.[7] From this:

$$K_{13,24}=2.3\times10^{-9}M;\ k'_{3,4}\,.\,\beta'_{3,4}=1.9\times10^{-3}M^{-2}.\text{sec}^{-1}.$$

There is excellent agreement between the observed k values and the ones calculated with the constants $K_{13,24}$ and $k_{3,4}{}^1\,.\,\beta_{3,4}{}^1$ (see Table III).

Also the value found for $K_{13,24}$ compares very well

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(14) V.E. Mironov, *Russian Chem. Rev.*, *39*, 319 (1970) (English translation).

(15) M.T. Beck, *Coordin. Chem. Rev.*, *3*, 91 (1968).

(16) T.I. Kozachenko, V.V. Bekman, and V.E. Mironov, *Russ. J. Inorg. Chem.*, *15*, 1192 (1970) (English translation).

(17) T.I. Kozachenko, V.V. Bekman, and V.E. Mironov, *Russ. J. Inorg. Chem.*, *16*, 1083 (1971) (English translation).

Table III. Reaction rate for solutions containing the aquahydroxocobalt(III) ion in measurable concentrations[a].

pH	(NH_3)	$10^4 . k . (NH_3)^{-1}$ $M^{-1} . sec^{-1}$	
	M	obsd.	calc.[b]
8.36	0.04	12.3	12.4
8.99	0.18	6.2	5.9
9.25	0.32	3.6	3.8
9.42	0.47	2.8	2.7

[a] $(NH_4ClO_4) = 1.70M$; $(Co) = 3.10^{-3}M$; $t = 25.5°C$. [b] see the text.

Table IV. Rate constant for the reaction of dihydroxotetraamminecobalt(III) with ammonia at constant ionic strength and varying pH and ammonia concentration[a].

pH	(NH_3) M	$10^6 . k$ sec^{-1}	$10^{-5} . k . (NH_3)^{-1} . [H^+]^{-1} . M^{-2} . sec^{-1}$.
9.90	0.19	5.2	2.2
10.01	0.19	4.2	2.2
10.14	0.19	3.0	2.2
10.00	0.28	6.0	2.2
10.15	0.38	5.7	2.1
10.24	0.48	5.3	2.0

[a] $t = 25.5°C$; $(Co) = 10^{-3} - 10^{-2} M$; $I = 0.10M$.

with the one obtained from stopped flow results:[7] $2.0 \times 10^{-9} M$ at 25.6°C and $I = 1.00 M$.

Influence of Ionic Strength. In Table IV the experimental data for the ionic strength $I = 0.10 M$ are collected. Applying equation (3), the value of $k . (NH_3)^{-1} . [H^+]^{-1}$ is seen to be constant and smaller than the one obtained earlier for $I = 0.20 M$ (Table I and Table II). On the basis of the proposed mechanism (equation (5)) the ionic strength dependence of the rate constant k for ammonia concentrations below 1 M and low pH will be given approximately by equation (7):

$$\frac{k}{(NH_3) . [H^+]} = C^0 . \frac{\gamma(Co(NH_3)_4(OH)_2^+)}{\gamma(Co(NH_3)_4(OH)(H_2O)^{2+})} \qquad (7)$$

where $\gamma(A)$ is the activity coefficient of complex A, and C^0 combines the values of the thermodynamic constants extrapolated to zero ionic strength. It is immediately clear that a Debye limiting law[18] predicts an increase of $b = k . (NH_3)^{-1} . [H^+]^{-1}$ (equation (3)) with increasing ionic strength. Unfortunately such a simple relation no longer holds at the ionic strengths employed. However, the existing empirical and semi-empirical relations for activity coefficients[19] in the ionic strength region used all predict an increase of the parameter b on going from $I = 0.10 M$ to $I = 0.20 M$, exactly as found.

Conclusions

Evidence has been presented that the formation of the pentaammine has as principal rate determining step a dissociative interchange reaction of the outer sphere complex between $Co(NH_3)_4(OH)(H_2O)^{2+}$ and NH_3. It has not become clear whether or not higher outer sphere complexes take part in the reaction. At higher pH values the observed rate is partly due to the complex $Co(NH_3)_4(OH)_2^{2+}$ and presumably also to an ammine conjugate base of the latter.

From the discussion of this paper it has emerged that more work is needed on the outer sphere complex mechanism and the conjugate base mechanism. These reactions are now under further investigation.

Acknowledgement. The author thanks Mrs. E.G. A.M. Bohte and Mr. R.J. Prent for their valuable help in performing the experiments described.

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(18) A.A. Forst and R.G. Pearson « Kinetics and Mechanism », sec. ed., New York (1961).

(19) B. Perlmutter-Hayman, *Progress in Reaction Kinetics*, 6, 239 (1971).