

Studies on Cobaltamines

II. Association of Ammonia with the Hexamine Cobalt(III) Ion in Aqueous Solution

RAGNAR LARSSON

Department of Inorganic and Physical Chemistry, Chemical Institute, University of Lund, Lund, Sweden

The solubilities of $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ and $\text{Ba}(\text{IO}_3)_2$ in 1 M NH_4ClO_4 are reported for mixed solvents, the non-aqueous component being ammonia, methanol, ethanol, acetone, glycerol and dioxane. Using these measurements, a method is devised for the calculation of the association constants when ammonia is associated with the $\text{Co}(\text{NH}_3)_6^{3+}$ ion. The first constant is reported. Evidence for an association of acetone with the $\text{Co}(\text{NH}_3)_6^{3+}$ ion is discussed. A spectrophotometric method is used which confirms the results from the solubility measurements.

From a solution containing some ammonium nitrate a solid phase has been isolated, having the composition $(\text{Co}(\text{NH}_3)_6 \cdot \text{NH}_3)(\text{ClO}_4)_2\text{NO}_3$.

The hexamine cobalt(III) ion, a complex seemingly saturated with respect to further coordination, has been the subject of several investigations on ion association. For example, the association of sulphate or thiosulphate ions has been investigated conductometrically¹ and spectrophotometrically^{2,3}, by measurements of solubility^{4,5} and dialysis⁶ as well as by a polarographic method⁷. Association of halide and pseudohalide ions has been studied both conductometrically⁸ and spectrophotometrically⁹⁻¹¹, whereas oxalate ion association has been studied by measurements of conductivity¹² and dialysis⁶.

It must be noted, however, that some of the interpretations of these experimental data are not generally accepted.

It seemed to be of interest to investigate the association of an uncharged, polar molecule with the $\text{Co}(\text{NH}_3)_6^{3+}$ ion. No such measurements have apparently been made though several authors^{13,14} have pointed out the importance of such an association in determining the velocity of inner-sphere substitutions.

In the first part¹⁵ of this series it was reported that there is an increase in the solubility of $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ in 1 M NH_4ClO_4 as the concentration of ammonia is increased. This fact was then explained as the result of an outer-

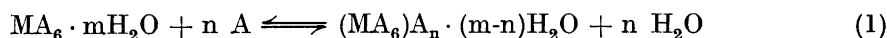
sphere ammine formation. In this work those solubility measurements have been extended in an effort to make possible the calculation of association constants.

As a check of the results obtained, an extincitometric method has also been used.

THEORY OF THE SOLUBILITY MEASUREMENTS

The notations will be those of the preceding paper¹⁵ except when otherwise stated.

The reactions under investigation may be written in the general form:



Excluding the solvating water, the corresponding association constant is defined by

$$\beta_n = \frac{[(\text{MA}_6)_n \text{A}_n] f_{(\text{MA}_6)_n \text{A}_n} \cdot a_{\text{aq}}^n}{[\text{MA}_6]^n \cdot f_{\text{MA}_6} \cdot [\text{A}]^n \cdot f_{\text{A}}^n} \quad (2)$$

where brackets mean free concentrations and f the activity coefficients of the species in question. a_{aq} is the activity of water. Now, $f_{(\text{MA}_6)_n \text{A}_n}$ and f_{MA_6} may be considered as almost equal, as they are related to ions of the same charge and almost nearly the same size. Thus eqn. (2) may be rewritten as

$$\beta_n = \frac{[(\text{MA}_6)_n \text{A}_n] a_{\text{aq}}^n}{[\text{MA}_6]^n \cdot a_{\text{A}}^n} \quad (3)$$

where $a_{\text{A}} = [\text{A}] \cdot f_{\text{A}}$

$$\text{We define } X = \sum_{n=1}^{\infty} \beta_n \cdot a_{\text{A}}^n / a_{\text{aq}}^n \quad (4)$$

$$\text{Thus } C_{\text{M}} = [\text{MA}_6] (1 + X) \quad (5)$$

In a solution saturated with $\text{MA}_6(\text{ClO}_4)_3$, we have

$$[\text{MA}_6] [\text{ClO}_4]^3 = L \quad (6)$$

and in the case when $C_{\text{A}} = 0$, *i.e.*, $C_{\text{M}} = [\text{MA}_6]_0$, we have

$$[\text{MA}_6]_0 [\text{ClO}_4]_0^3 = L_0 \quad (7)$$

If, as is the case in the present investigation, only the concentration of ammonia is changed, the salt medium being constantly kept 1 M NH_4ClO_4 , and if C_{M} is low, we can put

$$[\text{ClO}_4] = [\text{ClO}_4]_0 \quad (8)$$

Combining eqns. (6)—(8) we get

$$[\text{MA}_6] / [\text{MA}_6]_0 = L / L_0 \quad (9)$$

Inserting eqn. [9] into eqn. [5] we get

$$1 + X = \frac{C_{\text{M}}}{[\text{MA}_6]_0} \cdot \frac{L_0}{L} \quad (10)$$

Knowledge of L/L_0 as a function of $[\text{A}]$ would enable us to calculate X .

The evaluation of L/L_0

With this purpose in mind we will consider the effects on the solubility of a sparingly soluble salt in an aqueous solution of high ionic strength when a part of the water is exchanged for another solvent, *e.g.*, ammonia. This other solvent will be called here, for the sake of brevity, an "aquo-substitute".

The following items may be considered important:

1. The aquo-substitute may form complexes with the cation — or the anion — of the sparingly soluble salt.
2. A change in solvation conditions may result in a change in the "distance of closest approach" and thus cause activity changes of the ions in question.
3. The change in the dielectric constant of the solvent will cause a change in the activity coefficients of the ions. According to Owen¹⁶, two effects are operating: the primary and the secondary medium effects. The first one, arising from changes in ion-solvent interaction, is more or less correctly described by the theoretical equation of Born¹⁷ or by the empirical equation of Davies and Ricci¹⁸. However, it must be emphasized that none of those equations is generally valid. (*Cf.* Mayper, Clever and Verhoek¹⁹.) The secondary effect, connected with ion-ion interactions, is dependent on the ionic strength and is implied in the Debye-Hückel-Gronwall-LaMer equation.

One way to estimate the quotient L/L_0 for $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ in aqueous ammonia would be to use an ion of reference that does not form ammine complexes and is solvated as the $\text{Co}(\text{NH}_3)_6^{3+}$ ion. It should preferably be of the same size and have the same charge as this ion.

An ion fulfilling these demands is not easy to find, as most trivalent positive ions are hydrolyzed in aqueous ammonia, even at a high ammonium ion concentration.

As a reference ion Ba^{2+} has therefore been chosen. The measurements of Bjerrum²⁰, p. 145 indicate that this ion has a very low tendency of ammine formation.

However, the change of the solubilities of $\text{MA}_6(\text{ClO}_4)_3$ and a barium salt are not directly comparable for obvious reasons.

To overcome this difficulty, we might try to find another aquo-substitute, call it B, that does not form complexes with either $\text{Co}(\text{NH}_3)_6^{3+}$ or Ba^{2+} ions. Through a comparison of the solubility decrease of a barium salt in solutions of ammonia and in solutions of the aquo-substitute B, information might be obtained on the function $(L/L_0)_{\text{MA}_6}$. We now make the following definitions:

The formal solubility product* of $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ is given by $l_{\text{MA}_6} = C_{\text{MA}_6} \cdot C_{\text{ClO}_4}^3$. The formal solubility product of the barium salt to be used (BaX_2) is given by $l_{\text{Ba}} = C_{\text{Ba}} \cdot C_{\text{x}}^2$.

What we set out to measure is then the relative change of these formal quantities, l/l_0 , where $l_0 (= L_0)$ means l in solutions having $C_{\text{B}} (C_{\text{A}}) = 0$.

The reasoning will proceed as follows: If no $\text{MA}_6\text{-B}$ nor any $\text{Ba}^{2+}\text{-A}$ or $\text{Ba}^{2+}\text{-B}$ complexes are formed and if the solvation effects can be ignored, the quotients $(l/l_0)_{\text{MA}_6}$ and $(l/l_0)_{\text{B}}$ in the different solvents will depend only

* Note the difference between the usage of the symbol l in this paper and in the preceding one¹⁵.

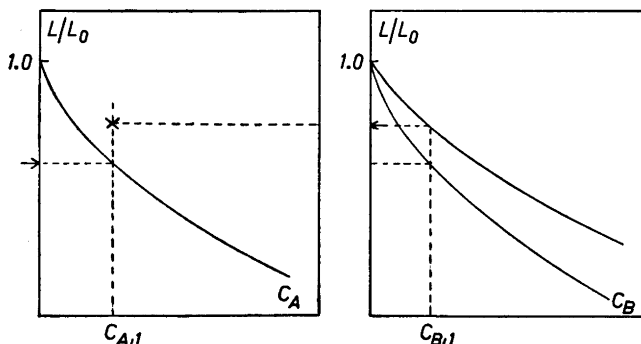


Fig. 1. Expected appearance of $(L/L_0)_{Ba}$ plotted against C_A (left figure) and $(L/L_0)_{MA}$, (right figure, upper curve) and $(L/L_0)_{Ba}$ (right figure, lower curve) plotted against C_B

on the dielectric constant of the solvent, as pointed out in item 3 previously mentioned. If now the quotients l/l_0 , which in these special cases turn into L/L_0 , are plotted against C_B — or C_A in the relevant case — we may expect curves of the form indicated in Fig. 1. For a certain value of L/L_0 , indicated by an arrow in the left diagram, we find the concentrations $C_{A,1}$ and $C_{B,1}$ for which the solubility product of the barium salt is decreased to the same amount. According to the assumptions made, these solutions must then have the same dielectric constant. At $C_B = C_{B,1}$ we can read the value of L/L_0 of $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ from the upper curve in the right diagram, indicated there by an arrow. This value of L/L_0 , however, must be that of $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ at the concentration $C_{A,1}$; this point is indicated by a cross in the left diagram.

Thus we may construct a set of points and from these draw a curve, describing the change of the solubility product of $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ in ammonia solution. This curve represents the function L/L_0 of eqn. (10) and insertion in this equation thus gives X , from which function the complexity constants may be obtained according to eqn. (4).

Calculation of f_A/a_{aq}

The standard state of the ammonia activity has been chosen so that $f_{\text{NH}_3} = 1$ in 1 M NH_4ClO_4 , $C_A = 0$. The activity of water is put = 1 in that same solution.

Following Bjerrum (Ref. ²⁰, p. 143) we assume that f_A as a function of C_A when $C_{\text{NH}_4\text{ClO}_4} = 1$ M will run approximately parallel to f_A when $C_{\text{NH}_4\text{ClO}_4} = 0$.

Thus the vapour pressure data of Perman ²¹ at zero ionic strength and 20°C can be used. From these it is found, if $C_A < 5$ M,

$$f_A = 1 + 0.066_3 C_A + 0.00106 C_A^2 \quad (11 a)$$

$$a_{aq} = 1 - 0.0244 C_A \quad (11 b)$$

EXPERIMENTAL

As the sparingly soluble barium salt $Ba(IO_3)_2$ was chosen. In order to make the best possible choice of the aquo-substitute B, the formal solubility products, l , for $Co(NH_3)_6(ClO_4)_3$ and $Ba(IO_3)_2$ were determined in 1 M NH_4ClO_4 at 20°C in aqueous solutions containing varying amounts of the following solvents: Methanol, ethanol, glycerol, acetone and dioxane.

For all these solvent mixtures the dielectric constant is known from the measurements of Åkerlöf²².

Chemicals used. The radioactive preparation of $Co(NH_3)_6(ClO_4)_3$ was the same as in Part I¹⁵.

The barium iodate was prepared from solutions of reagent quality barium chloride and potassium iodate.

The ammonium perchlorate and ammonia solutions were prepared as in Part I¹⁵. The solutions of methanol, ethanol, glycerol and acetone were made from weighed amounts of absolute, acetone-free methanol, absolute ethanol, glycerol, p.a., heated to 180°C to expel water, and acetone, p.a., respectively. The dioxane, Eastman 2144, was purified according to Eigenberger²³, and distilled at the constant boiling point 101.2°C. The melting point was found to be 11.5°C. The small amounts of impurities present certainly do not seriously affect the general features of the solubility curves.

Procedure. Solutions of 1 M NH_4ClO_4 , C_B M B (or C_A M A) were shaken with $Co^*(NH_3)_6(ClO_4)_3$ or $Ba(IO_3)_2$ in 100 ml flasks at 20°C in a thermostatically controlled room for two days to ensure saturation. The method of separation and measuring of the cobalt solutions was the same as in Part I¹⁵. The saturated solution of barium iodate was withdrawn with a 10 ml pipette provided with a filter-stick. The iodate content was determined iodometrically. The solubility product, l_{Ba} , was then easily calculated. As acetone and dioxane interfere in iodometric titrations, the solutions containing these solvents were freed from them before titration of the iodate content. The acetone solutions were made alkaline and boiled until all traces of ammonia were gone; it was then considered to be free from acetone also. The dioxane solutions were evaporated to dryness on the steambath. The quotient l/l_0 could be determined within ± 1 % for $Ba(IO_3)_2$ and ± 2 % for $Co(NH_3)_6(ClO_4)_3$.

RESULTS

The quotients l/l_0 found are reported in Tables 1 and 2. Along with these are given values, $(D)_{I=0}$, of the dielectric constants of the solvent mixtures that should be valid if the ionic strength, I , was zero. They are arrived at from density determinations of the stock solutions employed and linear interpolation from the data of Åkerlöf²². As the curves given by Åkerlöf describing D as a function of the concentration of aquo-substitute (given as weight-percentage) are not exactly linear, the values of Tables 1 and 2 are not quite accurate, but they will serve well enough to give a rough picture of the dependency of l/l_0 on D . It must also be remembered that these values of D are certainly not those of the actual solutions having an ionic strength $I = 1$ M. $(D)_{I=1}$ may be some 10 % lower than $(D)_{I=0}$, (cf. Hasted, Ritson and Collie²⁴). However, the quotient $(D_0/D)_{I=0} - D_0$ being the dielectric constant for $C_B = 0$ — will perhaps be more directly comparable to $(D_0/D)_{I=1}$ and has been used in Figs. 2 and 3.

It is seen that the curves of solubility of $Ba(IO_3)_2$ show the same relative positions as reported by Monk²⁵ at zero ionic strength.

Now, if the curves l/l_0 versus $(D_0/D)_{I=0}$ for different aquo-substitutes coincide, it might be inferred that the assumptions made on the exclusive dependency of l/l_0 on D are fulfilled. For $MA_6(ClO_4)_3$ this is the case in the

Table 1. Corresponding values of C_B , l/l_0 and $(D)_{I=0}$ · $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$.

Ammonia *		Methanol			Ethanol		
C_A M	l/l_0	C_B M	l/l_0	$(D)_{I=0}$	C_B M	l/l_0	$(D)_{I=0}$
0	1.00	0	1.00	80.4	0	1.00	80.4
0.250	1.02	0.339	0.94	79.8	0.223	0.87	79.7
0.500	1.05	0.508	0.88	79.6	0.557	0.78	78.8
1.000	1.13	0.846	0.82	79.0	1.114	0.64	77.1
1.500	1.23	1.354	0.74	78.2	1.560	0.55	75.8
2.500	1.47	2.030	0.64	77.2	1.782	0.50	75.2
3.50	1.88	3.38	0.49	75.0	2.228	0.43	73.9

Glycerol			Acetone			Dioxane		
C_B M	l/l_0	$(D)_{I=0}$	C_B M	l/l_0	$(D)_{I=0}$	C_B M	l/l_0	$(D)_{I=0}$
0	1.00	80.4	0	1.00	80.4	0	1.00	80.4
0.237	0.95	79.8	0.223	0.99	79.6	0.128	1.00	79.2
0.711	0.88	78.5	0.488	1.03	78.6	0.383	1.04	77.2
1.185	0.84	77.3	0.863	1.10	77.3	0.511	1.05	76.2
1.421	0.79	76.6	1.343	1.23	75.5	0.766	1.11	74.1
1.895	0.75	75.4	1.678	1.31	74.2	1.021	1.15	72.0
2.369	0.71	74.1	2.158	1.53	72.3	1.532	1.26	67.7

* These values are obtained by graphical interpolation from the values reported in Table 1 of Part I¹⁵.

Table 2. Corresponding values of C_B , l/l_0 and $(D)_{I=0}$. $\text{Ba}(\text{IO}_3)_2$.

Ammonia		Methanol			Ethanol		
C_A M	l/l_0	C_B M	l/l_0	$(D)_{I=0}$	C_B M	l/l_0	$(D)_{I=0}$
0	1.00	0	1.00	80.4	0	1.00	80.4
0.376	0.88	0.379	0.80	79.8	0.250	0.78	79.6
0.872	0.71	0.569	0.71	79.5	0.624	0.52	78.6
1.500	0.53	0.948	0.58	78.9	1.248	0.273	76.8
2.013	0.41	1.516	0.40	78.0	1.747	0.172	75.3
2.550	0.33	2.274	0.267	76.7	1.996	0.134	74.6
3.62	0.209	3.79	0.111	74.3	2.495	0.083	73.1

Glycerol			Acetone			Dioxane		
C_B M	l/l_0	$(D)_{I=0}$	C_B M	l/l_0	$(D)_{I=0}$	C_B M	l/l_0	$(D)_{I=0}$
0	1.00	80.4	0	1.00	80.4	0	1.00	80.4
0.796	0.93	78.3	0.223	0.80	79.6	0.286	0.71	78.0
1.327	0.90	76.9	0.558	0.55	78.4	0.572	0.54	75.7
1.592	0.89	76.2	0.893	0.37	77.2	0.715	0.47	74.5
2.122	0.87	74.8	1.339	0.231	75.5	1.144	0.268	70.9
2.653	0.85	73.4	1.678	0.162	74.2	1.430	0.231	68.5
			2.174	0.088	72.2	1.907	0.129	64.6

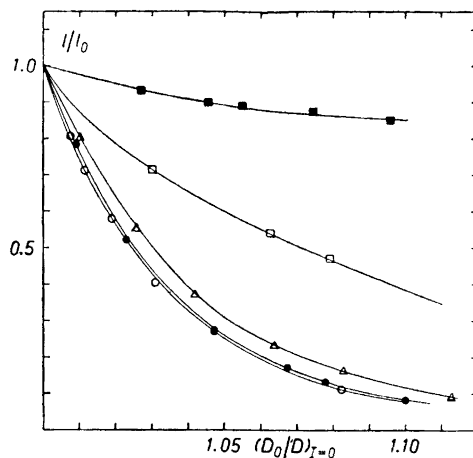


Fig. 2. The $\text{Ba}(\text{IO}_3)_2$ solubility curves; l/l_0 plotted against $(D_0/D)_{r=0}$. The symbols refer to the following aquo-substitutes: methanol (○); ethanol (●); acetone (△); dioxane (□); glycerol (■).

ethanol and methanol systems; for $\text{Ba}(\text{IO}_3)_2$ the ethanol, methanol and acetone curves lie rather close.

For these systems l/l_0 thus equals or nearly equals L/L_0 and the procedure indicated in Fig. 1 may be applied.

The measurements of Monk²⁵, also including the propanols, show that as the aquo-substitute molecule is made smaller, the solubility curves seem to converge to a common limit.

Thus, as ammonia, for which aquo-substitute we seek an analogue, is a small molecule, and as methanol is the smallest molecule of the reference aquo-substitutes investigated and also fulfills the demands stated, methanol will be chosen as the aquo-substitute to be used in the following calculations.

Discussion of anomalies

The l/l_0 -curves in dioxane and glycerol media do not coincide with the curves of the primary alcohol media (Figs. 2 and 3). Thus the change of the formal solubility products of the salts in question is not exclusively dependent on the dielectric constant of these solvents. Other factors must operate, such as an incorporation of the aquo-substitute in the solvation sheath of the ions (item 2 in the foregoing) or a complex formation (item 1). If a pure electrostatic attraction is operating, we should expect this effect to be greater for the Ba^{2+} ion than for the larger $\text{Co}(\text{NH}_3)_6^{3+}$ ion. The different courses of the curves of glycerol and dioxane media indicate that several factors are of importance, such as, *e.g.*, the degree of selective solvation and the dimensions of the aquo-substitute molecules. This latter effect may perhaps be accounted for by assuming the operation of London dispersion forces as discussed by Bockris, Bowler-Reed and Kitchener²⁶.

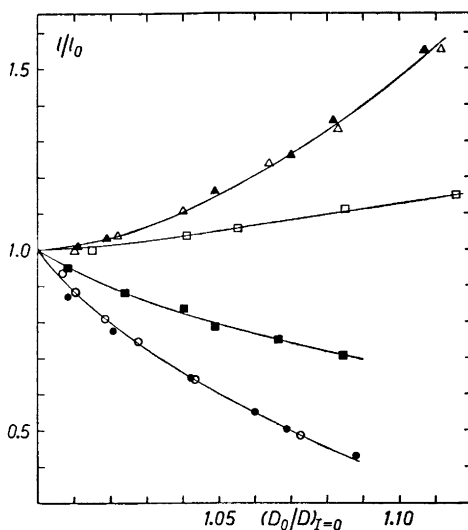


Fig. 3. The $\text{MA}_6(\text{ClO}_4)_3$ solubility curves; l/l_0 plotted against $(D_0/D)_{I=0}$. The symbols refer to the following aquo-substitutes: methanol (○); ethanol (●); glycerol (■); dioxane (□); acetone, when a small amount of chloride ions is present in the solutions (△); acetone, when perchlorate ions are the only anions in the solutions (▲).

Of course a distinction between a strongly selective solvation and complex formation is very difficult to make. In this connection reference²⁷ may be made to the well-known glycerol compounds of the alkaline earth metals.

The solubility curves in the acetone medium, however, exhibit a different picture. The $\text{Ba}(\text{IO}_3)_2$ -curve lies quite close to those of the primary alcohol media. The $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ -curve, on the other hand, indicates an increase of solubility. If we attribute the solubility increase of $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ in ammonia solutions to an ammonia complex formation, we must for the sake of consequence infer a complex formation between acetone and the $\text{Co}(\text{NH}_3)_6^{3+}$ ion. This is not entirely inconceivable as examples of ketonic complexes are known, *e.g.*, from the chemistry of the actinides (*cf.* Rydberg²⁸ and references quoted there).

In a recent review Katzin²⁹ has advanced the opinion that the increase in solubility found for salts in acetone-water solutions originates solely from an increased complex formation between the metal ion and the anions of the salt in question; this should be related to the small affinity of acetone for hydrogen ions and thus — according to Katzin — its small ability to compete with the anions for coordination sites when the water activity is diminished. However, it must be remembered that the parallel between complex formation and base strength, underlying that reasoning, holds true only for ligands of similar structure yielding pure σ -bonds; other factors would invalidate that parallelism.

Now, for practical reasons, the cobalt stock solution of the present work holds a certain amount of chloride ions, which are introduced in the solutions considered in concentrations of about 5 mM. Are these chloride ions responsible for the observed increase in solubility? The decisive experiment is, of course, to determine the solubility in solutions containing only perchlorate ions as anions — tacitly assuming that perchlorate ions do

Table 3. Corresponding values of C_A and C_B (B = methanol) yielding corresponding values of $(L/L_0)_{MA_s}$ and $(L/L_0)_{Ba}$. Calculation of $1 + X$.

C_A M	$(L/L_0)_{Ba}$ The ammonia system	C_B M	$(L/L_0)_{MA_s}$ The methanol system	$(C_M/C_{M_0})_{MA_s}$ The ammonia system	$1 + X$	$\frac{a_A}{a_{aq}}$
0.100	0.964	0.057	0.986	1.007	1.021	0.101
0.250	0.912	0.158	0.963	1.02	1.06	0.256
0.500	0.827	0.328	0.927	1.05	1.13	0.523
0.750	0.747	0.505	0.890	1.09	1.22	0.803
1.000	0.668	0.703	0.851	1.13	1.33	1.094
1.250	0.594	0.902	0.814	1.18	1.45	1.400
1.500	0.526	1.103	0.781	1.23	1.57	1.716
2.000	0.411	1.503	0.720	1.34	1.85	2.392
2.500	0.328	1.915	0.658	1.47	2.24	3.12
3.00	0.267	2.275	0.610	1.65	2.71	3.92
3.50	0.213	2.633	0.565	1.88	3.32	4.77

not form any complexes. Such measurements are reported in Fig. 2. The increase of solubility is not less than for the solutions containing chloride ions. Thus, in this case, an explanation as that proposed by Katzin²⁹ must be ruled out.

Calculations

In the first two columns of Table 3 are given some values of C_A and the corresponding relative decrease of the solubility product of $Ba(IO_3)_2$ in ammonia solution, obtained by graphical interpolation from the data of Table 2. The third column contains the methanol concentrations that give the same relative decrease of L_{Ba} , also obtained by graphical interpolation from Table 2. The relative decrease of L_{MA_s} , as obtained from the values of Table 1, for these values of C_B is given in column 4 of Table 3. This column thus gives L/L_0 of $MA_s(ClO_4)_3$ for the values of C_A in column 1 (Cf. Fig. 1). From the values of $(L/L_0)_{MA_s}$ thus obtained and the corresponding values of C_M/C_{M_0} , given in column 5, $1 + X_A$ has been calculated from eqn. (10).

In the definition of β_n (eqn. (2)) we have used the free ligand concentration $[A]$. However, as C_A is large, C_M very small and the complexity very weak, the approximation $[A] = C_A$ is not an improper one and will be used in the following.

In the last column of Table 3 a_A/a_{aq} is calculated from eqn. (11). In Fig. 4 $X \cdot (a_{aq}/a_A)$ is plotted against a_A/a_{aq} . It is seen that there exists a linear relation between these two quantities.

If we take only the first two terms of eqn. (4) into consideration, it may be transformed to

$$\frac{a_{aq}}{a_A} X = \beta_1 + \beta_2 \cdot \frac{a_A}{a_{aq}} \quad (12)$$

Thus, from the above-mentioned linear relation the first two complexity constants may be obtained.

$$\beta_1 = 0.24 \pm 0.05 \text{ M}^{-1}; \beta_2 \approx 0.05 \text{ M}^{-2}$$

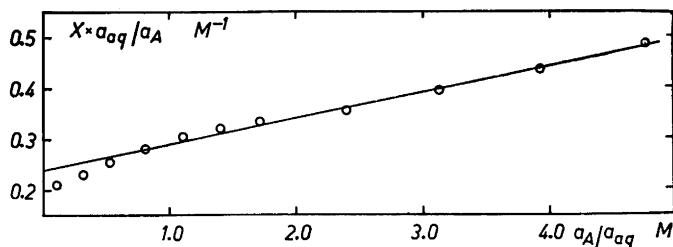


Fig. 4. $X \cdot \frac{a_{aq}}{a_A}$ as a function of a_A/a_{aq} .

However, if we assume the existence of the first complex only but take into consideration the increase of the complexity constant as the dielectric constant of the solvent diminishes (*cf.* Ref.³⁰), we also obtain a linear relation between $\frac{a_{aq}}{a_A} X$ and $\frac{a_A}{a_{aq}}$:

Making the simplifying assumptions of linear dependency of D on C_A and of β_1 on D_0/D , valid at not too large values of D_0/D , we may write

$$D = D_0 - k C_A \quad (13 a)$$

which equation becomes

$$D_0/D = 1 + k' C_A \quad (13 b)$$

and

$$\beta_1 = (\beta_1)_0 (1 + k'' D_0/D) \quad (14)$$

where k , k' and k'' are constants. Combining eqns. (13 b) and (14) we obtain the linear relation

$$\beta_1 = (\beta_1)_0 (1 + k'' + k' k'' C_A) \quad (15)$$

Thus

$$\frac{a_{aq}}{a_A} X = \beta_1 = (\beta_1)_0 (1 + k'') + k' k'' (\beta_1)_0 C_A \quad (16)$$

Or, as C_A is approximately proportional to a_A/a_{aq} (*cf.* eqns. (11)), $\frac{a_{aq}}{a_A} X$ will be a linear function of a_A/a_{aq} , as in Fig. 4.

It is difficult to see how to distinguish between the effects of eqns. (12) and (16). At least we can say that a value of β_2 calculated from eqn. (12) must be a maximum value.

FORMATION OF THE SOLID PHASE $[\text{Co}(\text{NH}_3)_6\text{NH}_3](\text{ClO}_4)_2\text{NO}_3$

Some solubility measurements have also been carried out in a salt medium consisting of 0.150 M NH_4NO_3 and 0.850 M NH_4ClO_4 .

The solubility curve then obtained is presented in Fig. 5. It is seen that at a certain value of the ammonia concentration the curve exhibits a distinct break, indicating that a new solid phase is formed. As the appearance of this

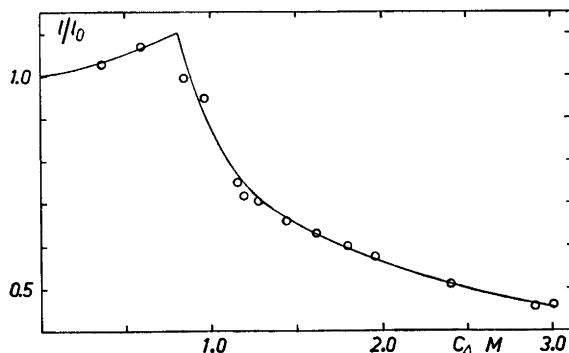


Fig. 5. $(l/l_0)_{MA}$ as a function of C_A in a salt medium of the composition 0.850 M NH_4ClO_4 , 0.150 M NH_4NO_3 .

new phase is obviously dependent on the presence of both nitrate ions and ammonia, we may expect it to be of the general composition $(Co(NH_3)_6)(NH_3)_x(ClO_4)_{3-y}(NO_3)_y$

Analysis of the solid phase. Some $Co(NH_3)_6(ClO_4)_3$ — unlabelled — was shaken with 100 ml of a solution of the following composition: 2.4 M NH_3 , 0.15 M NH_4NO_3 and 0.85 M NH_4ClO_4 . After a day the solid phase was separated and washed with alcohol until no ammonia could be detected, then washed with ether and air-dried. The substance thus obtained lost ammonia slowly on storage in open vessels at room temperature and rapidly at 100°C. The dried substance was analyzed for nitrate content according to Lindo³¹ and for cobalt by a colorimetric determination of the $Co(NH_3)_6^{3+}$ ion at 472 m μ . (NO_3^- : Calc. for $Co(NH_3)_6(ClO_4)_2NO_3$ 14.7 %; Found 14.8 %, Co: Calc. 13.97 %; Found 13.96 %.)

If the ether-dried substance was rapidly weighed and thereafter dried at 100°C, it lost 3.7 % of its weight. (Calc. for $[Co(NH_3)_6NH_3](ClO_4)_2NO_3$ 3.9 %.) This result is in agreement with solid phase studies of Ephraim³² and of Spacu and Voishescu³³, which indicate that $[Co(NH_3)_6NH_3]Cl_3$, though not stable, may be isolated at room temperature.

Thus we may conclude that the new solid phase is $[Co(NH_3)_6NH_3](ClO_4)_2NO_3$. However, as the composition of the solid phase gives no direct information on the composition of the ionic species in solution, no further investigation was made.

THE LIGHT ABSORPTION MEASUREMENTS

The absorption spectrum of the $Co(NH_3)_6^{3+}$ ion in ammonia solutions has been investigated once by Nakatsuka³⁴ who, however, reports no perceptible change with increasing ammonia concentration.

The low solubility of $Co(NH_3)_6(ClO_4)_3$ and the weak complexity under consideration render a complete extinctionsimetric investigation impossible. However, an approximate method has been attempted, under the assumption that only the first complex is present in appreciable amounts. (For a complete theory see, e.g., Ahrlund³⁵.) In order to reach higher values of C_M , the measurements have been performed at ionic strength 0.1 M.

The following notations are used:

ϵ_0 = extinction coefficient of the MA_6^{3+} ion
 ϵ_1 = " " " " " " " " $(\text{MA}_6)\text{A}^{3+}$ ion
 E = measured optical density
 d = cell thickness (cm)

The quantity ϵ_M is defined by

$$E = d\epsilon_M C_M \quad (17)$$

Hence,

$$\epsilon_M C_M = \epsilon_0 [\text{MA}_6] + \epsilon_1 [(\text{MA}_6)\text{A}] \quad (18)$$

Introducing the complexity constant β_1 from eqn. (3) we can rewrite eqn. (18)

$$\epsilon_M - \epsilon_0 = \frac{(\epsilon_1 - \epsilon_0)\beta_1 \cdot [\text{A}] \cdot f_A/a_{\text{aq}}}{1 + \beta_1 \cdot [\text{A}] \cdot f_A/a_{\text{aq}}} \quad (19)$$

If $q = \frac{\epsilon'_M - \epsilon_0}{\epsilon''_M - \epsilon_0}$ where ϵ'_M and ϵ''_M are measured at $C_A = C'_A$ and C_A'' respectively, and if we put $C'_A = [\text{A}]'$ and $C_A'' = [\text{A}]''$ we obtain from eqn. (19)

$$\beta_1 = \frac{q C_A'' f_A''/a''_{\text{aq}} - C'_A f'_A/a'_{\text{aq}}}{C'_A f'_A/a'_{\text{aq}} \cdot C_A'' f_A''/a''_{\text{aq}} (1-q)} \quad (20)$$

Here f'_A and a'_{aq} denote the activity coefficient of A and water activity at $C_A = C'_A$, etc.

These quantities are calculated from eqns. (11 a) and (11 b) under the same assumption as before, *i.e.*, that f_A and a_{aq} are functions dependent only on C_A . This means that f_A and a_{aq} are now determined by the condition that $f_A = 1$ and $a_{\text{aq}} = 1$ in solutions 0.1 M NH_4ClO_4 , $C_A = 0$.

From the paper³⁵ referred to it follows that if other complexes than the first one also exist, the value of β_1 will be too small.

On the other hand, if only the first complex exists, as assumed here, but the determination is performed at a rather high ammonia concentration, the value of β_1 thus found will be greater than that valid at zero ammonia concentration, as follows from eqn. (15).

From these measurements we can thus expect only an indication of the order of magnitude of β_1 .

Experimental. The measurements were performed in the ultraviolet wave length region, where outer-sphere association has previously been found to cause the greatest change in the absorption spectrum of the cobalt hexammine ion (Refs. ^{3,3,9-11}). The apparatus used was a Beckman Quartz Spectrophotometer (Model DU), changed as described by Adell³⁶.

The solutions were all 5.00 mM with respect to $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$. The ionic strength was kept 0.1 M by adding NH_4ClO_4 . Four sets of measurements were made, with $C_A = 0, 0.320, 0.640$ and 0.960 M. The reference cell contained ammonia at the same concentration and so much of NH_4ClO_4 that the perchlorate concentration was equal to that in the other cell.

For $E > 0.1$ the reproducibility was $\pm 2\%$, which may be accepted in view of the great systematic errors of the method.

Table 4. Calculation of the quotient q and β_1 from the experimental values of ϵ_M and ϵ_0 .

$C'_A = 0.320 \text{ M};$		$C''_A = 0.640 \text{ M};$		$C'''_A = 0.960 \text{ M}$		
$q_1 = \frac{\epsilon'_M - \epsilon_0}{\epsilon''_M - \epsilon_0}$				$q_2 = \frac{\epsilon''_M - \epsilon_0}{\epsilon'''_M - \epsilon_0}$		
$m\mu$	$\log \epsilon_0$	$\log \epsilon'_M$	$\log \epsilon''_M$	$\log \epsilon'''_M$	q_1	q_2
255	0.765	0.925	1.00	1.075	0.43	0.69
250	1.105	1.235	1.305	1.37	0.42	0.70
248	1.27	1.38	1.445	1.505	0.40	0.69
246	1.455	1.55	1.605	1.66	0.41	0.69
244	1.645	1.72	1.765	1.815	0.39	0.67
242	1.85	1.91	1.95	1.99	0.39	0.68
240	2.06	2.105	2.135	2.17	0.38	0.65
238	2.265	2.30	2.33	2.355	0.37	0.71
236	2.465	2.495	2.515	2.535	0.41	0.69
234	2.66	2.68	2.70	2.715	0.36	0.71
233	2.75	2.77	2.785	2.805	0.35	0.63
232	2.84	2.865	2.88	2.895	0.44	0.72
231	2.93	2.95	2.965	2.98	0.38	0.69
Mean					0.39	0.69
					$\beta_1 \text{ M}^{-1}$	
					0.38	0.20
					0.3 ± 0.2	

If we attribute the second-order term in a_A/a_{aq} , that was found from the solubility measurements, exclusively to the change in the dielectric constant we can introduce in eqn. (19) the correction:

$$\beta_1 = (\beta_1)_0 + 0.05 a_A/a_{aq}$$

This gives us a second-order equation in $(\beta_1)_0$ which renders $(\beta_1)_0 = 0.44$ and 0.32 , valid at $C_A = 0$ and $I = 0.1 \text{ M}$ and corresponding to the two values of q of Table 4.

This correction thus reduces the relative spreading appreciably.

Results. In Table 4 the calculations are shown for those wave lengths where the shift of the extinction coefficients is large enough to permit calculations of some degree of accuracy.

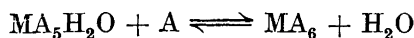
COMPARISON BETWEEN THE SOLUBILITY AND THE LIGHT ABSORPTION METHODS

As different standard states have been used for f_A in the solubility measurements and in the light absorption measurements, the constants obtained are not directly comparable.

However, from theoretical considerations Bjerrum (Ref.²⁰, p. 129) presents the formula,

$$\log \beta = \log \beta_0 + 0.03 C_{\text{NH}_4^+} \quad (21)$$

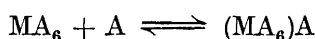
where β denotes the association constant for the association of one ammonia to a metal ion. Experimentally he finds very different values of the coefficient, both positive and negative ones, and especially for the reaction



he finds (Ref.²⁰, p. 281) for the equilibrium constant β

$$\log \beta = \log \beta_0 + 0.18 C_{\text{NH}_4^+} \quad (22)$$

If this surprisingly great coefficient is assumed to apply also for the very similar reaction considered here,



we must conclude that β_1 at ionic strength 1 M should be about 40 % greater than at ionic strength 0.1 M.

Thus for ionic strength 1 M we have:

$$\begin{aligned} \beta_1 &= 0.24 \pm 0.05 \text{ M}^{-1} && \text{(solubility method)} \\ \beta_1 &= 0.4 \pm 0.3 \text{ M}^{-1} && \text{(light abs. method)} \end{aligned}$$

If we prefer to make the "salt effect" correction with the help of eqn. (21), we obtain a smaller value $\beta_1 = 0.3 \pm 0.2 \text{ M}^{-1}$ (light abs. method).

Furthermore, if there exists a slight barium-ammonia complexity, which we have assumed not to be the case, the value of β_1 calculated from the solubility measurements should be somewhat greater. (The curve in the left diagram of Fig. 1 should be steeper and for a given value of C_A we should obtain a greater \bar{X} than that reported.)

To sum up, we can state that the results of the two methods are not inconsistent.

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