

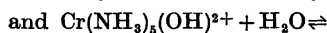
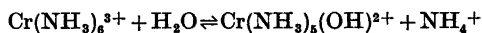
Equilibrium Studies of Chromium(III) Complexes. II. The Complex Formation between Chromium(III) and Ammonia in Aqueous Solution

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Equilibrium has been obtained between $\text{Cr}(\text{NH}_3)_6^{3+}$, $\text{Cr}(\text{NH}_3)_5\text{OH}^{2+}$, *cis*- $\text{Cr}(\text{NH}_3)_4(\text{OH})_2^+$, and *trans*- $\text{Cr}(\text{NH}_3)_4(\text{OH})_2^+$ in aqueous solutions with $C_{\text{NH}_4\text{Cl}} = 4.5 \text{ M}$, $C_{\text{NH}_3} = 2-10 \text{ M}$, and $C_{\text{Cr(III)}} = 0.05 \text{ M}$. Equilibrium was established within 5 days at room temperature due to the combined catalytic effect of chromium(II) and charcoal.

The hydrolysis constants of the reactions

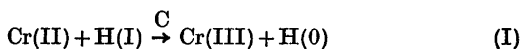


are found to be 195 M and 3.16 M, respectively, and the ratio between *cis*- and *trans*- $\text{Cr}(\text{NH}_3)_4(\text{OH})_2^+$ to be 4.9. The fifth and sixth consecutive stability constants are calculated to be $K_5 = 10^{1.6} \text{ M}^{-1}$ and $K_6 = 10^{1.5} \text{ M}^{-1}$, and on the basis of emf measurements the gross stability constant, β_6 , can be estimated to be 10^{13} M^{-6} .

The equilibrium solutions, with $[\text{NH}_3] = 9 \text{ M}$, contain ca. 5% of polynuclear chromium(III) species and this amount increases with decreasing ammonia concentration, but equilibrium has only been demonstrated between the mononuclear complexes mentioned above.

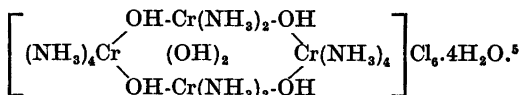
In a recent paper¹ we introduced a new method of obtaining equilibrium between chromium(III) and different amine ligands in aqueous solution. The method was applied to the ethylenediamine system and is based on the catalytic effect of charcoal and chromium(II), both of which must be present in the solutions to be equilibrated. During the 3–5 days of equilibration a steady state with a constant, small concentration of chromium(II) is maintained by electrolytic

reduction of chromium(III) to chromium(II). In this steady state the amount of chromium(II) generated by electrolysis equals the amount removed due to the charcoal-catalyzed oxidation by the medium:



This paper concerns the application of the method to the chromium(III)–ammonia system.

It is necessary to keep a high ammonium-ion concentration in the ammonia solutions in order to prevent the formation of basic chromium(III) precipitates. Several reactions in such ammonia-ammonium chloride buffers with all chromium initially present as chromium(II) have been described. Rhodo chloride, $[(\text{NH}_3)_5\text{CrOHCr}(\text{NH}_3)_5]\text{Cl}_5 \cdot \text{H}_2\text{O}$, is formed if such solutions are oxidized by air.² If the solutions are kept in an inert atmosphere, Jørgensen³ found that luteo chloride, $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3 \cdot \text{H}_2\text{O}$, was formed as well as some rhodoso chloride,^{3,4}



Later attempts to prepare the hexammine in this way have been futile unless one adds small amounts of, preferably group VIII, metals or metal ions.⁶ These metals have the effect that the small rate of oxidation of chromium(II) to chromium(III) under hydrogen evolution, which

is observed when no catalyst is present (reagent grade chemicals), is increased so that one obtains rates of oxidation and yields of hexamine similar to those observed by Jørgensen. Addition of charcoal likewise increases the rate of oxidation but the yield of hexamine is negligible. On the other hand addition of chromium(II) to such ammonia-ammonium chloride buffers containing hexamine and charcoal has the effect that the hexamine disappears within a few minutes.⁶ These observations led to equilibration experiments with the catalyst charcoal + chromium(II). In these experiments all the chromium was initially present as chromium(II)^{7,8} which, however, involved the difficulty that the chromium(II) might disappear according to reaction (I) before equilibrium was reached. With the new method by which it is possible continuously to keep part of the chromium as chromium(II) this problem has been solved, and we present here the results of an investigation of the complex formation under these circumstances in 4.5 M ammonium chloride with the ammonia concentration varying between 2 and 10 M.

EXPERIMENTAL

Procedure. The procedure and equipment has been described in a similar investigation with ethylenediamine.¹ All experiments were carried out at (24 ± 1) °C using $C_{Cr} = 0.05$ M, $C_{NH_4Cl} = 4.5$ M, and $C_{NH_3} = 2 - 10$ M. 2 g charcoal *per* l were used and the solutions were equilibrated for 3–10 days with a current of *ca.* 10 mA giving a chromium(II) concentration of *ca.* 10^{-3} M. The equilibration was followed by taking out samples which were analyzed as described below. Pairs of experiments with the same ammonia concentration, but different initial chromium(III) compound, within 3–5 days gave an identical distribution of at least the mononuclear complexes, and further equilibration did not change this distribution. Changes in $[NH_3]$ and $[NH_4^+]$ during the equilibration were negligible when 2 M H_2SO_4 was used in the anode chamber and the gas outlet was under ammonia of the same concentration as in the cathode chamber.

During the equilibration the emf was measured with a mercury electrode *vs.* a saturated calomel electrode and the Cr(II) content was determined in the same way as in the ethylenediamine system.¹

Analysis of the composition of the equilibrium solutions. $[NH_3]$ was determined by potentiometric titration with 0.1 M HCl. The distribution of the chromium(III) complexes was determined by atomic absorption spectro-

photometry after separation of the complexes by cation-exchange chromatography on columns of Sephadex SP-C-25. The robustness of the chromium(III) complexes, after removal of the catalyst, made this analytic procedure possible. The results of these analyses for a series of experiments, exp. 1–12, are given in Table 1.

The basic and acid chromatographic separations were very similar to those described for the ethylenediamine complexes.¹ A basic elution with an NH_4Cl/NH_3 buffer with $[NH_3] = 0.1$ M and $[NH_4^+]$ increasing from 0.5 to 2.0 M divided the mixture into the following bands of mononuclear complexes with increasing charge: A first band containing *cis-* and *trans-* $Cr(NH_3)_4(OH)_2^+$, a second one containing $Cr(NH_3)_5OH^{2+}$, and a third one containing $Cr(NH_3)_6^{3+}$. Four bands followed the $Cr(NH_3)_6^{3+}$ band. None of these purple species could be identified as mononuclear complexes and are therefore assumed to be polynuclear ones. A few per cent of the chromium remained on the column, even after elution with 2 M NH_4Cl . The first polynuclear band was at the end of the $Cr(NH_3)_6^{3+}$ -band but subsequent acid chromatography (0.7 M NH_4Cl , 10^{-3} M HCl) easily separated these two species.

The acid elution with 0.5 M NH_4Cl or NaCl ($pH \approx 2 - 3$) did not result in a complete separation of the mononuclear complexes, now having the same charge, but gave a check on the sum of these. We were able to separate the remaining polynuclear species in up to four bands by increasing the concentration of the eluting agent to 1–2 M.

Identification of the chromium(III) complexes. The same methods were used to identify the chromium species as were used for the ethylenediamine system.¹ The elution rates gave an indication of the charge and the visible spectra and the ESR spectra of the eluates, which, when necessary, were concentrated on separate columns, identified the well known mononuclear complexes. Analysis of the molar ratio between chromium and nitrogen in the eluates after removal of nitrogen not bound to chromium was used in attempts to identify the polynuclear species. Furthermore, the crystalline iodide of the chromium species in the third polynuclear band was isolated and analyzed.

As mentioned above we were not able to separate *cis-* and *trans-* $Cr(NH_3)_4(OH)_2^+$ completely by ion-exchange chromatography but the visible spectra and the ESR spectra of the diaqua complexes showed that they are both present, and from analysis of the spectra it was possible to determine the ratio between them.

Chemicals and apparatus. All chemicals used were reagent grade or analyzed by us. $[Cr(NH_3)_6]Cl_3$,⁹ *cis-* $[Cr(NH_3)_4Cl(H_2O)]Cl_2$,⁹ *cis-* $[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$,¹⁰ *trans-* $[Cr(NH_3)_4(OH)H_2O](ClO_4)_2$,¹¹ *trans-* $[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$,¹¹ and *cis-* $[Cr(NH_3)_2Cl_2(H_2O)_2]Cl$ ⁹

Table 1. The composition of the solutions from experiments 1 to 12. $C_{\text{NH}_4\text{Cl}} = 4.5 \text{ M}$. a_6 is $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$, $cis-a_2$ is $cis\text{-}[\text{Cr}(\text{NH}_3)_4\text{Cl}_2(\text{H}_2\text{O})_2]\text{-Cl}\cdot\text{H}_2\text{O}$, $cis-a_4$ is $cis\text{-}[\text{Cr}(\text{NH}_3)_4\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}_2$, and $trans-a_4$ is $trans\text{-}[\text{Cr}(\text{NH}_3)_4(\text{OH})(\text{H}_2\text{O})_3]\text{ClO}_4$. The content of mononuclear complexes are in mol % relative to the total chromium(III) content. () denote analyses repeated after six months. The equilibrium constants of the reactions II, III, and IV are given in the last three columns.

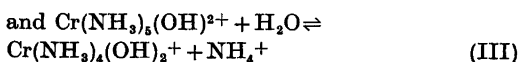
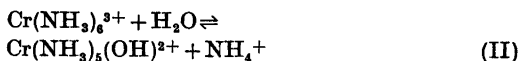
Exp. No.	$[\text{NH}_3]$ (M)	C_{Cr} (mM)	Initial Cr-comp.	% $\text{Cr}(\text{NH}_3)_6^{3+}$	% $\text{Cr}(\text{NH}_3)_5\text{OH}^{2+}$	% $\text{Cr}(\text{NH}_3)_4(\text{OH})_2^+$	$K_{\text{hs}/s}$ (M)	$K_{\text{hs}/4}$ (M)	$10^3 \times K_{\text{disp}}$
1	2.60	48.2	a_6	1.00	36.5	21.8	164	2.69	1.64
2	(2.61)	48.0		(0.55)	(20.5)	(12.6)	(168)	(2.77)	(1.65)
3	2.42	48.7	$cis-a_2$	0.92	36.1	21.0	177	2.62	1.48
4	3.78	48.7	a_6	1.40	47.7	23.1	153	2.18	1.42
5	3.62	49.5	$cis-a_4$	1.50	47.4	23.6	142	2.24	1.57
6	4.66	50.1	a_6	1.83	55.1	24.7	135	2.02	1.49
7	4.77	49.3	$cis-a_4$	1.78	54.6	24.2	138	1.99	1.44
8	6.64	49.4	a_6	2.48	64.6	24.2	117	1.69	1.44
9	6.55	50.2	$trans-a_4$	2.39	65.3	23.7	123	1.63	1.32
10	8.19	50.3	a_6	3.22	71.1	21.3	99.3	1.35	1.36
11	8.24	50.9	$cis-a_2$	3.01	71.8	20.9	107	1.31	1.23
12	9.27	48.2	a_6	4.04	74.4	17.1	82.8	1.03	1.24
	9.18	50.1	$trans-a_4$	3.97	74.1	17.6	84.0	1.07	1.27
	(9.21)			(3.57)	(68.8)	(16.0)	(86.7)	(1.05)	(1.21)

were prepared according to or analogously to the reference methods and were analyzed for Cr, N, and chloride. All analyses agreed within 1–2% (relative) with the given formulae. The charcoal used was a Norit W product.

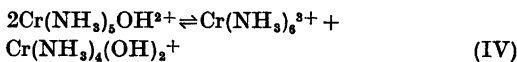
Visible spectra were taken on a Cary 14 or a Bausch and Lomb Spectronic 505 recording spectrophotometer and ESR spectra of frozen glasses (diluted $\times 2$ with glycerol) on a Jeol JES-ME-1X at -130°C and 9.3 GHz. The emf and pH measurements were performed with a Radiometer PHM 52, the G 202 C glass electrodes being tested in the relevant media according to Bjerrum.¹²

RESULTS

Equilibria. We have studied the following hydrolysis reactions:



which can be combined in the disproportionation reaction



$\text{Cr}(\text{NH}_3)_4(\text{OH})_2^+$ exists in a *cis*- and a *trans*-form and the equilibrium between these forms was also studied.

The composition of the equilibrium solutions are given in Table 1 for the series of experiments 1–12. Each solution was equilibrated *ca.* 5 days after which no further changes could be observed. Solutions with the same ammonia concentration but different initial chromium(III) compound had then attained the same distribution of mononuclear species. This distribution of $\text{Cr}(\text{NH}_3)_6^{3+}$, $\text{Cr}(\text{NH}_3)_5(\text{OH})^{2+}$, and $\text{Cr}(\text{NH}_3)_4(\text{OH})_2^+$ (*cis*- and *trans*-) are given in Table 1, and at the end of the table are the calculated values of the hydrolysis constants of reactions II and III, *i.e.* $K_{\text{h5/5}}$ and $K_{\text{h5/4}}$, respectively, together with the disproportionation constant K_{disp} of reaction IV.

The ratio $q_2 = [\text{cis-Cr}(\text{NH}_3)_4(\text{OH})_2^+]/[\text{trans-Cr}(\text{NH}_3)_4(\text{OH})_2^+]$ was determined in two ways, the results of which are given in Table 2. Both methods are based on analyses of the mixed *cis*- and *trans*-tetrammine eluates in 1 M perchloric acid.

Table 2. $q_2 = [\text{cis-Cr}(\text{NH}_3)_4(\text{OH})_2^+]/[\text{trans-Cr}(\text{NH}_3)_4(\text{OH})_2^+]$ determined in the tetrammine eluates (1 M HClO_4) from visible spectra (method A) and ESR spectra (method B).

Exp. No.	A	q_2	B
1	5.2		6
3	4.1		4
6	4.6		5
7	4.3		4
10	5.0		6
11	5.3		6
Average		4.9	

By method A, the visible spectra of the eluates and of the pure components were used for the calculation of the composition of the eluates, according to Mønsted.¹⁰

By method B, the ESR spectra of the frozen glasses of the eluates were used in a manner similar to the one by which we determined the equilibrium ratio between *cis*- and *trans*- $\text{Cr en}_2(\text{OH})_2^+$.¹ As shown in Fig. 1 the ESR spectrum of *trans*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$, unlike *trans*- $\text{Cr en}_2(\text{H}_2\text{O})_2^{3+}$, does not contain any narrow bands so that the method is not particularly well suited in this respect. It has, however, the advantage that the solutions are cooled rapidly to -130°C so that further reaction is prevented.

From these results it is possible to calculate the 5th and 6th consecutive stability constants, K_5 and K_6 , respectively. This is done in Table 3. The acid dissociation constants of the pentammine and tetrammines have been measured by other workers in 1 M salt medium^{13,14} and are in Table 3 estimated to be 0.7 pK units higher in 4.5 M NH_4Cl . This is the increase that one finds when extrapolating the measurements, by Bjerrum, of $\text{p}K_{\text{S pen}}$ for $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ in ammonium salt media with $[\text{NH}_4^+]$ varying between 0.25 and 2.0 M.¹²

The variation of $K_{\text{h5/5}}$ and $K_{\text{h5/4}}$ and the small variation of K_{disp} with the ammonia concentration are shown in Fig. 2. The values of $K_{\text{h5/5}}$ and $K_{\text{h5/4}}$ used in Table 3 are those obtained from extrapolation to $[\text{NH}_3] = 0$.

Estimation of the gross stability constant, β_6 , from emf-measurements. The electrode potential, E , was measured with a mercury electrode (saturated calomel as reference electrode) and

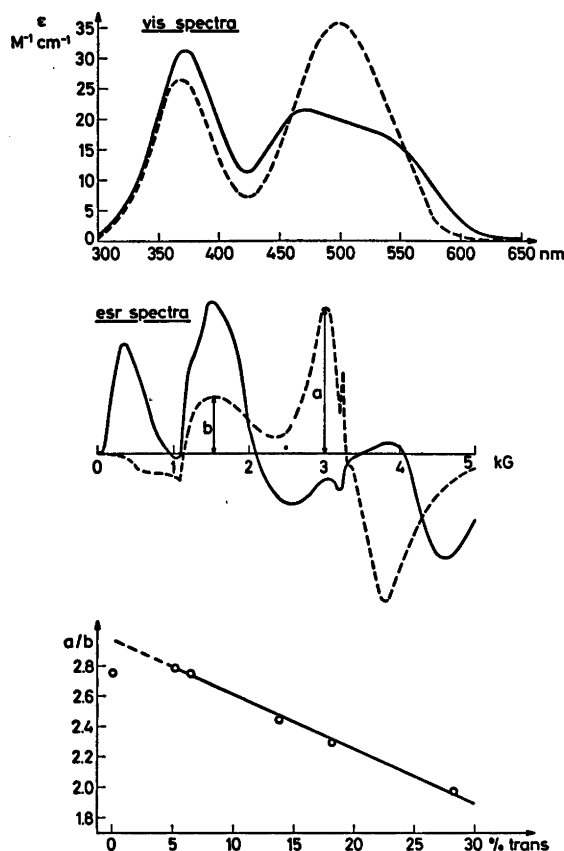


Fig. 1. Visible spectra and first derivative ESR spectra of *cis*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$ (---) and *trans*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$ (—). The ESR spectra were measured of frozen glasses of 1:1 mixtures of glycerol and aqueous 1 M HClO_4 solutions of the perchlorates at -130°C and 9.3 GHz.

The lowest figure gives the ratio between the peak heights *a* and *b* plotted as a function of mol per cent *trans*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$ relative to the sum of *cis* and *trans*, in different known mixtures of *cis*- and *trans*-tetrammine. In method B (Table 2) this plot was used to find q_2 in the tetrammine eluates from some of the exp. 1–12.

simultaneously $[\text{Cr}(\text{II})]$ was determined in similar ways to those described in our investigation with ethylenediamine as ligand.¹ Table 4 shows such measurements from exp. 1–12 when the solutions were at their final state of equilibration. It is possible, from these data, to make an estimate of the gross stability constant, β_6 , for the reaction $\text{Cr}(\text{H}_2\text{O})_6^{3+} + 6\text{NH}_3 \rightleftharpoons \text{Cr}(\text{NH}_3)_6^{3+} + 6\text{H}_2\text{O}$:

$$\log \beta_6 = \log \beta_4^{\text{II}} - (E + 652)/59 +$$

$$\log \frac{[\text{Cr}(\text{NH}_3)_6^{3+}]}{[\text{Cr}(\text{NH}_3)_4^{2+}][\text{NH}_3]^2}$$

$$\beta_4^{\text{II}} = \frac{[\text{Cr}(\text{NH}_3)_4^{2+}]}{[\text{Cr}(\text{H}_2\text{O})_4^{2+}][\text{NH}_3]^4}$$
 can be estimated to

be 10^5 M^{-4} by comparison with the chromium(II)–ethylenediamine system¹⁵ and with other metal ammine and ethylenediamine systems (mainly copper(II)).^{12,15} “652” is the sum of the standard potentials of the $\text{Cr}^{2+} - \text{Cr}^{3+}$ couple and of the saturated calomel electrode (410 mV¹⁶ and 242 mV, respectively). Under our conditions all chromium(II) is likely to be present as $\text{Cr}(\text{NH}_3)_4^{2+}$. We determined \bar{n} to be 4, within the experimental error, in solutions

Table 3. Calculation of the stability constants K_6 , $K_5 \text{ cis}$, $K_5 \text{ trans}$ and K_6 in 4.5 M NH_4Cl .

$$\begin{aligned}
 K_6 &= \frac{[\text{Cr}(\text{NH}_3)_6^{3+}]}{[\text{Cr}(\text{NH}_3)_6(\text{H}_2\text{O})_2^{3+}][\text{NH}_3]} &= \frac{K_{\text{S pen}}}{K_{\text{hs/6}} \cdot K_{\text{S NH}_4^+}} &= 10^{1.5} \text{ M}^{-1} \\
 K_5 \text{ cis} &= \frac{[\text{Cr}(\text{NH}_3)_6(\text{H}_2\text{O})_2^{3+}]}{[\text{cis-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}][\text{NH}_3]} &= \frac{K_{\text{S1 cis}} \cdot K_{\text{S2 cis}}}{K_{\text{hs/4 cis}} \cdot K_{\text{S pen}} \cdot K_{\text{S NH}_4^+}} &= 10^{1.6} \text{ M}^{-1} \\
 K_5 \text{ trans} &= \frac{[\text{Cr}(\text{NH}_3)_6(\text{H}_2\text{O})_2^{3+}]}{[\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}][\text{NH}_3]} &= \frac{K_{\text{S1 trans}} \cdot K_{\text{S2 trans}}}{K_{\text{hs/4 trans}} \cdot K_{\text{S pen}} \cdot K_{\text{S NH}_4^+}} &= 10^{2.5} \text{ M}^{-1} \\
 K_6 &= \frac{[\text{Cr}(\text{NH}_3)_6(\text{H}_2\text{O})_2^{3+}]}{\{[\text{cis-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}] + [\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}]\}[\text{NH}_3]} &= \frac{K_5 \text{ cis} \cdot K_5 \text{ trans}}{K_5 \text{ cis} + K_5 \text{ trans}} &= 10^{1.6} \text{ M}^{-1}
 \end{aligned}$$

From Fig. 2: $K_{\text{hs/6}} = 195 \text{ M}$ and $K_{\text{hs/4}} = 3.16 \text{ M}$. $q_2 = 4.9$

$$K_{\text{hs/4 cis}} = \frac{q_2}{1 + q_2} \times K_{\text{hs/4}} = 2.62 \text{ M}, \quad K_{\text{hs/4 trans}} = \frac{1}{1 + q_2} \times K_{\text{hs/4}} = 0.54 \text{ M}$$

Acid dissociation constant for NH_4^+

$$\begin{array}{ll}
 \gg \text{Cr}(\text{NH}_3)_6(\text{H}_2\text{O})_2^{3+} & : K_{\text{S NH}_4^+} = 10^{-9.6} \text{ M}^{12} \\
 \gg \text{constants} \gg \text{cis-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+} & : K_{\text{S pen}} = 10^{-6.0} \text{ M}^{13} \\
 \gg \gg \text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+} & : K_{\text{S1 cis}} = 10^{-5.7} \text{ M}, K_{\text{S2 cis}} = 10^{-8.1} \text{ M}^{13,14} \\
 \gg \gg \gg & : K_{\text{S1 trans}} = 10^{-5.1} \text{ M}, K_{\text{S2 trans}} = 10^{-8.5} \text{ M}^{14}
 \end{array}$$

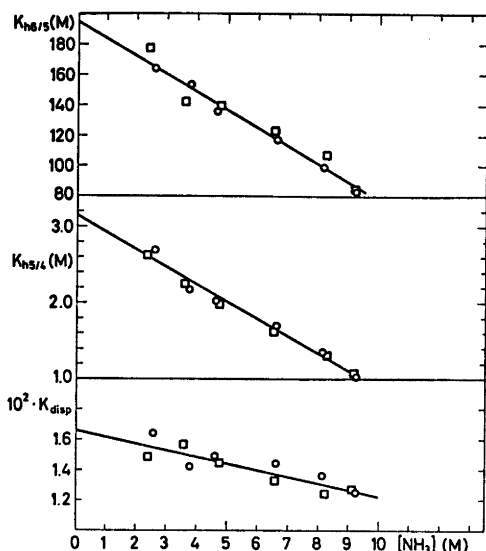


Fig. 2. The hydrolysis constants $K_{h6/5}$ and $K_{h5/4}$ and the disproportionation constant $K_{disp} = K_{h5/4}/K_{h6/5}$ as a function of $[NH_3]$, with $[Cr(NH_3)_6]Cl_3$ (O) and lower ammine complexes (\square) as initial Cr(III) compound (exp. 1–12).

Table 4. $\log \frac{\beta_6}{\beta_4^{II}} (= -(E + 652)/59 +$

$$\log \frac{[Cr(NH_3)_6^{3+}]}{[Cr(II)][NH_3]^2})$$

determined from measurements of $[Cr(II)]$ and the electrode potential, E , between a mercury and a saturated calomel electrode in solutions 1 to 12 at their final state of equilibration.

Exp. No.	$-E$ (mV)	$[Cr(II)]$ (mM)	$\log \frac{\beta_6}{\beta_4^{II}}$
1	1126	0.25	7.5
2	1140	0.31	7.7
3	1181	0.54	7.9
4	1201	1.0	8.1
5	1155	0.35	7.6
6	1120	0.10	7.5
7	1182	0.37	7.9
8	1162	0.28	7.6
9	1210	0.97	7.9
10	1150	0.21	7.5
11	1230	2.3	7.8
12	1205	0.52	8.0
Average:			7.7 ₅

with $C_{NH_4Cl} = 4.5$, $C_{Cr(II)} = 0.25$ M and with $[NH_3]$ varying between 1.1 and 2.3 M. These measurements were made with a glass electrode according to Bjerrum.¹² The calculated values of $\log(\beta_6/\beta_4^{II})$ in exp. 1–12 are given in Table 4, giving an estimated value of $\beta_6 = 10^{13} M^{-6}$.

Polynuclear complexes. From Table 1 the mononuclear complexes comprise nearly 100 % of the total chromium content at high ammonia concentrations. The content of polynuclear complexes increases as the ammonia concentration decreases. From the separations by ion-exchange chromatography we know that there are at least four different polynuclear species in the solutions but we have not yet been able to identify any of these. Analyses show that the molar ratio between Cr and N is 1:3 for the polynuclear species in the first three bands. We isolated the third polynuclear species as the iodide and this crystalline salt analyzed as $\{Cr_2(NH_3)_6(OH)_3I_3(H_2O)_4\}_n$ (Found: Cr 14.62; I 53.21; N 12.18. Calc.: Cr 14.64; I 53.62; N 11.84).

DISCUSSION

We conclude from the results given in the previous section that equilibrium has been obtained among the mononuclear amines mentioned, just as we found when using the catalyst with the ethylenediamine system. Part of the equilibrium solutions from exp. 1–12 was filtered after the equilibration and kept in glass ampoules for six months after which they were reanalyzed. The results of such repeated analyses are given in Table 1 and show that the molar ratio between the mononuclear complexes is unchanged. The total amount of mononuclear complexes has, however, decreased at the expense of polynuclear complexes, especially at low ammonia concentration.

Table 1 shows that the amount of polynuclear species is highest at low ammonia concentrations. This is what one would expect from the equilibria when ammonia and hydroxide ions are the only ligands bound to chromium(III)⁸ as ammonia is released when OH-bridges are formed, e.g.

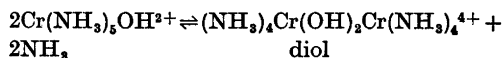


Table 5. Comparison of stability constants, at room temperature, for Cr(III), Co(III), and Ni(II) with ammonia (extrapolated values) and ethylenediamine (en).

	NH ₃			en	
	log K _s	log K ₆	log β ₆	log K _s	log β _s
Cr(III) ¹	1.6	1.5	13	6.4	19.5
Co(III) ^{12,20,21}	5.5	4.9	38	13.3	48.7
Ni(II) ^{12,22}	0.9	0.2	10	4.4	18.3
Medium	4.5 M NH ₄ Cl			1 M 1:1 salt	

The analyses, repeated after six months, show, however, that equilibria involving polynuclear complexes are attained much more slowly, if at all. We are at present continuing our investigations of these complexes.

The change in the water activity is probably the main reason why $K_{\text{hs/5}}$ and $K_{\text{hs/4}}$ decrease with increasing ammonia concentration as shown in Fig. 2. K_{disp} for the reaction involving the complex ions only is less dependent on the ammonia concentration in the investigated interval. At very high ammonia concentrations and correspondingly low water concentrations one would expect equilibrium II to be displaced in favour of $\text{Cr}(\text{NH}_3)_6^{3+}$.

This was confirmed by an experiment with $C_{\text{NH}_4\text{Cl}} = 4.5 \text{ M}$, $C_{\text{NH}_3} = 15 \text{ M}$ (continuous NH₃-gas flow) and $C_{\text{Cr}} = 0.10 \text{ M}$ (initially as *cis*-[Cr(NH₃)₄Cl(H₂O)]Cl₂), which after equilibration gave 12.4 % Cr(NH₃)₆³⁺.¹⁷

The results of this work are summarized in Table 5 which, for comparison, also shows the corresponding stability constants for the chromium(III) ethylenediamine system and also those for Co(III) and Ni(II). The stability constants for chromium(III) and ammonia are intermediate between those for Ni(II) and Co(III) and closer to Ni(II) as we have found for ethylenediamine¹ and EDTA.⁹ Stability constants for complexes of ammonia are very close to those with ethylenediamine when bound as a monodentate ligand¹ ($10^{1.6}$ and $10^{1.4}$, respectively, for Cr(III)), as it has been found also for Ag(I)¹⁸ and Hg(II).¹⁹

The determination of the gross stability constant is only an estimate because β_4^{II} is based on an estimate. β_3 for Cr en₃³⁺ seems a little low when compared to β_3 for Ni en₃³⁺. Any small error in the emf due to the Cr(III)/

Cr(II) couple as measured in this way with the mercury electrode will most probably be in the direction which would give low gross stability constants, because possible formation of hydrogen at the mercury surface will tend to make the initial (very negative) potentials less negative. We have, however, investigated the reliability of the mercury electrode more thoroughly in connection with a similar determination of the stability constant between chromium(III) and EDTA⁹ and found that in this EDTA case the mercury electrode does work satisfactorily.

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