

Metal Ammine Formation in Solution. XIX. On the Formation of Tetraamminedi- μ -hydroxodicopper(II) and Hydroxotetraammine Complexes in Ammoniacal Copper(II) Solutions

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It is shown that the UV absorption of weakly ammoniacal copper(II) solutions which are almost saturated with basic salt is caused by small concentrations of the tetraamminedi- μ -hydroxodicopper(II) complex, which has $\epsilon_{\max} \approx 200$ at 317 nm. The monomeric hydroxotriammine copper(II) complex also present in such solutions with low ammonium ion concentrations has no absorption in the near UV. For copper(II) ammine solutions stabilized with an excess of ammonia and made more basic by addition of sodium hydroxide it was found that their absorption curves have an isosbestic point when the concentration of ammonia was kept constant. It could be shown that the complex formed is a pentacoordinated hydroxotetraammine complex with $\epsilon_{\max} = 39.7$ at 597 nm. The formation constant K'_{OH} for the uptake of the hydroxide ion at constant ammonia concentration was found to be 11.3 for $[\text{NH}_3] = 0.997$ M and 4.6 for $[\text{NH}_3] = 4.45$ M. The decrease in the value of K'_{OH} with increasing ammonia concentration can be quantitatively explained when it is considered that the pentaammine complex present in the solutions liberates an ammonia molecule when the hydroxotetraammine complex is formed. The following constants corresponding to the expressions (9), (10) and (11) in the paper were determined for $I = 1$ M and 23 °C to be: $K_5 = 0.418$, $K_{4,\text{OH}} = 9.3$ and $K_{5,\text{OH}} = 22.3$.

In Jannik Bjerrum's early papers¹⁻³ on copper ammine formation the individual stability constants and spectra in the visible region for all the copper(II) complexes from monoammine to pentaammine

were determined under conditions (high ammonium salt concentration) such that only the monomeric aqua-ammine complexes were present.

Copper(II) ammonia solution of low ammonia concentration and not stabilized by ammonium salt have an absorption band at 317 nm in the near UV. This band has been observed by several authors⁴⁻⁶ and has been assumed to be caused by monomeric hydroxoammine complexes. Under this assumption Reeves and Bragg,⁷ using pH-measurements, and Fisher and Hall,⁸ using polarographic measurements, have calculated constants for the hydrolysis of copper(II) ammonia and other copper(II) ammine complexes. However, Sakamoto and Kida⁹ assume that the intense band in the near UV is due to the presence of dimeric species of the type $(\text{NH}_3)_2\text{Cu}(\text{OH})_2\text{Cu}(\text{NH}_3)_2^{2+}$, a result which is confirmed in the present paper. Dimeric species of the type $\text{L}_2\text{Cu}(\text{OH})_2\text{CuL}_2^{2+}$ have also been shown to be hydrolysis products of copper(II) systems with pyridine⁸ and diamines^{11,12} as well as of the aqua copper(II) ion.¹³⁻¹⁶

The second part of the paper deals with a study, by spectrophotometric measurements in the visible, of the influence of strong base (NaOH) on copper(II) ammonia solutions stabilized with ammonia in concentrations from 1 to 5 M. Rather unexpectedly it was found that the tetraammine ion under these conditions instead of hydrolyzing to hydroxotriammine takes up a hydroxyl ion forming a pentacoordinated hydroxotetraammine complex. The pentaammine ion which exists in equilibrium with the tetraammine ion^{2,17,18} should correspondingly lose an ammonia molecule when the hydroxo-

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tetraammine complex is formed, and the constants calculated from the data were in quantitative agreement with this assumption.

EXPERIMENTAL

Reagents and solutions. All reagents were of analytical grade. The various solutions were prepared in volumetric flasks by weighing, pipetting or titrating from stock solutions. Carbon dioxide-free sodium hydroxide solutions were prepared from 19 M Sørensen lye.

pH-Measurements were performed in a jacketed vessel with thermostatted water flow. A selected Radiometer glass electrode (Type GK-1) with the theoretical pH-dependence was used, and a saturated KCl-calomel electrode (Type K 401) was used

as reference. The potentiometer used was a Radiometer PHM 52 digital pH Meter, the mV-scale being preferred to the direct reading pH-scale.

Spectrophotometric measurements (UV and Vis.) were performed with a Cary 118 spectrophotometer at room temperature. The most suitable absorbance range was chosen to achieve greatest accuracy and the spectra were corrected for base line adjustment.

MEASUREMENTS OF THE DIMERIZATION OF THE DIAMMINE COPPER(II) ION

The experimental data for the solutions (Nos. 1–14) are shown in Table 1a. Columns 2–6 give the stoichiometric concentrations of the components CuCl_2 , NH_4Cl or NaOH , NH_3 and KCl in molar units. The concentration of free ammonia (7th

Table 1a. Measurements of the ultraviolet absorption for the copper(II) ammine system at different ammonia and ammonium ion concentrations in 1 M (K, NH_4 , Na)Cl at $\sim 23^\circ\text{C}$.

No.	C_{CuCl_2}	$C_{\text{NH}_4\text{Cl}}$	C_{NaOH}	C_{NH_3}	C_{KCl}	$[\text{NH}_3]$	C'_{NH_4}	$\Delta E(\text{mV})$	$[\text{NH}_4^+]$	A_{317}
1	0.00996	0	0.00907	1.012	0.97	0.97	0.0034	8.1	0.0046	0.0546
2	0.01992	0	0.01814	1.012	0.94	0.93	0.00205	15.55	0.00365	0.262
3	0.01992	0	0.00907	1.012	0.95	0.93	0.0033	14.2	0.0056	0.154
4	0.01992	0	0	1.012	0.96	0.93	0.0064	10.3	0.0091	0.0732
5	0.00996	0.00992	0	0.2302	0.97	0.190	0.0106	9.5	0.0129	0.203
6	0.00249	0.00992	0	0.2302	0.98	0.220	0.0107	2.55	0.0104	0.0161
7	0.00996	0.0248	0	0.2302	0.96	0.190	0.0251	6.1	0.0264	0.081
8	0.00498	0.0248	0	0.2302	0.97	0.210	0.0252	2.8	0.0257	0.020
9	0.00996	0.0992	0	0.2302	0.88	0.190	0.1000	5.0	0.1010	0.0166
10	0.00996	0.496	0	0.2302	0.48	0.190	—	—	0.496	0.003
11	0.01992	0.992	0	0.2302	0	0.150	—	—	0.992	0.003
12	0.01992	0	0	0.228	0.96	0.148	0.00257	38.55	0.00945	1.20
13	0.01992	0.00992	0	0.228	0.95	0.148	0.0105	20.2	0.0156	0.700
14	0.00498	0.0992	0	0.0575	0.89	0.038	—	—	0.0100	0.043

Table 1b. Calculation of apparent constants for the dimerization of the diammine copper(II) ions. $\beta_1 = 10^{4.15}$, $\beta_2 = 10^{7.67}$, $\beta_3 = 10^{10.57}$, $\beta_4 = 10^{12.71}$, $\beta_5 = 10^{12.22}$

No.	α_1	α_2	α_3	\bar{n}	α_{OH}	$\beta'_{2,2}$	$-\log[\text{H}^+]$
1	0.23×10^{-8}	0.73×10^{-5}	0.00565	4.23	0.12	2.9×10^8	11.824
2	0.27×10^{-8}	0.81×10^{-5}	0.00597	4.22	0.08	1.8×10^8	11.906
3	0.27×10^{-8}	0.81×10^{-5}	0.00597	4.22	0.12	2.7×10^8	11.720
4	0.27×10^{-8}	0.81×10^{-5}	0.00597	4.22	0.125	3.4×10^8	11.509
5	0.37×10^{-6}	2.3×10^{-4}	0.0346	4.02	0.23	3.0×10^8	10.668
7	0.37×10^{-6}	2.3×10^{-4}	0.0346	4.02	0.13	3.2×10^8	10.357
8	0.28×10^{-6}	1.87×10^{-4}	0.0314	4.03	~ 0	$(3.8) \times 10^8$	10.412
12	0.79×10^{-6}	3.8×10^{-4}	0.0446	4.00	0.345	2.0×10^8	10.695
13	0.79×10^{-6}	3.8×10^{-4}	0.0446	4.00	0.26	2.5×10^8	10.478
14	0.42×10^{-5}	5.2×10^{-3}	0.157	3.84	—	$(4.1) \times 10^8$	10.080
						Av. 2.7×10^8	

column) is given by the relation: $[\text{NH}_3] = C_{\text{NH}_3} - \bar{n}C_{\text{Cu}}$, where \bar{n} (shown in Table 1b) is calculated by means of the known stability constants for the copper(II) aquaammine system in one molar salt solution at $\sim 23^\circ\text{C}$.¹⁹ The actual ammonium ion concentration in the solutions (10th column) was determined from the relationship:

$$\log [\text{NH}_4^+] = \frac{\Delta E}{N} + \log \left(\frac{[\text{NH}_3]C'_{\text{NH}_4^+}}{C_{\text{NH}_3}} \right)$$

where ΔE (9th column) is the measured glass electrode potential between the solution and a copper-free solution with identical concentrations of the other components. N is the Nernst factor at the temperature in question and $C'_{\text{NH}_4^+}$ (8th column) is the actual ammonium concentration in the copper-free solution calculated from the stoichiometric concentration by means of the base constant for ammonia $K_{\text{NH}_3} = 4.4 \times 10^{-5}$ ($I = 1 \text{ M}$, 23°C). The difference $[\text{NH}_4^+] - C'_{\text{NH}_4^+}$ is a measure of the hydrolysis of the aqua-ammine ions, and $\alpha_{\text{OH}} = ([\text{NH}_4^+] - C'_{\text{NH}_4^+})/C_{\text{Cu}}$ (given in the 6th column of Table 1b) is the fraction of hydroxyl ions taken up per copper atom. The absorbance of the ultraviolet band at 317 nm: $A_{317} = \epsilon_{317}C_{\text{Cu}}$ is given in the last column of Table 1a. Some of the absorbance curves (A_λ versus λ) for the ultraviolet band with either a shoulder or a maximum at 317 nm are shown in Fig. 1. At lower wavelengths than 317 nm is a considerable background absorption but it will be seen from the figure that the absorbance at 317 nm (as well as at somewhat higher wavelengths) can be considered as a relative measure for the concentration of the complex responsible for the UV absorp-

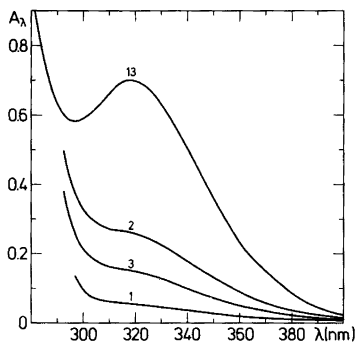


Fig. 1. UV absorption curves $A_\lambda = \epsilon_\lambda \times C_{\text{Cu}}$ versus the wavelength for some copper(II) ammonia solutions (Nos. 1, 2, 3 and 13 in Table 1a).

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tion. The literature⁹⁻¹⁶ gives, as already discussed, evidence that this complex is the di- μ -hydroxo dimer $(\text{NH}_3)_2\text{Cu}(\text{OH})_2\text{Cu}(\text{NH}_3)_2^{2+}$. A stability constant for this complex is given by the expression (1).

$$\beta_{2,2} = \frac{[\text{Cu}_2(\text{NH}_3)_4(\text{OH})_2^{2+}][\text{NH}_4^+]^2}{[\text{Cu}(\text{NH}_3)_2^+]^2[\text{NH}_3]^2} \quad (1)$$

Now assuming that the concentration of the dimer (abbreviated [D]) is proportional to A_{317} (more accurately to $A_{317} - 0.003$, where 0.003 is a small background absorption) and substituting $C_{\text{Cu}}\alpha_2(1 - \alpha_{\text{OH}})$ for $[\text{Cu}(\text{NH}_3)_2^+]$, a new constant is defined, eqn. (2).

$$\beta'_{2,2} = \frac{(A_{317} - 0.003)[\text{NH}_4^+]^2}{C_{\text{Cu}}^2\alpha_2^2(1 - \alpha_{\text{OH}})^2[\text{NH}_3]^2} \quad (2)$$

The concentration $C_{\text{Cu}}\alpha_{\text{OH}}$ is assumed to be $[\text{Cu}(\text{NH}_3)_3\text{OH}^+] + 2[\text{D}]$. The quantity $1 - \alpha_{\text{OH}}$ is therefore a rough measure of the fraction of the total copper(II) concentration which is present as aqua-ammine copper. Values of α_1 , α_2 and α_3 , the fractions of the mono-, di- and triammine aqua ions, respectively, are calculated from the known stability constants¹⁹ and tabulated in Table 1b. Values for $\beta'_{2,2}$ are calculated in Table 1b for all of the measured solutions where A_{317} is sufficiently large (> 0.02) to be defined. The constancy of $\beta'_{2,2}$ is seen to be satisfactory considering the approximately 100-fold variation in the involved quantities A_{317} , α_2 and $[\text{NH}_4^+]$, and can therefore be taken as confirming the correctness of our assumption.

With the assumption that $\frac{1}{2}\alpha_{\text{OH}}C_{\text{Cu}}$ alone (neglecting the concentration of hydroxotriammine) represents the concentration of the dimer, it can be estimated from the data that $\epsilon_{\text{D}} \gtrsim 200$. Assuming ϵ_{D} to be 200 and introducing $(A_{317} - 0.003) = A_{\text{D}} = 200 \times [\text{D}]$ in the expression for $\beta'_{2,2}$, the true constant, $\beta_{2,2}$ is calculated from the average value for $\beta'_{2,2}$ in Table 1b to be 1.4×10^6 . The more commonly used constant, eqn. (3), can now be calculated from

$$\beta_{2,2}^* = \frac{[\text{D}][\text{H}^+]^2}{[\text{Cu}(\text{NH}_3)_2^+]^2} \quad (3)$$

the relationship $\beta_{2,2}^* = \beta_{2,2}K_{\text{NH}_4^+}^2$. Introducing the value $K_{\text{NH}_4^+} = 10^{-9.50}$, $\beta_{2,2}^*$ is calculated to be $10^{-12.85}$. The corresponding constant for the aqua copper(II) ion is according to Pedersen¹³ and Berecki-Biedermann¹⁴ $\sim 10^{-11.5}$. There is evidence¹⁹ that the diammine aqua ion is a weaker acid

than the aqua copper(II) ion and this is probably the main reason for the lower value for $\beta_{2,2}^*$ found in our case.

ON THE FORMATION OF HYDROXOTETRAAMMINE COPPER(II) IONS

When sodium hydroxide is added to ammoniacal copper(II) solutions, the absorption in the visible region decreases. This effect was studied in 1 M and 4.50 M ammonia, *i.e.* under conditions where the solutions contain only aquatetraammine and pentaammine complexes.² Two of the measured series with $C_{Cu} = 0.00797$ and 0.00996 M, respectively, are tabulated in Table 2, and the absorption curves are shown in Fig. 2. A further series in 1 M ammonia solution with the same hydroxide ion concentrations, but with $C_{Cu} = 0.00299$ M, was also measured and the molar extinction coefficients are plotted as o points in the lower part of Fig. 2. The identity of the absorption curves for the two series with the same concentration of free ammonia ($[NH_3] = 0.997$ M) can be taken as proof that only mononuclear complexes are present in the solutions. It further appears from Table 2 and Fig. 2 that the series in 1 M ammonia has an isosbestic point at 524 nm up to $[OH^-] \sim 0.5$ M, and the series in 4.5 M ammonia an isosbestic point at 547 nm up to $[OH^-] \sim 1$ M. The existence of isosbestic points shows that only one new complex is formed in the sodium hydroxide containing solutions and analysis of the data shows that this complex is the hydroxotetraammine copper(II) ion.

The formation constants for uptake of a hydroxide ion by the tetraammine-pentaammine equilibrium mixture at constant ammonia concentration were determined by use of eqn. (4), which is a special

$$\frac{[OH^-]}{\epsilon_0 - \epsilon} = \frac{1}{\epsilon_0 - \epsilon_{OH}} [OH^-] + \frac{1}{K'_{OH}(\epsilon_0 - \epsilon_{OH})} \quad (4)$$

form of the Benesi-Hildebrand equation.²⁰ In this equation, K'_{OH} [eqn. (5)] is the apparent formation

$$K'_{OH} = \frac{[Cu(NH_3)_4OH^+]}{(C_{Cu} - [Cu(NH_3)_4OH^+])[OH^-]} \quad (5)$$

constant at constant ammonia concentration. ϵ_{OH} indicates the extinction coefficients of the hydroxo complex, and ϵ_0 the starting extinction coefficients slightly higher than those measured at $C_{NaOH} = 0$

and extrapolated from the measured extinction coefficient to $[OH^-] = 0$. The hydroxide ion concentration is equal to C_{NaOH} corrected with a contribution from the dissociation of the ammonia (estimated with $K_{NH_3} = 4.4 \times 10^{-5}$ and 5.6×10^{-5} appropriate to our conditions ($I = 1.0$, $23^\circ C$) in 1 M and 4.5 M ammonia solution, respectively). In the final calculation an almost negligible correction for the hydroxide ion concentration bound in the complex was also introduced.

In Fig. 3, $X = [OH^-]/(\epsilon_0 - \epsilon)$ is plotted *versus* $[OH^-]$ at two wavelengths for both the ammonia

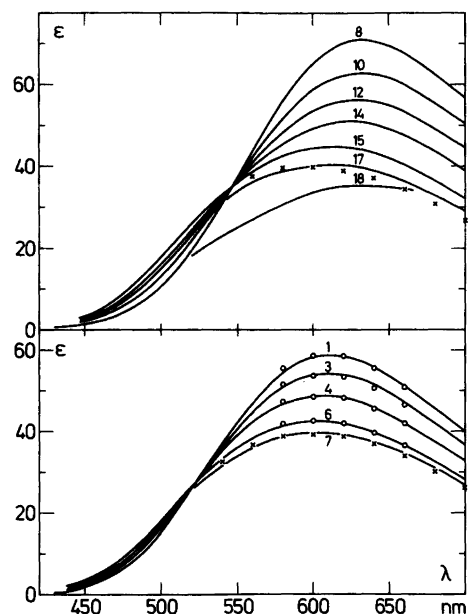


Fig. 2. Molar extinction coefficients of copper(II) ammonia solutions *versus* wavelength.

Lower part ($[NH_3] = 0.997$ M). The figure shows the absorption curves of sols. Nos. 1, 3, 4, 6 and 7 in Table 2a with $C_{CuCl_2} = 0.00797$ M. The O-points are plotted from a similar series with the same hydroxide ion concentrations but with $C_{CuCl_2} = 0.00299$ M. The x-points show the extinction coefficients (ϵ_{OH}) for the hydroxotetraammine complex calculated with $K'_{OH} = 11.3$.

Upper part ($[NH_3] = 4.45$ M). The figure shows the absorption curves of sols. Nos. 8, 10, 12, 14–15, 17 in Table 2b. No. 18 shows the absorption curve of an ammonia-free copper chloride solution $C_{CuCl_2} = 0.00996$ M) in concentrated lye ($C_{NaOH} = 18.2$ M) with $\epsilon_{max} = 35.4$ at 632 nm. The x-points show the extinction coefficient (ϵ_{OH}) for the hydroxotetraammine calculated with $K'_{OH} = 4.6$.

Table 2a. Molar extinction coefficients of copper(II)-ammonia solutions with $[\text{NH}_3]=0.997$ M and varying hydroxide ion concentration at $\sim 23^\circ\text{C}$. Nos. 1–7 with $C_{\text{CuCl}_2}=0.00797$ M, $C_{\text{NH}_3}=1.03$ M, $C_{\text{NaOH}}+C_{\text{KCl}}\cong 1$ M, and No. 1 with $C_{\text{NH}_4\text{Cl}}=0.0198$ M.

No.	C_{NaOH}	$[\text{OH}^-]$	ϵ_{317}	ϵ_{524}	ϵ_{580}	ϵ_{600}	ϵ_{620}	ϵ_{640}	ϵ_{660}
1	0	0.0066	0.81	29.0	54.5	58.0	58.3	55.7	51.2
2	0.0136	0.0153	0.62	29.0	52.5	55.4	55.7	53.5	49.0
3	0.0272	0.0270	1.01	29.0	51.0	53.7	53.8	51.5	47.2
4	0.0985	0.0949	1.98	28.2	46.7	48.5	48.3	46.0	42.2
5	0.1970	0.192	1.73	28.2	44.1	45.3	45.0	43.0	39.4
6	0.492	0.485	1.79	28.2	41.3	42.1	41.7	39.9	36.6
7	0.985	0.977	0.94	26.4	38.8	39.6	39.25	37.5	34.6
Calc. with $K'_{\text{OH}}=11.3$			$\epsilon_{\text{OH}}(\lambda)$	28.6	39.0	39.2	38.7	37.1	34.0
Calc. from slope			K'_{OH}		10.9	11.5	11.7	11.4	10.9
			$\epsilon_{\text{OH}}(\lambda)$		38.7	39.3	38.9	36.7	33.1

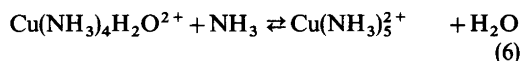
Table 2b. Molar extinction coefficients as in Table 2a, but with $[\text{NH}_3]=4.46$ M. Nos. 8–17 with $C_{\text{CuCl}_2}=0.00996$ M, $C_{\text{NH}_3}=4.50$ M, and Nos. 8–15 with $C_{\text{NaOH}}+C_{\text{KCl}}\cong 1$ M.

No.	C_{NaOH}	$[\text{OH}^-]$	ϵ_{317}	ϵ_{547}	ϵ_{600}	ϵ_{620}	ϵ_{640}	ϵ_{660}	ϵ_{680}
8	0	0.016	0.63	35.1	65.1	70.0	70.7	67.7	62.5
9	0.0394	0.0450	1.43	35.1	61.6	65.8	66.2	63.5	58.5
10	0.0788	0.0819	2.24	35.1	58.7	62.0	62.6	60.1	55.5
11	0.1182	0.1203	2.75	35.1	56.0	59.3	59.6	57.2	52.7
12	0.197	0.198	3.60	35.1	53.6	55.8	56.0	53.3	49.1
13	0.315	0.316	4.25	35.1	50.8	52.3	52.0	49.3	45.2
14	0.394	0.394	3.82	35.1	49.3	50.9	50.2	47.6	43.7
15	0.985	0.985	3.82	35.1	44.4	44.5	43.2	40.3	36.5
16	1.97	1.97	4.12	34.5	42.3	42.1	40.9	38.0	34.2
17	3.94	3.94	3.11	33.8	40.3	40.4	39.0	36.4	32.9
Calc. with $K'_{\text{OH}}=4.6$			$\epsilon_{\text{OH}}(\lambda)$	35.1	39.8	38.8	37.0	34.2	30.7
Calc. from slope			K'_{OH}		4.8	4.9	4.7	4.2	4.4
			$\epsilon_{\text{OH}}(\lambda)$		40.6	39.5	38.9	34.4	32.3

concentrations employed. Such plots were made for all of the wavelengths used for which $\epsilon_0-\epsilon$ is defined, and from the slope and intercept K'_{OH} and ϵ_{OH} are calculated. The result of these calculations are shown in Tables 2a and 2b, and it will be seen that the agreement between the values obtained for K'_{OH} at the different wavelengths is as good as can be expected. The tables also give the values for ϵ_{OH} calculated with the average values for K'_{OH} 11.3 at $[\text{NH}_3]=0.997$ and 4.6 at $[\text{NH}_3]=4.46$ M. These values for ϵ_{OH} agree well with those determined directly and show the consistency of the measurements. However, it is especially remarkable that the extinction coefficients for the hydroxo complex determined at two different ammonia concentrations agree so well with each other. This proves that

it is the same hydroxo complex which is formed in the ammonia concentration range $1 \lesssim [\text{NH}_3] \lesssim 5$ M. Copper(II) solutions with ammonia concentrations ≥ 1 M and negligible hydroxide ion concentrations contain almost exclusively aquatetraammine and pentaammine complexes. The aquatetraammine complex is only present in very small amounts ($<0.3\%$)¹ and less than 1% of the copper is present as the tetraamminedi- μ -hydroxodicopper(II) complex according to the measured extinction coefficients at 317 nm ($\epsilon_D \geq 200$).

Our results, therefore, can be explained by assuming only the equilibria (6)–(8).



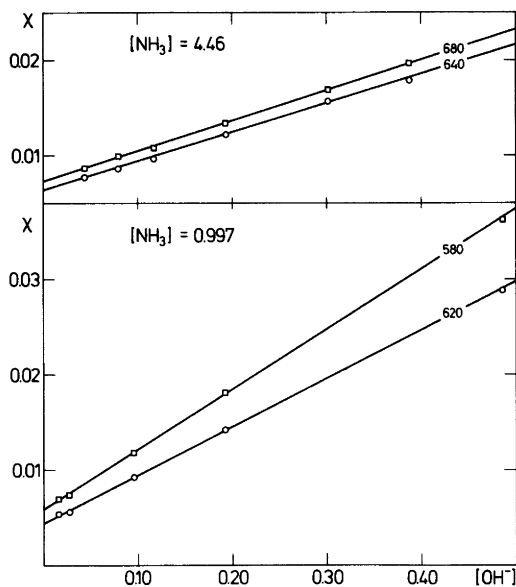
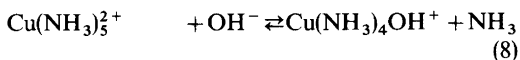
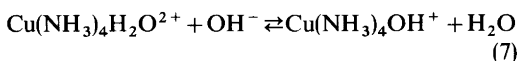


Fig. 3. Plots of $X = [\text{OH}^-]/(\epsilon_0 - \epsilon)$ versus $[\text{OH}^-]$ for different ammonia concentrations. $[\text{NH}_3] = 0.997$ M. 580 nm calc. $K'_{\text{OH}} = 10.9$, $\epsilon_{\text{OH}} = 38.7$. 620 nm calc. $K'_{\text{OH}} = 11.7$, $\epsilon_{\text{OH}} = 38.9$. $[\text{NH}_3] = 4.46$ M. 680 nm calc. $K'_{\text{OH}} = 4.40$, $\epsilon_{\text{OH}} = 32.3$. 640 nm calc. $K'_{\text{OH}} = 4.75$, $\epsilon_{\text{OH}} = 38.9$.



The formation constants corresponding to eqns. (6)–(8) are denoted as eqns. (9)–(11), from which eqn. (12) follows; a knowledge of $K_{4,\text{OH}}$ and $K_{5,\text{OH}}$

$$K_5 = \frac{[\text{Cu}(\text{NH}_3)_5^{2+}]}{[\text{Cu}(\text{NH}_3)_4^{2+}][\text{NH}_3]} \quad (9)$$

$$K_{4,\text{OH}} = \frac{[\text{Cu}(\text{NH}_3)_4\text{OH}^+]}{[\text{Cu}(\text{NH}_3)_4^{2+}][\text{OH}^-]} \quad (10)$$

$$K_{5,\text{OH}} = \frac{[\text{Cu}(\text{NH}_3)_4\text{OH}^+][\text{NH}_3]}{[\text{Cu}(\text{NH}_3)_5^{2+}][\text{OH}^-]} \quad (11)$$

$$K_5 = K_{4,\text{OH}}/K_{5,\text{OH}} \quad (12)$$

also determines K_5 . The apparent constant for the hydroxo complex formation at constant ammonia concentration can be expressed as in eqn. (13),

$$K'_{\text{OH}} = \frac{[\text{Cu}(\text{NH}_3)_4\text{OH}^+]}{(\alpha_4[\text{Cu}(\text{NH}_3)_4^{2+}] + \alpha_5[\text{Cu}(\text{NH}_3)_5^{2+}][\text{OH}^-]} \quad (13)$$

where α_5 and $\alpha_4 = 1 - \alpha_5$ are the degrees of formation of pentaammine and tetraammine complexes, respectively, as determined from K_5 and the ammonia concentration. Using (10), (11) and (12) in (13) we obtain the simple relation (14).

$$\frac{K_5 \times K_{5,\text{OH}}}{K'_{\text{OH}}} = \alpha_4 + \alpha_5 K_5 [\text{NH}_3] \quad (14)$$

Since K'_{OH} has been determined at two ammonia concentrations, two equations of the form (14) (with $K'_{\text{OH}} = 11.3$ and 4.6, respectively) are at our disposal for the calculation of K_5 , $K_{5,\text{OH}}$ and $K_{4,\text{OH}}$. The activity coefficient of ammonia increases strongly with the ammonia concentration. Therefore ammonia activities instead of concentrations were used in the calculations (with $f_{\text{NH}_3} = 1.00$ for $[\text{NH}_3] = 0.997$ M and 1.30 for $[\text{NH}_3] = 4.46$ M^{2,19}). The calculations themselves were performed as successive approximations and the following values were obtained for the constants: $K_5 = 0.418$, $K_{4,\text{OH}} = 9.3$, and $K_{5,\text{OH}} = 22.3$. The pentaammine constant K_5 has previously been determined spectrophotometrically² to be 0.345 in 2 M NH_4NO_3 at 18 °C and from EMF-measurements³ to be 0.355 under similar conditions. The agreement with the value $K_5 = 0.418$ obtained here is satisfying and can be taken as demonstrating the correctness of our assumptions.

There is evidence that the tetraammine copper(II) ion in solution contains a reasonably strongly coordinated water molecule,^{21,22} as also assumed in eqns. (6)–(7). On the other hand it is still an open question whether the pentaammine ion in aqueous solution is anhydrous or contains a coordinated water molecule.^{23,24} The extinction coefficients and wavelengths for the absorption maxima of the tetraammine, hydroxotetraammine and pentaammine ions are shown in Table 3. When the

Table 3. Absorption maxima of the complexes.

	$\lambda(\text{nm})$	ϵ_{max}
$\text{Cu}(\text{NH}_3)_4\text{H}_2\text{O}^{2+}$	590	53
$\text{Cu}(\text{NH}_3)_4\text{OH}^+$	597	39.7
$\text{Cu}(\text{NH}_3)_5^{2+}$	640	83

tetraammine ion takes up an ammonia molecule, the wavelength maximum is shifted 50 nm towards the red. This is the so-called "pentaammine effect" and the table shows that also the uptake of a hydroxide ion causes a small effect of the same kind. The shift of the absorption maximum towards higher wavelengths continues when the hydroxide ion at sufficiently high concentration begins to displace one of the four strongly bound ammonia molecules. (Compare the calculated spectrum of hydroxotetraammine in Fig. 2 with the measured spectrum for $[\text{OH}^-] = 3.94 \text{ M}$ (curve 17), and with the spectrum in ammonia-free lye (curve 18)). However, this shift towards higher wavelengths caused by the exchange of the strongly bound ammonia molecule with hydroxide ions is in better agreement with the lower position of the hydroxide ion than ammonia in the spectrochemical series.

19. Bjerrum, J. *Metal ammine formation in aqueous solution*, P. Haase and Søn, 1941, reprinted 1957.
20. Benesi, H. A. and Hildebrand, J. H. *J. Am. Chem. Soc.* 71 (1949) 2703.
21. Yamaguchi, T. and Ohtaki, H. *Bull. Chem. Soc. Jpn.* 52 (1979) 415.
22. Schneider, W. and Baccini, P. *Helv. Chim. Acta* 52 (1969) 1955.
23. Jørgensen, C. K. *Topics in Current Chem.* 56 (1975) 1.
24. Romano, V. and Bjerrum, J. *Acta Chem. Scand.* 24 (1970) 1551.

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REFERENCES

1. Bjerrum, J. K. *Dan. Vidensk. Selsk., Mat.-Fys. Medd.* 11 (1931) No. 5.
2. Bjerrum, J. K. *Dan. Vidensk. Selsk., Mat.-Fys. Medd.* 11 (1932) No. 10.
3. Bjerrum, J. K. *Dan. Vidensk. Selsk., Mat.-Fys. Medd.* 12 (1934) No. 15.
4. Winther, C. and Mynster, E. H. *Z. Wiss. Photograph. Photoph. Photochem.* 24 (1926) 90.
5. Ley, H. *Z. Anorg. Chem.* 164 (1927) 392.
6. Kubota, M. *Nippon Kagaku Kaishi* 62 (1941) 509.
7. Reeves, R. E. and Bragg, P. *J. Am. Chem. Soc.* 84 (1962) 2491.
8. Fisher, J. F. and Hall, J. L. *Anal. Chem.* 39 (1967) 1550.
9. Sakamoto, M. and Kida, S. *Bull. Chem. Soc. Jpn.* 46 (1973) 3298.
10. Leusing, D. L. and Hansen, R. C. *J. Am. Chem. Soc.* 79 (1957) 4270.
11. Perrin, D. D. and Sharma, V. S. *J. Inorg. Nucl. Chem.* 28 (1966) 1271.
12. Arenare, E. and Paoletti, P. *J. Chem. Soc. Dalton Trans.* (1972) 736, 740.
13. Pedersen, K. J. K. *Dan. Vidensk. Selsk., Mat.-Fys. Medd.* 20 (1943) No. 7.
14. Berecki-Biedermann, C. *Ark. Kemi* 9 (1956) 175.
15. Perrin, D. D. *J. Chem. Soc.* (1960) 3189.
16. Sylva, R. N. and Davidson, M. R. *J. Chem. Soc. Dalton Trans.* (1979) 232.
17. Rosenblatt, F. *Z. Anorg. Chem.* 204 (1932) 351.
18. Bjerrum, J., Ballhausen, C. J. and Jørgensen, C. K. *Acta Chem. Scand.* 8 (1954) 1275.