

Metal Ammine Formation in Solution. XXV. The Stability Constant of the Triammine Copper(I) Complex

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In 1934 the two consecutive stability constants for the diammine copper(I) ion were determined by EMF measurements without finding evidence for higher ammine complexes.¹ Jørgensen² found that ammoniacal diammine copper(I) perchlorate solutions showed UV absorption at wavelengths lower than 300 nm. However, it was not until 1984 that Stevenson and coworkers³ made a closer study of this UV absorption and concluded that it must be due to the formation of a triammine copper(I) complex. They found that the absorption curves had a shoulder at 290 nm and that the molar absorbance ϵ_{290} increased almost proportionally with the ammonia concentration up to saturation. However, they did not take into account the fact that the ammonia activity is much higher than the concentration in strong ammonia solutions, and because of the proportionality of the molar absorbance to the ammonia concentration found they were unable to calculate trustworthy values for the stability constant for the reaction:



When the concentration of ammonia is substituted by a_{NH_3} the stability constant:

$$K_3 = [\text{Cu}(\text{NH}_3)_3^+]/([\text{Cu}(\text{NH}_3)_2^+]a_{\text{NH}_3}) \quad (1)$$

can be calculated directly from the relationship:

$$K_3 = \frac{a''_{\text{NH}_3}(\epsilon' - \epsilon_2) - a'_{\text{NH}_3}(\epsilon'' - \epsilon_2)}{a'_{\text{NH}_3}a''_{\text{NH}_3}(\epsilon'' - \epsilon')} \quad (2)$$

in which $a''_{\text{NH}_3} > a'_{\text{NH}_3}$ and represent the ammonia activities and $\epsilon'' > \epsilon'$ and represent the molar absorbances of two solutions. ϵ_2 is the nearly negligible molar absorbance of the diammine complex. This expression is easily derived by combining the relationship for the fractions of the triammine complex in the two solutions

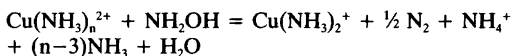
$$\alpha_3'/\alpha_3'' = (\epsilon' - \epsilon_2)/(\epsilon'' - \epsilon_2) \quad (3)$$

with the expression

$$\alpha_3 = K_3 a_{\text{NH}_3}/(1 + K_3 a_{\text{NH}_3}) \quad (4)$$

Experimental and Results

The absorbance *A* of the copper(I)ammine solutions were measured at 290 nm in 1 cm quartz cells using a Cary 118 spectrophotometer at room temperature 22–23°C. Measurements were made at varying ammonia concentrations in 0.426 and 0.0426 M NH_4ClO_4 and in 0.100 M NaOH solutions in most cases at a nearly constant ionic strength of 0.5 M. All the experimental data are tabulated in Table 1. The copper(I)ammine solutions were prepared from the copper(II)-ammonia solutions by reduction with hydroxylamine:



The concentration of free ammonia in the NH_4ClO_4 solutions was therefore corrected for the bound ammonia by the expression: $[\text{NH}_3] = C_{\text{NH}_3} - 3 C_{\text{Cu(II)}}$. The activity coefficients of ammonia at 25°C used to calculate the ammonia activities were calculated from Perman's vapour pressure measurements⁴ (cf. Bjerrum^{1,5,6}). The copper(I)ammine solutions were prepared by adding a slight excess of solid $(\text{NH}_3\text{OH})_2\text{SO}_4$, thereby discol-

Table 1. Data and results of calculations at 290 nm.

No.	C_{NH_3}	$[\text{NH}_3]$	f_{NH_3}	a_{NH_3}	$C_{\text{Cu(II)corr.}}$	C_{NaClO_4}	A	ϵ	ϵ_3
$C_{\text{NH}_4\text{ClO}_4} = 0.426 \text{ M}$							$K_3 = 0.038$	$\epsilon_2 = 1.3$	
1	0.197	0.137	1	0.137	0.0202	0	0.060	2.97	322
2	0.329	0.269	1	0.269	0.0202	0	0.090	4.46	312
3	0.658	0.598	1.01	0.604	0.0202	0	0.16	7.92	295
4	0.938	0.878	1.02	0.896	0.0202	0	0.22	10.89	291
5	1.876	1.816	1.06	1.925	0.0195	0	0.43	22.1	305
6	3.752	3.692	1.20	4.43	0.0184	0	0.83	45.1	304
7	4.69	4.63	1.28	5.93	0.0182	0	0.99	54.4	289
8	7.39	7.33	1.54	11.29	0.0172	0	1.58	91.9	302
$C_{\text{NH}_4\text{ClO}_4} = 0.0426 \text{ M}$							$K_3 = 0.036$	$\epsilon_2 = 1.3$	
9	1.876	1.816	1.06	1.925	0.0202	0.40	0.45	22.3	303
10	7.504	7.444	1.55	11.54	0.0196	0.40	2.00	102	343
11	7.504	7.474	1.55	11.585	0.0100	0.40	0.98	98	329
12	10.52	10.49	1.95	20.46	0.0100	0.40	1.35	135	315
$C_{\text{NaOH}} = 0.100 \text{ M}$							$K_3 = 0.046$	$\epsilon_2 = 1.3$	
13	1.876	1.836	1.06	1.946	0.0202	0	0.50	24.7	285
14	7.504	7.464	1.55	11.57	0.0202	0	2.00	99	281
15	1.876	1.836	1.06	1.946	0.0202	0.30	0.49	24.3	280
16	3.752	3.712	1.20	4.454	0.0202	0.30	0.99	49.0	281
17	7.504	7.484	1.55	11.60	0.0101	0.30	0.96	95	269
18	10.52	10.50	1.95	20.47	0.0101	0.30	1.40	139	284

ouring the copper(II)ammonia solutions. The reduction to copper(I) was complete in all cases except for the solutions with $C_{\text{NH}_4\text{ClO}_4} = 0.426 \text{ M}$ and C_{NH_3} higher than $\sim 1 \text{ M}$. In these cases a small correction was introduced for the unreduced copper(II) by measuring the absorbance at the wavelength 574 nm where the molar absorbances of the copper(II)ammine complexes ($\epsilon_{574} = 50.4$) are independent of the ammonia concentrations.⁵ Hydroxylammonium sulphate has no absorption at 290 nm and the copper(II)ammonia solutions have much weaker absorption than the copper(I) solutions at this wavelength. As well as N_2 , a little N_2O is possibly formed on reduction of the copper(II) solutions. For this reason it was checked that a saturated aqueous solution of N_2O has no UV absorption above 230 nm.

Discussion

Average values for the stability constant were computed by use of equation (2) for each of the three media employed. It is obvious that the uncertainty of the constants is dependent on the magnitude of the differences $\epsilon'' - \epsilon'$ and $a'' - a'$. The average value $K_3 = 0.038$ in 0.426 M NH_4ClO_4 was obtained by combining sol. 8 with

sols. 4, 5 and 6, and sol. 7 with sol. 5 for ϵ_2 inserting the value 1.3 which gives the best fit with special regard to sols. 1–3 with the lowest ammonia concentrations. The value $K_3 = 0.036$ in 0.0426 M NaClO_4 was obtained by combining sol. 9 with sols. 11 and 12 using the value 1.3 for ϵ_2 estimated from the data in 0.426 M NH_4ClO_4 . The value $K_3 = 0.046$ in 0.100 M NaOH is in a similar way obtained by combining sol. 15 with sols. 14 and 17, and sol. 13 with sol. 18. The results are shown in Table 1, and the value: $K_3 \approx 0.04$ (with an uncertainty of about 10 per cent) shows clearly that K_3 is independent of pH in the range from ~ 9 to 13. The influence of the salt concentration is also small (cf. e.g. sols. 13 and 15). A relatively high ammonia concentration ($> 1 \text{ M}$) is necessary in order to stabilize copper(I)ammine solution in 0.1 M NaOH and copper(I) solutions in 0.426 M NH_4ClO_4 are unstable and precipitate Cu_2O , aq for $[\text{NH}_3] \leq 0.1 \text{ M}$. It was therefore difficult to estimate directly the molar absorbance of the diammine complex at 290 nm.

The values of ϵ_3 , the molar absorbance of the triammine complex at the wavelength of the

shoulder at 290 nm calculated for each of the measured solutions by means of the obtained average values of K_3 and the expression $\epsilon_3 = (\epsilon - 1.3)/a_3$, in which α_3 (equation 4) is the fraction of the triammine complex, are shown in the last column of Table 1. The relatively good constancy found for ϵ_3 in the whole range of ammonia activities from <0.1 to <20 confirms the assumption that the UV absorption results from the formation of a triammine complex. The lack of dependence on pH further shows that hydroxy and amide complex formation is without influence on the ammine formation. Raman spectroscopy⁷ gives evidence that the silver ion forms a tetraammine complex in liquid ammonia and the same is probably also the case for the copper(I) ion. It is therefore possible that the copper(I) ion in 10 M NH_3 with α_3 as high as ~ 0.4 already contains minor concentrations of a tetraammine complex.

The measurements of Braish *et al.*³ are in reasonable agreement with those in our study and their absurd results ($K_3 \sim 0.002$ and $\epsilon_3 \sim 7035$) are due only to their use of the classic mass action law without correction for the activity in concentrated ammonia solutions.

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