

Metal Ammine Formation in Solution

VII. Cupric-Pentammine Formation with *n*-Butylamine

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Complexes with three typical chelate ligands bound to the central atom normally have octahedral configuration, but in a paper by J. Bjerrum and Nielsen ¹ it has been made evident that the tri-ethylenediamine cupric complex is a pentammine complex in which two of the ethylenediamine molecules are chelate-bound to the cupric ion, while the third molecule is bound only with one of its amino groups. This suggestion was supported by a number of facts, *e. g.* the similarity of the absorption curves of the tri-ethylenediamine cupric ion and the previously ²⁻⁴ studied pentammine complexes: $\text{Cu}(\text{NH}_3)_5^{++}$ and $\text{Cu en}_2\text{NH}_3^{++}$.

As the cupric ion has the characteristic coordination number 4, and cupric complexes with 4 bound ligand groups have been shown by X-ray data to have a planar square configuration, Bjerrum ⁵ assumed that the 4 strongly bound amine groups were also planar arranged in the pentammine complex, and that the fifth and much more loosely bound ligand molecule is placed perpendicular to this plane. It deserves notice that such a configuration, in which the bound ligand groups are placed at the corners of a tetragonal pyramid with the central atom at the base, was postulated in 1945 on quantum-mechanical basis by Daudel and Bucher ⁶. These investigators were not thinking of the pentammine complex in this connection, and they searched for cases where the configuration mentioned might be found. In the best known configurations with the coordination number 5, such as in the pentahalogen compounds of phosphorus and in iron pentacarbonyl, it has been shown (*cf.* ref. 7) that the five ligands are placed in a trigonal bipyramid around the central atom, but quite recently Jensen and Nygaard ⁷ have prepared a tervalent nickel complex with triethylphosphine $\text{NiBr}_3(\text{Et}_3\text{P})_2$, which like the cupric-

pentamine complex seems to exemplify the configuration theoretically treated by Daudel and Bucher.

In this paper is reported some extinction measurements of cupric-butylamine solutions. These measurements show that it is also possible with aliphatic primary amines to follow the amine formation beyond the tetrammine step. However, it is only possible to determine the order of magnitude of the affinity constant for taking up the fifth butylamine molecule owing to an extremely high medium effect, which for example is shown by the fact that the absorption curves at high amine concentrations are not going through a common point of intersection as in the analogous ammonia- and ethylenediamine systems (see Fig. 1).

Aliphatic monamines have an essentially lesser affinity to metal ions than ammonia, coincident with their greater affinity to the hydrogen ion (*cf.* Tables 1 and 2). These two facts combined necessitate very great amine concentrations in order to prevent the complex solutions separating out as basic precipitates. Thus, in the case of cupric-butylamine solutions, it is only possible to make measurements at high amine concentrations $> 7 N$, and even in 1 N butylammonium salt solutions rather high concentrations of amine are required.

GLASS ELECTRODE MEASUREMENTS

The hydrogen ion affinity constants

$$k_{\text{am,H}^+} = \frac{[\text{am H}^+]}{[\text{am}] [\text{H}^+]}$$

for *n*-butylamine and methylamine in 1 N (or 0.5 N) alkylammonium salt solution at 25° were determined by glass electrode measurements in the same way as previously described for ammonia (*cf.* ref. 5, p. 122). The values found are recorded in Table 1 and for comparison the previously determined values for ammonia, re-calculated under similar conditions and at the same temperature, are given.

The concentration of free amine in some cupric-*n*-butylamine and methylamine * solutions were determined in the limited range where the concentration values were suitable for the calculation of the formation function:

* For the making of the measurements with methylamine the authors are indebted to Mr. Bent Morsing.

Table 1. The hydrogen ion affinity constant $k_{\text{am,H}^+}$ of *n*-butylamine, methylamine and ammonia at 25°.

Amine	C_{amHNO_3}	C_{KNO_3}	C_{am}	$\log k_{\text{am,H}^+}$
<i>n</i> -butyl	0.50		0.01—0.2	10.70 ± 0.02
»	1.00		0.02	10.75 ± 0.02
»	0.50	0.50	0.01	10.75 ± 0.02
methyl	0.50		0.004—0.08	10.72 ± 0.02
ammonia	0.50		0.01	9.30 ± 0.02
»	1.00		0.01	9.36 ± 0.02

$$\bar{n} = \frac{C_{\text{am}} - [\text{am}]}{C_{\text{Cu}(\text{NO}_3)_2}}$$

(C_x = total molar concentration of X).

In order to correct for the salt effect and the deviation of the glass electrode from theoretical pH-dependence in the rather basic range ($\text{pH} \gtrsim 10$), the solutions were measured against standard solutions with the same alkylammonium and very nearly the same amine concentration as in the complex solutions.

The solutions were made from stock solutions of cupric nitrate, alkylammonium nitrate and amine. The stock solutions of ammonium nitrate were 2.5 *N* and were prepared by careful neutralization of the amine with the calculated amount of 5 *N* HNO_3 . The *n*-butylamine (Heyl & Co., gereinigt) was carefully dried over KOH and distilled through a column. The methylamine was a Kahlbaum product.

The results of glass electrode measurements are shown in Table 2. In Table 2 are given, for comparison, the concentrations of free ammonia for the corresponding values of the formation function in the cupric ammonia system. These values are calculated by using the known complexity constants in this system:

$$\begin{aligned} \log k_n &= \log k_n^0 + 0.080 C_{\text{NH}_4\text{NO}_3} + 0.013 (30^\circ - t^\circ) \\ \log k_1^0 &= 3.99; \log k_2^0 = 3.34; \log k_3^0 = 2.73; \log k_4^0 = 1.97 \\ \log k_5^0 &= -0.52 + 0.008 (18^\circ - t^\circ). \end{aligned}$$

From the figures in the table it may be estimated that

$$k_4 = \frac{[\text{Cu}(\text{am})_4^{++}]}{[\text{Cu}(\text{am})_3^{++}] [\text{am}]}$$

Table 2. Free amine concentration [am] and formation function \bar{n} of some cupric-amine solutions at 25°.

Amine	C_{amHNO_3}	$C_{\text{Cu(NO}_3)_2}$	C_{am}	$p[\text{am}]$	[am]	\bar{n}
<i>n</i> -butyl	1.00	0.0816	0.4298	0.791	0.162	3.29
»	1.00	0.03238	0.2676	0.796	0.160	3.32
»	1.00	0.0816	0.5076	0.635	0.232	3.38
methyl	0.50	0.1229	0.5714	0.823	0.150	3.42
»	0.50	0.1148	0.5358	0.823	0.150	3.36
ammonia	1.00			2.193	0.0064	3.30
»	1.00			2.093	0.0081	3.40
»	0.50			2.054	0.0088	3.40

the fourth consecutive constant in the methylamine and *n*-butylamine system is approximately 20—25 times smaller than in the ammonia system.

EXTINCTION MEASUREMENTS

The extinction measurements were made at 25° with a König-Martens spectrophotometer, but some control experiments were made with a Beckman spectrophotometer. Figs. 1a and 1b give a compilation of the experimental data. As abscissa is plotted the wavelengths in $m\mu$ and as ordinate the extinction coefficient

$$\epsilon = \frac{\log I_0/I}{C_{\text{Cu(NO}_3)_2} \cdot d}$$

where I_0 and I denote the intensity of the incident and the transmitted light, respectively, and d the thickness of the absorbing layer in cm. The composition of the solutions in mols per liter and some of the extinction coefficients measured are given in Table 3. The solutions were all about 0.01 molar with respect to cupric nitrate and contained varying concentrations of butylamine (C_{bu}). Fig. 1a gives the ϵ, λ -curves for solutions nos. I—IV without added ammonium salt, and Fig. 1b the curves for solutions nos. V—X, which were 0.5 *N* with respect to butylammonium salt. Curves V and VII were repeated with a Beckman spectrophotometer (o-points), and, as the figure shows, with very nearly the same results.

The cupric nitrate and the amine were added by weight either pure or from stock solutions; in the case of the "waterfree" solutions nos. I and V, a weighed amount of cupric nitrate stock solution, respectively cupric nitrate + butyl-

Table 3. Composition and molar extinction coefficients of the solutions measured.

No.	I	II	III	IV	V	VI	VII	VIII	IX	X
C_{buHNO_3}	0	0	0	0	0.50	0.50	0.50	0.50	0.50	0.50
$C_{\text{Cu}} \cdot 10^2$	1.20	0.95	1.12	1.00	1.10	1.20	1.05	1.12	1.15	0.98
C_{bu}	9.90	9.89	9.68	8.62	9.39	8.15	3.95	1.013	0.508	0.264
$C_{\text{H}_2\text{O}}$	~ 0	0.52	2.27	9.49	~ 0	8.53	30.3	47.2	49.5	50.8
690 $m\mu$	117.5	116.3	104.5	79.7	123.5	102.3	66.6	53.7	46.3	43.2
670	125.4	125.9	110.6	83.6	136.0	112.2	75.6	61.2	52.6	47.8
650	131.4	129.8	114.8	88.1	143.6	118.6	82.9	68.3	58.3	53.1
630	133.2	130.0	111.8	87.5	146.2	122.3	89.6	74.5	64.1	58.8
610	127.6	122.5	104.8	84.1	140.2	118.4	92.4	77.5	67.0	62.4
590	114.6	108.0	90.3	75.2	122.3	106.0	92.1	78.0	66.8	62.1
570	91.1	87.3	70.1	62.8	96.9	87.2	83.7	72.5	63.7	58.4
550	66.1	62.6	49.3	48.6	67.0	64.1	70.2	63.8	54.0	51.9

ammonium stock solution, was evaporated in a graduated flask in a vacuum desiccator with concentrated sulphuric acid, and the residue dissolved in waterfree amine. The water content and molar water concentration $C_{\text{H}_2\text{O}}$ of the solutions was calculated as the difference between the total weight of the contents of the graduated flask filled to the mark and the weight of the added equivalents of cupric nitrate, butylammonium nitrate and butylamine. For butylamine was used the equivalent weight 73.7 found by titration of the product used, instead of the theoretical value 73.1.

DISCUSSION

The extinction measurements give strong evidence of the existence of a tetrammine-pentammine equilibrium in cupric-butylamine solutions. This is easily seen by comparing the absorption curves especially in Fig. 1b with corresponding curves in the cupric ammonia and ethylenediamine systems (Fig. 1c and d); the fact, however, that the curves in the butylamine solutions have no common point of intersection, requires an explanation.

At the lowest amine concentrations examined, it is evident that the formation of the tetra-butylamine complex is not completed. The fourth consecutive constant in the butylamine system is, according to the glass electrode measurements already mentioned, ~ 25 times smaller than the corresponding constant in the copper ammonia system. In the last mentioned system is $\bar{n} = 4$ for $[\text{NH}_3] \cong 0.1$, and it is therefore reasonable to conclude that the absorption curve for the tetra-butylamine copper complex is situated somewhere between

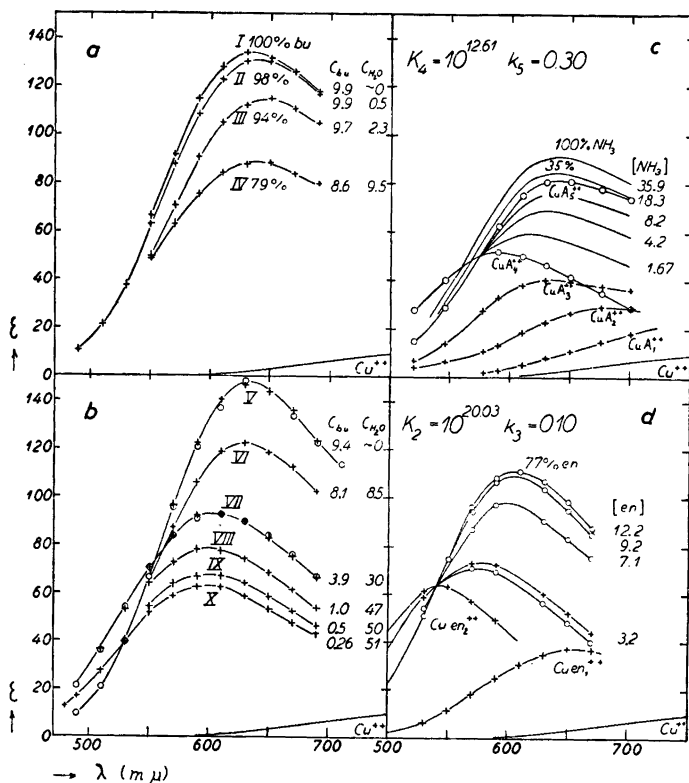


Fig. 1. Extinction curves for cupric complexes with *n*-butylamine, ammonia and ethylenediamine.

- a: Curves for aqueous cupric nitrate butylamine solutions.
 b: The same in 0.5 *N* butylammonium nitrate solutions. Measurements with König-Martens (+) and Beckman spectrophotometer (O).
 c: Curves ^{2,3} for cupric ammonia solutions and tetrammine and pentammine ions (O) in water and for the lower ammine ions (+) in 2 *N* NH_4NO_3 .
 d: Curves ¹ for cupric ethylenediamine solutions and complexes in water (O) and in 1 *N* KNO_3 (+).

the curves VIII and VII corresponding to $C_{\text{bu}} = 1.01$ and 3.95. Fig. 1b shows that sol. VIII has maximum of absorption at a little shorter wavelength than the solutions with higher as well as lower butylamine concentration (comp. Fig. 1c and d), and this makes it probable that curve VIII very nearly represents the curve for the tetra-ammine complex.

If we assume that the waterfree solution V represents the curve for the penta-butylamine complex, Fig. 1b shows that the pentammine formation is about two thirds complete in sol. VI with $C_{\text{bu}} = 8.15$ and $C_{\text{H}_2\text{O}} = 8.53$. Weget

in this way a rough estimate of the very slight stability of the penta-butylamine complex, but cannot treat the data quantitatively due to the unknown influence of the great change in medium.

If one compares the absorption curves of the cupric-butylamine solutions in Fig. 1b with curves with same butylamine concentration in Fig. 1a, it will be seen (comp. *e. g.* sols. VI and IV) that the presence of butylammonium salt brings about a rather strong increase in the extinction coefficient. A corresponding increase in absorption by salt addition is shown to exist in ammoniacal copper salt solutions (see ref. 2, Fig. 7) as well as in ethylenediamine-containing copper salt solutions (see Fig. 1d), but the effect in these solutions is much smaller. When addition of butylammonium salt has so great an influence on the extinction coefficients of the complexes, it is reasonable to assume that a change in the butylamine concentration also has a considerable influence, which explains that the curves have no common point of intersection. In the ethylenediamine system it is noteworthy that the curves in the whole range from nearly pure water to 77 weight per cent ethylenediamine behave very nearly as if they are belonging to a system of only two absorbing components, whilst in the ammonia system one has a raise in absorption and a not negligible shift of the pentamine curve towards blue, when the solvent is changed from about 20 to 100 per cent ammonia: an effect which is particularly manifest in the butylamine system (comp. Fig. 1a and c). But why do changes in concentration in the butylamine system have a stronger influence on the extinction coefficients of the complexes than corresponding changes in the composition of the medium in the ammonia and ethylenediamine systems?

It is probable that the cause of this is that we have a lower dielectric constant in butylamine solutions and, therefore, we must reckon with a stronger interaction between cations, anions and solvent molecules⁸ than in corresponding ammonia and ethylenediamine solutions.

In the literature the dielectric constant of liquid ammonia is determined to 15.6 at 20°⁹, but no data are available for butylamine and ethylenediamine hydrate. We therefore express our thanks to Professor Kai Arne Jensen, who has kindly determined for us the order of magnitude of the dielectric constant of the following solutions:

<i>n</i> -Butylamine	Dielectric constant
~ 100 weight per cent (corresp. to sol. I)	4.9 ± 0.2
94 » » » (» » » III)	6.8 ± 0.3
79 » » » (» » » IV)	17.5 ± 0.7
Ethylenediamine	
77 weight per cent (ethylenediamine hydrate)	~ 30

It will be seen from these figures that we have actually in butylamine solutions a much smaller dielectric constant than in corresponding ammonia solutions: 80 per cent butylamine corresponds about to 100 per cent ammonia, which again has a much smaller dielectric constant than ethylenediamine hydrate. This agrees well with the observations made in this paper and supports the already earlier maintained assumption^{3,5}, that the deviations from additivity are caused by the changes of the solvent and not by formation of hexammine.

As the cupric ion is able to bind five amino groups, it is reasonable to assume that the tetrammine ion contains a complex-bound water molecule^{2,3,5}, and we had originally hoped that a study of the light absorption of cupric butylamine solutions would throw some light on this problem. But due to lack of knowledge of the activity coefficients of amine, water, etc. and the great influence of the medium on the light absorption in the range where the change in water concentration is relatively highest (*cf.* the molar concentrations of butylamine and water in the solutions examined), we cannot say with certainty that the tetrammine complex contains a complex-bound water molecule. On the other hand, the removal of the last traces of water from the solvent (comp. sols. I and II in Fig. 1a) has no influence on the light absorption, which can be taken as a proof that the pentammine complex does not contain any water of constitution.

SUMMARY

The complex formation between cupric ion, methylamine and especially *n*-butylamine is studied by means of glass electrode and spectrophotometer measurements. The glass electrode measurements show that k_4 , the fourth consecutive complexity constant, is about 20—25 times smaller than in the corresponding ammonia system. The extinction measurements show that a pentammine complex is formed at high amine concentrations, but due to a strong medium effect on the light absorption much higher than in corresponding ammonia and ethylenediamine solutions, it was not possible to give a quantitative treatment of the measurements.

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