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Copper(II) Ion and Nickel(II) Ion Complexes with 2-Amino-2-(hydroxymethyl)-1,3-propanediol. Reactions with Sodium Hydroxide¹

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The solid compounds $\text{Cu}(\text{AOH})_2\text{SO}_4$, $\text{Cu}(\text{AO}^-)_2\cdot\text{H}_2\text{O}$, and $\text{Ni}(\text{AOH})_2(\text{ClO}_4)_2$ have been prepared from 2-amino-2-(hydroxymethyl)-1,3-propanediol⁴ and the corresponding copper(II) or nickel(II) salts. In the presence of an excess of the amine salt, copper(II) and amine complexes may be formed in the ratios, in the order named, 1:1, 1:2 and 1:3. The successive formation constants are, in terms of $\log K$, 3.98, 3.49, and 3.2. At and above pH 10 the stable species present in solution is $\text{Cu}(\text{AO}^-)_2$. In solution $\text{Ni}(\text{AOH})^{+2}$ and $\text{Ni}(\text{AO}^-)^{+1}$ species are formed. For $\text{Ni}(\text{AOH})^{+2}$, $\log K$ is approximately 2.86. Above pH 9 a polynuclear species is formed.

Introduction

Ligands which have an amine nitrogen atom and a hydroxyl oxygen atom separated by two carbon atoms, such as ethanolamine and hydroxyethyl ethylenediamine, have been of interest to this Laboratory for several years. Such molecules have the possibility of forming five-membered chelate rings with coordination at the nitrogen and oxygen atoms. It has been shown that the copper(II) complexes of such ligands react in solution with strong base⁵ and it has been presumed that in this reaction a proton is lost from a hydroxyl oxygen atom of the ligand and that this oxygen atom is coordinated to the metallic ion.

The present study concerns the copper(II) and nickel(II) ion complexes of 2-amino-2-(hydroxymethyl)-1,3-propanediol.⁴

Experimental

Apparatus and Methods.—Spectrophotometric studies were made with a Beckman Model DU spectrophotometer using 1-cm. cells. Unless otherwise specified the solvent

was water and the solutions were made 0.5 *M* in potassium nitrate for the copper(II) complexes or 0.5 *M* in sodium perchlorate for the nickel(II) complexes. Wave lengths for analysis of the data by the method of continuous variations were selected following the method given by Vosburgh and Cooper.⁶ The potentiometric titration method as used in this Laboratory has been described recently.^{6d} For the determination of the data for \bar{n} and pA , advantage was taken of the expanded scale of the Beckman Model GS pH meter. The solutions for determination of \bar{n} and pA were made 0.05 *M* in the amine, 0.06 *M* in nitric acid, 0.005 *M* in the metallic ion, and 0.1 *M* in potassium nitrate. Titration was with 0.985 *N* sodium hydroxide.

Crystalline Compounds. **Bis-(2-amino-2-(hydroxymethyl)-1,3-propanediol)-copper(II) Sulfate.**—Dissolve $\text{Cu}\cdot\text{SO}_4\cdot 5\text{H}_2\text{O}$ in the minimum amount of water. Add the amine in 1:2 ratio; then add about 2 volumes of ethanol and cool on an ice-bath. The fine blue crystals may be recrystallized from water. *Anal.* Calcd. for $\text{Cu}(\text{C}_4\text{H}_{11}\text{O}_3\text{N})_2\text{SO}_4$: Cu, 15.81; N, 6.97. Found: Cu, 15.79; N, 6.85.

Bis-(2-amino-2-(hydroxymethoxy)-1,3-propanediol)-copper(II) 1-Hydrate.—Dissolve freshly precipitated and washed copper(II) hydroxide in the minimum amount of amine in ethanol, with cooling. Dilute the solution with ethanol and allow to evaporate slowly. Deep blue crystals form which may be washed with acetone, but may not be recrystallized. *Anal.* Calcd. for $\text{Cu}(\text{C}_4\text{H}_{10}\text{O}_3\text{N})_2\cdot\text{H}_2\text{O}$: Cu, 19.75; C, 29.85; H, 6.89; N, 8.70. Found⁷: Cu, 19.41; C, 29.72; H, 6.86; N, 8.68. The sample showed no loss of weight upon drying at 100° for two weeks, indicating that the water molecule is quite firmly bound.

Bis-(2-amino-2-(hydroxymethyl)-1,3-propanediol)-nickel(II) Perchlorate.— $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ and amine, in 1:2 ratio, are dissolved in the minimum amount of methanol. The solution is allowed to evaporate slowly. The blue crystalline compound which separates is washed with 1-propanol. *Anal.* Calcd. for $\text{Ni}(\text{C}_4\text{H}_{11}\text{O}_3\text{N})_2(\text{ClO}_4)_2$: Ni, 11.75; N, 5.60. Found: Ni, 11.83; N, 5.85.

Attempts to prepare a compound of the type $\text{Ni}(\text{AO}^-)_2$

(1) Presented before the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

(2) In part abstracted from M.S. Theses at West Virginia University by J. A. Swisher (1959), D. G. Brannon (1960), and T. M. Liden (1961).

(3) A portion of this work was supported under contract with the Office of Ordnance Research, U. S. Army.

(4) The amine, $\text{H}_2\text{NC}(\text{CH}_2\text{OH})_2$, is commonly known as tris-(hydroxymethyl)-aminomethane. It will be abbreviated AOH in the formulas. AO^- indicates the ion formed by loss of a proton from one of the hydroxyl groups.

(5) (a) J. L. Hall, F. R. Jones, C. E. Delchamps, and C. W. McWilliams, *J. Am. Chem. Soc.*, **79**, 3361 (1957); (b) J. L. Hall and W. E. Dean, *ibid.*, **80**, 4183 (1958); (c) J. L. Hall and W. E. Dean, *ibid.*, **82**, 3300 (1960); (d) J. L. Hall, W. E. Dean, and E. A. Pacofsky, *ibid.*, **82**, 3303 (1960); (e) A. E. Martell, S. Chaberek, Jr., R. C. Courtney, W. Westerback, and H. Hyytiainen, *ibid.*, **79**, 3036 (1957). See this last article for several references to previous work.

(6) W. C. Vosburgh and G. R. Cooper, *ibid.*, **63**, 457 (1941).

(7) Carbon and hydrogen analyses by Galbraith Microanalytical Laboratories.

resulted in a solid in which the nickel(II) ion, amine, and sodium hydroxide had reacted, in the order named, in the ratio 1:2:3. This compound could not be purified, however.

Results and Discussion

Spectrophotometric Studies.—Unlike ammonia and the ethanolamines,^{8,9} tris-(hydroxymethyl)-aminomethane and copper(II) salts may be mixed in any proportion in dilute aqueous solution to form stable, clear solutions. Hence the spectrophotometric method of continuous variations may be used to study this system. In the present work these studies showed reaction of the copper(II) ion and amine in the ratios, in the order named, of 1:1, 1:2, and 1:3, and indicated that there was some further, incomplete reaction with an excess of the amine. Figure 1 shows Y, Y', and Y'' curves at selected wave lengths as calculated from spectra for solutions which had a total concentration of amine plus copper(II) salt of 0.02 M.

Figure 2 shows spectra of several solutions containing copper(II) ion and the amine in various ratios and in addition shows the spectra of two solutions to which sodium hydroxide had been

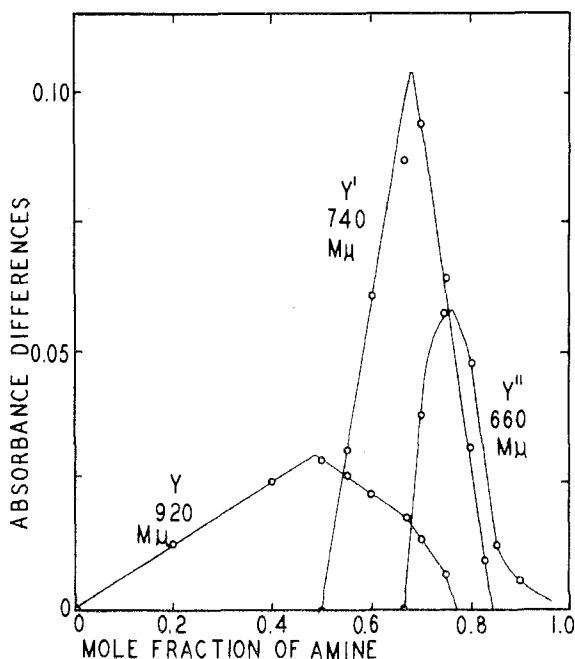


Fig. 1.—Derived curves from the spectrophotometric method of continuous variations for the system copper(II) ion and tris-(hydroxymethyl)-aminomethane.

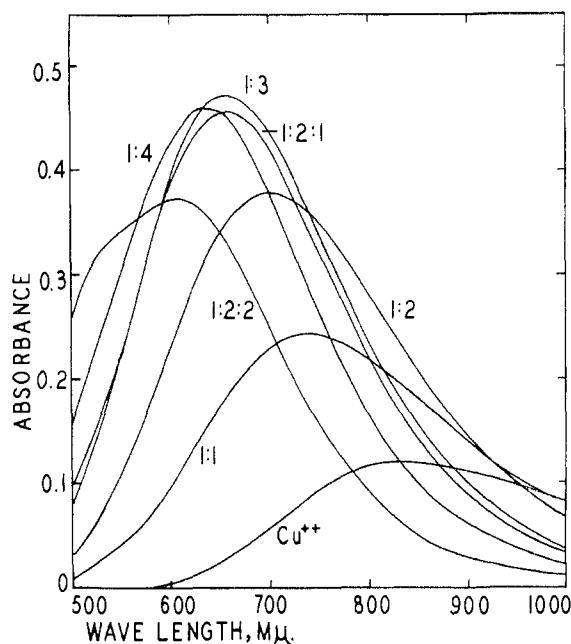
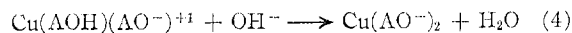
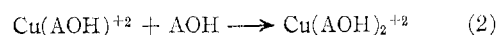
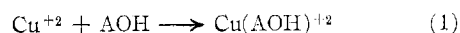


Fig. 2.—Absorption spectra of solutions 0.01 M in copper(II) perchlorate and containing various ratios of tris-(hydroxymethyl)-aminomethane and of sodium hydroxide.

added. The near identity of the spectra for the 1:3 solution, copper(II) ion to amine, to that for the 1:2:1 solution, copper(II) ion to amine to sodium hydroxide, suggests that the colored species formed in these two solutions are identical. Spectral curves for solutions having ratios 1:5, 1:6, 1:7, and 1:8 as well as for ratios 1:3:1 and 1:4:1 were intermediate between the ones shown for ratios 1:3 and 1:2:2. All solutions containing more amine and/or more sodium hydroxide than the 1:2:2 solution produced spectra nearly identical with that of the 1:2:2 solution. Reactions represented by the following equations are consistent with the spectrophotometric observations. Coördinated water molecules are omitted from the formulas.



In the absence of an excess of the amine salt, the amine is a sufficiently strong base to bring reaction 3 nearly to completion but is not strong enough to bring about reaction 4 to any considerable extent. Sodium hydroxide, however, brings reaction 4 to completion. The potentiometric studies, below, indicate that $\text{Cu}(\text{AOH})_3^{2+}$ may be

(8) J. L. Hall and P. S. James, *Proc. W. Va. Acad. Sci.*, **33**, 49 (1961).

(9) B. Kirson and L. Barsily, *Bull. soc. chim. France*, 1926 (1959); H. Ojima and K. Sone, *Z. anorg. u. allgem. Chem.*, **309**, 110 (1961).

formed also in the presence of a large excess of the amine salt.

Similar spectrophotometric studies involving this amine and nickel(II) ion were less conclusive. Figure 3 shows spectra for the visible range for some nickel(II) ion-amine and nickel(II) ion-amine-sodium hydroxide mixtures. The spectra strongly suggest that the colored complex species present in these solutions contain only one

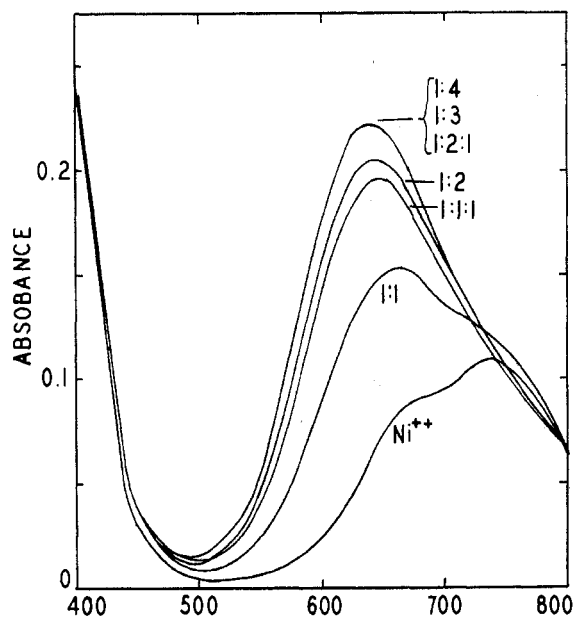


Fig. 3.—Absorption spectra of solutions 0.05 *M* nickel(II) perchlorate and containing various ratios of tris-(hydroxymethyl)-aminomethane and of sodium hydroxide.

amine molecule per nickel(II) ion, and that the further reactions involving either amine or sodium hydroxide result in removal of a proton from the 1:1 complex. Since these spectra do not absolutely exclude higher ratios of amine to nickel(II) ion, continuous variations studies between the nickel(II) ion and amine were made at constant values of *pH*. The 1:1:1 and 1:2:1 solutions were stable but solutions having a higher proportion of sodium hydroxide showed precipitates. The *pH* of each of the two stable solutions was near 8.3 and this value was selected for a continuous variations study. The results of this study (see Fig. 4) show that all solutions with less than 0.5 mole fraction of amine precipitated immediately and the Y curves were straight lines for mole fraction of amine greater than 0.5. While this proves only that at this *pH* no complex exists with the mole ratio of amine to metallic ion greater than 1:1, this observation, together with the other evidence, makes it probable that the

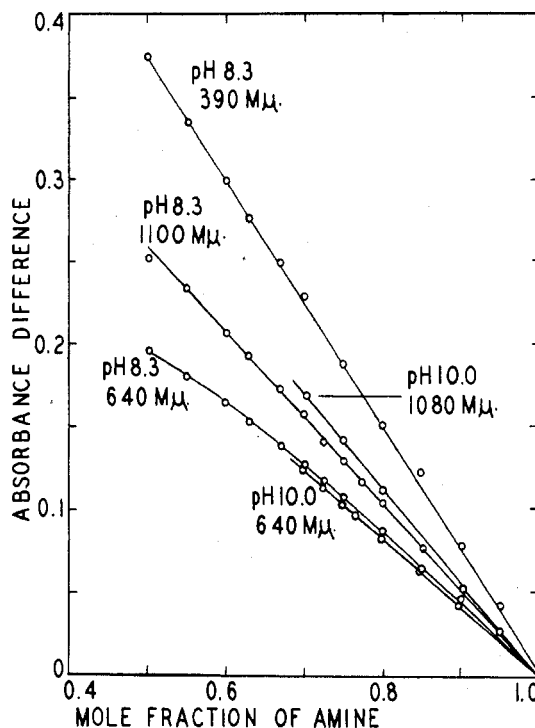


Fig. 4.—Derived Y-curves for continuous variations studies of the nickel(II) ion and tris-(hydroxymethyl)-aminomethane system at *pH* 8.3 and *pH* 10.0.

stable complex species in these solutions is $\text{Ni}(\text{AO}^-)^{+1}$. A similar study at *pH* 10 showed that all solutions with less than about 0.7 mole fraction of amine formed precipitates immediately and the solutions with this or greater concentration of amine precipitated within a few days. No clear solutions could be obtained at *pH* 11.5. In such alkaline solutions evidently the hydroxyl ion is able to displace the coordinated amine molecule. The approximately 2:1 ratio of amine to nickel(II) ion at *pH* 10 which is required to prevent immediate precipitation is not assumed to represent the composition of a stable species present. The potentiometric results given below show formation of a small amount of $\text{Ni}(\text{AOH})_2^{+2}$ below *pH* 7.2 in the presence of a large excess of the amine salt.

Potentiometric Titrations.—Whenever an acidified solution of an amine salt in an excess of nitric acid is titrated with a strong base such as sodium hydroxide, two end points are observed. The first, at *pH* 4.5 for tris-(hydroxymethyl)-aminomethane, represents complete neutralization of the strong acid and the second one, about *pH* 10.2, represents the completion of the conversion of the HAOH^+ ion to free amine. If this titration is repeated, except that the initial solution

contains, in addition, some of a complexing metallic ion, the curve will be displaced from that of the amine only at intermediate values of pH . The amount of this displacement is the basis for the calculation of the stability constants of the complex ions by the method of Bjerrum as modified by Chaberek and Martell.¹⁰ Complete details of the method as used in this Laboratory have been described recently.^{5d}

If the reactions in the solution between the metallic ion, amine, and base result in the formation of complexes of the type $M(AOH)_n^{+m}$ only, then the two titration curves should converge in the vicinity of the second end point. If, however, there is additional reaction between the complex $M(AOH)_n^{+m}$ and the strong base to form, for example, $Cu(AO^-)_2$, the two curves will remain displaced from one another at and beyond the second end point and the amount of displacement will show the number of hydroxyl ions reacted per metallic ion. While the method of Bjerrum has been used for many years, the additional information which may be obtained by extending the titration curves to and beyond the second end point frequently has been neglected.

Table I shows, at selected values of pH , for a solution initially 0.05 M in $HAOH^+$ and 0.005 M

copper(II) ion. For the titration described by Table I there is a maximum displacement of about three equivalents of hydroxyl ion between pH 7 and 7.5. Also shown in the table is, at each pH , the approximate number of nitrogen atoms, n , which would be made available for coordination, assuming that all of the hydroxyl ion is used for this purpose. This approximate value of n is calculated by multiplying the $\Delta[OH^-]/[Cu^{+2}]$ ratio by $(1 + K_{AH^+}/[H^+])$. The rapid increase in this function above pH 7.5 shows that from this pH on an increasing proportion of the base added in the titration is used for purposes other than releasing nitrogen atoms for coordination. The third and fourth columns of Table I show the approximate amount of base, in terms of $\Delta[OH^-]/[Cu^{+2}]$, required to produce $Cu(AOH)_2^{+2}$ and $Cu(AOH)_4^{+2}$ in the solution, respectively. These are obtained by dividing $(1 + K_{AH^+}/[H^+])$ into 2 and 4, respectively.

From the results and calculations shown in Table I, and from similar results and calculations based on solutions containing other ratios of amine salt to metallic ion, several conclusions may be drawn. First, as the ratio of amine salt to metallic ion is made greater than 2:1, some $Cu(AOH)_3^{+2}$ is formed as the pH is raised above about 6.2. In the 10:1 solution there is near complete formation of $Cu(AOH)_3^{+2}$ at pH 7.2 and there is probable formation of some $Cu(AOH)_4^{+2}$ in the range pH 7.2 to 7.6. Second, as the pH is increased above about 7.0 to 7.5, depending on the concentration of the amine salt, there is reaction of these complexes to form $Cu(AO^-)_2$, and the conversion of all complex species to this last one is complete at pH 10 and above. Third, for the 10:1 and 20:1 solutions, it is evident that the values of pA and \bar{n} which were calculated by the modified method of Bjerrum are valid only for values of \bar{n} of 2.8 and less.

A study, similar to that of Table I, for the titration of $HAOH^+$ and nickel(II) ion showed that $\Delta[OH^-]/[Ni^{+2}]$ increased from zero at pH 5.0 to 1.05 at pH 7.6, decreased to 0.77 at pH 8.4, then increased to 1.5 at pH 10 and above. The formation of $Ni(AOH)^{+2}$ evidently was complete at about pH 6.9 but possibly not more than one-fifth of the nickel(II) ion was converted to $Ni(AOH)_2^{+2}$ at pH 7.5. Above pH 7 protons are removed from these complexes and at pH 10 and above a polynuclear species must be present with the ratio of nickel(II) ion to reacted hydroxyl ion being 1:1.5. The values of \bar{n} and pA as calculated

TABLE I

RESULTS FROM TITRATION CURVES FOR ADDITION OF SODIUM HYDROXIDE TO $HAOH^+$ AND TO $HAOH^+$ -COPPER(II) ION MIXTURE

pH	$\Delta[OH^-]/[Cu^{+2}]$	n	1:2	1:4
4.5	0.10	0.10		
5.0	.31	.31		
5.5	.76	.76		
6.0	1.67	1.67		
6.5	2.44	2.58	1.95	
7.0	2.87	3.06	1.87	
7.5	2.92	3.56	1.64	
8.0	2.76	4.69	1.18	2.36
8.5	2.36	7.5	0.66	1.32
9.0	2.13	17.1	.25	0.50
9.5	2.00	46	.09	.18
10.0	1.97	400	.03	.06

in copper(II) ion, the displacement, $\Delta[OH^-]/[Cu^{+2}]$ between the two titration curves. For this and other titrations involving ratios of metallic ion to amine from 1:1 to 1:20, the displacement at and beyond the final end point was always two equivalents of hydroxyl ion per mole of

(10) S. Chaberek, Jr., and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5052 (1952).

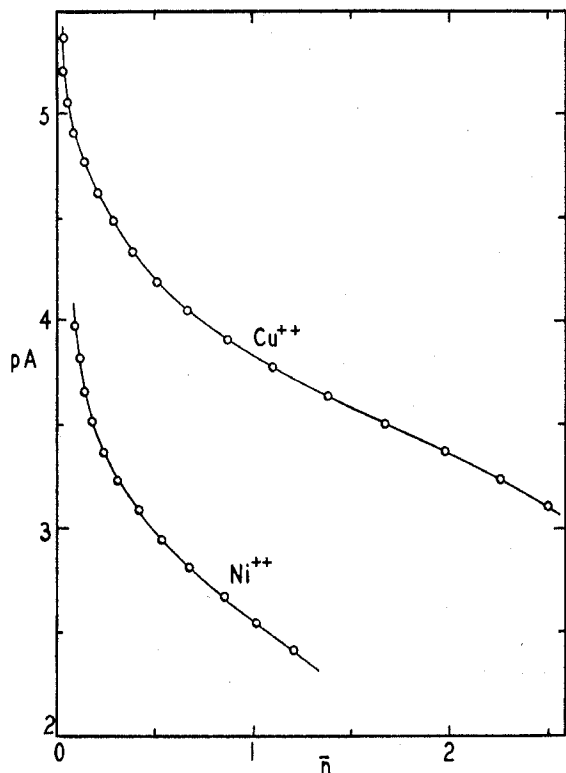


Fig. 5.—Plots of pA as a function of \bar{n} for tris-(hydroxymethyl)-aminomethane with copper(II) ion and with nickel(II) ion.

by the modified method of Bjerrum¹¹ should be valid if \bar{n} is 1.2 or less.

Figure 5 shows the values of \bar{n} as a function of pA for the copper(II) ion and nickel(II) ion and amine systems. These data are for solutions in which the ratio of amine species to metallic ion was 10:1. Only very slightly different values were obtained in solutions in which the ratio was 20:1. These curves are plotted only over the

range for which the values were shown to be valid, above. For the copper(II) and amine system, the values of pA given by the curve are 4.20, 3.57, and 3.13 at \bar{n} equal to 0.5, 1.5, and 2.5, respectively. Estimating that the true value of pA is 2.5 at $\bar{n} = 3.5$ and using the method of obtaining the temporary constants and the convergence equations given by Bjerrum,¹¹ the successive formation constants for addition of the amine to copper(II) ion were calculated. This method should yield reliable values for $\log K_1$ and $\log K_2$ and these are 3.98 and 3.49, respectively. A value of $\log K_3$ of 3.2 is a reasonable estimate and of $\log K_4$ of 2.7 is a rough approximation.

For the plot of pA as a function of \bar{n} for the nickel(II) ion, the value of pA of 2.99 at $\bar{n} = 0.5$ is reliable. To obtain K_1 , however, it is necessary to estimate the true value of pA at $\bar{n} = 1.5$. Making this estimate as 1.95, assuming that only 1:1 and 1:2 complexes are formed, and using the convergence equations, there results a reasonable value of $\log K_1$ of 2.86 and a rough estimate for $\log K_2$ of 2.1.

Conductometric Studies.—Conductometric titrations, made in solution in methanol, revealed the existence in such solutions of metastable polynuclear species of the type $Cu_x(AOH)_y(OH)_z$, where x may be 4 or 5 and y plus z may be from 6 to 12. Protons removed from the amine are included in z . These results are similar to those reported for the copper(II)-monoethanolamine-sodium hydroxide⁸ and copper(II)-diethanolamine-sodium hydroxide systems.¹²

(11) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, pp. 36-38.

(12) W. E. Dean and J. L. Hall, *Proc. W. Va. Acad. Sci.*, **33**, 55 (1961).