February, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (2), 415—419 (1979) 415

X-Ray Diffraction Studies on the Structures of Tetra- and Higher-ammine Complexes of Copper(II) Ion in Aqueous Solution

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(Received June 11, 1978)

From X-ray scattering measurements on ammoniacal aqueous solutions of copper(II) chloride at the NH_3/Cu mole ratios of 4.8 and 5.0, four ammonia molecules at the equatorial position and other two water molecules at the axial one were found to be coordinated to a copper(II) ion at the distance of 2.03 and 2.33 Å, respectively. The radial distribution curve obtained for an aqueous solution of copper(II) chloride saturated with ammonia (NH_3/Cu=11.2) showed that a higher ammine copper(II) complex than the tetraamminecopper(II) ion is formed in the solution. The complex has a distorted octahedral form in which the equatorial Cu–N bond distance is 1.93 Å. The axial apices of the octahedron at the distance of 2.30 Å are occupied by either an ammonia molecule and a water molecule or two ammonia molecules. The present study shows that the structures of the tetra- and higher-ammine copper(II) complexes in solution are different from those in crystal.

A number of methods have been applied for investigating the formation of ammine complexes of copper(II) ion. For a long time the tetraamminecopper(II) ion has been believed to have a square planar structure. In 1968 Tomlinson and Hathaway[1] studied the structures of pentaammine- and hexaamminecopper(II) salts in the solid state by means of electronic, ESR, and infrared spectra, together with magnetic moment measurements, and they suggested that the configuration of the pentaammine complex of copper(II) ion is a tetragonal pyramid and that the hexaammine complex has also the pentaammine moiety so that the complex should be described as $Cu(NH_3)_5X_2 \cdot NH_3$ having a free ammonia molecule in the lattice. Romano and Bjerrum[2] also proposed the tetragonal pyramid form for the pentaammine complex in aqueous solution.

While numerous crystal structures have been reported for the tetraammine complexes of copper(II) ion,[3-6] no structural data have been reported for the complex in solution. For penta- and hexaamminecopper(II) complexes, many powder X-ray data have been reported,[7,8] but few crystallographic data are available because of low stability of the crystals.

The present X-ray diffraction study for ammoniacal aqueous solutions of copper(II) chloride with the NH_3/Cu mole ratios of 4.8 and 5.0 has been undertaken in order to clarify the structure of the tetraamminecopper(II) complex in solution. An aqueous solution of copper(II) chloride saturated with ammonia has also been examined to determine the structure of a higher-ammine complex of copper(II).

Experimental

Preparation and Analysis of Sample Solutions. The tetraammine copper(II) chloride solutions were prepared by dissolving recrystallized copper(II) chloride (Wako Pure Chemicals. Co., reagent grade) into concentrated ammoniacal aqueous solutions (Wako Pure Chemicals. Co., reagent grade) and by adding gaseous ammonia (99.99%) to the solutions (A and B) in order to obtain prescribed stoichiometric ratios of NH_3/Cu, in which the tetraaminecopper(II) ion is expected to be predominant in the solutions according to the formation constants of ammine copper(II) complexes.[9] The distribution of the ammine complexes of copper(II) ion is shown in Fig. 1. An ammoniacal copper(II) chloride solution (C) of a high ammonia concentration was also prepared by introducing gaseous ammonia into a tetraammine copper(II) chloride solution to saturation (the NH_3/Cu mole ratio was about 11).

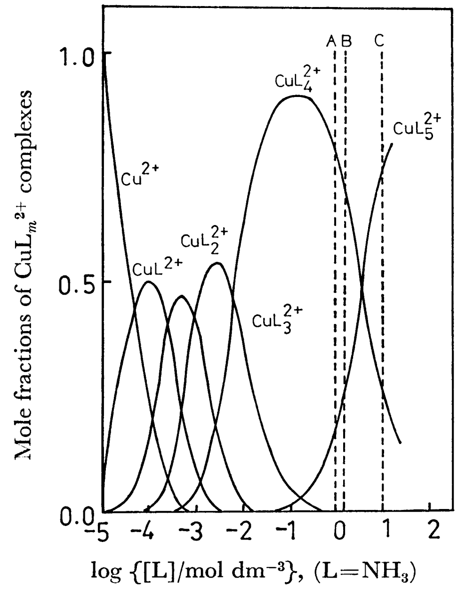

Fig. 1. The distribution of copper(II) ammine complexes as a function of the free ammonia concentration by assuming the formation constants in the literature[16] to be valid.

The concentration of the copper(II) ion was determined both by EDTA titration using a BT indicator and by electrogravimetry as metallic copper on a platinum gauze. The results of the two different methods agreed each other within 0.2%. The concentration of total ammonia was determined by the Kjeldahl method. The concentration of the chloride ion was determined from the stoichiometry of copper(II) chloride.

The density of the solutions was determined pycnometrically.

The compositions of the solutions are given in Table 1.

X-Ray Scatterings. The X-ray diffractometer used, methods of measurements and data treatment have been previously described.[10-12] Mo $K\alpha$ radiation (λ=0.7107 Å) was used for the measurements. The measurements were

Table 1. The composition (g-atoms/dm^3) and the stoichiometric volume V per copper atom in the solutions

Solution	Cu	Cl	N	O	H	$\frac{NH_3}{Cu}$	$\frac{V}{Å^3}$	$\frac{\text{Density}}{\text{g cm}^{-3}}$
A	2.108	4.217	10.21	39.60	109.9	4.8	787.6	1.171
B	2.180	4.360	10.87	39.91	112.4	5.0	761.6	1.171
C	1.541	3.083	17.30	30.70	113.3	11.2	1077.0	1.055

carried out over the range of $1° < \theta < 70°$ (2θ is the scattering angle), corresponding to the range 0.31 Å$^{-1} < s < 16.6$ Å^{-1} $s = 4\pi \sin \theta/\lambda$). Times required to accumulate 40000 counts at each angle were recorded. The whole angle range was scanned twice. The scattered intensities were corrected for background, polarization, absorption and Compton modified radiation, and then scaled to absolute units by conventional ways.[10–12] The values of coherent, incoherent and anomalous scatterings were the same as those used in previous papers.[11,12] The reduced intensities $i(s)$ obtained by subtraction of independent atomic scatterings from the scattered intensities thus deduced, were Fourier transformed into radial distrícution functions, $D(r)$, after smoothing correction.[12] Residual systematic errors appearing in the small r region of the $D(r)$ curves were also corrected. The theoretical peak for a given atom pair i-j was calculated in the previous manner.[12]

Results and Discussion

The scaled coherent intensity curves, the observed $s \cdot i(s)$ values, the $D(r)$, and $(D(r) - 4\pi r^2 \rho_0)$ curves where ρ_0 is the bulk electron density obtained for solutions A, B, and C are shown in Figs. 2—5, respectively.

Solutions A and B. As can be seen in Fig. 1, the tetraamminecopper(II) ion is the predominant species in solutions A and B. The $D(r)$ and $(D(r) - 4\pi r^2 \rho_0)$ curves obtained for the both solutions are very similar except for $r > 5$ Å and show four peaks around 1.0, 2.1, 3.3, and 4.3 Å. The smallest broad peak around 1 Å is attributed to both O–H and N–H bonds within water and ammonia molecules, respectively. The peak centered at 3.3 Å is mainly attributed to the interaction between chloride ions and water molecules.[13]

The location of the second major peak at about 2.1 Å is consistent with interatomic distances between Cu(II) and nitrogen atoms within the square-planar tetraamminecopper(II) ion in the crystalline state.[3–6] However, the area under the peak was found to be larger than the area calculated from only four Cu–N bonds. Therefore, it is expected that the copper complex may have an octahedral structure and the axial copper–ligand bond within the octahedral coordination may also contribute to the area under the peak. By assuming that the equatorial Cu(II)–N bonds are the same as those in the crystalline state, the interactions due to the four Cu–N bonds were subtracted from the $D(r)$ and $(D(r) - 4\pi r^2 \rho_0)$ curves. The values of 2.03 Å for the Cu–N distance and 0.0020 Å^2 for the temperature factor calculated from spectroscopic data[14] were adopted for the calculation. The result is shown in Fig. 6 (fine solid line). A hump still remaining around 2.3 Å may be due to the axial copper(II)–ligand bonds. The location of this hump ruled out the possibility of axial Cu(II)–Cl bonding, since the Cu–Cl distance was reported to be about 2.6 Å.[15] It is therefore assumed that water molecules occupy the axial sites of Cu(II). The Cu–OH_2(axial) distance, as well as the Cu–NH_3(equatorial) one, within the tetraamminecopper(II) complex were determined by the trial-and-error method so that subtraction of the calculated peaks of the assumed structure of the tetraamminecopper(II) complex from the $D(r)$ and $(D(r) - 4\pi r^2 \rho_0)$ curves led to a smooth background curve with no indication of any other intramolecular interactions in the first coordination sphere of copper(II) ion. From the analysis, we found that two water molecules should coordinate to the tetraamminecopper(II) ion in solutions A and B.

Table 2 gives the final values estimated from the

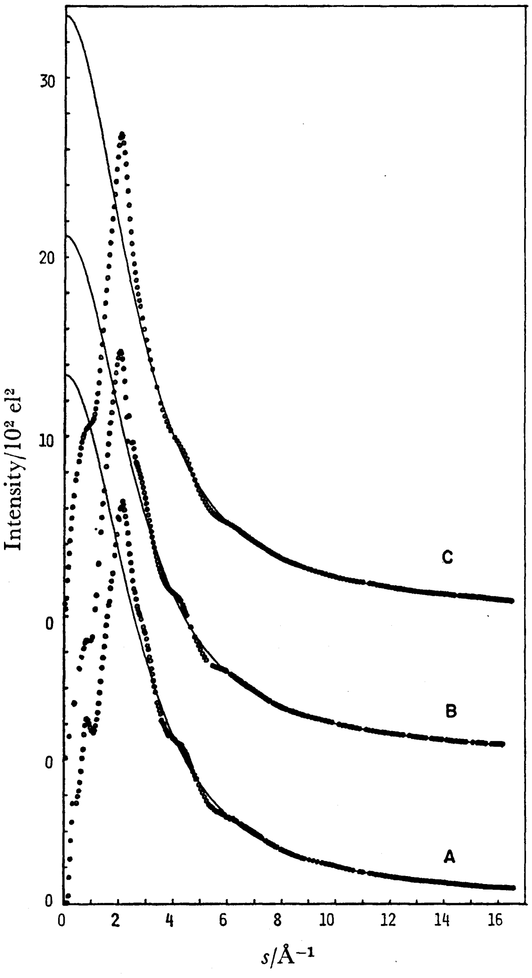

Fig. 2. Scaled coherent intensity functions (circle) and calculated independent scatterings (solid line) for ammoniacal aqueous solutions of copper(II) chloride. A. $NH_3/Cu = 4.8$; B. $NH_3/Cu = 5.0$; C. $NH_3/Cu = 11.2$.

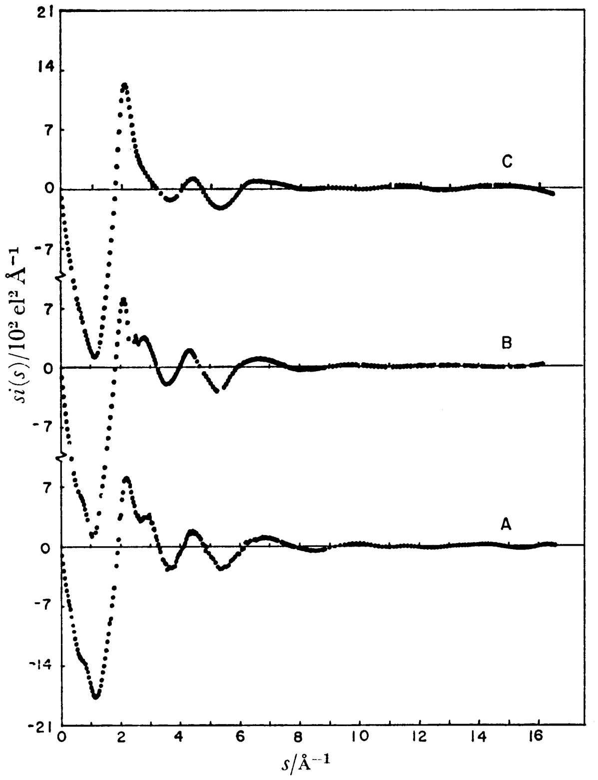

Fig. 3. Observed $s\cdot i(s)$ values of solutions A, B, and C.

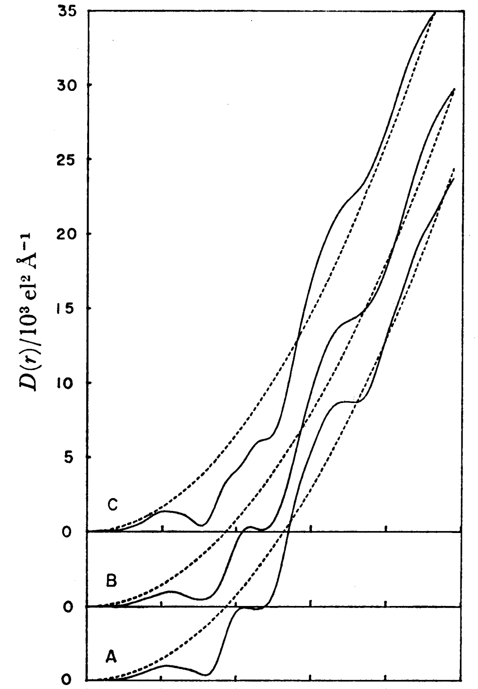

Fig. 4. Radial distribution functions $D(r)$ (solid line) and $4\pi r^2\rho_0$ (dashed line) for solutions A, B and C.

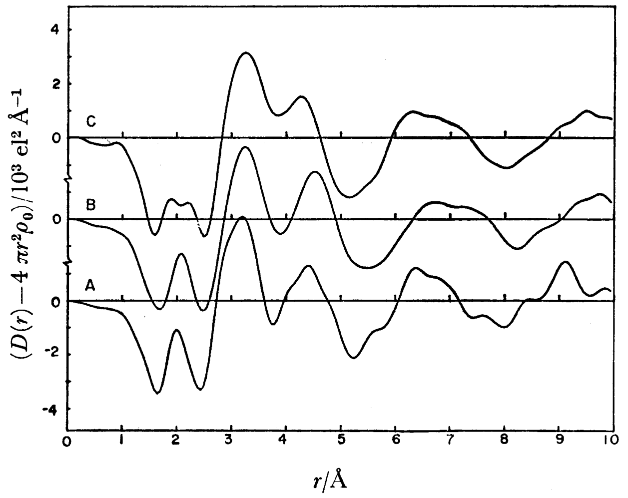

Fig. 5. The $(D(r)-4\pi r^2\rho_0)$ curves for solutions A, B, and C.

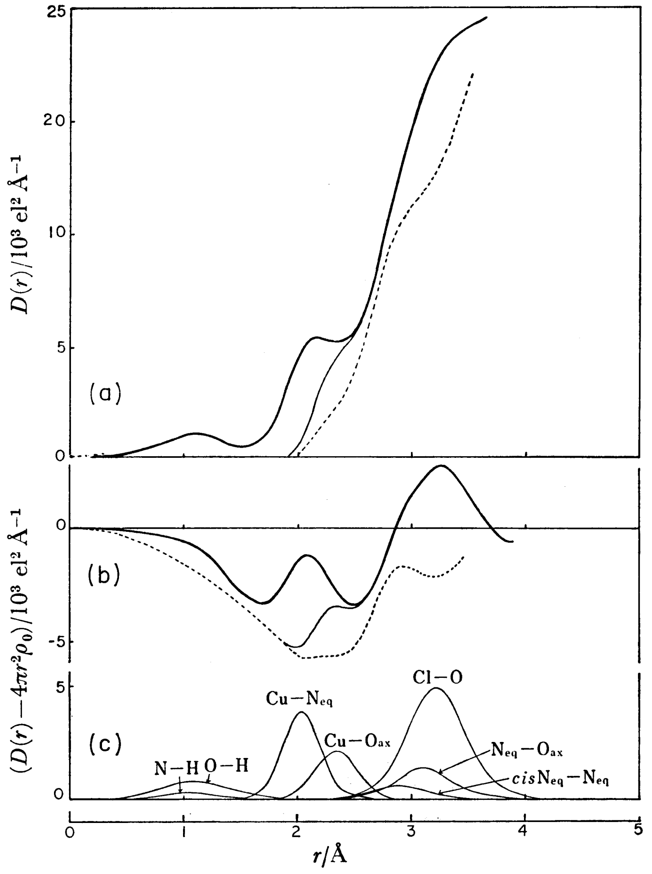

Fig. 6. (a). The $D(r)$ curve for solution A (NH_3/Cu = 4.8). The fine solid line shows the residual curve obtained subtraction of theoretical peak shape for four Cu-N$_{eq}$ bonds from the $D(r)$ curve and the broken curve the difference between the $D(r)$ curve and theoretical peak shapes shown in (c). (b). The corresponding $(D(r)-4\pi r^2\rho_0)$ curve. (c). The theoretical peak shapes with the parameters given in Table 2.

shape of the $D(r)$ curve in Fig. 6. The broad peak at around 2.9 Å still left in the residual radial distribution curve (broken line) may be ascribed to the O–O bonds of bulk water. The maximum at 4.3 Å in the $D(r)$ and $(D(r)-4\pi r^2\rho_0)$ curves (Figs. 4 and 5) may include the interaction between Cu(II) and water molecules within the secondary hydration shell,[16] as well as the interaction of *trans*-N···N.

TABLE 2. THE FINAL PARAMETER VALUES FOR THE DISTORTED OCTAHEDRAL STRUCTURE OF THE TETRAAMMINE COPPER(II) COMPLEX. THE VALUES IN PARENTHESES ARE THEIR ESTIMATED ERRORS

	$\frac{r_{ij}}{Å}$	$\frac{b_{ij}}{Å^2}$	n_{ij}
$Cu(NH_3)_4(OH_2)_2^{2+}$			
$Cu-N_{eq}$	2.03(±0.02)	0.003	4
$Cu-O_{ax}$	2.33(±0.03)	0.005	2
cis-$N_{eq}\cdots N_{eq}$	2.87(±0.05)	0.01	4
$N_{eq}\cdots O_{ax}$	3.09(±0.05)	0.01	8
$Cl(H_2O)_6^-$			
Cl-O	3.20(±0.05)	0.01	6

Solution C. Figure 1 shows that the predominant species is a pentaamminecopper(II) ion in solution C. As can be seen in Figs. 4 and 5, the $D(r)$ and $(D(r)-4\pi r^2\rho_0)$ curves for solution C show double peaks in the range of $r=2.0$—2.5 Å. The double peaks may be easily resolved into a peak with the maximum at about 1.95 Å and another one at about 2.3 Å. Other peaks at 3.3 Å and 4.2 Å also appeared in the curve C.

The first small peak located at 1.0 Å is due to the O-H bonds within water molecules and partly due to the N-H bonds within ammonia molecules. The peak at about 1.95 Å may be ascribed to the Cu(II)-N bond in the square-plane and the peak at about 2.3 Å may be ascribed to the interaction between Cu(II) and the ligands at the axial sites. The peaks located at 3.3 Å and 4.2 Å are mainly related to the Cl-O and to the $Cu-OH_2$ (in the second coordination layer) interactions, respectively, as previously described.

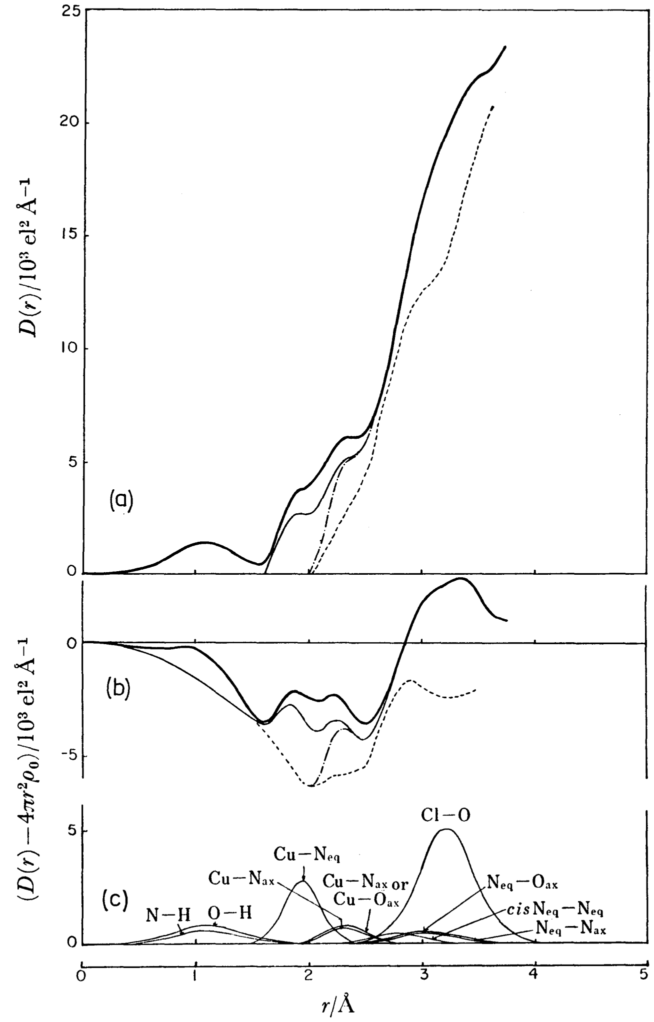

Fig. 7. (a). The $D(r)$ curve for solution C ($NH_3/Cu=11.2$). The fine solid line (——) shows the residual curve obtained by subtracting the contribution of the tetraamminecopper(II) ion from the $D(r)$ curve, the chain line (-•-•-) gives the difference between the residual curve and the calculated peak shape for four $Cu-N_{eq}$ bonds and the broken line (----) the residual curve obtained by subtraction of the theoretical peak shapes shown in (c) from the residual curve.
(b). The corresponding $(D(r)-4\pi r^2\rho_0)$ curve. (c). The theoretical peak shapes with the parameters given in Table 3.

TABLE 3. THE FINAL PARAMETER VALUES FOR THE DISTORTED OCTAHEDRAL STRUCTURE OF THE $Cu(NH_3)_5X^{2+}$ ($X=NH_3$ or H_2O) THE VALUES IN PARENTHESES ARE THEIR ESTIMATED ERRORS

	$\frac{r_{ij}}{Å}$	$\frac{b_{ij}}{Å^2}$	n_{ij}
$Cu(NH_3)_5X^{2+}$			
$Cu-N_{eq}$	1.93(±0.02)	0.003	4
$Cu-N_{ax}$	2.30(±0.03)	0.005	1
$Cu-X_{ax}$	2.30(±0.03)	0.005	1
cis-$N_{eq}\cdots N_{eq}$	2.73(+0.05)	0.01	4
$N_{eq}\cdots N_{ax}$	3.00(±0.05)	0.01	4
$N_{eq}\cdots X_{ax}$	3.00(±0.05)	0.01	4
$Cl(H_2O)_6^-$			
Cl-O	3.20(±0.05)	0.01	6

After subtracting the appropriate intramolecular interactions within the tetraamminecopper(II) ion present, as well as O-H and N-H interactions in solution C, the second and third peaks of the residual curves (fine solid line in Fig. 7) were analyzed for determining the structure of a higher-ammine complex of copper ion as illustrated in Fig. 7. The clearly defined peak at 1.93 Å was assigned to the equatorial Cu-N distance and the area under this peak gave four Cu-N bonds per Cu(II). The distance and the number of the axial copper(II)-ligand bonds were estimated after subtraction of the four equatorial Cu-N interactions from the $D(r)$ curve. The resulting curve is drawn by the chain line (—•—) in Fig. 7. The area under the peak at 2.3 Å corresponded to the $Cu-NH_3$ and $Cu-OH_2$ bonds with an equal distance (see Fig. 7c), if it is assumed that the pentaamminecopper complex is formed. However, it must be noted that another assumption of the formation of the hexaamminecopper complex can equally well explain the data. The final parameter values thus determined are summarized in Table 3. The residual radial distribution curve after subtraction of all the intramolecular interactions of the species is shown in Fig. 7 with dashed lines. The broad peak remaining at about 2.9 Å in the residual radial distribution curve may be due to the O–O interactions within bulk water. The maximum at 4.3 Å in the $D(r)$ curve (Fig. 4, curve C) may be attributable to the interaction between Cu(II) and water molecules within the secondary hydration shell.

Although it is not conclusive whether the copper(II) ion combines with five ammonia molecules and a water molecule or with six ammonia molecules in solution C, it is obvious that the complex present in the solution has not a tetragonal-pyramidal form, but a distorted octahedral structure.

In the hexaaquacopper(II) ion the Cu–OH_2-(equatorial) distance is 1.94 Å[17] and the Cu–NH_3-(equatorial) one within the tetraamminecopper(II) complex is 2.03 Å. However, we observed that the Cu–NH_3(equatorial) distance is shortened to 1.93 Å by further combination of ammonia molecules with the tetraamminecopper(II) complex. Although the reason of the change in the bond distance is not clear yet, it may be due to the lowering of the symmetry of the complex ion. The electron density of the bonds between the central copper(II) ion and the ammonia molecules at the equatorial position may also be changed with varying ligand molecules at the axial position. This may reflect to the change in the bond distances between the copper(II) ion and ligand molecules.

References

1) A. A. G. Tomlinson and B. J. Hathaway, *J. Chem. Soc., Part A*, 1905 (1968).
2) V. Romano and J. Bjerrum, *Acta Chem. Scand.*, **24**, 1551 (1970).
3) B. Morosin, *Acta Crystallogr., Sect. B*, **31**, 2220 (1975).
4) J.-C. Tedenac, É. Philippot, and M. Maurin, *Bull. Soc. Fr. Mineral Cristallogr.*, **98**, 36 (1975).
5) B. Morosin, *Acta Crystallogr., Sect. B*, **25**, 19 (1969); **32**, 1237 (1976).
6) E. Dubler and L. Linowsky, *Helv. Chim. Acta*, **58**, 2604 (1975).
7) H. Elliot and B. J. Hathaway, *Inorg. Chem.*, **5**, 885 (1966).
8) T. Distler and P. A. Vaughan, *Inorg. Chem.*, **6**, 126 (1967).
9) L. G. Sillén and A. E. Martel, "Stability Constants," Special Publication No. 17, The Chemical Society, London (1964).
10) H. Ohtaki, M. Maeda, and S. Ito, *Bull. Chem. Soc. Jpn.*, **47**, 2217 (1974).
11) H. Ohtaki, T. Yamaguchi, and M. Maeda, *Bull. Chem. Soc. Jpn.*, **49**, 701 (1976).
12) T. Yamaguchi and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **51**, 3227 (1978).
13) A. H. Narten, F. Vaslow, and H. A. Levy, *J. Chem. Phys.*, **58**, 5017 (1973).
14) B. N. Cyvin, S. J. Cyvin, K. H. Schmidt, W. Wiegeler, A. Müller, and J. Brunvoll, *J. Mol. Struct.*, **30**, 315 (1976).
15) D. L. Wertz and J. L. Tyvoll, *J. Inorg. Nucl. Chem.*, **36**, 3713 (1974).
16) W. Bol and T. Welzen, *Chem. Phys. Lett.*, **49**, 189 (1977).
17) H. Ohtaki and M. Maeda, *Bull. Chem. Soc. Jpn.*, **47**, 2197 (1974).