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X-Ray Diffraction Study on the Coordination Structure of Chlorocopper(II) Complexes in Highly Concentrated Methanolic $CuCl_2$ Solution

Mitsuyoshi Ichihashi, Hisanobu Wakita,* and Isao Masuda
Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma, Jonan-ku, Fukuoka 814-01

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The structures of the solute complexes existing in methanolic $CuCl_2$ solutions with the concentrations of 1.055—3.250 mol dm^{-3} were investigated by X-ray diffraction analysis. The solute complexes which were predominantly present could be formulated as $[CuCl_n(CH_3OH)_{6-n}]$ (n= 1—3); they have an axially elongated octahedral structure including Cl^- at the equatorial site. The Cu–O bond distance was 2.230—2.238 Å. Methanol molecules were coordinated at the equatorial site with the Cu–O bond distance of 1.926—1.950 Å and at the axial site with that of 2.423—2.473 Å. When the initial concentration of $CuCl_2$ was kept within the range examined here, almost all of the Cu^{2+} ions formed chloro complexes.

Solution X-ray diffraction investigations have established that the stereo structure of the hexaaqua complex existing in aqueous $CuSO_4$ and $Cu(ClO_4)_2$ solutions is characteristic for the elongated octahedral geometry having two axial bonds with the longer distance (2.34—2.43 Å) and four equatorial bonds with the shorter distance (1.94—1.98 Å).[1,2] In concentrated aqueous $CuBr_2$ solutions (1.016—4.364 mol dm^{-3}), the coordination of Br^- ion was demonstrated to occur at the equatorial sites.[3] As for an aqueous $CuCl_2$ solution (2.952 mol dm^{-3}), Magini proposed from the investigation by X-ray diffraction analysis the presence of a monomeric complex which included two Cl^- ions at the equatorial sites,[4] similar to the above bromo complex. On the other hand, Wertz *et al.* reported the polymeric complexes to be present in aqueous $CuCl_2$ solutions (3.18 and 4.35 mol dm^{-3});[5] in these complexes the Cl^- ion bridged between two Cu^{2+} ions.

Since the coordination ability of methanol molecules is generally expected to be lower than that of water, the Cl^- ion may have a higher coordination ability than solvent molecules in methanol than in water. In fact, it was shown by the X-ray diffraction analysis that in methanolic $FeCl_3$ (6.0 and 11.0 mol kg^{-1}) and $CoCl_2$ (3.91 mol kg^{-1}) solutions, polymeric species bridged through Cl^- ions were present.[6] On the other hand, in aqueous $FeCl_3$ (2.332 mol dm^{-3}) and $CoCl_2$ (2.973 mol dm^{-3}) solutions, only the monomeric octahedral complex was known to be present in the form of either a mono- or a dichloro complex including H_2O molecules as another ligand.[4,7]

These facts suggest the increased coordination ability of Cl^- ion in methanol than in water. Accordingly, if a polynuclear chlorocopper(II) complex species were present, it might be demonstrated more distinctly with a methanolic $CuCl_2$ solution. In the present investigation the X-ray diffraction analysis has been carried out for concentrated methanolic $CuCl_2$ solutions. Observed $D(r)$ curves have been well explained by assuming that the solutions predominantly include three complexes, formulated as $[CuCl_n(CH_3OH)_{6-n}]$ where n=1, 2, and 3, in nearly equivalent amounts; the complexes have a distorted octahedral structure and the equatorial sites are occupied preferentially by Cl^- ions. The existence of a polymeric species was improbable.

Experimental and Data Treatment

Sample Solutions. Commercially available $CuCl_2 \cdot 2H_2O$ crystals were recrystallized from distilled water. The hydrate was dehydrated by keeping it at 100 °C, *in vacuo*, for 48 h. The sample solutions were prepared by dissolving the anhydrous $CuCl_2$ into anhydrous methanol. The copper ion concentration of the solutions was determined by EDTA titration method. The chloride ion concentration was calculated from the copper concentration. The amount of methanol in the solution was calculated from the copper ion concentration and from the density determined pycnometrically. The composition of the sample solutions is given in Table 1.

X-Ray Diffraction Measurements and Data Treatments. The measurements and the data treatments were carried out as described elsewhere.[3,8] The time required for accumulating 80000 counts was recorded for solutions A and B, and that for 40000 counts for solution C. The $s \cdot i(s)$ curves in Fig. 1 with circles were obtained by multiplying the observed reduced intensities $i(s)$ by the s value ($s=4\pi\sin\theta/\lambda$).

The radial distribution function was calculated from the reduced intensities $i(s)$ according to Eq. 1:

$$D(r) = 4\pi r^2\rho_0 + \frac{2r}{\pi}\int_0^{15} s\cdot i(s)\cdot M(s)\cdot\sin(r\cdot s)\mathrm{d}s. \tag{1}$$

In Eq. 1, $\rho_0=[\sum_i n_i f_i(0)]^2/V$. It denotes the average scattering power per unit volume V. $M(s)=[\sum_i n_i f_i(0)^2]/[\sum_i n_i f_i(s)^2] \times \exp(-0.01s^2)$; r is the distance in Å. The theoretical intensities, $i(s)_{\text{calcd}}$, of the interactions for the given pairs of the atoms were calculated from Eq. 2:

$$i(s)_{\text{calcd}} = \sum_i\sum_j^{i\neq j} n_{ij}\cdot f_i(s)\cdot f_j(s)\,\frac{\sin(r_{ij}\cdot s)}{r_{ij}\cdot s}\exp(-b_{ij}\cdot s^2), \tag{2}$$

where $f_i(s)$ and $f_j(s)$ are the scattering factors of atoms i and j; and n_{ij}, r_{ij}, and b_{ij} are the frequency factor, the distance (Å), and the temperature factor (Å^2) of the interactions between atoms i and j. Least-squares refinements of the above structural parameters n, r, and b were made by the use of the NLPLSQ program[1] utilizing a selected s (Å^{-1}) range so as to

Table 1. Composition of methanolic $CuCl_2$ solutions

Solution	$CuCl_2$[a]	CH_3OH[a]	V/Å^3	ρ/g cm^{-3}	μ/cm^{-1}
A	1.055	24.36	1574	0.9224	4.996
B	2.575	23.84	644.8	1.110	11.13
C	3.251	22.96	510.7	1.173	13.83

a) mol dm^{-3}. V, Stoichiometric volume containing one copper atom; ρ, density; μ, linear absorption coefficient of the solution for Mo $K\alpha$ radiation.

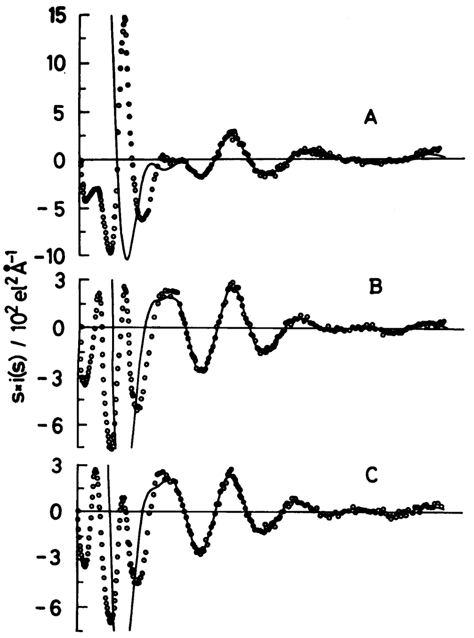

Fig. 1. Observed (oooo) and calculated (——) $s \cdot i(s)$ curves for solutions A, B, and C.

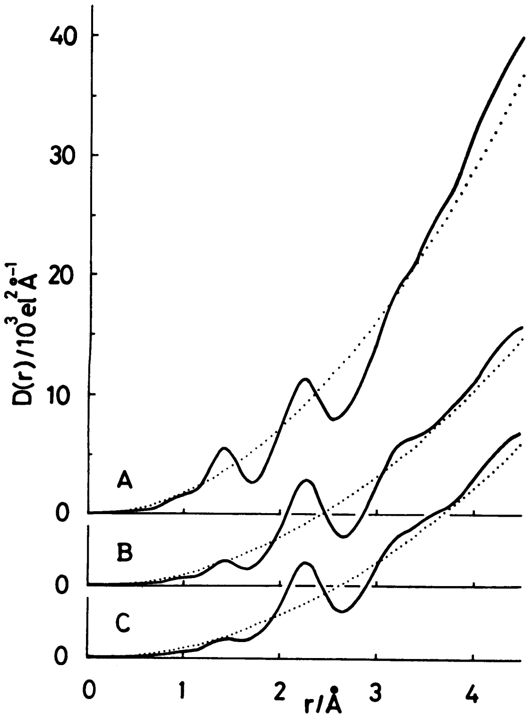

Fig. 2. $D(r)$ (——) and $4\pi r^2\rho_0$ (······) curves for solutions A, B, and C.

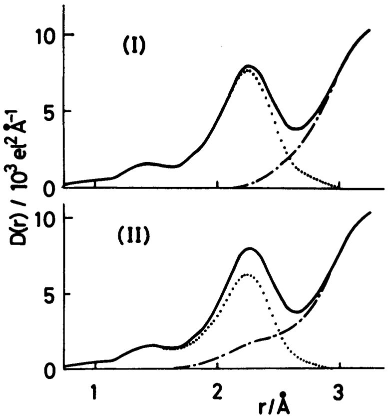

Fig. 3. Residual (—·—) $D(r)$ curves obtained by subtracting calculated $D(r)$ curves (······) from observed $D(r)$ curve (——) for solution C.

(I); Calculated $D(r)$ curve is obtained by assuming the formation of "$CuCl_2(CH_3OH)_4$". (II); Calculated $D(r)$ curve is obtained by assuming the formation of $[Cu(CH_3OH)_6]^{2+}$.

minimize the U value in Eq. 3:

$$U = \Sigma s^2[i(s)-i(s)_{\mathrm{calcd}}]^2. \qquad (3)$$

Results and Discussion

The $D(r)$ curves for solutions A, B, and C are given in Fig. 2. These show a common pattern exhibiting a shoulder around 1.0 Å, two distinct peaks with the maxima at 1.5 and 2.3 Å, and a shoulder between 3.0—3.5 Å.[9] The shoulder around 1.0 Å and the peak at 1.5 Å can be attributed to free and complexed CH_3OH molecules; the former is caused by the C—H and O—H interactions and the latter by the C—O interaction. In $D(r)$ curves obtained for methanol or methanolic solutions, the peak due to the C—O interaction has ordinarily been seen around 1.5 Å.[10] The shoulder located in the 3.0—3.5 Å region, judging from the position, may be ascribed to the mutual interactions among the ligands which are bound in the first coordination sphere and to the interactions between these ligands and the solvent CH_3OH molecules. The peak at 2.3 Å could be most informative for the interactions between Cu^{2+} and the ligands including CH_3OH and Cl^-. This peak appears to be quite symmetric, but, as will be discussed below, it can not be ascribed to solely one sort of interaction.

In order to analyze the $D(r)$ curve quantitatively, the area of the above peak has been taken into account. By supposing tentatively the presence of only one species of complex as $[Cu(CH_3OH)_6]^{2+}$,[11] the calculated peak area due to the six Cu–O interactions amounts to only 6/8 of the observed one, as shown in Fig. 3. Similarly, supposing only $[Cu(CH_3OH)_4]^{2+}$ to be present, the calculated peak area was not coincident with the observed one. Therefore, it appears necessary to accept the occurrence of the coordination of Cl^- to Cu^{2+} ion. In fact, Doe and Kitagawa recently reported that the stepwise formation constants of the chloro-copper complex species in methanol are $K_1 = 1.2 \times 10^5$, $K_2 = 2.5 \times 10^3$, and $K_3 = 1.7 \times 10^3$ (mol^{-1} dm^3).[12] On the basis of these data, the amounts of the complex species that include unitary bonding as $CuCl^+$, $CuCl_2$, and $CuCl_3^-$ are calculated to be 30.5, 37.6, and 31.5%, of the initial Cu^{2+} concentration in solutions A—C.[13] In addition, a survey of the bond distance data for the numerous chloro-copper(II) complex crystals suggested the following:

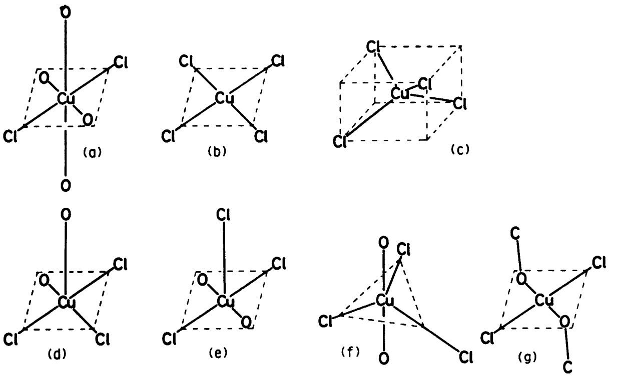

Fig. 4. Assumed structural models.

If the Cu^{2+} ion in methanolic solution had two sorts of coordination distances, one shorter and the other longer, and if it coordinated Cl^- ion with the longer one, the interaction due to such Cu—Cl bonding could be expected to appear at 2.6—3.0 Å. But, actually, no such peak appeared on the $D(r)$ curves in Fig. 2, so occurrence of the bonding in the above manner is unlikely. By taking into account the stability data, we assumed that the complexes including the unitary $CuCl^+$, $CuCl_2$, and $CuCl_3^-$ bonds are present in an elongated octahedral form wherein the Cu^{2+} ion coordinated the Cl^- ion with a bond distance shorter than 2.6 Å. These complexes are generally formulated as $[CuCl_n(CH_3OH)_{6-n}]$ (n=1—3), and on the basis of the stability data the mean composition of the complexes with n=1—3 existing in the solutions may be represented with a formula "$CuCl_2(CH_3OH)_4$". Therefore, the calculation of the peak area was carried out on "$CuCl_2(CH_3OH)_4$". As shown in Fig. 3, the calculated peak area agreed well with the observed one.

The structural model shown in Fig. 4-a was depicted. The model has axially elongated octahedral geometry and possesses two O atoms and two Cl^- ions at the equatorial sites, with the bond distances of 1.95 and 2.25 Å, respectively, and the other two O atoms at the axial sites with the bond distance of 2.45 Å. In order to determine the parameter values (n, r, and b values), the $s \cdot i(s)_{calcd}$ curves were calculated from Eq. 2 by employing a set of the parameter values selected tentatively for the Fig. 4-a. The refinements of these values were carried out by a least-squares method so that these gave an $s \cdot i(s)_{calcd}$ curve which agreed with the observed $s \cdot i(s)$ curve in the region of $s > 5$ Å^{-1}. It was found that using the model, Fig. 4-a, the calculated $D(r)$ curve show a peak at 2.3 Å with the peak area closely agreed with the observed one. And, as shown in Fig. 1, a good agreement between the calculated and observed $s \cdot i(s)$ curves is seen in the region of $s > 4$ Å^{-1}. The final parameter values used in these calculations are given in Table 2: it is noteworthy in Table 2 that the n values for the interactions, Cu-Cl, Cu-O (equatorial), and Cu-O (axial), are always nearly 2; this is consistent with the assumed six-coordinate complex. In Fig. 5 the smoothing of the observed $D(r)$ curves for solution C is demonstrated. The subtraction of the peaks due to the interactions expected for the model, Fig. 4-a, from the observed $D(r)$ curve gives finally a residual curve which is satisfactorily smooth.

Table 2. Structural parameter values of the $[CuCl_n(CH_3OH)_{6-n}]$ (n=1—3) complexes

Solution (mol dm^{-3})	Parameter[a]	Interaction		
		$Cu-O_{eq}$	$Cu-O_{ax}$	$Cu-Cl_{eq}$
A	r	1.950	2.458	2.230
(1.055)	b	0.0011	0.0084	0.0031
	n	2.109	1.938	2.019
B	r	1.947	2.423	2.236
(2.575)	b	0.0016	0.0072	0.0025
	n	1.982	2.089	2.085
C	r	1.926	2.473	2.238
(3.251)	b	0.0015	0.0074	0.0021
	n	1.919	2.023	2.048

a) r: Bond distance, Å; b: temperature factor, Å^2; n: frequency factor; eq, equatorial; ax, axial.

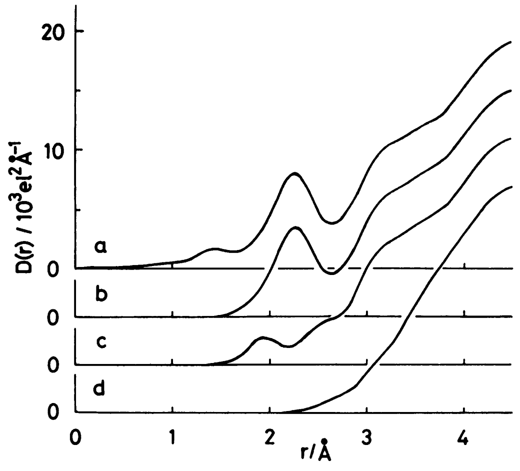

Fig. 5. Smoothing of $D(r)$ curve.
(a); $D(r)$ curve for solution C. (b); Obtained by subtracting the calculated peak due to the interactions within the methanol molecules from curve (a). (c); Obtained by subtracting the calculated peak due to the $Cu-Cl_{eq}$ interactions from curve (b) (the clear peaks due to the $Cu-O_{eq}$ and $Cu-O_{ax}$ interactions are left at about 1.9 and 2.5 Å). (d); Final residual curve obtained by subtracting from curve (c) the calculated peaks due to the $Cu-O_{eq}$ and $Cu-O_{ax}$ interactions along with those due to the other expected intramolecular interactions (*cf.* Fig. 4-a).

A similar result of the $D(r)$ curve analysis could be deduced for the solution which was considered to include nearly equivalent amounts of the three complexes of n=1—3 in $[CuCl_n(CH_3OH)_{6-n}]$. It may be said from the formation data that almost all of the Cl^- ions are consumed for the above complexation; this makes the presence of chloro-bridged polymeric complexes improbable, for such polymer formation results in the presence of free Cl^- ions in the solution. In the concentrated methanolic 1.055—3.250 mol dm^{-3} $CuCl_2$ solutions, therefore, three monomeric complexes of the formula, $[CuCl_n(CH_3OH)_{6-n}]$ (n=1—3), were predominantly present; these possessed the axially elongated octahedral structure and coordinated the Cl^- ion equatorially.

The other structural models, b—g in Fig. 4, were also examined. As long as one considered the peak area and position of $D(r)$ curve, these models gave rise a peak with area and position similar to those of the observed peak at 2.3 Å. However, all of these models had to be discarded for the following reason. The temperature factors (b value) of the Cu–Cl bonding for the models b, c, and d were 0.02, 0.03, and 0.01 Å^2; these are too large, as compared with 0.0052 Å^2, a value known for the equatorial Cu–Cl bonding.[4] In the models e, f, and g, the b values, 0.0023—0.0032 Å^2, were not necessarily unreasonable, but these models had to be rejected for the following reasons. In model e, one of the Cl^- ions has to be at the apex apart from the Cu^{2+} ion with a very short distance, 2.45 Å, which is not plausible for the axial Cu–Cl bond distance. In model f, the Cu^{2+} ion binds two O atoms, two Cl^- ions, and one Cl^- ion with the distances of 1.95, 2.25, and 2.45 Å, respectively. This geometry resembles that in the $CuCl_2 \cdot 2DMSO$ crystal.[14] And this model gave an $s \cdot i\,(s)_{calcd}$ curve which fit the observed one well. But, the residual distribution curve obtained by using the model was not satisfactorily smooth in the 3—4 Å region. Model g gave an $s \cdot i\,(s)_{calcd}$ curve similar to that obtained by using model a. However, this geometry forces the the ∠Cu–O–C to be about 91°: This is not probable for the methanol molecule coordinated to the metal ions. The ∠Hg–O–C is 117° in the $HgCl_2 \cdot 2CH_3OH$ crystal,[15] and the ∠Cu–O–C is 119.5° in the $[Cu_2\{(CH_3)_2N(CH_2)_3NH(CH_2)_2O\}_2(CH_3OH)_2](ClO_4)_2$ crystal.[16]

References

1) H. Ohtaki, T. Yamaguchi, and M. Maeda, *Bull. Chem. Soc. Jpn.*, **49**, 701 (1976).

2) H. Ohtaki and M. Maeda, *Bull. Chem. Soc. Jpn.*, **47**, 2197 (1974); M. Magini, *Inorg. Chem.*, **21**, 1535 (1982).

3) M. Ichihashi, H. Wakita, T. Mibuchi, and I. Masuda, *Bull. Chem. Soc. Jpn.*, **55**, 3160 (1982).

4) M. Magini, *J. Chem. Phys.*, **74**, 2523 (1981).

5) J. R. Bell, J. L. Tyvoll, and D. L. Wertz, *J. Am. Chem. Soc.*, **95**, 1456 (1973).

6) D. L. Wertz and R. F. Kruh, *J. Chem. Phys.*, **50**, 4013, 4313 (1969).

7) M. Magini and T. Radnai, *J. Chem. Phys.*, **71**, 4255 (1979).

8) H. Wakita, M. Ichihashi, T. Mibuchi, and I. Masuda, *Bull. Chem. Soc. Jpn.*, **55**, 817 (1982).

9) The $D(r)$ curves reported by Wertz *et al.*[5] for the aqueous $CuCl_2$ solutions (3.18 and 4.35 mol dm^{-3}) showed five peaks at 1.95, 2.43, 3.2, 3.9, and 5.1 Å and one shoulder at 4.4 Å. They ascribed the peak at 3.9 Å to "secondary" Cu···O and Cu···Cl interactions between adjacent unitary molecules in the chloro-bridged polymeric complexes. On the $D(r)$ curves of the methanolic solutions subjected to our investigation, no peak around 3.9 Å was observed to appear.

10) G. G. Harvey, *J. Chem. Phys.*, **6**, 111 (1938); D. L. Wertz and R. F. Kruh, *ibid.*, **47**, 388 (1967).

11) T. Ichikawa and L. Kevan, *J. Phys. Chem.*, **84**, 1955 (1980).

12) H. Doe and T. Kitagawa, *Inorg. Chem.*, **21**, 2272 (1982).

13) When the initial concentration of $CuCl_2$ is given as C mol dm^{-3}, the respective concentrations of the species, $CuCl^+$, $CuCl_2$, and $CuCl_3^-$, can be calculated from the following equations: $[CuCl^+]=K_1[Cu][Cl]$; $[CuCl_2]=K_1K_2[Cu][Cl]^2$; $[CuCl_3^-] = K_1K_2K_3[Cu][Cl]^3$, and $[Cu] = C/\{1+K_1[Cl]+K_1K_2[Cl]^2+K_1K_2K_3[Cl]^3\}$, $2C = [Cl] + K_1[Cu][Cl] + 2K_1K_2[Cu][Cl]^2 + 3K_1K_2K_3[Cu][Cl]^3$.

14) R. D. Willett and K. Chang, *Inorg. Chim. Acta*, **4**, 447 (1970).

15) H. Brusset and F. Madaule-Aubry, *Bull. Soc. Chim. Fr.*, **1966**, 3121.

16) N. Matsumoto, S. Kida, and I. Ueda, *J. Coord. Chem.*, **9**, 133 (1979).