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An X-Ray Diffraction Study on the Structures of Mono(glycinato)copper(II) and Tris(glycinato)-cuprate(II) Complexes in Aqueous Solution

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The structures of mono(glycinato)copper(II) and tris(glycinato)cuprate(II) complexes in solution were determined by means of X-ray diffraction at 20 °C. The radial distribution curve obtained for solution A, in which comparable amounts of hexaaqua- and mono(glycinato)copper(II) complexes coexisted (the mole ratio $C_{gly}/C_{Cu}=0.700$, where C_i represents the total concentration of species i), showed that the mono(glycinato)copper(II) complex combined with four water molecules, two of which were at the distance of (1.98±0.01) Å at the equatorial position and the other two were of (2.27±0.01) Å at the axial one. The equatorial Cu–OH_2 bond length within the mono(glycinato)copper(II) was longer than that within the hexaaquacopper(II) ion (1.94 Å), whereas the axial Cu–OH_2 bond distance within the former complex was shorter than that within the latter (2.43 Å). Both lengths of the Cu–O and Cu–N bonds within the mono(glycinato)copper(II) ion were (1.99±0.02) Å. Thus the $[Cu(gly)(OH_2)_4]^+$ complex has an axially elongated octahedral structure. The X-ray scattering data of solution B with the C_{gly}/C_{Cu} mole ratio of 13.7, in which almost all Cu(II) ions formed the tris(glycinato)cuprate(II) complex were well explained in terms of a regular octahedral structure of the complex having the same Cu–O and Cu–N bond distances of (2.02±0.01) Å. The structure of the bis(glycinato)copper(II) complex was not determinable owing to its low solubility.

Many kinds of polyhedra appear in stereochemistry of copper(II) complexes, in which the coordination number of copper(II) ion is three, four, five or six. Of these a hexacoordinated copper(II) complex tends to have a distorted octahedral structure. A tetragonal distortion is frequently observed with the elongation of two bonds along the axis of the octahedron. Gažo *et al.*[1] collected crystal data for CuO_6, CuN_6, and CuN_4O_2 type complexes and discussed the correlation between equatorial and axial bond distances. The observation was that the equatorial and axial bond lengths correlated asymptotically with an increase of the interatomic distances within the equatorial plane, resulting in shortening the bond lengths along the axial direction.

Structures of copper(II) complexes have been extensively studied crystallographically. However, an axial bond distance in crystal may be significantly affected by an interaction between a ligand at the apex of a complex and counter ions around the complex ion, since an axial bond is essentially weak relative to an equatorial one. Thus, it seems to be desirable to investigate structures of copper(II) complexes without an effect of counter ions on copper(II)-ligand bonds along the axis.

Hexaaqua-,[2,3] some ammine-[4] and bis- and tris-(ethylenediamine)copper(II)[5] complexes in aqueous solution have been investigated so far by the X-ray diffraction method. All of the hexacoordinated complexes have an axially elongated octahedral structure. The equatorial bond distances are between 1.93 Å and 2.05 Å, whereas the axial bond lengths vary widely (2.3—2.9 Å). Recently the structures of tetraammine- and bis(ethylenediamine)copper(II) complexes in aqueous solution have been reported with a laboratory EXAFS apparatus.[6] Only four equatorial Cu–N bonds (≈2.03 Å) were detectable and the axial bond length was not determinable by the EXAFS measurement. The structure of a copper(II) chloride aqueous solution was studied by means of X-ray diffraction,[7] and it was reported that the equatorial sites of copper(II) ion were occupied by water molecules and chloride ions at 1.95 Å and 2.25 Å, respectively. However, the axial Cu–OH_2 and/or Cu–Cl bonds, which would appear at 2.2—2.3 Å for the former and at 2.8—3.0 Å for the latter, were not clearly observable because of overlapping of the peak owing to the axial bonds with that of the Cu–Cl (eq) bond within the complex and with the peak of the Cl–H_2O bond (≈3.1 Å) within the hydrated chloride ion. Distorted octahedral structures of copper(II)–chloro complexes were also found in methanol.[8]

Although there have been presented some structural data of copper(II) complexes in solution by the X-ray diffraction and EXAFS methods, no investigation has been carried out for structures of chelate complexes, except for ethylenediamine complexes, in solution. Therefore, in the present study we have attempted to determine the structures of glycinato copper(II) complexes in aqueous solution by the X-ray diffraction method.

In spite of a great importance of structural information of glycinato copper(II) complexes in the view point of coordination chemistry and biochemistry, the structure of only the bis(glycinato)copper(II) complex has been determined in crystal,[9] and structural data have been given for other complexes in neither solution nor the solid state. Therefore, we investigated the structures of the mono(glycinato)copper(II) and tris (glycinato)couprate(II) complexes in aqueous solution. The structure of the bis(glycinato)copper(II) complex in solution was not determinable by the present X-ray diffraction method due to its low solubility in water.

Experimental

Preparation and Analysis of Sample Solutions. All chemicals used were of reagent grade. Sample solutions were prepared by the similar way to that described in a previous

Table 1. The composition (mol dm^{-3}) and stoichiometric volume V per copper atom in solution A and per sodium atom in solutions B and C

	A	B	C
Cu	1.234	0.5842	—
Na	—	6.840	6.166
O	57.78	48.30	50.28
N	2.468	8.008	6.166
C	1.727	16.02	12.33
H	105.9	96.59	100.6
V/Å^3	1346	242.8	269.3
C_{gly}/C_{Cu}	0.700	13.7	—
density/g cm^{-3}	1.165	1.369	1.282
ρ_o/Å^{-3}	195.1	46.67	46.29

paper.[10] *Solution A,* in which the mono(glycinato)copper(II) complex was mainly formed, was prepared by dissolving powder of the bis(glycinato)copper(II) complex to a copper(II) nitrate solution. *Solution B* was prepared by mixing the bis(glycinato)copper(II) and sodium glycinate in water. Almost all copper(II) ions formed the tris(glycinato)cuprate(II) complex in this solution. *Solution C* was an aqueous sodium glycinate solution.

Bis(glycinato)copper(II) was prepared by mixing an aqueous copper(II) sulfate solution with a glycine solution which had been neutralized with $NaHCO_3$ and then recrystallized from water. Sodium glycinate was obtained by the same manner previously reported.[10] Copper(II) nitrate and copper(II) sulfate of reagent grade were recrystallized from water.

The total concentration of copper(II) ions (C_{Cu}) in the test solutions was electrogravimetrically determined as metallic copper. The total glycine concentration (C_{gly}) in the solutions was determined by the Kjeldahl method. Concentrations of nitrate ions in solution A and of sodium ions in solutions B and C were evaluated from the material balance of ions in the solutions. Densities of the sample solutions were measured by using a pycnometer. The composition of the solutions is given in Table 1.

Method of Measurement and Treatment of X-Ray Scattering Data. The apparatus used and method of measurements were described previously.[2,10,11] Mo $K\alpha$ radiation (λ= 0.7107 Å) was used and the scattered intensities were measured at discrete points of θ over the range 1°—70° (2θ is the scattering angle). Times required to accumulate 120000 counts were recorded at each point. The scattered intensities were scaled to the absolute ones after corrections for absorption, polarization and multiple scatterings of X-rays by a usual manner.[11]

The reduced intensities $i(s)$ were extracted from the scaled intensities $I(s)$ by subtracting independent coherent scatterings according to Eq. 1:

$$i(s) = I(s) - \sum_i n_i[\{f_i(s)+\Delta f_i'\}^2 + (\Delta f_i'')^2]. \quad (1)$$

The reduced intensities multiplied by s ($=4\pi\lambda^{-1}\sin\theta$) of the sample solutions are shown in Fig. 1. The radial distribution function $D(r)$ was calculated by the Fourier transform of the reduced intensities as follows:

$$D(r) = 4\pi r^2\rho_o + \frac{2r}{\pi}\int_0^{s_{max}} s\cdot i(s)\cdot M(s)\cdot\sin(rs)ds, \quad (2)$$

where ρ_o ($=\{\sum_i n_i\cdot f_i(0)\}^2/V$) is the average scattering density in the stoichiometric volume V of the solution, and s_{max} represents the maximum s-value attained in the measurement. The modification function $M(s)$ had the form given in Eq. 3,

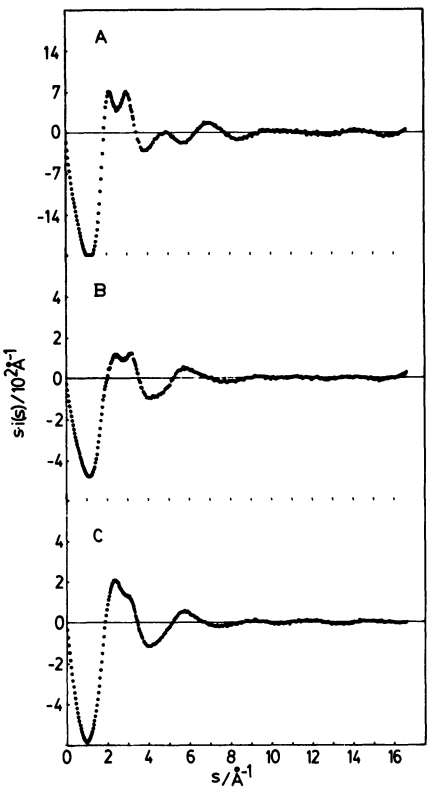

Fig. 1. The reduced intensities multiplied by s for solutions A, B, and C.

$$M(s) = \frac{[\sum_i n_i\cdot f_i(0)^2]}{[\sum_i n_i\cdot f_i(s)^2]}\cdot\exp(-k\cdot s^2). \quad (3)$$

The damping factor k was chosen as 0.01 Å^2 in the present case. In Eqs. 1—3 $f_i(0)$ and $f_i(s)$ denote the atomic scattering factors of atom i at s=0 and s, respectively. n_i is the number of atom i in the stoichiometric volume. $\Delta f_i'$ and $\Delta f_i''$represent the real and imaginary parts of anomolous dispersion of atom i, respectively. The radial ($D(r)$) and differential radial ($D(r)-4\pi r^2\rho_o$) distribution curves of the test solutions are depicted in Figs. 2 and 3, respectively.

Calculations were performed by using by KURVLR[12] and NLPLSQ[13] programs with the computer at the Tokyo Institute of Technology and partly with the computer at the Institute for Molecular Science in Okazaki.

Results and Discussion

According to the formation constants of copper(II)–glycine complexes,[14] comparable amounts of the hexaaquacopper(II) and mono(glycinato)copper(II) complexes existed in solution A. The tris(glycinato)cuprate(II) complex is predominantly formed in solution B as a large excess of glycinate ions are contained. The coexistence of the bis(glycinato)copper(II) complex in both solutions needs not to be taken into consideration in the course of the analysis of the data, since the solubility of the bis(glycinato)copper(II) is low (about 0.025 mol dm^{-3}).

Structure of Mono(glycinato)copper(II) Complex. Figure 4 represents the radial distribution and differential radial distribution functions of solution A,

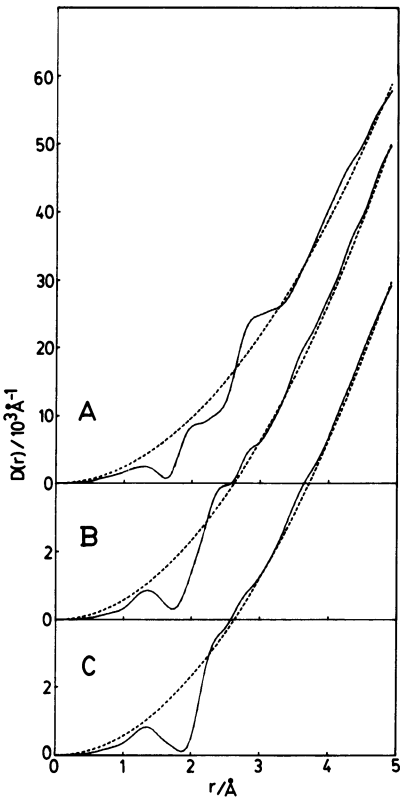

Fig. 2. The radial distribution curves, $D(r)$, for solutions A, B, and C. The curves of $4\pi r^2\rho_o$ are shown by dashed lines.

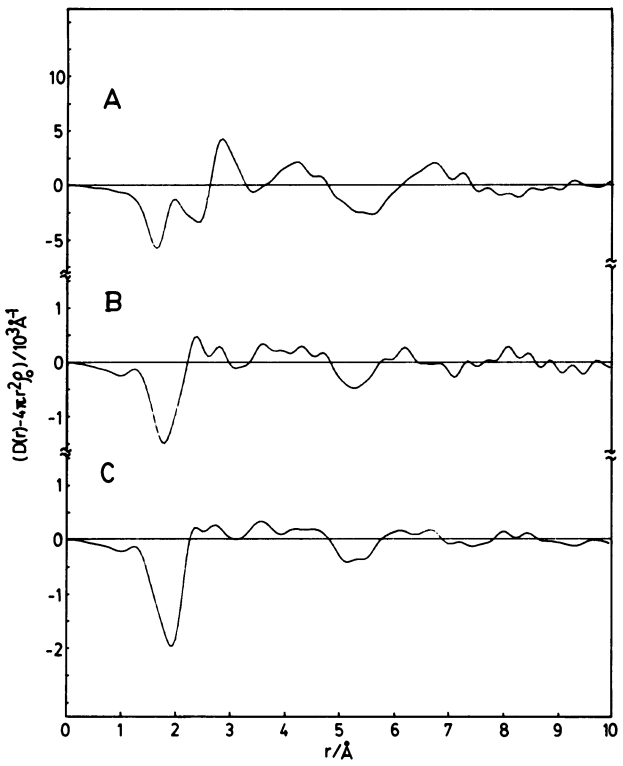

Fig. 3. The $(D(r)-4\pi r^2\rho_o)$ curves for solutions A, B, and C.

as well as the calculated peak shapes of each atom pair in the system which will be discussed in the later section. In the radial distribution curves (Figs. 4a and 4e) we see four peaks around 1.3, 2.0, 2.9, and 4.3 Å.

The small and broad peak appearing at 1.3 Å is due to the O–H bonds within water molecules, the N–O bonds within nitrate ions and N–H, C–H, C–C, C–N, and C...O bonds within glycinate ions. The second peak observed around 2.0 Å is attributable to the interactions of copper(II) ion with the ligand atoms in the first coordination shell. Nonbonding C···N, C···O, and O···O interactions within glycinate ions and O···O contacts within nitrate ions also contribute to the peak. The third peak at about 2.9 Å is ascribed to the nonbonding Cu···C interactions within the mono(glycinato)copper(II) ion, to the interactions between atoms within the ligands in the first coordination sphere of the complexes and to the O···O contacts of water mole-

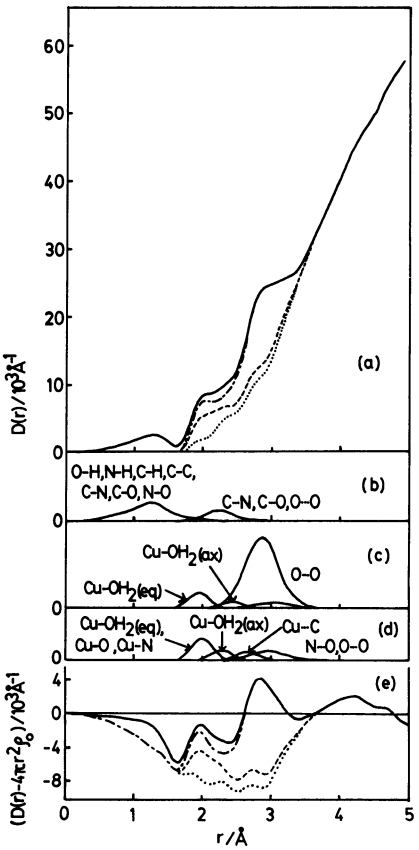

Fig. 4. (a) The radial distribution curve for solution A. (b) The theoretical peak shapes for O–H bonds within water molecule, intramolecular interactions within glycinate ion, and N–O and O···O pairs within nitrate ion. (c) The theoretical peaks for Cu–OH_2(eq), Cu–OH_2(ax), and O···O pairs within the hexaaquacopper-(II) complex and O···O contacts of water molecules in the bulk. (d) The theoretical peaks calculated for Cu–OH_2(eq), Cu–O, Cu–N, Cu–OH_2(ax), Cu···C, N···O, and O···O pairs within the mono-complex. (e) The corresponding $(D(r)-4\pi r^2\rho_o)$ curve to the $D(r)$ in (a). The chain, dashed, and dotted lines indicate the residual curves after subtraction of the theoretical peaks in (b), (c), and (d), respectively.

cules in the bulk. The fourth peak is composed of peaks owing to longer intramolecular interactions as well as intermolecular interactions between ions in the solution, which will not be taken into account in the present analysis.

In the first step of the analysis of the radial distribution curve, we subtracted the calculated peak shapes owing to the intramolecular interactions of water molecules, glycinate and nitrate ions. The parameter values used were the same as those described in the previous paper.[10] The residual curve thus obtained is shown in Fig. 4 by the chain line. The broad peak at about 2.0 Å suggested that the mono(glycinato)copper(II) as well as the hexaaquacopper(II) complexes had a distorted octahedral structure.

In order to estimate the structural parameters for the mono(glycinato)copper(II) complex, the concentration ratio of the $[Cu(OH_2)_6]^{2+}$ to $[Cu(gly)]^+$ ions in the solution must be evaluated. In the second step of the analysis, we assumed the concentration ratio of the hexaaquacopper(II) to mono(glycinato)copper(II) complexes to be 40:60 according to the stability constants reported in dilute solutions,[14] and the theoretical peaks owing to the intramolecular interactions of $[Cu(OH_2)_6]^{2+}$ and the O···O contacts in the bulk water were subtracted. In the course of the calculation, the structure parameters for the $[Cu(OH_2)_6]^{2+}$ ion and the bulk water were quoted from the works by Ohtaki and Maeda[2] and by Narten,[15] respectively. The analysis of the residual curve (···) indicated that the broad peak around 2.0 Å consisted of two peaks centered at 2.0 and 2.3 Å. The peak area corresponded to four Cu-O and Cu-N bonds for the former and two Cu-O bonds for the latter,[16] and hence the mono(glycinato)copper(II) complex has a form of a distorted octahedron with one glycinate ion and four water molecules. Thus, the glycinate ion and two of the water molecules coordinated to the Cu(II) ion at the equatorial positions and additional two water molecules bound at the axial ones. The distances of the nonbonding Cu···C pairs and the interactions between the ligand atoms in the first coordination shell were evaluated by employing the above structure model.

The least-squares calculations were carried out by using $s \cdot i(s)$ values in the high angle region ($s > 5$ Å^{-1}) (Fig. 5). In order to avoid errors introduced by neglecting long-range interactions, the lower limit of the s-value was varied from 5 to 7 Å^{-1}. The intramolecular interactions of water molecules, glycinate and nitrate ions and of hexaaquacopper(II) complex and the O···O contacts in the bulk water were fixed at the literature values during the refinements. The calculations were performed by inserting bond distances roughly estimated from the analysis of the radial distribution curve as initial value. Various sets of the initial values were examined in the course of the least-squares calculations: in one case the length of the Cu-OH_2 (eq), Cu-O, and Cu-N bonds were assumed to be 2.00 Å, while the length of the Cu-OH_2 (ax) within the $[Cu(gly)(OH_2)_4]^+$ complex was 2.30 Å. Another assumption was made for the initial bond lengths inserted to be 1.94 Å for the Cu-OH_2 (eq) in the $[Cu(gly)(OH_2)_4]^+$, which was the same as that of the Cu-OH_2 (eq) within the hexa-

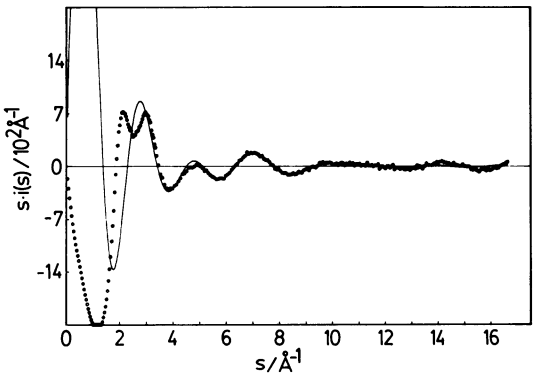

Fig. 5. The $s \cdot i(s)$ values for solution A. The observed curve is shown by circles and calculated one using parameter values listed in Table 2 by the solid line.

aquacopper(II) ion. Other bond lengths were assumed to be the same as those examined in the previous case.[10] Two additional assumptions were tested, in which the length of the Cu-OH_2 (eq) bond within $[Cu(gly)(OH_2)_4]^+$ was either 1.94 or 2.00 Å and the Cu-N and Cu-O bond distances were set to be a value between 1.95 to 2.05 Å. The different assumptions thus made, however, did not affect the result, and independent of the assumptions for the initial values inserted for the bond length within the $[Cu(gly)(OH_2)_4]^+$ complex, the values converged to those listed in Table 2.

In the course of the refinement described above, the concentration ratio of the hexaaquacopper(II) to mono(glycinato) copper(II) complexes was fixed at 40:60. At the next step of calculation, we changed the concentration ratio of the $[Cu(OH_2)_6]^{2+}$ to $[Cu(gly)(OH_2)_4]^+$ ions from 60:40 to 30:70 and performed the data refinement in the same way as described in the preceding section. The converged values coincided with those given in Table 2 within the standard deviations given in the previous calculations and were practically independent of the concentration ratio. The error square sum U,

$$U = \sum_{s_{min}}^{s_{max}} s^2(i(s)_{obsd} - i(s)_{calcd})^2 \quad (4)$$

for each set of the concentration ratios at different s-ranges examined are summarized in Table 3.

The minimum error square sum was obtained for the set in which the concentration ratio of the hexaaquacopper(II) to mono(glycinato)copper(II) complexes was 40:60, regardless of the s-ranges examined in the least-squares calculations.

From the result we concluded that the Cu-OH_2(eq), Cu-O and Cu-N bond lengths within the $[Cu(gly)(OH_2)_4]^+$ complex were approximately the same, and therefore, the complex has a distorted octahedral structure with a regular square plane. The concentration ratio of the $[Cu(OH_2)_6]^{2+}$ to $[Cu(gly)(OH_2)_4]^+$ complexes was 40:60 in the test solution.

Structure of Tris(glycinato)cuprate(II) Complex.
The stability constant of the tris(glycinato)cuprate(II) complex has been reported to be small (log (K_3/mol^{-1} dm^3)≈0—1) and thus the solution in which the tris(glycinato)cuprate(II) complex is predominantly formed must contain a large excess of glycinate tions. In

TABLE 2. RESULTS OF THE LEAST-SQUARES REFINEMENT OF SOLUTION A.[a]
STANDARD DEVIATIONS ARE GIVEN IN PARENTHESES
r: bond distance (Å), b: temperature factor (Å^2).

Interaction	Parameter	$5<s/Å^{-1}<16$[c]	$6<s/Å^{-1}<16$	$7<s/Å^{-1}<16$
Cu-OH_2(eq)	r	1.98(1)	1.98(1)	1.97(1)
	b	0.0020(4)	0.0019(4)	0.0018(4)
Cu-O	r	1.99(2)	1.99(2)	1.99(2)
	b	0.0020(4)	0.0019(4)	0.0018(4)
Cu-N	r	1.99(2)	1.99(2)	1.99(2)
	b	0.0021(4)	0.0019(4)	0.0018(4)
Cu-OH_2(ax)	r	2.27(1)	2.27(1)	2.27(1)
	b	0.004[b]	0.004[b]	0.004[b]
N···O O···OH_2(eq) N···OH_2(eq) OH_2(eq)···OH_2(eq)	r	2.8[b]	2.8[b]	2.8[b]
	b	0.010[b]	0.010[b]	0.010[b]
O···OH_2(ax) N···OH_2(ax) OH_2(eq)···OH_2(ax)	r	3.0[b]	3.0[b]	3.0[b]
	b	0.010[b]	0.010[b]	0.010[b]
Cu···C	r	2.66(4)	2.69(4)	2.70(4)
	b	0.006[b]	0.006[b]	0.006[b]

a) The mole ratio of Cu^{2+} to $[Cu(gly)]^+$ complexes was assumed to be 40 : 60. b) The values were kept constant during the calculation. c) The calculated $s\cdot i(s)$ values shown in Fig. 5 were obtained by using the parameter values of this type.

TABLE 3. ERROR SQUARE SUMS (U) CALCULATED FOR THE BEST FIT VALUES OBTAINED BY THE LEAST-SQUARES REFINEMENT USING VARIOUS SETS OF s-RANGE AND MOLE FRACTION OF Cu^{2+} TO $[Cu(gly)]^+$

	mole fraction			
	Cu^{2+}=0.3	0.4	0.5	0.6
	$[Cu(gly)]^+$=0.7	0.6	0.5	0.4
s-range	$U\times10^{-4}$/Å^{-2}			
$5<s/Å^{-1}<16$	6.7	*6.4*	7.2	8.0
$6<s/Å^{-1}<16$	6.2	*6.1*	6.5	7.0
$7<s/Å^{-1}<16$	5.7	*5.6*	5.7	6.0

solution B in which the C_{gly}/C_{Cu} mole ratio was 13.7, almost all of the Cu(II) ions were expected to be present as the $[Cu(gly)_3]^-$ complex. However, the concentration of Cu(II) ions was much lower than that of sodium and glycinate ions in the solution (see Table 1).

Since the large contribution of the hydrated sodium and free glycinate ions to the measured intensities hid the structural information of the tris(glycinato)-cuprate(II) complex in this solution, it was difficult to obtain the structural parameters for the tris(glycinato)-cuprate(II) complex with a reasonable accuracy with a direct analysis of the reduced intensities for solution B. Therefore, we tried to determine the structure of the tris(glycinato)cuprate(II) complex by subtracting the contribution of sodium and free glycinate ions from the X-ray scattering data for solution B by taking into account the scattered intensities of solution C (an aqueous sodium glycinate solution).

The radial distribution and differential radial distribution curves of solutions B and C depicted in Figs. 2 and 3 showed simlar patterns over the whole r range. A slight different shape, however, was observed around 2 Å, which was attributable to the interaction of copper(II) ion with donor atoms in its first coordination sphere. A direct comparison of the data for solutions B and C could be made because the ρ_0 value (the average scattering density in a stoichiometric volume of a solution) of solution B was approximately the same as that of solution C (see Table 1).

The radial distribution functions of solutions B and C could be compared provided that the Fourier transform (Eq. 2) of their intensities would be carried out by using the same modification function. Since the modification functions were different for these solutions because of different atomic compositions of the solutions, the direct comparison of the radial distribution curves of solutions B and C offered only qualitative information about the structural difference of these solutions. Therefore, the structural data for the tris(glycinato)cuprate(II) complex in solution B was extracted by subtracting the reduced intensities of solution C from those of solution B. The difference of the reduced intensities of the two solutions, $i(s)_{diff}$, which includes any structural difference between the two solutions, is shown in Fig. 6. Since the stoichiometric volume of the solutions was normalized to that containing one sodium atom, the contribution of hydrated sodium ions to the reduced intensities of the solutions was entirely eliminated from the $i(s)_{diff}$ curve. The difference in the concentrations of glycinate ions in the two solutions could remain to some extent in the $i(s)_{diff}$ curve, but the number of glycinate ions in the stoichiometric volumes of solutions B and C was 1.17 and 1.0, respectively, and thus the difference was very small.

The $i(s)_{diff}$ curve, therefore, contained only intensities owing to interactions between copper(II) ions and ligand atoms within the coordination sphere and the nonbonding Cu···C interactions. Intensity difference due to different numbers of water molecules in the stoichiometric volumes of solutions B and C (which were 4.72 and 6.15, respectively) might appear as a part of the $i(s)_{diff}$ curve.

The Fourier transform of the $i(s)_{diff}$ data gave only one peak centered at about 2.02 Å, which should be ascribed to the Cu-O and Cu-N interactions within the tris-(glycinato)cuprate(II) complex (see Fig. 7). A small hump appearing at the right wing of the peak was thought to be a spurious one, because the shape of the hump changed when the s_{max} value of the Fourier transform of the $i(s)_{diff}$ data was changed. Since the $i(s)_{diff}$ data had large uncertainties in the high angle region, the s_{max} value did not exceed 13 Å^{-1}.

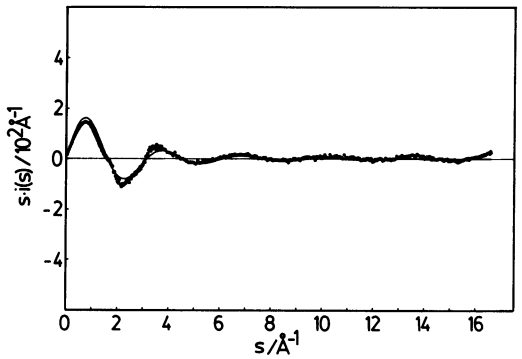

Fig. 6. The $s \cdot i(s)_{diff}$ curve (circles) obtained after subtracting reduced intensities of solution C from those of solution B. The solid line indicates the calculated values with the parameter values given in Table 4.

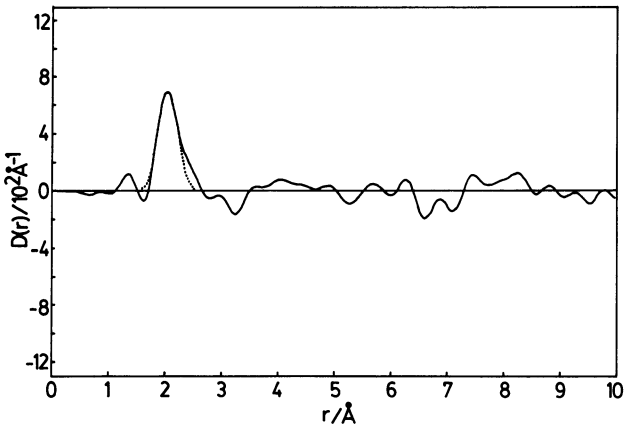

Fig. 7. The $D(r)$ curve obtained by the Fourier transform of the $s \cdot i(s)_{diff}$ values. Dotted line represents the theoretical peak shape for Cu-O and Cu-N bonds within the tris-complex.

Analysis of the peak shape (dotted line in Fig. 7) led to the Cu-O and Cu-N bond distances to be 2.02 Å and the temperature factors of the bonds to be 0.002 Å^2. The frequency factor of the sum of those of the Cu-O and Cu-N bonds was evaluated to be 6 from the area under the peak. The length of the nonbonding Cu···C interactions was estimated to be about 2.8 Å by using a suitable structure model of chelating glycinate ions within the tris(glycinato)cuprate(II) complex. However, no distinct peak corresponding to the Cu···C distance was observed in the curve in Fig. 7, probably the Cu···C peak having been cancelled by a part of the O···O peak due to the bulk water in solution C.

The structural parameters of the tris(glycinato)-cuprate(II) complex were determined by using a least-squares method for the $s \cdot i(s)_{diff}$ data over the range $s<13$ Å^{-1}. The lower limit of the s-values was changed from 0 to 2 Å^{-1}. In type-I refinement only two interactions, Cu-O and Cu-N, were taken into consideration. In type-II calculation contributions arising from intramolecular interactions within water molecules and glycinate ions were also taken into account, because the numbers of them in the stoichiometric volumes in solutions B and C were different. The frequency factors were kept constant to be 3 for both the Cu-O and Cu-N interactions in the course of the calculations. The results obtained by the two calculations were practically the same and were given in Table 4. When we inserted different lengths for the Cu-O and Cu-N bonds as initial values, they converged to indifferent values of the bond lengths through the least-squares calculations. Therefore, we concluded that the tris-(glycinato)cuprate(II) complex has a regular octahedral structure.

The lengths of Cu-OH_2(eq), Cu-O, Cu-N, and Cu-OH_2(ax) bonds within the $[Cu(OH_2)_6]^{2+}$,[2] $[Cu(gly)(OH_2)_4]^-$, and $[Cu(gly)_3]^-$ complexes in solution, together with those within the *cis*-$[Cu(gly)_2(OH_2)_2]$ in crystal, are tabulated in Table 5. In the *cis*-$[Cu(gly)_2(OH_2)_2]$ complex four sites in the square plane of the copper(II) ion were filled with two oxygen and two nitrogen atoms within the two glycinate ions coor-

Table 4. Least-squares refinements of the structural parameters for tris(glycinato)-cuprate(II) complex. Standard deviations are given in parentheses

Interaction	Parameter	I		II	
		$0<s/Å^{-1}<13$	$2<s/Å^{-1}<13$	$0<s/Å^{-1}<13$	$2<s/Å^{-1}<13$[a]
Cu-O	r/Å	2.01(1)	2.02(1)	2.01(1)	2.02(1)
	b/Å^2	0.0019(7)	0.0017(8)	0.0019(6)	0.0018(8)
Cu-N	r/Å	2.01(1)	2.02(1)	2.01(1)	2.02(1)
	b/Å^2	0.0021(6)	0.0020(7)	0.0021(6)	0.0020(6)

a) The calculated $s \cdot i(s)$ curve shown in Fig. 6 was drawn by using the parameter values given here.

TABLE 5. COPPER(II)-LIGAND BOND DISTANCES (r/Å) IN THE HYDRATED COPPER ION AND GLYCINATO-COPPER(II) COMPLEXES

Complex	Cu-OH_2(eq)	Cu-O	Cu-N	Cu-OH_2(ax)	Cu-O(ax)[c]
$[Cu(OH_2)_6]^{3+}$ [a]	1.94	—	—	2.43	—
$[Cu(gly)(OH_2)_4]^+$	1.98	1.99	1.99	2.27	—
cis-$[Cu(gly)_2(OH_2)]$[b]	—	1.946 1.957	1.984 2.021	2.404	2.742
$[Cu(gly)_3]^-$	—	2.02	2.02	—	—

a) Ref. 2. b) In crystal: Ref. 9. c) Carbonyl oxygen of a glycinate ion within an adjacent complex unit.

dinated and one apex of the distorted octahedron of the copper(II) ions was occupied by a water molecule. The oxygen atom at the other apex of the octahedron was a carbonyl oxygen of a glycinate ion combined with an adjacent copper(II) ion in the crystal.

The tris(glycinato)cuprate(II) complex has a regular octahedral structure, although the structure of the other copper(II)-glycinato complexes distorted. Regular octahedral structures of copper(II) complexes have been found for the $[Cu(en)_3]SO_4$,[17] $K_2Pb[Cu(NO_2)_6]$[18] and $[Cu(OMPA)_3](ClO_4)_2$[19] (OMPA refers to octamethylpyrophosphoramide) complexes in crystal. The indifferent bond length within a copper(II) complex was often explained in terms of the dynamic Jahn-Teller effect. However, we found that the regular octahedral $[Cu(en)_3]^{2+}$ complex in crystal had different Cu-N(eq) and Cu-N(ax) bond lengths in solution,[5] and thus the dynamic Jahn-Teller effect was not observed in the complex in solution. Since the dynamic Jahn-Teller effect can hardly be observed in principle in the structural analysis of complexes in solution by the X-ray diffraction method, the regular octahedral structure of the $[Cu(gly)_3]^-$ complex found in the present study is not an averaged structure of a dynamically distorted octahedron, but a relatively rigid regular one. The small temperature factors of the Cu-O and Cu-N bonds within the complex support this conclusion.

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