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

Kazuhiko Ozutsumi and Hitoshi Ohtaki*
Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, 4259,
Nagatsuta-cho, Midori-ku, Yokohama 227

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The structure of zinc(II) complexes with glycinate ion in solution was investigated by the X-ray diffraction method. The measurements were performed at 20 °C for the solutions with the C_{gly}/C_{Zn} mole ratios of 1.49 (solution A) and 5.09 (solution B), where C_i denotes the total concentration of species i. From the analysis of the radial distribution curve of solution A, in which comparable amounts of the hexaaqua- and mono(glycinato)-zinc(II) complexes existed, it was found that the mono(glycinato)zinc(II) complex combined with four water molecules at the distance of (2.12±0.01) Å. The Zn-OH_2 bond length within the complex was longer than that within the hexaaquazinc(II) ion (2.08 Å). The Zn-O and Zn-N distances, where O and N denote oxygen and nitrogen atoms within the glycinate ion in the $[Zn(gly)(OH_2)_4]^+$ complex, were both (2.12±0.02) Å. Thus the mono(glycinato)zinc(II) complex had a regular octahedral structure. The nonbonding Zn···C distance was found to be (2.84±0.02) Å. The X-ray diffraction data of solution B, which contained the $[Zn(gly)_3]^-$ ion as a predominant species, showed that the tris(glycinato)zincate(II) complex had a regular octahedral structure with the both Zn-O and Zn-N bond distances of (2.12±0.01) Å. The nonbonding Zn···C(COO), Zn···C(CH_2), and Zn···O(O=C) lengths were (2.87±0.03) Å, (2.93±0.03) Å, and (4.10±0.04) Å, respectively. The solubility of the bis(glycinato)zinc(II) complex was so low that the structural determination of the complex by the present X-ray diffraction method was not possible.

Zinc(II) ion often changes the structure in the course of ligand substitution reactions. The hexaaquazinc(II) ion has been reported to be regular octahedral in perchlorate, sulfate and nitrate solutions.[1,2] The Zn-OH_2 bond distance was found to be 2.08 Å in the former two solutions[1] and 2.093 Å in the latter.[2]

Yamaguchi and Ohtaki[3] found that the tetraamminezinc(II) complex has no water molecules in the first coordination shell and thus the tetraamminezinc(II) complex has a regular tetrahedral structure with the Zn–N bond length of 2.03 Å. The triamminemonochlorozinc(II) complex found in a dilute ammoniacal solution has a distorted tetrahedral structure. The Zn–N and Zn–Cl bond distances were determined to be 2.00 Å and 2.30 Å, respectively.

The structure of the bis(ethylenediamine)zinc(II) ion is a regular tetrahedron with the Zn–N bond length of 2.131 Å, although the structure of the tris(ethylenediamine)zinc(II) complex is a regular octahedron with a longer Zn–N bond distance of 2.276 Å.[4] Thus the coordination number of zinc(II) ion changed from 6 to 4 in the course of the formation of the ammine complexes, while the coordination number of zinc(II) ion within the ethylenediamine complexes varied from 6 within the hexaaquazinc(II) ion to 4 within the bis(ethylenediamine)zinc(II) and then again to 6 within the tris(ethylenediamine)zinc(II) complex.

Structural changes in complex formation reactions with increasing number of ligands coordinated were found in Zn(II)–chloro[5] and Zn(II)–bromo complexes[6] in solution.

In previous studies[7,8] we determined the structures of the mono- and tris(glycinato) complexes of nickel(II) and copper(II) ions in aqueous solutions by the X-ray diffraction method. In the present work we have attempted to determine the structure of glycinato–zinc(II) complexes in a series of structural study of chelate complexes of transition metals in solution.

Many crystallographic data are available for amino carboxylato complexes. Though zinc(II) ion plays an important role in biochemical reactions as copper(II) ion does, less structural information on the zinc(II)–amino carboxylato complexes has been presented than that on the copper(II) complexes. The structure of the bis(glycinato)zinc(II) complex has been determined to be octahedral with two more carbonyl oxygen atoms within glycinate ions coordinated to adjacent zinc(II) ion in crystal.[9] However, structures of other complexes of zinc(II) ion with glycine have not been known even in crystal due to difficulty in preparation of stable single crystals of the mono- and tris(glycinato) complexes of zinc(II) ion. Therefore, we studied the structure of the mono(glycinato)zinc(II) and tris(glycinato)-zincate(II) complexes in aqueous solution. To find a structural change, if it occurs, of the complexes with changing number of the ligand is another aim of this investigation. The structure of the bis(glycinato)zinc(II) complex in solution was not determinable by the X-ray diffraction method due to its low solubility in water.

Raman spectroscopic measurements have been carried out as a supplement to the structural determination of the complexes.

Experimental

Preparation and Analysis of Sample Solutions. All chemicals used were of reagent grade. Two test solutions were prepared in the similar way to that reported in previous papers.[7,8] *Solution A*, which contained the mono(glycinato)zinc(II) complex as a predominant species, was prepared by dissolving crystals of the bis(glycinato)zinc(II) to a zinc(II) nitrate solution. In order to prevent hydrolysis of zinc(II) ion, a small amount of glycine was added to this solution. *Solution B*, in which the tris(glycinato)zincate(II) com-

Table 1. The composition (mol dm^{-3}) and stoichiometric volume V per zinc atom in the solutions

	A	B
Zn	2.031	1.245
Na	—	3.843
O	57.09	50.03
N	5.085	6.333
C	6.070	12.67
H	102.9	100.1
V/Å^3	817.6	1334
C_{gly}/C_{Zn}	1.49	5.09
density/g cm^{-3}	1.294	1.312

plex was formed as a main species, was prepared by mixing the bis(glycinato)zinc(II) and sodium glycinate in water. *Bis(glycinato)zinc(II)* was prepared by mixing powder of zinc(II) oxide and glycine in boiling water and then recrystallized from a sodium glycinate solution. Sodium glycinate was obtained by the same manner previously reported.$^{7)}$ Zinc(II) nitrate and glycine were recrystallized from water.

The total concentration of zinc(II) ions (C_{Zn}) in the sample solutions was determined by EDTA titration and gravimetry as $ZnNH_4PO_4$. The results of the two independent methods agreed each other within 0.2%. The total glycine concentration (C_{gly}) was determined by the Kjeldahl method. The concentrations of nitrate ions in solution A and sodium ions in solution B were evaluated by the material balance of ions in the solutions. Densities of the test solutions were measured pycnometrically. The composition of the solutions is listed in Table 1.

X-Ray Scattering Measurements. X-Ray scattering measurements were performed with a JEOL θ—θ diffractometer by using Mo $K\alpha$ radiation (λ=0.7107 Å). The observed range of scattering angle (2θ) was from 2° to 140°. Times required to acummulate 120000 counts at each angle were recorded. The method of measurements and data treatments were described in previous papers.$^{1,8,10)}$ Calculations were carried out by using KURVLR$^{11)}$ and NLPLSQ$^{12)}$ programs with the computer at the Tokyo Institute of Technology and partly with the computer at the Institute for Molecular Science in Okazaki.

Raman Spectroscopic Measurements. Raman spectra for the sample solutions were measured with a JEOL laser Raman spectrophotometer JRS-Sl with the use of the 5145 Å excited line of Ar$^+$ laser.

Results and Discussion

According to the stability constants of zinc(II)–glycine complexes,$^{13)}$ solution A contains comparable amounts of the hexaaqua- and mono(glycinato)zinc(II) complexes and a small amount of the bis(glycinato)zinc(II) complex. However, the concentration of the bis(glycinato)zinc(II) is so small that the formation of the complex was neglected in the course of the analysis of the X-ray scattering data. In solution B almost all of the zinc(II) ions are expected to form the tris(glycinato)zincate(II) complex, since the C_{gly}/C_{Zn} mole ratio is 5.09.

The observed $s\cdot i(s)$ and $D(r)$ curves for solutions A and B are shown in Figs. 1 and 2, respectively.

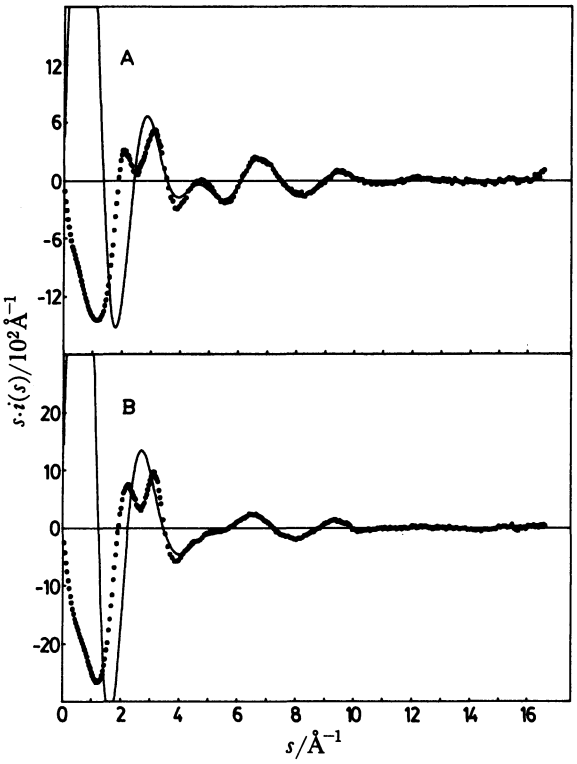

Fig. 1. The reduced intensities multiplied by s for solutions A and B. The observed $s\cdot i(s)$ values are shown by dotted lines and calculated ones by solid lines.

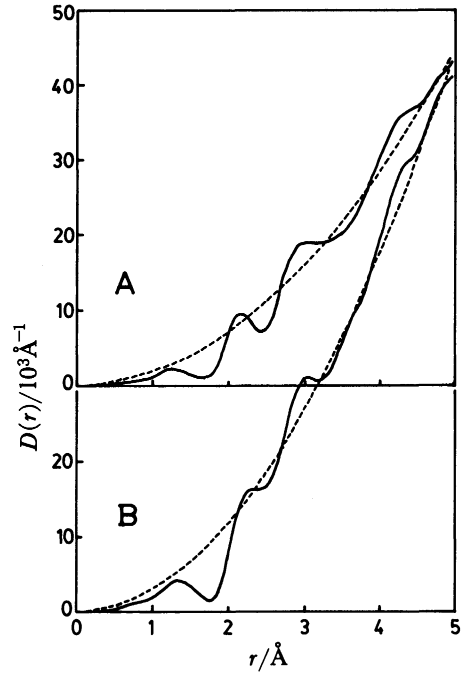

Fig. 2. The $D(r)$ curves for solutions A and B. The dashed lines indicate the curve of $4\pi r^2\rho_0$.

The parameter values for the intramolecular structure within glycinate ion, as well as those within water molecule and nitrate ion, used for the computation of the X-ray scattering data are the same as those described in a previous paper.$^{7)}$ Numbering of the atoms within the glycinate ion coordinated to the

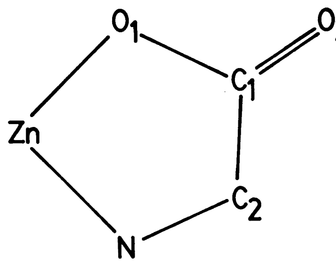

Fig. 3. The numbering of the atoms within the glycinate ion coordinated to the zinc(II) ion.

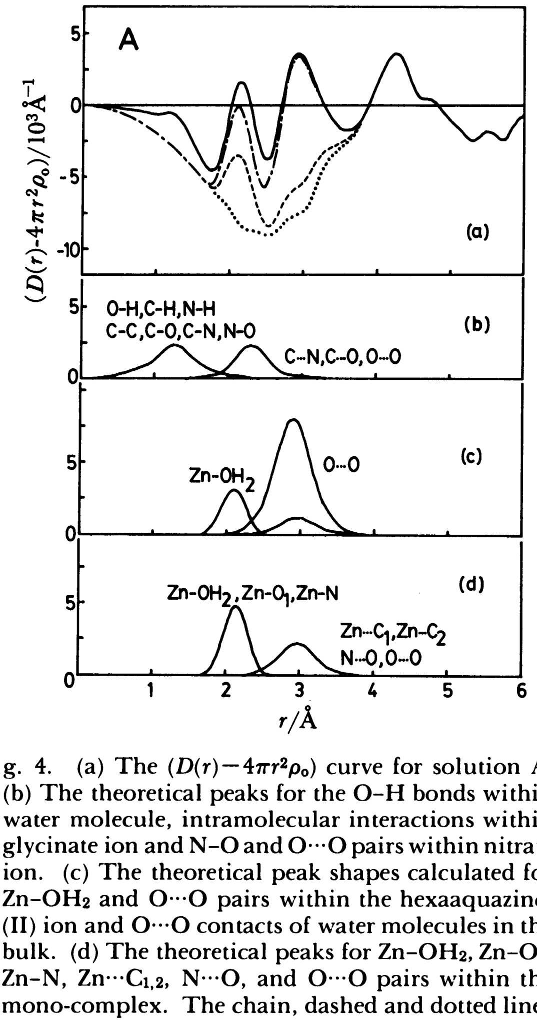

Fig. 4. (a) The $(D(r)-4\pi r^2\rho_0)$ curve for solution A. (b) The theoretical peaks for the O–H bonds within water molecule, intramolecular interactions within glycinate ion and N–O and O$\cdots$O pairs within nitrate ion. (c) The theoretical peak shapes calculated for Zn–OH_2 and O$\cdots$O pairs within the hexaaquazinc(II) ion and O$\cdots$O contacts of water molecules in the bulk. (d) The theoretical peaks for Zn–OH_2, Zn–O_1, Zn–N, Zn$\cdots C_{1,2}$, N$\cdots$O, and O$\cdots$O pairs within the mono-complex. The chain, dashed and dotted lines indicate the residual curves after subtracting the theoretical peaks in (b), (c), and (d), respectively.

zinc(II) ion is given in Fig. 3.

Solution A. In the $D(r)$ (Fig. 2A) and $D(r)-4\pi r^2\rho_0$ (Fig. 4a) curves, where ρ_0 represents the average scattering density in the stoichiometric volume V per zinc atom of the solution, we see four peaks at about 1.3, 2.2, 2.9, and 4.2 Å. The small and broad peak around 1.3 Å is owing to the O–H bonds within water molecules, the C–H, N–H, C_1–C_2, C_2–N, $C_1\overset{\ldots}{-}O_1$, and $C_1\overset{\ldots}{-}O_2$ bonds within glycinate ions and the N–O bonds within nitrate ions. The second peak appearing at 2.2 Å is mainly ascribed to the Zn–OH_2 bonds within the hexaaquazinc(II) ion and the Zn–OH_2, Zn–O_1, and Zn–N bonds within the mono(glycinato)zinc(II) complex. Nonbonding $C_2\cdots O_1$, $C_2\cdots O_2$, $C_1\cdots N$, and $O_1\cdots O_2$ interactions within glycinate ions and O$\cdots$O contacts within nitrate ions also contribute, in part, to the peak. The third peak at about 2.9 Å is composed of peaks owing to nonbonding Zn$\cdots C_1$ and Zn$\cdots C_2$ interactions within the mono(glycinato)zinc(II) ion and interactions between ligand atoms in the first coordination sphere within the complexes, as well as the O$\cdots$O contacts of the bulk water. In the fourth peak at 4.2 Å various longer range interactions, which will not be taken into account in the present analysis, may be included.

In order to evaluate the structure parameters of the mono(glycinato)zinc(II) complex, we firstly subtracted the theoretical peaks of the known interactions within water molecules, glycinate and nitrate ions from the observed radial distribution curve. The residual curve obtained (chain line in Fig. 4a) showed the peak at about 2.1 Å and the peak was well interpreted in terms of the octahedral configuration of six oxygen and nitrogen atoms around all zinc atoms in the solution, independent of the concentration ratio of the $[Zn(OH_2)_6]^{2+}$ to $[Zn(gly)]^+$ complexes. Since the Zn–O and Zn–N bonds were practically indistinguishable by the X-ray analysis, the result indicated that the mono(glycinato)zinc(II) complex should have six ligand atoms in the first coordination shell. Thus, we concluded that the $[Zn(gly)]^+$ complex has an octahedral structure combined with one glycinate ion and additional four water molecules.

The structure parameters of the mono(glycinato)zinc(II) complex were refined by using a least-squares method for the $s\cdot i(s)$ data over the range $s>5$ Å^{-1}. In order to avoid the introduction of errors by neglecting long-range interactions, the lower limit of the s-value was changed from 5.0 to 7.0 Å^{-1}. The concentration ratio of the $[Zn(OH_2)_6]^{2+}$ to $[Zn(gly)(OH_2)_4]^+$ complexes was assumed to be 40:60 in the present stage of the calculation. The parameter values first guessed from the analysis of the radial distribution curve of the mono(glycinato)zinc(II) ion were refined by the least-squares procedure at the fixed composition of the solution. The structural parameters of the hexaaquazinc(II) ion and the O$\cdots$O contacts of bulk water were taken from the works by Ohtaki *et al.*[1] and by Narten[14] and were fixed at the literature values during the calculation. Since the lengths of the Zn–O_1 and Zn–N bonds were not determinable separately with a reasonable accuracy, we assumed that the Zn–O_1 and Zn–N bonds had the same structure parameters. The results obtained were listed in Table 2. We also tested another assumption for initial values inserted in the least-squares calculation. A tetrahedral coordination around the Zn(II) ion within the mono(glycinato)zinc(II) complex was assumed and the number of the Zn–OH_2 bond was set to be 2. When the refinement was carried out by floating the number of the Zn–OH_2

TABLE 2. RESULTS OF THE LEAST-SQUARES REFINEMENTS OF SOLUTION A. PARAMETER VALUES REFINED WERE BOND DISTANCES (r/Å), TEMPERATURE FACTORS (b/Å^2) AND FREQUENCY FACTORS (n). THE VALUES IN PARENTHESES REPRESENT STANDARD DEVIATION

Interaction	Parameter	A-I (s>5.0 Å^{-1})	A-II (s>6.0 Å^{-1})	A-III (s>7.0 Å^{-1})
Zn-OH$_2$	r	2.12(1)	2.12(1)	2.12(1)
	b	0.003(1)	0.003(1)	0.003(1)
	n	3.9(1)	4.0(1)	4.0(1)
OH$_2$···OH$_2$	r	3.0(1)	3.0(1)	3.0(2)
	b	0.010$^{a)}$	0.010$^{a)}$	0.010$^{a)}$
Zn-O$_1$ Zn-N	r	2.12(2)	2.13(2)	2.12(2)
	b	0.003(1)	0.003(1)	0.003(1)
	n	1.9(1)	2.0(2)	1.9(2)
OH$_2$···O$_1$ OH$_2$···N	r	3.0$^{a)}$	3.0$^{a)}$	3.0$^{a)}$
	b	0.010$^{a)}$	0.010$^{a)}$	0.010$^{a)}$
N···O$_1$	r	2.8$^{a)}$	2.8$^{a)}$	2.8$^{a)}$
	b	0.010$^{a)}$	0.010$^{a)}$	0.010$^{a)}$
Zn···C$_1$ Zn···C$_2$	r	2.84(2)	2.87(2)	2.79(2)
	b	0.010(2)	0.009(2)	0.007(2)

a) The values were kept constant during the calculation.

bonds at fixed frequency factor of the Zn–O$_1$ and Zn–N bonds, the number of the Zn–OH$_2$ bonds reached nearly 4 in the course of the calculation. Thus the octahedral structure of the mono(glycinato)zinc(II) complex was confirmed by the least-squares calculation. The Zn–OH$_2$ bond length was determined to be 2.12 Å and the distance of the Zn–O$_1$ and Zn–N bonds was also evaluated to be 2.12 Å.

Since we assumed that the Zn–O$_1$ and Zn–N bonds had the same structure parameters in the least-squares calculation described above, a possibility of the different lengths of the Zn–O$_1$ and Zn–N bonds was not well excluded. At the next step of calculation we examined assumptions of various lengths of the Zn–O$_1$ and Zn–N bonds. The residual radial distribution curve ascribed to the Zn–O and Zn–N bonds was extracted from the second peak of the distribution curve in Fig. 2A by subtracting intramolecular interactions of water molecules, glycinate and nitrate ions (Fig. 5). The curve consisted of peaks attributed to the interactions between Zn(II) ion and donor atoms within the complex around 2.1 Å and longer-range interatomic interactions at r>2.5 Å. The peak at 2.1 Å was drawn by assuming that it was a symmetrical Gaussian curve.

Calculations were carried out in order to minimize the error-square sum defined by Eq. 1 for various sets of the temperature factors of the Zn–OH$_2$ bond, lengths of the Zn–O$_1$ and Zn–N bonds and the concentration ratio of $[Zn(OH_2)_6]^{2+}$ to $[Zn(gly)(OH_2)_4]^+$.

$$U = \sum w\{D(r)^{2nd}_{calcd} - D(r)^{2nd}_{obsd}\}^2 \tag{1}$$

In Eq. 1, $D(r)^{2nd}$ represents the second peak extracted from the original radial distribution curve by the procedure described above. w is given as $\exp(-\alpha \cdot \Delta l^2)$, where $\Delta l = r_o - r$ and r_o denotes the r-value at the center of the peak. In this case we assumed that the r_o value was 2.11 Å and the value α was evaluated from the half-width of the second peak. In the course of the calculation the lengths of the Zn–O$_1$ and Zn–N bonds as well as the concentration ratio of $[Zn(OH_2)_6]^{2+}$ to $[Zn(gly)(OH_2)_4]^+$, were stepwise changed. In addition, the temperature factor of the Zn–OH$_2$ bond within the mono(glycinato)zinc(II) complex was varied from 0.003 Å^2 to 0.005 Å^2. On the other hand, we fixed the values of the structure parameters of the $[Zn(OH_2)_6]^{2+}$ complex at the literature values,[1] as well as the length of the Zn–OH$_2$ bond within the mono(glycinato)zinc(II) complex at 2.12 Å and the temperature factor of the Zn–O$_1$ and Zn–N bonds at 0.003 Å^2.

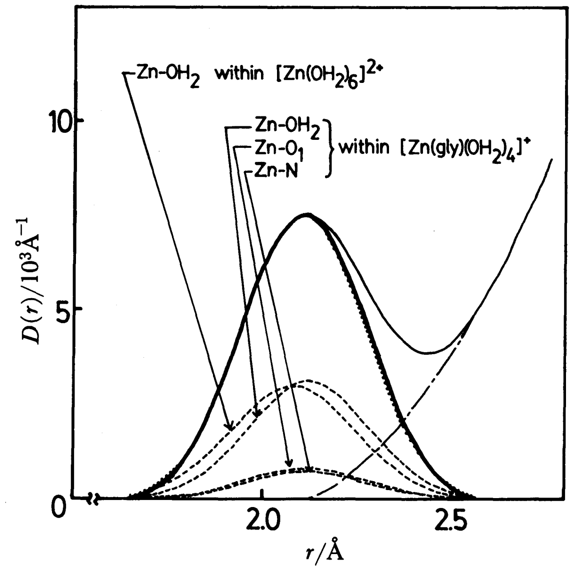

Fig. 5. The second peak of the radial distribution curve for solution A. The thin and thick solid lines show the experimental and extracted $D(r)$ curves, respectively, and the chain line indicates the residual curve after extraction. The theoretical peak shapes owing to the Zn–OH$_2$ bonds within the $[Zn(OH_2)_6]^{2+}$ ion, and the Zn–OH$_2$, Zn–O$_1$, and Zn–N bonds within the $[Zn(gly)(OH_2)_4]^+$ complex are shown by dashed lines. The dotted line represents the peak by summing peak shapes shown by dashed lines.

At the temperature factor of 0.003 Å^2 for the Zn–OH$_2$ bond within the mono(glycinato)zinc(II) complex, a

Table 3. Results of the analysis of the second peak in the $D(r)$ curve of solution A. Error-square sums ($U\times10^{-4}/\text{Å}^{-2}$) were calculated according to Eq. 1. The Zn–OH_2 bond distance and all temperature factors within the monocomplex were kept constant at 2.12 Å and 0.003 Å^2, respectively, in the course of the calculation

			mole fraction			
		Zn^{2+} :	0.3	0.4	0.5	0.6
		Zn(gly)$^+$:	0.7	0.6	0.5	0.4
Bond distance r/Å			$U\times10^{-4}/\text{Å}^{-2}$			
Zn–O_1 Zn–N	2.08 2.16		11.2	8.9	17.2	36.2
Zn–O_1 Zn–N	2.10 2.14		10.8	6.7	14.3	33.0
Zn–O_1 Zn–N	2.12 2.12		10.3	*6.2*	13.0	31.2

minimum error-square sum was obtained at each set of the lengths of Zn–O_1 and Zn–N bonds. When we changed the length of the Zn–O_1 and Zn–N bonds and the concentration ratio of $[Zn(OH_2)_6]^{2+}$ to $[Zn(gly)(OH_2)_4]^+$ at the value of 0.003 Å^2 for the temperature factor of the Zn–OH_2 bond, the minimum error-square sum was obtained when we assumed that the Zn–O_1 and Zn–N bonds have the same distance of 2.12 Å and the concentration ratio of the $[Zn(OH_2)_6]^{2+}$ to $[Zn(gly)(OH_2)_4]^+$ was approximately 40:60 in the test solution (Table 3). Figure 5 represents the shape of the calculated curve from the Zn–OH_2 bonds within the $[Zn(OH_2)_6]^{2+}$ ion and the Zn–OH_2, Zn–O_1, and Zn–N bonds within the $[Zn(gly)(OH_2)_4]^+$ complex. The curve fitted well the extracted peak shape. Thus we concluded that the $[Zn(gly)(OH_2)_4]^+$ complex is regular octahedral.

Solution B. The $(D(r)-4\pi r^2\rho_0)$ curve given in Fig. 6a shows four peaks around 1.3, 2.3, 2.9, and 4.2 Å and a small hump at 3.4 Å. The peak at 1.3 Å was attributed to the O–H bonds within water molecules and the C–H, N–H, C_1–C_2, C_2–N, $C_1\overset{...}{-}O_1$, and $C_1\overset{...}{-}O_2$ bonds within glycinate ions. The second peak appearing at 2.3 Å mainly consisted of the Zn–O_1 and Zn–N interactions within the tris(glycinato)zincate(II) complex. Nonbonding $C_2\cdots O_{1,2}$, $C_1\cdots N$, and $O_1\cdots O_2$ interactions within glycinate ions and Na–O pairs within hydrated sodium ions were also included in the peak. The peak around 2.9 Å was composed of peaks owing to the nonbonding $Zn\cdots C_{1,2}$ pairs and the interactions between ligand atoms in the first coordination sphere within the tris(glycinato)zincate(II) complex. The $O\cdots O$ contacts of water molecules in the bulk also contributed to the peak. In the fourth peak at about 4.2 Å nonbonding $Zn\cdots O_2$ and other long range interactions were contained.

In order to estimate the structural parameters of the $[Zn(gly)_3]^-$ complex, the peak shapes owing to interactions among water molecules, glycinate and sodium ions should be subtracted from the radial distribution function. We assumed an octahedral hydration of a sodium ion since there was a small hump at 3.4 Å which might be ascribable to the $O\cdots O$ contacts within a hydrated sodium ion as was previously pointed out.[7] The peak remained at 2.12 Å (chain line in Fig. 6a) must be attributed to the Zn–O_1 and Zn–N interactions within the tris(glycinato)zincate(II) complex. From the analysis of the peak shape the Zn–O_1 and Zn–N bonds were found to have the same length of 2.12 Å and the temperature factor of the bonds was evaluated to be about 0.003 Å^2. The peak area corresponded to the sum of the peak areas of six bonds of Zn–O_1 and Zn–N. Thus the structure of the tris(glycinato)zincate(II) complex was concluded to be regular octahedral. The distance of longer range interactions within the tris(glycinato)zincate(II) complex were estimated by using a suitable structure model of chelating glycinate ions. Subtraction of the above peaks from the radial distribution curve led to a smooth background curve (dotted line in Fig. 6a) having no appreciable peak over the range $r<4$ Å.

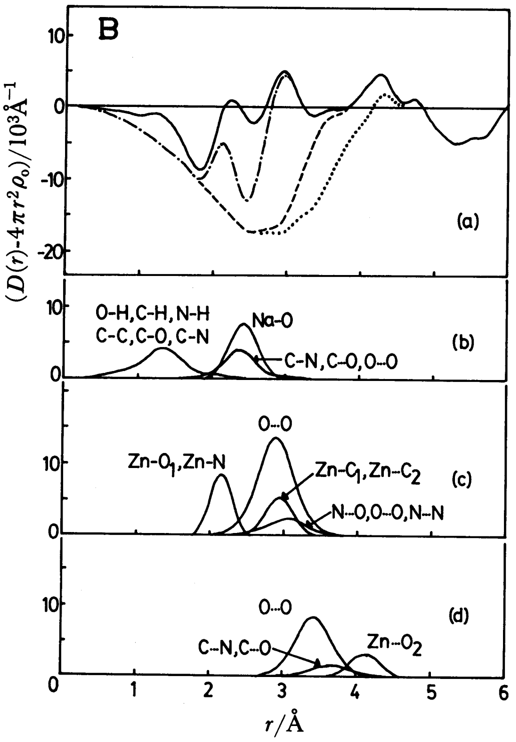

Fig. 6. (a) The $(D(r)-4\pi r^2\rho_0)$ curve for solution B. (b) The theoretical peak shapes calculated for the O–H bonds within water molecule, intramolecular interactions within glycinate ion and Na–O pairs within hydrated sodium ion. (c) The theoretical peaks for Zn–O_1, Zn–N, $Zn\cdots C_{1,2}$, $N\cdots O$, $N\cdots N$, and $O\cdots O$ pairs within the tris-complex and $O\cdots O$ contacts of water molecules in the bulk. (d) The theoretical peaks for $O\cdots O$ contacts within hydrated sodium ion and $Zn\cdots O_2$, $C_{1,2}\cdots N$, $C_{1,2}\cdots O_1$ pairs within the tris-complex. The chain, dashed and dotted lines show the residual curves after subtracting the theoretical peaks in (b), (c), and (d), respectively.

The structure parameters of the tris(glycinato)zin-

TABLE 4. RESULTS OF THE LEAST-SQUARES REFINEMENTS OF SOLUTION B. PARAMETER VALUES REFINED WERE BOND DISTANCES (r/Å), TEMPERATURE FACTORS (b/Å^2) AND FREQUENCY FACTORS (n). STANDARD DEVIATIONS ARE GIVEN IN PARENTHESES

Interaction	Parameter	B-I	B-II	B-III
Zn–O$_1$	r	2.12(1)	2.12(1)	2.12(1)
	b	0.0031(6)	0.0029(7)	0.0028(9)
	n	3.0(1)	3.0(1)	3.0[b]
Zn–N	r	2.12(1)	2.12(1)	2.12(1)
	b	0.0029(6)	0.0026(8)	0.0025(9)
	n	3.0(1)	3.0(1)	3.0[b]
N···O$_1$[a]	r	2.7(2)	2.8[b]	2.8[b]
O···O[a]	r	3.1(2)	3.1[b]	3.1[b]
N···O[a]	r	3.1(2)	3.0[b]	3.0[b]
N···N[a]	r	3.1(2)	3.2[b]	3.2[b]
Zn···C$_1$	r	2.87(2)	2.86(2)	2.87(3)
	b	0.008(2)	0.010(3)	0.009(3)
	n	3.1(1)	3.2(2)	3.0[b]
Zn···C$_2$	r	2.93(2)	2.93(2)	2.93(3)
	b	0.009(2)	0.010(3)	0.008(3)
	n	3.1(1)	3.3(2)	3.0[b]
Zn···O$_2$	r	4.08(4)	4.07(4)	4.10(4)
	b	0.010(2)	0.011(3)	0.011(3)
	n	3.1(1)	3.2(2)	3.0[b]

a) Temperature factors of these interactions were fixed at 0.006 Å^2. b) The values were kept constant during the calculation.

cate(II) complex were finally determined by a least-squares calculation for the $s \cdot i(s)$ curve over the range $s > 4$ Å^{-1}. The calculations were performed by inserting the values for each interatomic interaction evaluated by the analysis of the radial distribution function. Three types of calculations were carried out on slightly different assumptions. In the B-I type calculation all the parameter values listed in Table 4 were floated as independent variables. In the B-II treatment some interatomic distances were allowed to remain unchanged. On the B-III assumption, similar to the B-II treatment, the frequency factors of all atom pairs in the table were fixed at the given values. No significant difference was found in the bond lengths in the three calculations.

In the course of the calculation the existence of the *fac-* and *mer-*isomers of the tris(glycinato)zincate(II) complex was taken into consideration. However, the structural difference between the isomers was too small to improve the result by the introduction of the existence of the isomers.

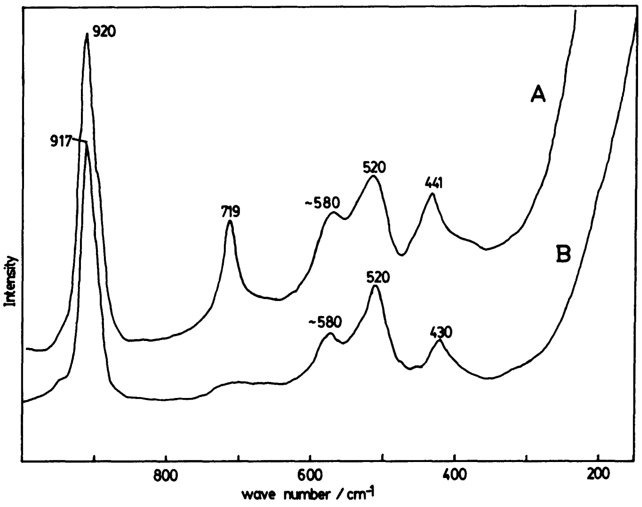

Fig. 7. Raman spectra of solutions A and B.

Raman Spectra of Solutions A and B. Krishnan and Plane[15] reported Raman spectra for aqueous zinc(II) nitrate–glycine solutions in the pH range 2.0—7.0. From a Job plot with the total concentration of zinc(II) ion plus glycinate ion keeping approximately constant, the Zn–N stretching frequencies for the mono(glycinato)zinc(II), bis(glycinato)zinc(II) and tris(glycinato)zincate(II) complexes were assigned to be *ca.* 445, 430, and 425 cm^{-1}, respectively. In solution A of the present work (Fig. 7) the line at 441 cm^{-1} was assignable to the Zn–N stretching vibration for the mono(glycinato)zinc(II) complex. Other lines at 520, 580, and 920 cm^{-1} were attributable to the CO_2^- rocking, CO_2^- wagging and C–C stretching vibrations, respectively, within glycinate ion. The $\tilde{\nu}_4$-band of the nitrate ion appeared at 720 cm^{-1}. In solution B we found a band ascribed to the Zn–N stretching for the tris(glycinato)zincate(II) complex at 430 cm^{-1}. Since solution B contained the tris(glycinato)zincate(II) complex as a main species, our result of the Zn–N frequency for the tris(glycinato)zincate(II) complex may be more reliable than that observed by Krishnan and Plane, because the concentration of the complex is sufficiently high in our solution. On the other hand the concentration of the tris-complex may be low under their experimental conditions where they kept the total concentration of zinc(II) and glycinate ions almost constant. The Raman spectra measured in the present work showed that the Zn–N stretching frequency was higher in the mono(glycinato)zinc(II) complex than in the tris(glycinato)zincate(II) ion, although the length of the Zn–N bond within the both complexes was practically the same. The Zn–O and Zn–N bond lengths determined in the former complex may contain larger uncertainties than those in the latter do, because in the course of the structural analysis of the $[Zn(gly)(OH_2)_4]^+$ complex we have to evaluate lengths of three different kinds of bonds whilst the $[Zn(gly)_3]^-$ complex has bonds of two different kinds.

The mono(glycinato)zinc(II) and tris(glycinato)zincate(II) complexes in solution have a regular octahedral structure with the lengths between zinc(II) and ligand atoms of 2.12 Å. In crystal of the $[Zn(gly)_2]\cdot H_2O$[9] the equatorial square plane around the zinc(II) ion was occupied by chelating two glycinate ions and two apices of the distorted octahedron were filled with carbonyl oxygen atoms of glycinate ions combined with adjacent zinc(II) ions, though the bond distances between the Zn(II) ion and donor atoms were not determined. All the structures of the zinc(II)–glycinato complexes were octahedral and the metal-ligand bond lengths were practically indifferent in the complexes with varying numbers of the ligand coordinated, in contrast to the case of zinc(II)–ammine[3] and zinc(II)–ethylenediamine complexes.[4]

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