An X-Ray Diffraction Study on Zinc(II) Complexes with α-Alaninate Ion in Aqueous Solution

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The structures of mono(α-alaninato)zinc(II), bis(α-alaninato)zinc(II), and tris(α-alaninato)zincate(II) complexes in aqueous solutions were determined by the X-ray diffraction method. All the three complexes have the octahedral structure in the form $[Zn(\alpha\text{-ala})(H_2O)_4]^+$, $[Zn(\alpha\text{-ala})_2(H_2O)_2]$, and $[Zn(\alpha\text{-ala})_3]^-$. The structures of the complexes were different from those of the glycinato complexes of zinc(II) ion, which were all regular octahedral. The length of the Zn-O bond in the α-alaninato complexes was shorter than that of the Zn-N bond due to the inductive effect of the substituted methyl group at the α-carbon on the oxygen atom in the amino acid. The lengths of the Zn-O and Zn-N bonds in the complexes determined are, respectively, as follows: $[Zn(\alpha\text{-ala})(H_2O)_4]^+$, 202 and 214 pm; $[Zn(\alpha\text{-ala})_2(H_2O)_2]$, 203 and 214 pm; $[Zn(\alpha\text{-ala})_3]^-$, 202 and 213 pm.

In spite of a number of structural studies of chelate compounds of transition metals by the X-ray crystallographic method, no information has been available for the structural change with varying ligand numbers in a series of chelate complexes of a given metal ion with one kind of ligand, besides solvent molecules, because of difficulties of preparing single crystals of all kinds of the chelate complexes formed in solutions. The liquid X-ray diffraction method has an advantage for the structural analysis of complexes over the crystallographic method because in the former method we need not isolate the complexes as single crystal, but we can determine their structures in solution even though some complexes coexist.

Although zinc(II) ion does not belong to the transition metals, chelate complexes of this ion are of special interest due to its ability to form a great variety of complexes with coordination number of four and six and to its importance in biochemical reactions. It is well known that the aqua complex of zinc(II) ion is octahedral in solution.[1-4] However, the structure is changed from octahedral to tetrahedral when ethylenediamine is introduced as the ligand to form the bis-complex.[5] The tris(ethylenediamine)zinc(II) complex is certainly octahedral.[5] On the other hand, the glycinato complexes of zinc(II) ion are all regular octahedral, i.e., $[Zn(gly)(H_2O)_4]^+$, $[Zn(gly)_2(H_2O)_2]$ and $[Zn(gly)_3]^-$, in water, the lengths of Zn-O and Zn-N bonds being the same and constant at 210 pm within an uncertainty of ±2 pm.[6-9] In the present work we extended our studies to the zinc(II) complexes with α-alanine (α-ala) by liquid X-ray diffraction to examine the effect of the substituted methyl group on the structure of the metal complexes.

Experimental

Preparation and Analysis of Sample Solutions. All chemicals used were of reagent grade. Two test solutions were prepared. *Solution A*, which contained the tris(α-alaninato)zincate(II) complex as the predominant species, was prepared by dissolving crystals of the bis(α-alaninato)zinc(II) complex in an aqueous solution of lithium α-alaninate. According to the distribution curves of the complexes calculated from the stability constants of the zinc(II)-α-alaninato complexes,[10,11] about 95% of the complexes in the solution should be the tris-complex. *Solution B*, in which about 45% of mono(α-alaninato)-zinc(II), 45% of the bis(α-alaninato)zinc(II) and 10% of the tris(α-alaninato)zincate(II) complexes were present, was prepared by dissolving crystals of the bis-complex in an aqueous zinc(II) perchlorate solution.

The bis(α-alaninato)zinc(II) complex was prepared from α-alanine dissolved in a hot sodium hydroxide solution and zinc(II) oxide by the addition of acetic acid in the mixture. Crystals of the bis(α-alaninato)zinc(II) complex thus obtained were recrystallized twice from water.

Lithium α-alaninate was prepared by dissolving α-alanine in a methanol solution of lithium hydroxide. Crystals obtained were recrystallized from ethanol.

The total concentration of zinc(II) ions was determined by EDTA titration. Densities of the test solutions were measured pycnometrically. The composition and the densities of the solutions are given in Table 1.

X-Ray Scattering Measurements. X-Ray scattering measurements were performed with a JEOL θ-θ type diffractometer by using Mo $K\alpha$ radiation (λ=71.07 pm). The

Table 1. The Composition (mol dm^{-3}) and Stoichiometric Volume per Zinc Atom in the Sample Solutions

	Solution A	*Solution B*
Zn	1.189	1.189
Li	1.513	—
Cl	—	1.157
O	49.41	55.43
N	3.891	1.660
C	11.67	4.980
H	106.6	106.6
$V/10^6$ pm^3	1.397	1.397
Density/g cm^{-3}	1.181	1.196

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observed range of scattering angle (2θ) was from 1.5° to 140°. Times required to accumulate 100000 counts at each angle were recorded. The method of measurements and data treatments were the same as those described in the measurement of Zn(II)-glycinate solutions.[6-8] Calculations were carried out using KURVLR[12] and NLPLSQ[13] programs with the computers of the Tokyo Institute of Technology.

Results and Discussion

Method of Structural Analysis. Numbering of atoms in the coordinated α-alaninato ion is given in Fig. 1. The observed structural functions, $s \cdot i(s)$, and pair-correlation functions, $g(r)$, for the two solutions are shown in Figs. 2 and 3, respectively. The analysis of the results was carried out by the nonlinear least-squares (LSQ) method by varying structural parameters obtained from the radial distribution curves and models constructed as the initial values. The fit was monitored through the R-factor as defined as follows:

$$R = \frac{\sum [s \cdot i(s)_{\mathrm{exp}} - s \cdot i(s)_{\mathrm{model}}]^2}{\sum [s \cdot i(s)_{\mathrm{exp}}]^2}, \quad (1)$$

where s is the scattering variable ($s = 4\pi \sin\theta/\lambda$).

The contributions to the structure of each solution, in principle, can be divided into four parts: the intramolecular structure of α-alaninate and perchlorate ions, the structure of the complexes, the hydration structure of the cations and anions, and the bulk structure of water. The intramolecular O-H and H···H interactions as well as the H-bonding O···H interactions can be neglected in the course of the LSQ calculations.

The first broad peak around 100 pm in the $g(r)$'s are evidently due to intramolecular contribution predominantly arising from atom-pairs in the α-alaninate ions and Cl-O pairs in perchlorate ions in *Solution B*. The peak at ca. 210 pm contains the peak due to the Zn-OH_2 bonds in the complexes. The Zn-N and Zn-

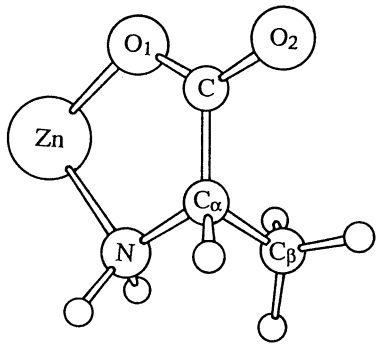

Fig. 1. A view of an α-alaninato ion with central zinc(II) ion. The atoms without letters are hydrogen atoms.

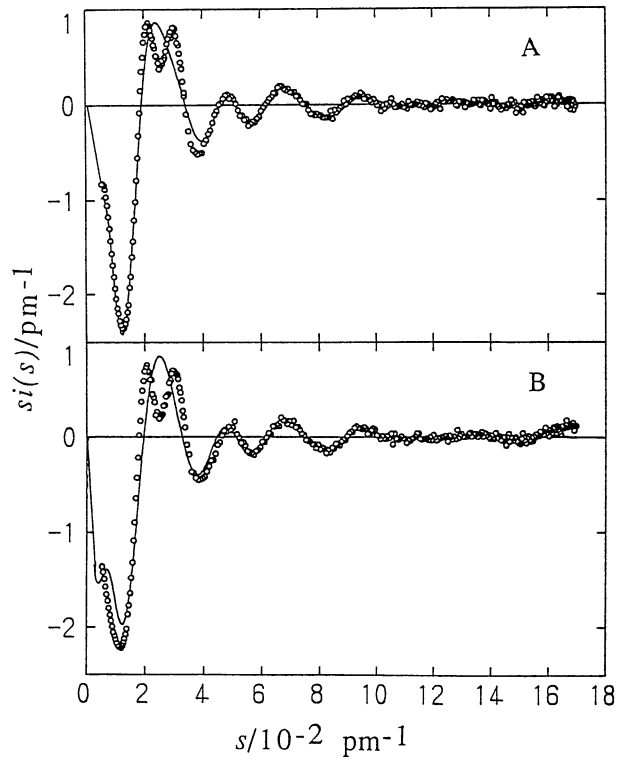

Fig. 2. Experimental (circles) and calculated (lines) structure functions of aqueous zinc(II)-α-alaninate solutions *A* and *B*.

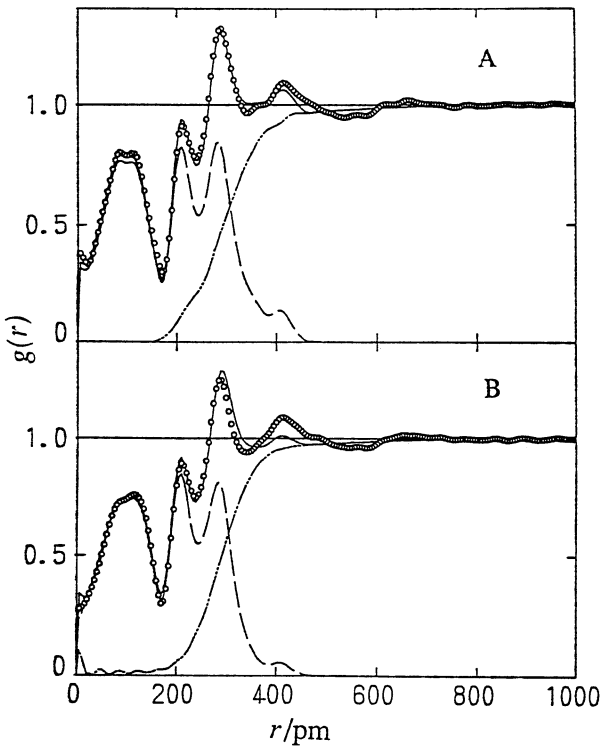

Fig. 3. Pair-correlation functions of aqueous zinc(II)-α-alaninate solutions *A* and *B*. Experimental (circles), calculated (lines) functions and the sum of the contributions of the discrete structure units (dashed). The chain line with two dots shows the contribution of the continuum.

O bonds between zinc(II) ion and α-alaninate ions in the complex should also appear in this region. Peaks due to nonbonding atom-atom pairs within α-alaninato ions and the Li-O bonds within the hydrated lithium ions may appear in the same region. The peak centered at about 300 pm can be ascribed to nonbonding atom-pairs of other types in the complexes and in the hydration structure of the ions. The maximum around 420 pm may be attributable to the water-water distance at the second neighbor in the bulk structure and other long range nonbonding atom-atom distances in the complicated ligand anions. In order to obtain reliable structural parameters, the coordination number n_{pq}, the mean interatomic distance r_{pq} and the temperature factors b_{pq} of the p-q atom pair in the complexes, therefore, a careful analysis of the experimental data must be needed with additional information at the construction of the structural models of the complexes in the solutions.

For long range interactions beyond the discrete distributions of these distances, terms of the continuous distribution of electrons were introduced in order to fully reproduce the experimental structure functions. The mathematical form of the theoretical structure function is given as follows:

$$s \cdot i(s) = s \cdot i_d(s) + s \cdot i_c(s), \quad (2)$$

where $s \cdot i_d(s)$ includes the discrete part of contributions

$$s \cdot i_d(s) = s \cdot \sum\sum n_{pq} c_{pq} j_0(s r_{pq}) \exp(-b_{pq} s^2), \quad (3)$$

and $s \cdot i_c(s)$ describes the continuum:

$$s \cdot i_c(s) = -4\pi\rho_0 \sum\sum c_{pq} R_{pq}^2 j_1(s R_{pq}) \exp(-B_{pq} s^2). \quad (4)$$

Here c_{pq} refers to the weight of the contribution of the interaction of a p-q atom pair to the total intensity of scattered X-rays comprising the scattering powers of atoms and their stoichiometric weights, $j_m(x)$ is the spherical Bessel-function of the mth order.[14] The structural parameters describing the continuum terms are the distance R_{pq} beyond which a continuous distribution of electrons of atom q around the central p atom. B_{pq} is a parameter describing the sharpness of the boundary R_{pq}.

The LSQ fitting procedure was extended over the whole s-region for the calculations. Systematic checks were also made by varying the minimum s value from 0.02 to 0.06 pm^{-1}, but no significant change could be observed in the structural parameters obtained. Introduction of the structural parameter values found in pure water to the calculations was not successful to reproduce the double peak appearing at s=0.02—0.03 pm^{-1}, because the water structure in the electrolyte solutions may be significantly changed due to intermolecular interactions between water molecules and solute species. Such disagreements between experimental and calculated $s \cdot i(s)$ values have been seen in previous papers.[6-8] Therefore, we did not extend the improvement of the LSQ calculations to obtain a better fit in the s-range smaller than 0.04 pm^{-1}.

Intramolecular Structure of α-Alaninate Ion. The parameter values for the intramolecular structure of α-alaninate ion were taken from the result of neutron diffraction studies in the solid phase.[15] The parameter values were allowed to vary during the fitting procedures. No significant change in the parameters could be observed, however. The parameter values finally obtained are summarized in Table 2. The first peak in the $g(r)$ functions of both solutions A and B were satisfactorily reproduced by using the values. Moreover, the agreement among the intramolecular structural parameters of α-alaninate, glycinate,[6] and β-alaninate ions[16] was also satisfactory within the limits of errors.

The Structure of Perchlorate Ion. The structure of the perchlorate ion present in *Solution B* was described with four parameters as follows: the distances $r_{Cl\text{-}O}$=143 and $r_{O\cdots O}$=234 pm, and the temperature factors $b_{Cl\text{-}O}$=10 and $b_{O\cdots O}$=100 pm^2.[17]

The Hydration Structure of Ions. The hydration structures of free Li^+ and Zn^{2+} ions were taken into consideration in the course of the structural analysis of the solutions.

Lithium ions were only present in *Solution A* and the contribution of the hydrated lithium ions to the structural function was not significant. In the fitting procedure the tetrahedral[18] and octahedral[19] structures were assumed with the Li-O distance of 200—220 pm and the O···O nonbonding distances calculated from either regular tetrahedral or octahedral structure of the hydrated complex. No significant influence of the supposed structural forms of the hydrated lithium ion on the R-factor was observed, and thus the tetrahedral structure was retained at the final analysis of the total

Table 2. Intramolecular Structural Parameters, Distances r_{pq} and Temperature Factors b_{pq} for the α-Alaninate Ion[a]

p-q	r_{pq}/pm	$b_{pq}/10^2$ pm^2
N-H	103.6(5)	0.3(1)
C_β-H_β	108.2(5)	0.3(1)
C_α-H_α	109.3(5)	0.3(1)
C-O_1	124.2(5)	0.1(1)
C-O_2	125.8(5)	0.1(1)
C_α-N	148.7(5)	0.1(1)
C_α-C_β	152.4(5)	0.1(1)
C_α-C	153.1(5)	0.1(1)
$O_1 \cdots O_2$	222.4(5)	0.3(1)
$C_\alpha \cdots O_2$	236.9(5)	0.3(1)
$C_\alpha \cdots O_1$	238.6(5)	0.3(1)
$C_\beta \cdots N$	246.3(5)	0.3(1)
$C \cdots N$	247.3(5)	0.3(1)
$C_\beta \cdots C$	251.9(5)	0.3(1)

a) Uncertainties given in parentheses are probable values estimated from experimental errors.

structure function of *Solution A*.

Hydrated Zn^{2+} ions exist in *Solution B* according to stoichiometric considerations. The structural parameters of the hydrated zinc(II) ions were also introduced to the fitting procedure by assuming the regular octahedron for the structure. The parameters obtained are listed in Table 4, together with the parameters of the complexes in *Solution B*. The parameter values for the hydrated zinc(II) ion thus obtained were very close to the literature values.[1-4]

Structure of the Zinc(II)-α-Alaninato Complexes. During the calculations it was assumed that the distribution of the complexes in the solutions was the same as that predicted from the stability constants.

Solution A. The detailed LSQ structural analysis on the $s \cdot i(s)$ function confirmed that the main species formed in the solution was the tris(α-alaninato)-zincate(II) complex. The zinc(II) ion has the coordination number of six consisting of three oxygen and three nitrogen atoms. Since we cannot a priori exclude any other combinations of $(6-n)$ oxygen atoms and n nitrogen atoms in the coordination sphere of the zinc(II) ion, models with varying n were tested during the LSQ analysis. The best result was obtained with the unique 3O and 3N combination. The carboxylato oxygen atom in the coordination sphere is denoted as O_1 as shown in Fig. 1, while the carbonyl oxygen is referred to O_2.

At the LSQ procedure, the Zn-O_1 and Zn-N distances and their temperature coefficients were taken as independent parameters, while the frequency parameters were fixed at 3O and 3N. The structural parameters finally obtained for the complex are summarized in Table 3. The result in Table 3 shows that the Zn-O_1 bond is shorter than the Zn-N bond by about 10 pm. In the tris(glycinato)zincate(II) complex we found the equal lengths of the Zn-O_1 and Zn-N bonds.[8] On the other hand, different Zn-O_1 and Zn-N bond lengths were observed for the tris(glycinato)-nickelate(II) complex.[6]

The LSQ procedure was examined for various combinations of the Zn-O_1 and Zn-N bond lengths. The R-factors were calculated for various models with different combinations of the Zn-O_1 and Zn-N bond lengths. In the calculations one of the lengths of the bonds was fixed at a given value shown in the note of Fig. 4 and the length of the other bond was stepwise varied over the range from 195 to 220 pm. The R-factors thus obtained for the various combinations are plotted against either the Zn-O_1 or Zn-N bond length in Fig. 4. The minimum of the R-factor was obtained for the combination of Zn-O_1=202 pm and Zn-N=213 pm (open circles in Fig. 4A). As expected, approximately the same value of the R-factor was obtained for the combination of Zn-N=202 pm and Zn-O_1=213 (closed circles in Fig. 4A). The X-ray

Table 3. Structural Parameters for the Tris(α-alaninato)zincate(II) Complex in *Solution A*: Distances r_{pq}, Temperature Factors b_{pq}, and Coordination Numbers n_{pq}. Standard Deviations for Independent Parameters are given in Parentheses

p-q	r_{pq}/pm	$b_{pq}/10^2$ pm^2	n_{pq}
Zn-O_1	202(1)	0.3(1)	3[a]
Zn-N	213(1)	0.4(1)	3[a]
Zn···C	281(2)	0.4(2)	3[a]
Zn···C_α	287(2)	0.5(2)	3[a]
O···O	291(2)	4.9(1)	3.6(3)
N···O_1	293[b]	1.0[a]	6[a]
N···N	301[b]	1.0[a]	3[a]
O_1···O_1	285[b]	1.0[a]	3[a]
C_β···O_1	366(2)	1.0[a]	1[a]
C_β···O_2	316(2)	1.0[a]	1[a]
N···O_2	366(3)	1.0[a]	1[a]
Zn···O_2	407(4)	0.5(2)	3[a]
Zn···C_β	425(5)	1.4(9)	3[a]

a) Fixed. b) Calculated from the bond lengths in the first coordination shell.

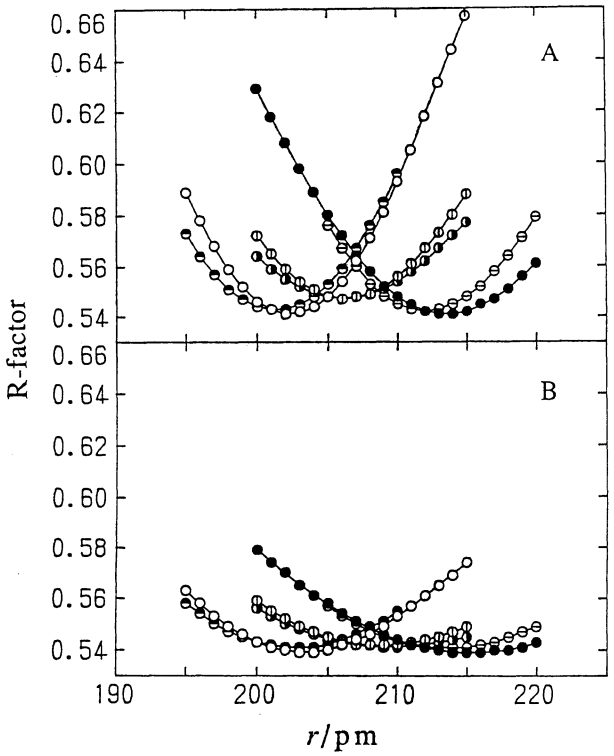

Fig. 4. Values of the R-factor as a function of the Zn-X distance at the LSQ procedures for solutions *A* and *B*. Symbols in the figure are indicated as follows:

Symbol	X	Bond fixed	Distance/pm
○	O_1	Zn-N	213
●	N	Zn-O_1	202
◐	O_1	Zn-N	208
◑	N	Zn-O_1	208
⊖	O_1	Zn-N	202
◓	N	Zn-O_1	213

diffraction technique can hardly distinguish between oxygen and nitrogen atoms and it happens especially in the liquid X-ray diffraction method in which less precise structural information is usually given compared with the crystallographic X-ray diffraction method. Thus the set of structural parameters of shorter Zn-N bonds than Zn-O bonds gave the same results in the *R*-factor as those for the set of shorter Zn-O bonds than Zn-N ones. However, the former combination could be excluded because the shorter Zn-N bond than the Zn-O_1 bond resulted in a significant distortion of the α-alaninato ion in the coordination shell, as we have seen in the case of the $[Ni(gly)_3]^-$ complex[6]. The value of the *R*-factor obtained for the combination of the same length of the Zn-O_1 and Zn-N bond at 208 pm (◐ and ◑) was larger than the minimum value obtained for the different Zn-O_1 and Zn-N bond lengths.

The different lengths of the Zn-O_1 and Zn-N bonds in the $[Zn(\alpha\text{-ala})_3]^-$ complex may be caused by the inductive effect of the methyl group which gives more electrons to the O_1 atom than the N atom having a less electronegativity than the former. On the other hand, the different bond lengths in the tris(glycinato) complexes of zinc(II) and nickel(II) ions may be due to the different electron configurations of these metal ions, the latter has a larger π-electron accepting ability from the carboxylato oxygen atom than the former which has the d^{10} electrons.

Solution B. In the course of the LSQ analysis, various geometrical forms were tested for the complexes $[Zn(\alpha\text{-ala})]^+$ and $[Zn(\alpha\text{-ala})_2]$. For the former $[Zn(\alpha\text{-ala})(H_2O)_4]^+$ and $[Zn(\alpha\text{-ala})(H_2O)_2]^+$ was assumed, while for the latter octahedral $[Zn(\alpha\text{-ala})_2(H_2O)_2]$ and the tetrahedral $[Zn(\alpha\text{-ala})_2]$ structures were taken into consideration. The frequency factors of the atom pairs were fixed at a given combination of the geometrical forms assumed for the complexes in the course of the LSQ refinement of the structural parameters. The bond lengths and the temperature factors of atom pairs in the first coordination shell of the zinc(II) ions were freely floated around the initial values inserted at the beginning of the calculations. The initial values were taken from the values of the hydrated zinc(II) ion and the tris-complex. Some other structural parameters of nonbonding atom-pairs were also allowed to vary independently from other parameter values. The amounts of the complexes in the solution were fixed at the given values calculated from the stability constants.

The results were summarized in Table 4. In this case different Zn-O_1 and Zn-N bond lengths were obtained for both mono- and bis(α-aninato)zinc(II) complexes. The length of the Zn-OH_2 bond in the complexes was practically the same as that in the aqua complex. All the complexes existing in the solution were six-coordinated ones. Any attempt to reduce the coordination number of the zinc(II) ion in the complexes led to a significant increase in the *R*-factor. Similarly, the peak around 200—220 pm in the $g(r)$ curve were not well reproduced under an assumption of the coordination number of the zinc(II) ion less than 6.

Table 4. Structural Parameters for the Hydrated Zinc(II) Ion, Mono(α-alaninato)zinc(II) and Bis(α-alaninato)-zinc(II) Complexes in *Solution B*: Distances r_{pq}, Temperature Factors b_{pq}, and Coordination Numbers n_{pq}. Standard Deviations for Independent Parameters are given in Parentheses

p-*q*	r_{pq}/pm	$b_{pq}/10^2$ pm^2	n_{pq}
$[Zn(H_2O)_6]^{2+}$			
Zn-O	208[a]	0.3(1)	6[a]
O···O	294[a]	1.0[a]	12[a]
$[Zn(\alpha\text{-ala})(H_2O)_4]^+$			
Zn-O_1	202(1)	0.3(1)	1[a]
Zn-N	214(1)	0.4(1)	1[a]
Zn-OH_2	208(1)	0.3(1)	4[a]
OH_2···OH_2	290[b]	1.0[a]	5[a]
O_1···OH_2	289[b]	1.0[a]	3[a]
N···OH_2	296[b]	1.0[a]	3[a]
N···O_1	294[b]	1.0[a]	1[a]
Zn···C	287(2)	0.4(2)	1[a]
Zn···C_α	288(2)	0.5(2)	1[a]
$[Zn(\alpha\text{-ala})_2(H_2O)_2]$			
Zn-O_1	203(1)	0.3(1)	2[a]
Zn-N	214(1)	0.4(1)	2[a]
Zn-OH_2	208(1)	0.3(1)	2[a]
O_1···OH_2	289[b]	1.0[a]	4[a]
N···OH_2	296[b]	1.0[a]	4[a]
N···O_1	295[b]	1.0[a]	4[a]

a) Fixed. b) Calculated from the bond lengths in the first coordination shell.

The same examination for checking the reliability of the conclusion of different Zn-O_1 and Zn-N bond lengths as demonstrated for the tris-complex was carried out. The results were graphically summarized in Fig. 4B. Very similar patterns of changes in the *R*-factors plotted against the Zn-O_1 or Zn-N bond length were obtained as found for the tris-complex. The minimum value of the *R*-factor appeared at Zn-O_1=202—203 pm and Zn-N=214 pm. The minimum obtained at Zn-O_1=Zn-N=208 pm was slightly larger than that obtained in the preceding case. Thus, we concluded that the lengths of the Zn-O_1 and Zn-N bonds were different in the α-alaninato complexes of zinc(II) ion.

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