An X-Ray Diffraction Study on the Structures of Bis- and Tris-(ethylenediamine)zinc(II) Complexes in Solution

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An X-ray diffraction study has been carried out at 25 °C for aqueous ethylenediamine(en) solutions of zinc(II) nitrate, the mole ratios, en/Zn, in the solutions being 2.252 and 3.204. In the former solution bis(ethylenediamine)-zinc(II) complex existed as the main species, while in the latter tris(ethylenediamine)zinc(II) complex was predominant. The X-ray scattering data of the solution containing the bis-complex showed that four nitrogen atoms within the two ethylenediamine molecules were tetrahedrally coordinated to the zinc(II) ion at a distance of 2.131 (9) Å. The nonbonding Zn···C distance was also determined to be 2.89(2) Å. In the tris-complex in which the zinc(II) ion was coordinated with the six nitrogen atoms, the Zn–N and Zn···C distances were 2.276(5) Å and 3.00(1) Å, respectively. Raman spectra of the solutions supported the structures of the complexes.

X-Ray diffraction studies on complexes in solution have been markedly developed in these years, and the structural data of metal complexes with various unidentate ligands, such as halide and hydroxide ions and water and ammonia molecules, have been accumulated to provide the most fundamental knowledge on elucidating behavior of metal complexes in solution. Recent progresses in techniques and apparatus for X-ray diffraction analysis allow to investigate structures of polynuclear complexes containing relatively heavy metals. However, structures of metal chelates in solution have never been examined by the X-ray diffraction method.

In the present work, as a first step of investigation of structures of metal chelates, we choose ethylenediamine complexes of zinc(II) ion, because ethylenediamine is one of the simplest chelating agents. To find the structural difference, if it presents, of the complexes with varying numbers of the ligand coordinated is another aim of this investigation, since no crystallographic study of these complexes has been made so far.

Raman spectroscopic measurements have been employed to provide a supplement to the structural determination of the complexes.

Experimental

Preparation and Analysis of Sample Solutions. Anhydrous ethylenediamine of guaranteed reagent grade was obtained from Tokyo Kasei Co., Ltd. and was purified by refluxing and distilling over sodium (bp 167 °C). Zinc(II) nitrate of reagent grade was purchased from Wako Pure Chemical Co., Osaka and was recrystallized twice from water. The samples were prepared by dissolving zinc nitrate into aqueous ethylenediamine solutions.

The concentration of zinc(II) ions in the test 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 concentration of the nitrate ion was determined from the stoichiometry of the zinc(II) nitrate.

TABLE 1. THE COMPOSITION (g-atom/dm³) AND THE STOICHIOMETRIC VOLUME V PER ZINC ATOM IN THE SOLUTIONS

	Solutions	
	A	B
Zn	1.846	1.295
N	15.52	8.422
C	11.83	5.832
O	47.11	49.28
H	119.4	106.4
en/Zn	3.204	2.252
V/Å³	899.5	1282
Density/g cm^{-3}	1.239	1.171

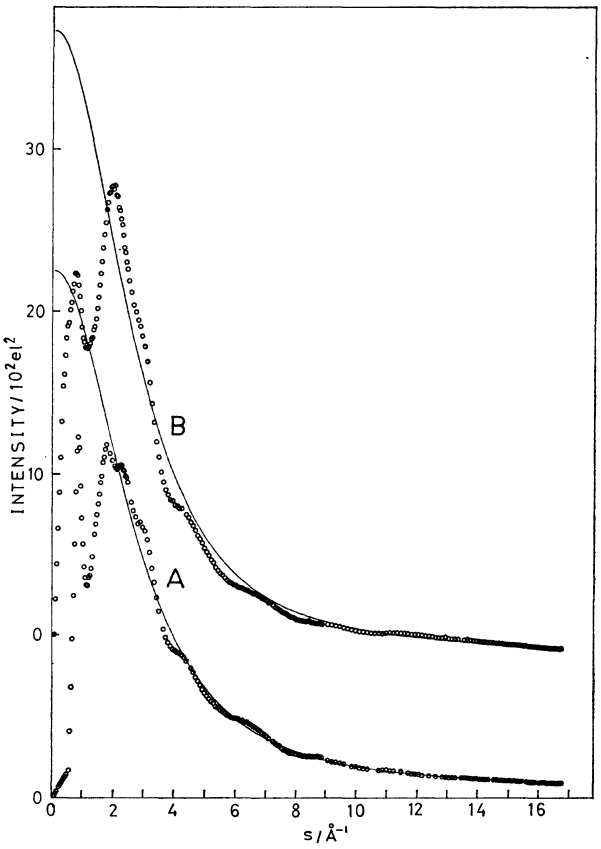

Fig. 1. Coherent scattering intensities of the sample solutions A and B. Experimentally obtained intensities I^{coh} are shown by circles and calculated independent scattering intensities by solid lines.

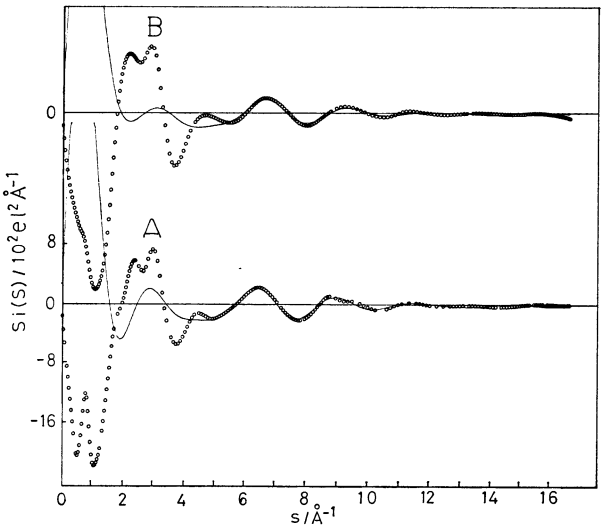

Fig. 2. The reduced intensities multiplied by s for solutions A and B. Open circles indicated experimentally obtained $s \cdot i(s)$ values and full lines are calculated ones by using parmeter values finally proposed.

The density of the test solutions was measured pycnometrically.

The composition of the test solutions is given in Table 1.

Method of Measurements and Treatment of X-Ray Scattering Data. The method of measurements and the apparatus used were essentially the same as those in previous papers.[1] Coherent and reduced intensities of the test solutions are given in Figs. 1 and 2, respectively. The radial distribution function $D(r)$ was calculated by the following equation:

$$D(r) = 4\pi r^2\rho_0 + \frac{2r}{\pi}\int_0^{s_{max}} s \cdot i(s) \cdot M(s) \cdot \sin(rs)\mathrm{d}s, \quad (1)$$

where ρ_0 is the average scattering density in the stoichiometric volume V of the solution per Zn atom, and s_{max} denotes the maximum s-value attained in the measurements ($s_{max}=16.7$ Å). $M(s)$ represents the modification function[2] and the reduced intensities $i(s)$ are given by

$$i(s) = I^{coh}(s) - \sum n_i\{(f_i(s)+\Delta f_i')^2+(\Delta f_i'')^2\}, \quad (2)$$

where n_i is the number of atom i and $f_i(s)$ denotes the scattering factor of atom i at s. $\Delta f_i'$ represents the real part of the anormalous dispersion, whereas $\Delta f_i''$ is the imaginary one.[3] The radial distribution curves $D(r)$ of the solutions were drawn after the Fourier transform of the reduced intensities which had been smoothed by the method described previously.[1]

The theoretical scattering intensities due to atom pairs of all possible combinations in the system were given as follows:

$$i_{calcd}(s) = \sum_{i}\sum_{i\neq j}^{j} n_{ij}\{(f_i(s)+\Delta f_i')(f_j(s)+\Delta f_j') + (\Delta f_i'')(\Delta f_j'')\} \cdot \frac{\sin(r_{ij}s)}{(r_{ij}s)} \cdot \exp(-b_{ij}s^2), \quad (3)$$

where r_{ij}, b_{ij}, and n_{ij} denote the distance, the temperature factor, and the frequency factor of an atom pair i-j, respectively.

All calculations were performed with the aid of electronic computers M 160 and M 180 by means of KURVLR program.[4]

Raman Spectroscopic Measurements. A JEOL JRS-S1 Raman spectrometer was employed with the use of the 4880 Å excitation line of Ar^+ laser.

Results and Discussion

Since no formation constants of the complexes has been reported in the literature in such concentrated solutions examined here, distributions of the zinc(II)–ethylenediamine complexes in the solutions were not estimated in advance of the X-ray measurements. However, we can approximately evaluate the formation constants of the ethylenediamine zinc(II) complexes in the solutions used in the present work by simply extrapolating the literature values.[5] The extrapolated values, as well as the literature values obtained in relatively low ionic strengths, suggested that both bis- and tris(ethylenediamine)zinc(II) complexes may coexist in each solution. In solution A the tris-complex may be the main species, whereas the bis-complex may be

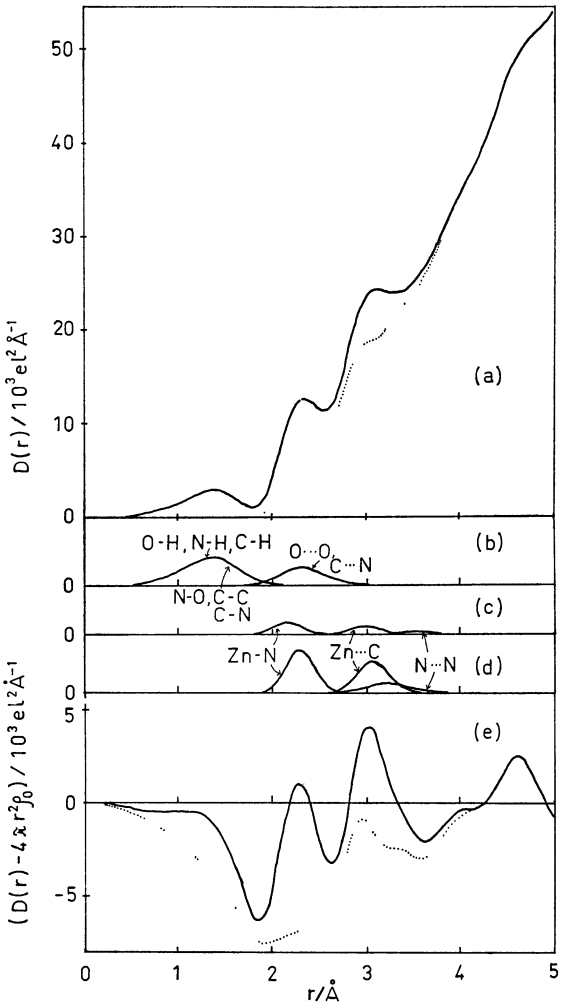

Fig. 3. (a) The radial distribution curve for solution A. (b) The theoretical peak shapes for the O–H bond within water, the N–H, C–H, C–C, C–N, and C···N pairs within ethylenediamine molecule, and the N–O and O···O contacts within nitrate ion. (c) The theoretical peak shapes for the Zn–N, Zn···C, and N···N pairs within the $Zn(en)_2^{2+}$ complex. (d) The theoretical peak shapes for the Zn–N, Zn···C, and N···N pairs within the $Zn(en)_3^{2+}$ complex. (e) The corresponding $(D(r)-4\pi r^2\rho_0)$ curve to the $D(r)$ in (a). The dotted lines in (a) and (e) show the residual radial and residual differential radial distribution curves, respectively, after subtraction of these theoretical peaks.

predominant in solution B. In the analyses of the radial distribution curves of solutions A and B, the both complexes were taken into consideration at the same time in the following manner; at a first approximation the $D(r)$ curve of solution A was analyzed by assuming that the only tris-complex was contained. The parameter values for the structure of the complex thus estimated was used for analyzing the $D(r)$ curve of solution B in order to determine the structural parameters of the bis-complex so as to obtain a smooth background of the $D(r)$ curve. The parameter values thus obtained for the bis-complex were turned back to the calculation of the $D(r)$ curve of solution A in order to evaluate better parameter values of the tris-complex. The improved values of the tris-complex were again used for analyzing the $D(r)$ curve of solution B. The successive approach of the analysis was continued until no appreciable peak was left in the background of the radial distribution curves of both solutions A and B.

The parameter values, the bond distance(r), temperature factor(b), and frequency factor(n) of the models used for calculations of intensities due to intramolecular interactions were refined by using the data at high angle regions of the $s \cdot i(s)$ curves of solutions A and B. The refinements were carried out so as to obtain an error-square sum $U=\sum s^2\{i_{\mathrm{obsd}}(s)-i_{\mathrm{calcd}}(s)\}^2$ to be a minimum. The lower s limit in the calculation was varied in order to avoid introduction of errors to the refined parameters from intermolecular interactions. The least-squares calculations were performed by using the NLPLSQ program.[1]

Solution A. The radial distribution curve of solution A showed four major peaks over the range $r=$ 1—5 Å (Fig. 3a). A small peak at about 1.3 Å is composed of peaks due to the O–H bond within water, the N–H, C–H, C–C, and C–N bonds within ethylenediamine molecules and the N–O bond within nitrate ions (Fig. 3b). The second peak appearing at around 2.2 Å may be attributed to the interactions between zinc(II) ion and the nitrogen atoms of the ethylenediamine molecules coordinated to the central metal ion (Fig. 3, c and d). The distances corresponding to the nonbonding C···N pair in ethylenediamine molecules and the O···O contact within NO_3^- ion may also partly contribute to the peak. The third peak at 2.95—3.05 Å may be mainly ascribed to the nonbonded interactions of zinc(II) ion with the carbon atoms within ethylenediamine molecules coordinated. The broad peak at around 4—5 Å may include contributions among the complexes, free ligand and solvent molecules, which we will not discuss in this paper.

We assumed that the bond lengths of the N–H, C–H, C–C, C–N and C···N pairs within the ethylenediamine molecules are practically the same as those within free ligand molecules in the gas phase.[6] The structural parameters of nitrate ion were taken from the work by Maeda, *et al.*[7] and Caminiti, *at al.*[8] The values used in this work are summarized in Table 2. The Zn–N and Zn···C distances within the bis- (Fig. 3c) and tris-complexes (Fig. 3d) were estimated from the radial distribution curve of solution A. Successive approaches for the estimation have been employed as mentioned previously. The Zn–N and Zn···C bond lengths within the tris-complex were thus estimated to be 2.28 and 3.02 Å, respectively. The temperature factor of the former was determined to be 0.003 Å^2, while that of the latter was 0.006 Å^2. The area under the peak at 2.28 Å corresponded to six Zn–N bonds (see Fig. 3d), which were expected from the composition of the tris-complex. Subtraction of the peaks due to Zn–N and Zn···C interactions from the residual radial distribution curve led to a smooth background having no appreciable peak over the range $r<4$ Å, except for the peak at about 2.9 Å which was ascribed to the adjacent O···O interactions in the bulk water and hydrated nitrate ions[8] (Fig. 3, a and e).

The parameter values thus estimated from the analysis of the radial distribution curve were refined by the least-squares method for the intensity curve

Table 2. Bond distances (r) and temperature factors (b) for water and ethylenediamine molecules and nitrate ions

		r/Å	b/Å^2
H_2O	O–H	0.955[a]	0.010[a]
en	N–H	0.870[b]	0.003[b]
	C–H	1.11[b]	0.003[b]
	C–C	1.55[b]	0.001[b]
	C–N	1.47[b]	0.001[b]
	C···N	2.47[b]	0.003[b]
NO_3^-	N–O	1.26[c]	0.0009[d]
	O···O	2.19[c]	0.002[e]

a) R. Triolo and A. H. Narten, *J. Chem. Phys.*, **63**, 3624 (1975). b) A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **44**, 2926 (1971). c) R. Caminiti, G. Licheri, G. Piccaluga, and G. Pinna, *J. Chem. Phys.*, **68**, 1967 (1968). d) M. Maeda, Y. Maegawa, T. Yamaguchi, and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **52**, 2545 (1979). e) Estimated from the value of b_{N-O}.

Table 3. Results of the least-squares refinements of solution A

The refined parameters for the bond, distance (r), temperature factor (b) and frequency factor (n) are obtained from the reduced intensity curve. The units of r and b are Å and Å^2, respectively. Standard deviations are given in parentheses.

Interaction	Parameter	A-1	A-2
O···O(NO_3^-)	r	2.19(2)	2.19(2)
C···N(en)	r	2.41(4)	2.41(4)
Bis-complex			
Zn–N	r	2.16(3)	2.17(3)
N···N[a]	r	4.2(8)	4.1(8)
Zn···C	r	2.89(7)	2.90(7)
Tris-complex			
Zn–N	r	2.276(5)	2.276(5)
	b	0.0029(3)	0.0028(3)
	n	6.2(1)	6[b]
N···N[a]	r	3.16(6)	3.16(6)
Zn···C	r	3.00(1)	3.00(1)
	b	0.0053(6)	0.0053(6)
	n	6.1(2)	6[b]

a) The temperature factor of this interaction is estimated to be 0.01, quoted from Ref. 6. b) Fixed.

(Fig. 2). Two types of refinement (A-1 and A-2) were performed for solution A.

In type A-1, all the twelve parameters listed in Table 3 were allowed to change independently, a tetrahedral structure of the bis-complex being assumed. The frequency factors of the Zn–N bond and the nonbonding Zn···C interaction were close to six as expected in all the sets of data examined over the different s-regions from 5.0, 6.0, and 7.0 to 16.7 Å^{-1}.

In type A-2, an octahedral structure of the tris-complex as the main species was also assumed and the distances and the temperature factors of the Zn–N and nonbonding Zn···C interactions were refined. Since no appreciable difference was found in the results of the two calculations, the octahedral structure of the tris-complex having the parameter values given in Table 3 was concluded.

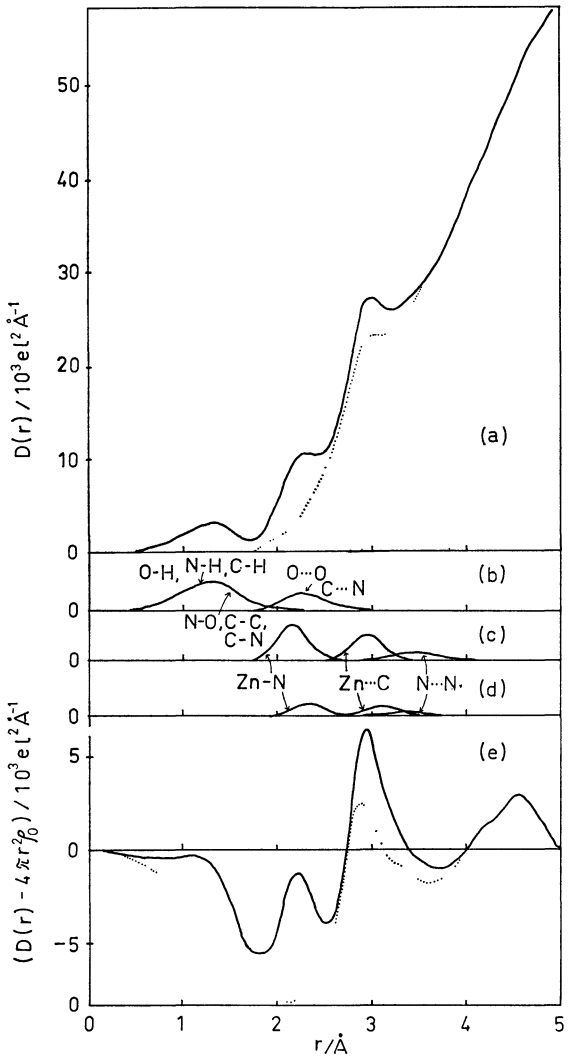

Fig. 4. (a) The radial distribution curve for solution B. (b) The theoretical peak shapes for the O–H bond within water, the N–H, C–H, C–C, C–N, and C···N pairs within ethylenediamine molecule, and the N–O and O···O contacts within nitrate ion. (c) The theoretical peak shapes for the Zn–N and Zn···C and N···N pairs within the $Zn(en)_2^{2+}$ complex. (d) The theoretical peak shapes for the Zn–N, Zn···C, and N···N pairs within the $Zn(en)_3^{2+}$ complex. (e) The corresponding $(D(r)-4\pi r^2\rho_0)$ curve to the $D(r)$ in (a). The dotted lines in (a) and (e) show the residual radial and residual differential radial distribution curves, respectively, after subtraction of these theoretical peaks.

Solution B. The essentially same procedure as that used for solution A was employed for analyzing the radial distribution curve of solution B. The contribution of the tris-complex coexisting to the curve was taken into account in the analysis. The structural parameters of the N–H, C–H, C–C, C–N, and C···N bonds within ethylenediamine molecules in the complexes were the same as those used in the previous section. The peaks due to the Zn–N and Zn···C distances within the tris-complex were eliminated from the radial distribution curve by the trial-and-error method.

The Zn–N and Zn···C distances within the biscomplex were evaluated as 2.14 and 2.93 Å, respectively, from the analysis of the radial distribution curve (Fig. 4). The area under the peak at 2.14 Å showed the four-coordinated zinc atom. A peak still remained at about 2.9 Å in the radial distribution curve (dotted lines in Fig. 4, a and e) was attributed to the structure of the bulk water and hydrated nitrate ions[8] as has been discussed in the previous section.

TABLE 4. RESULTS OF THE LEAST-SQUARES REFINEMENTS OF SOLUTION B

The refined parameters of the bond distance (r), temperature factor (b), and frequency factor (n) are obtained from the reduced intensity curve. The units of r and b are Å and Å^2, respectively. Standard deviations are given in parentheses.

Interaction	Parameter	B-1	B-2	B-3
O···O(NO_3^-)	r	2.20(2)	2.18(2)	2.18(2)
C···N(en)	r	2.31(5)	2.37(5)	2.29(6)
Bis-complex				
Zn–N	r	2.113(7)	2.134(7)	2.131(9)
	b	0.0035(4)	0.0027(4)	0.0026(5)
	n	4.10(8)	4.09(8)	4[b]
N···N[a]	r	3.9(2)	4.0(2)	3.8(2)
Zn···C	r	2.90(1)	2.90(2)	2.89(2)
	b	0.0057(6)	0.006[b]	0.006[b]
	n	4.7(2)	4[b]	4[b]

a) The temperature factor of this interaction is estimated to be 0.01, quoted from Ref. 6. b) Fixed.

The least-squares refinements were carried out for the parameter values of the bis-complex in order to obtain the best-fit curve to the experimentally obtained $s\cdot i(s)$ curve. In the case of solution B, three types of refinement (B-1, B-2, and B-3) were examined. In type B-1, all the nine parameters given in Table 4 were changed simultaneously. The frequency factor of the Zn–N bond of the bis-complex was always close to four in the various sets with lower s limits of 5.0, 6.0, and 7.0 Å^{-1}. In type B-2, the temperature and frequency factors of the nonbonding Zn···C interaction were held constant and the parameters for the Zn–N bond were refined because the frequency factor was strongly correlated to the temperature factor in the nonbonding Zn···C interaction. The possibility of the existence of $Zn(en)_2(H_2O)_2^{2+}$ as the bis-complex instead of $Zn(en)_2^{2+}$ could also be checked by this treatment; if the former

complex were formed, the frequency factor of the Zn–N in the calculation of B-2 would be six, because no distinction between Zn–O and Zn–N bonds was possible in the calculation. In type B-3, a tetrahedral structure of the bis-complex was assumed and the distances and temperature factors for the Zn–N and nonbonding Zn···C interactions were refined. The refined parameter values in the B-3 set were almost the same as those in the B-2 set.

The observed intensities are compared with the calculated ones (Eq. 3) by using the parameter values in Tables 3 (A-2) and 4 (B-3) (see Fig. 2). The agreement between the two curves is satisfactory except at the low-angle part of the curves where the intermolecular interactions significantly contribute to the $s \cdot i(s)$ curves. From the independent refinements of the parameter values for solutions A and B, the bis- and tris-complexes were confirmed to be tetrahedrally and octahedrally constructed in aqueous solution.

The Zn–N bond within the bis-complex was shorter than that within the tris-complex. The results are consistent with those reported in the literature[9] that the crystal ionic radius of a zinc(II) ion having the coordination number of 4 is smaller than that of a zinc(II) ion of the six-coordination.

Raman Spectra of Solutions A and B. Raman spectra of the tris(ethylenediamine)zinc(II) complex in aqueous solution have been studied by Krishnan and Plane.[10] They reported that the line at 423 cm^{-1} was due to the totally symmetric Zn–N stretching vibration of the tris-complex. In solution A of the present work (Fig. 5) we also found the line at 427 cm^{-1}. Since the line is strongly polarized, it is distinguishable from the skeletal deformation vibration band of free ethylenediamine of the *trans*-conformation which would appear at 475 cm^{-1} in solution.[11] Another strong line was observed at 883 cm^{-1}, for which Krishnan and Plane gave no assignment (in their work the line appeared at 878 cm^{-1}). The line may be ascribed to the rocking vibration of the $-CH_2-$ groups[11] within the ethylenediamine molecules. The band at 722 cm^{-1} was assignable to the ν_4-band of the nitrate ion. In the low frequency region of 170—300 cm^{-1}, some Raman lines were observed. However, no reasonable assignments to the lines were given.

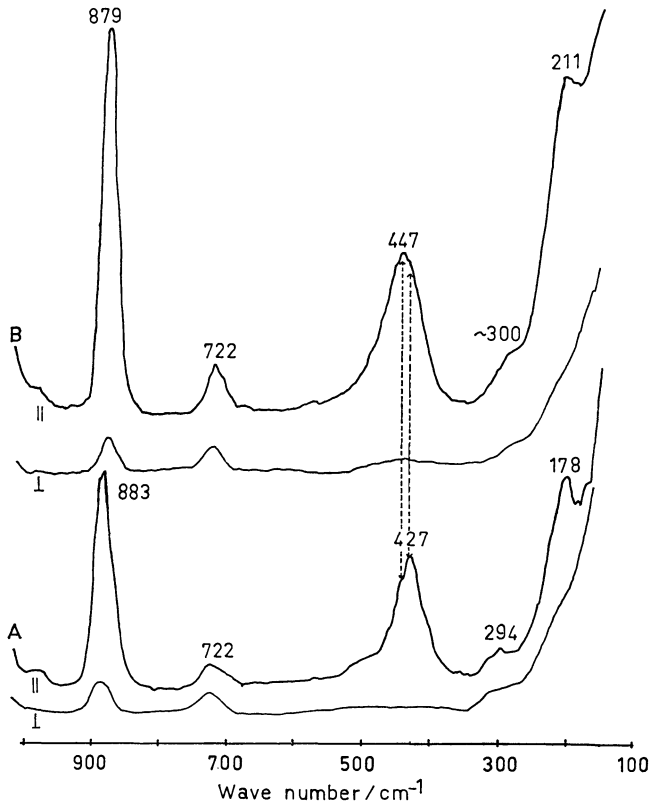

Fig. 5. Raman spectra of solutions A and B. The lines are the components parallel (||) and perpendicular (⊥), respectively, to the direction of polarization of the incident light.

Krishnan and Plane have also measured the Raman spectrum of the bis-complex.[10] However, since their measurements were carried out in a very diluted solution (*ca.* 0.1 mol dm^{-3} for zinc(II) ion) and the test solution contained both bis- and tris-complexes to some extent, assignments of the bands observed for the bis-complex may be less reliable. Solution B in the present work contained the bis-complex with a relatively high concentration, which might be suitable for measuring the Raman spectrum of the bis-complex. The spectrum of solution B showed three major lines at 447, 722, and 879 cm^{-1} (Fig. 5B). The 722 and 879 cm^{-1} bands were readily assigned to the nitrate-ν_4 and CH_2-rocking vibrations, respectively, as have been described previously. The polarized line at 447 cm^{-1}, which was ascribed to the Zn–N sterching in the bis-complex, was in good agreement with the line found at about 450 cm^{-1} by Krishnan and Plane.[10] The frequency of the line was apparently higher than those of the corresponding lines of the tris-complex (427 or 423 cm^{-1} [10]) and the $Zn(NH_3)_4^{2+}$ complex (429[2] or 427 cm^{-1} [12]). These results indicated that the bis-complex has a stronger metal–nitrogen interaction than the other two complexes. This conclusion is supported by the fact that the bis-complex has a shorter Zn–N bond than the tris-complex. The Zn–N distance within the bis-complex is, however, longer than the Zn–NH_3 distance within the tetraammine–zinc(II) complex. The stronger interaction between zinc(II) ion and amino groups within the ethylenediamine molecules may be due to a greater basicity of the NH_2-groups in the ethylenediamine molecules by donating electrons from the CH_2 groups to the amino groups.

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