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

Tadao FUJITA and Hitoshi OHTAKI*
Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta,
Nagatsuta-cho, Midori-ku, Yokohama 227

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The structures of cadmium(II) complexes with ethylenediamine(en) have been determined by means of X-ray diffraction. The measurements were performed at 25 °C for aqueous ethylenediamine solutions of cadmium nitrate, the mole ratios (en/Cd) in the solutions being 2.188 and 3.387. In the solution of the lower en/Cd mole ratio, the bis(ethylenediamine)cadmium(II) complex was predominant, whereas in the other solution the tris(ethylenediamine)cadmium(II) complex was contained as the main species. From the analysis of the X-ray scattering data of the solutions, it was shown that in the bis-complex four nitrogen atoms within the two ethylenediamine molecules were tetrahedrally coordinated to the cadmium(II) ion at a distance of 2.339(4) Å. The nonbonding Cd···C distance within the bis-complex was also determined to be 3.04(1) Å. In the tris-complex the cadmium(II) ion was coordinated with six nitrogen atoms and the Cd–N and Cd···C distances were 2.371(5) and 3.19(1) Å, respectively. The strength of the Cd–N bond with changing coordination number of the complexes was discussed in terms of the frequencies of the Cd–N bond in the Raman spectra of these solutions and the bond lengths found from the X-ray scattering measurements.

In a previous paper,[1] the structures of the bis- and tris(ethylenediamine)zinc(II) complexes in solution have been investigated by the X-ray diffraction method. In the present study, we have attempted to determine the structures of the bis- and tris(ethylenediamine)cadmium(II) complexes in aqueous nitrate solutions in a series of structural studies of chelate complexes of transition metals in solution. No crystallographic investigation of ethylenediamine complexes of cadmium(II) has been reported so far.

Raman spectra of the test solutions were also studied for comparing the strength of the Cd–N bonds within the bis- and tris-complexes.

Experimental

Preparation and Analysis of Sample Solutions. Ethylenediamine was purified by the method previously described.[1] Cadmium(II) nitrate of reagent grade was purchased from Wako Pure Chemical Co., Osaka and was recrystallized twice from water. The sample solutions were prepared by dissolving cadmium(II) nitrate into aqueous ethylenediamine solution as in the similar way to that in the previous paper.[1]

Concentrations of cadmium(II) ions in the test solutions were determined by EDTA titration and electrogravimetry. 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 cadmium nitrate. The density of the solutions was determined pychnometrically. The composition of the test solutions is given in Table 1.

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

	Solution	
	A	B
Cd	1.916	1.760
N	16.81	11.22
C	12.98	7.702
O	38.03	46.95
H	105.0	103.6
en/Cd	3.387	2.188
V/Å³	866.6	946.6
Density/g cm⁻³	1.321	1.303

Method of Measurements and Treatment of X-Ray Scattering Data. The X-ray diffractometer used, the method of measurements and treatment of X-ray scattering data were the same as those described elsewhere.[1,2] Mo $K\alpha$ radiation (λ=0.7107 Å) was used for the measurements over the range $1° < \theta < 70°$ (2θ is the scattering angle). The data were recorded twice over

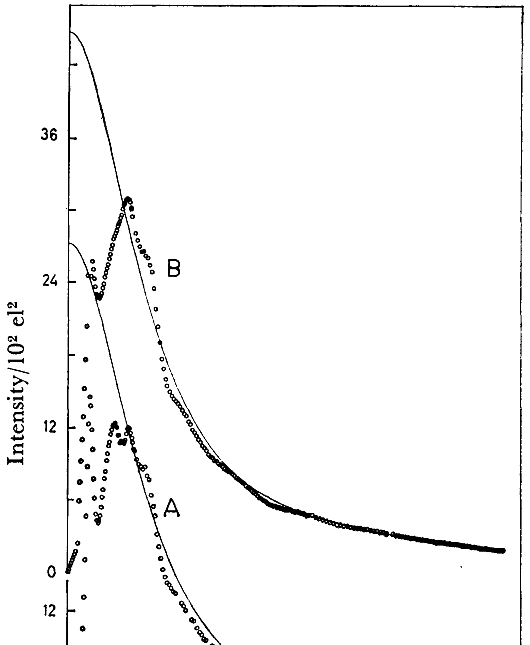

Fig. 1. Coherent scattering intensities of the sample solutions A and B. Experimentally obtained intensities I^{coh} are shown by circles and calculated independent scattering intensities by solid lines.

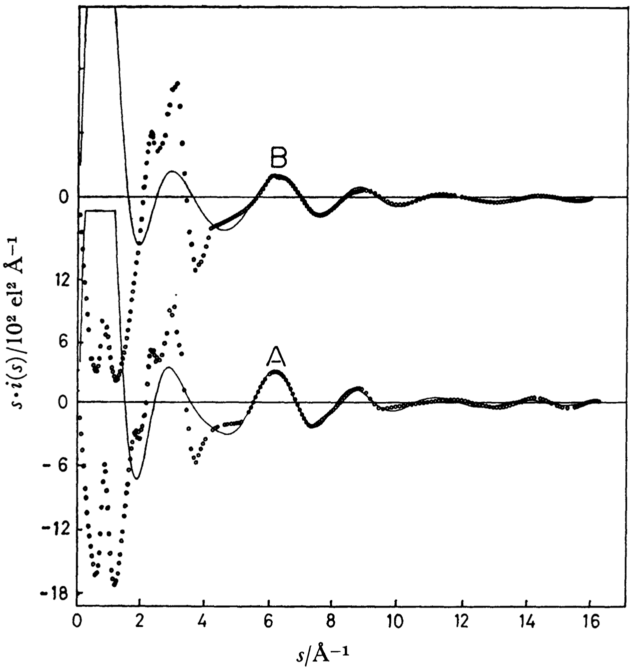

Fig. 2. The reduced intensities multiplied by s for solutions A and B. The observed $s\cdot i(s)$ curve is shown by circles and the calculated one by solid lines.

the whole angle range. The corrections and analysis of the scattering data were performed in the same ways as those in the previous papers.[1,2] Coherent intensities and reduced intensities multiplied by s of the test solutions are given in Figs. 1 and 2, respectively. The radial distribution function $D(r)$ was calculated by the usual method:

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

where ρ_0 is the average scattering density in the stoichiometric volume V of the solution per cadmium atom, and $s_{\max}$ denotes the maximum s-value ($s=4\pi\sin\theta/\lambda$) attained in the measurement ($s_{\max}=16.7$ Å^{-1}). $M(s)$ is the modification function, the function $[f_{\mathrm{Cd}}(0)^2/f_{\mathrm{Cd}}(s)^2]\cdot\exp(-0.01\,s^2)$ being chosen. The reduced intensities $i(s)$ are given by

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

where n_i is the number of atom i and $f_i(s)$ denotes the scattering factor of atom i at s. $\Delta f_i'$ and $\Delta f_i''$ represent the real and imaginary parts of the anomalous dispersion, respectively. The radial distribution curve $D(r)$ of the solutions was drawn after the Fourier transform of the reduced intensity multiplied by s.

Results and Discussion

Solution A contains the tris(ethylenediamine)-cadmium(II) complex as the main species according to the formation constants so far reported.[3] In solution A, however, coexistence of the bis-complex may not be neglected. In solution B the bis(ethylenediamine)-cadmium(II) complex may be contained with a small amount of the tris-complex. Therefore, a successive approach of the analysis as described in the preceding paper[1] was employed in order to obtain the best fitted results for both radial distribution and reduced intensity curves of the test solutions.

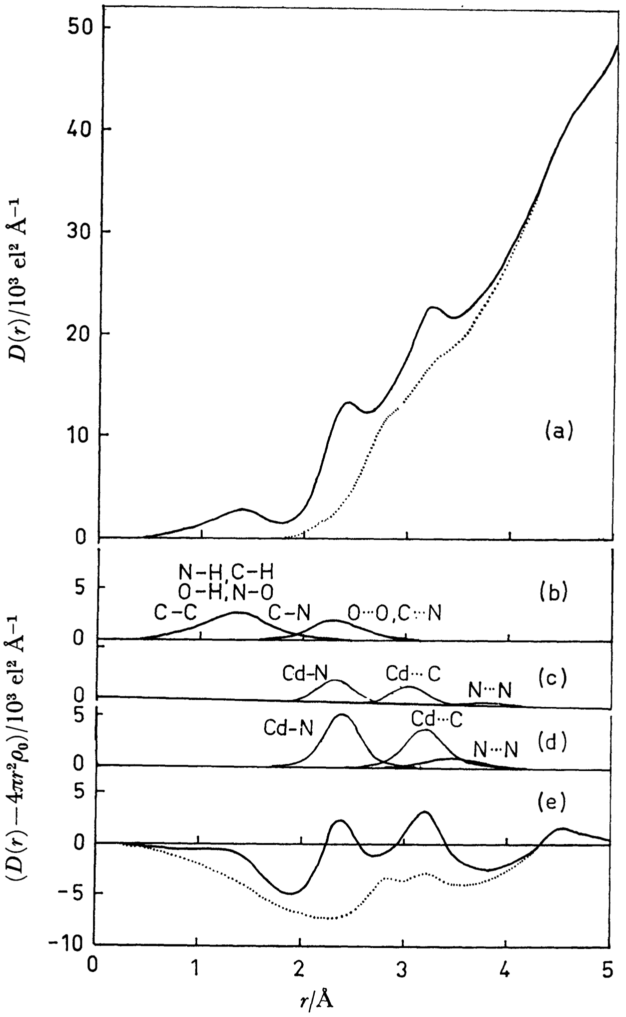

Fig. 3. (a) The radial distribution curve for solution A. (b) The theoretical peak shapes for the O–H bond within water, the N–H, C–H, C–C, C–N, and C···N pairs within an ethylenediamine molecule, and the N–O and O···O contacts within a nitrate ion. (c) The theoretical peak shapes for the Cd–N, Cd···C, and N···N pairs within the $\mathrm{Cd(en)_2}^{2+}$ complex. (d) The theoretical peak shapes for the Cd–N, Cd···C and N···N interactions within the $\mathrm{Cd(en)_3}^{2+}$ 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 A. The radial distribution curve of solution A showed four major peaks over the range 1—5 Å (Fig. 3a). A small peak at about 1.3 Å is composed of the peaks due to the O–H bond within water, the N–H, C–H, C–C and C–N bonds within an ethylenediamine molecule and the N–O bond within a nitrate ion (see Fig. 3b). The second peak appearing at 2.4 Å may be attributed to the interaction between a cadmium(II) ion and the nitrogen atoms of the ethylenediamine molecules coordinated to the central metal ion. The distances corresponding to the nonbonded C···N pairs within an ethylenediamine molecule and the O···O contacts within an $\mathrm{NO_3}^-$ ion may partly contribute to the peak. The third peak at 3.2 Å may be ascribed to the nonbonded interactions between cadmium(II) ion and the carbon atoms within the ethylenediamine molecules coordinated. The broad peak at around 4—5 Å may include contributions from the relatively long range intermolecular interactions among the complexes, free ligands and solvent molecules, which we will not discuss in this paper. The temperature factors of atom pairs within water and ethylenediamine molecules and a nitrate ion used in this investigation were the same as those used in Ref. 1.

At a first approach, the Cd–N and Cd···C distances within the tris-complex were estimated from the radial distribution curve by assuming that the only tris-complex existed in the solution. The bond distances of 2.38 and 3.18 Å for the Cd–N and Cd···C interactions, respectively, were found, the temperature factor of the former bond being about 0.003 Å^2 and that of the latter 0.008—0.01 Å^2. The parameter values thus obtained for the tris-complex were inserted into the analytical procedure of determining the parameter values of the bis-complex in solution B. The procedure was continued until a smooth background of the radial distribution curve was obtained by assuming suitable concentrations of the bis- and tris-complexes in the solutions and parameter values of the former complex. The parameter values thus estimated for the both bis- and tris-complexes were again turned back to the calculation of the radial distribution curve of solution A in order to refine the values of the tris-complex at a fixed parameter values of the bis-complex and changing concentration ratio of the tris-complex to the bis-complex. The successive analyses were continued until no appreciable peak was left in the background of the radial distribution curves of the both solutions A and B. The values thus obtained were further refined by the least-squares method applied to the reduced intensities of the solutions.

Solution B. A successive approach for analyzing the radial distribution curve of solution B was employed as described in the previous section. The Cd–N and Cd···C distances within the bis-complex were estimated to be 2.35 and 3.05 Å, respectively (Fig. 4). The temperature factor of the former bond was about 0.003 Å^2, while that of the latter one was 0.006—0.008 Å^2.

A peak still remained at around 2.9—3.3 Å in the residual radial distribution curves of the both systems (dotted lines in Figs. 3 and 4) were attributed to the structures of bulk water and hydrated nitrate ions.[4)]

Least-Squares Refinements. The parameter values (bond distance r, temperature factor b and frequency factor n) of the interactions in the models adopted were refined by comparing the observed $s\cdot i(s)$ curves with theoretical ones of solutions A and B .at high angle regions. The refinements were carried out so as to obtain a minimum error-square sum $U=\sum s^2\{i_{\text{obsd}}(s)-i_{\text{calcd}}(s)\}^2$ by using the NLPLSQ program.[5)] The s-region was varied in the calculations in order to avoid introduction of errors due to relatively long range intermolecular interactions, which mainly contribute to the intensity data at a low angle region, to the refined parameters.

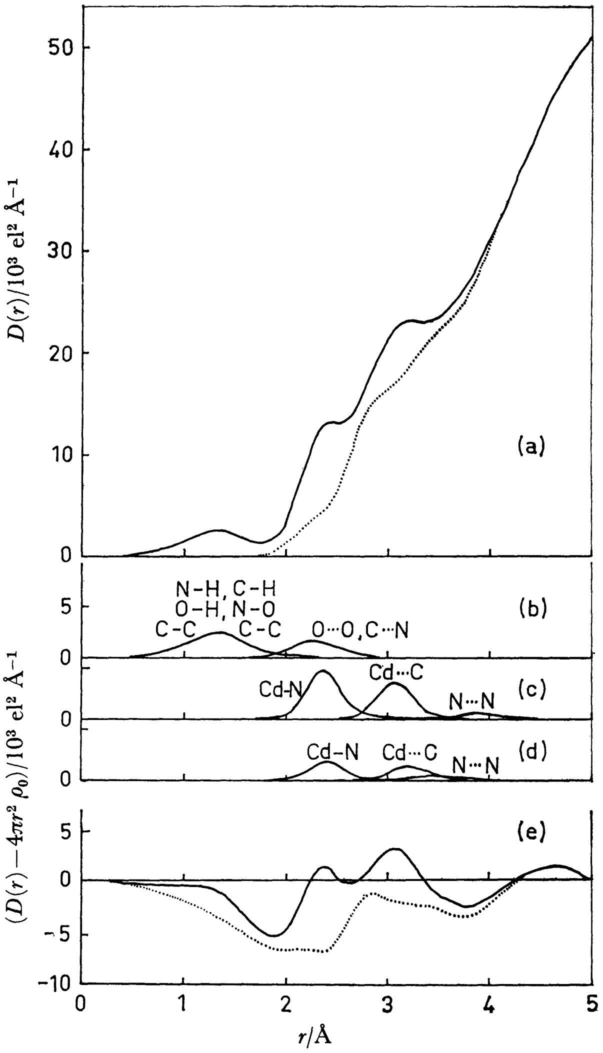

Fig. 4. (a) The radial distribution curve for solution B. (b) The theoretical peak shapes for the O–H bond within water, the N–H, C–H, C–C, C–N, and C···N pairs within an ethylenediamine molecule, and the N–O and O···O contacts within a nitrate ion. (c) The theoretical peak shapes for the Cd–N and Cd···C and N···N pairs within the Cd(en)$_2^{2+}$ complex. (d) The theoretical peak shapes for the Cd–N, Cd···C and N···N pairs within the Cd(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.

For the tris-complex the parameter values were refined with four ways (A-1, A-2, A-3, and A-4). In type A-1, fourteen parameter values (indicated by italic letters) listed in Table 2 were allowed to change simultaneously on the assumption of the tetrahedral structure of the bis-complex, which is confirmed as described later. In type A-2, an octahedral structure of the tris-complex was also assumed, that is, the frequency factor of the Cd–N and Cd···C interactions were fixed at 6 and the only bond distances and temperature factors of the models were refined. In both treatments, the frequency factors of the interactions within

TABLE 2. RESULTS OF THE LEAST-SQUARES REFINEMENTS OF SOLUTION A
The parameter values, r=distance (Å), b=temperature factor (Å^2) and n=number of distance per cadmium(II) atom were refined. Standard deviations are given in parentheses.

Interaction	Parameter	A-1	A-2	A-3	A-4
O···O(NO_3^-)	r	*2.19*(2)	*2.19*(2)	*2.20*(2)	*2.20*(2)
C···N(en)	r	*2.49*(5)	*2.48*(4)	*2.53*(4)	*2.53*(4)
Bis-complex					
Cd–N	r	*2.34*(1)	*2.33*(1)	*2.33*(1)	*2.33*(1)
	b	*0.0033*(6)	*0.0032*(5)	*0.0031*(5)	*0.0031*(5)
	n	4[a]	4[a]	4[a]	4[a]
N···N	r	*3.9*(4)	*3.8*(3)	3.80[a]	3.80[a]
	b	0.01[a,b]	0.01[a,b]	0.006[a]	0.006[a]
Cd···C	r	*3.03*(3)	*3.03*(3)	*3.02*(3)	*3.01*(3)
	b	*0.010*(2)	*0.012*(2)	*0.009*(1)	*0.009*(1)
	n	4[a]	4[a]	4[a]	4[a]
Tris-complex					
Cd–N	r	*2.378*(6)	*2.371*(4)	*2.371*(5)	*2.371*(5)
	b	*0.0032*(3)	*0.0033*(2)	*0.0031*(5)	*0.0031*(5)
	n	*5.94*(9)	6[a]	*6.0*(1)	6[a]
N···N	r	*3.32*(9)	*3.44*(9)	3.35[a]	3.35[a]
	b	0.01[a,b]	0.01[a,b]	0.006[a]	0.006[a]
Cd···C	r	*3.17*(2)	*3.18*(2)	*3.18*(1)	*3.19*(1)
	b	*0.0098*(7)	0.01[a]	*0.0074*(6)	*0.0075*(5)
	n	*6.0*(2)	6[a]	*5.6*(2)	6[a]

a) Fixed. b) Y. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **44**, 2926 (1971).

the bis-complex were fixed and the temperature factors of the N···N interactions within both bis- and tris-complexes were held constant at 0.01 Å^2, which was obtained in the gas phase. Beside A-2, various attempts were made for the sets of the parameters with descretely changing temperature factors of the N···N interactions of the complexes over the range $b_{N\cdots N}$ from 0.01 to 0.006 Å^2 (twice of the $b_{Cd\cdots N}$ value). However, no appreciable change for all parameter values was found, typical results being shown in A-3 and A-4 of Table 2. In these treatments $r_{N\cdots N}$ and $b_{N\cdots N}$ of the bis- and tris-complexes were fixed and $n_{Cd\cdots C}$ of the tris-complex was varied in A-3, while $n_{Cd\cdots C}$ of the tris-complex was fixed at 6 in A-4. Thus, it was found that the temperature factor of the N···N interactions within the complexes were insensitive to the parameter values given in Table 2. The parameter values were not practically influenced by changing $s_{\min}$ from 4.5 to 7.0 Å^{-1} ($s_{\max}$ was 16.7 Å^{-1}).

Similar treatments were examined for evaluating parameter values of the bis-complex. Thus, for solution B four types of the refinement (B-1, B-2, B-3, and B-4 in Table 3) were carried out. In types B-1 and B-3, the frequency factors of the Cd–N and nonbonding Cd···C interactions, as well as other parameter values indicated by italic, were refined. In types B-2 and B-4, on the other hand, a tetrahedral structure of the bis-complex was assumed. In B-1 and B-2, the temperature

TABLE 3. RESULTS OF THE LEAST-SQUARES REFINEMENTS OF SOLUTION B
The parameter values, r=distance (Å), b=temperature factor (Å^2) and n=number of distance per cadmium(II) atom were refined. Standard deviations are given in parentheses.

Interaction	Parameter	B-1	B-2	B-3	B-4
O···O(NO_3^-)	r	*2.17*(1)	*2.18*(2)	*2.17*(2)	*2.18*(2)
C···N(en)	r	*2.50*(4)	*2.54*(7)	*2.56*(5)	*2.57*(5)
Bis-complex					
Cd–N	r	*2.341*(3)	*2.341*(5)	*2.338*(4)	*2.339*(4)
	b	*0.0032*(1)	*0.0032*(3)	*0.0034*(2)	*0.0034*(2)
	n	*3.98*(4)	4[a]	*3.97*(5)	4[a]
N···N	r	*3.7*(1)	*3.6*(1)	3.82[a]	3.82[a]
	b	0.01[a,b]	0.01[a,b]	0.006[a]	0.006[a]
Cd···C	r	*3.05*(1)	*3.04*(1)	*3.04*(1)	*3.04*(1)
	b	*0.0067*(3)	*0.007*(1)	0.007[a]	0.007[a]
	n	*3.88*(7)	4[a]	*3.79*(9)	4[a]

a) Fixed. b) Y. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **44**, 2926 (1971).

factor of the N···N interaction within the bis-complex was assumed to be 0.01 Å^2, whereas the value was fixed at 0.006 Å^2 in the treatments of B-3 and B-4. In these four refinements, all of the parameter values of the tris-complex were fixed, because the concentration of the tris-complex was so low compared with that of the bis-complex that a reasonable refinement of the parameter values of the tris-complex could not be achieved by the least-squares method for the reduced intensities of the solution. Therefore, the parameter values of the tris-complex determined in the previous section were used in these calculations. In the refinement of the values of solution A, however, the parameter values of the bis-complex were also optimized, together with those of the tris-complex, since the concentration of the bis-complex was about 30 mol%.

The results obtained by these refinements obviously exclude the existence of the octahedral $Cd(OH_2)_2(en)_2^{2+}$ complex as the bis-species. If the $Cd(OH_2)_2(en)_2^{2+}$ complex would form, instead of $Cd(en)_2^{2+}$, the frequency factor for the Cd–N interaction within the bis-complex would be optimized to 6 in the treatments of B-1 and B-3, because the Cd–O bond would not be clearly distinguished from the Cd–N bond by the present measurements. When we fixed the $n_{\text{Cd–N}}$ values of the bis-complex at 6, a fairly large error-square sum was resulted compared with that of B-4 in which $n_{\text{Cd–N}}$ was fixed at 4. Moreover, the $n_{\text{Cd–N}}$ value of the bis-complex tended to decrease and approached 4 in the course of the least-squares refinement of the $s \cdot i(s)$ values. Therefore, we concluded that the formation of the $Cd(en)_2^{2+}$ complex of a tetrahedral structure was confirmed and the existence of the $Cd(OH_2)_2(en)_2^{2+}$ was excluded. The parameter values listed in Table 3 were practically independent of varying s-regions from 5.0, 6.0, and 7.0 to 16.7 Å^{-1}. Since almost the same parameter values were obtained for the bis-complex regardless of the assumptions set for the calculations in the both solutions, the pre-assumption of $n_{\text{Cd–N}}=4$ for the bis-complex made in the treatment of solution A was confirmed as a reasonable one.

The observed intensities were compared with the calculated ones by using parameter values given in Tables 2 (A-2) and 3 (B-2) and Eq. 3:

$$i_{\text{calcd}}(s) = \sum\sum n_{ij}\{(f_i(s)+\Delta f_i')(f_j(s)+\Delta f_j') + (\Delta f_i'')(\Delta f_j'')\} \cdot \frac{\sin(r_{ij}s)}{(r_{ij}s)} \exp(-b_{ij}s^2). \quad (3)$$

A reasonable agreement was found for both curves A and B in Fig. 2 except at the low angle part of the intensity curves where long range intermolecular interactions significantly contribute to the curves.

In the bis- and tris(ethylenediamine)zinc(II) complexes,[1] the Zn–N bond of the former complex is shorter than that of the latter, as is expected from the smaller crystal ionic radius of zinc(II) ion within a complex of a tetrahedral structure than that of an octahedral one. In crystal the ionic radius of cadmium(II) ion having the coordination number 4 is also smaller than that of the coordination number 6.[6] However, in cadmium(II) iodide complexes in solution, we have found that the Cd–I bond distance within the distorted octahedral $CdI(H_2O)_5^+$ complex does not appreciably change by replacing the five water molecules to three iodide ions to form the tetrahedral CdI_4^{2-} complex.[2,7] In the case of cadmium ethylenediamine complexes, the change in the Cd–N bond distance with changing coordination number of the cadmium(II) ion was only a few hundredths ångstroms, which is much smaller than the difference of the bond length in the crystalline state.[6] The distance of the Cd–NH_3 bond within the $Cd(NH_3)_6^{2+}$ complex is also 2.37 Å.[8]

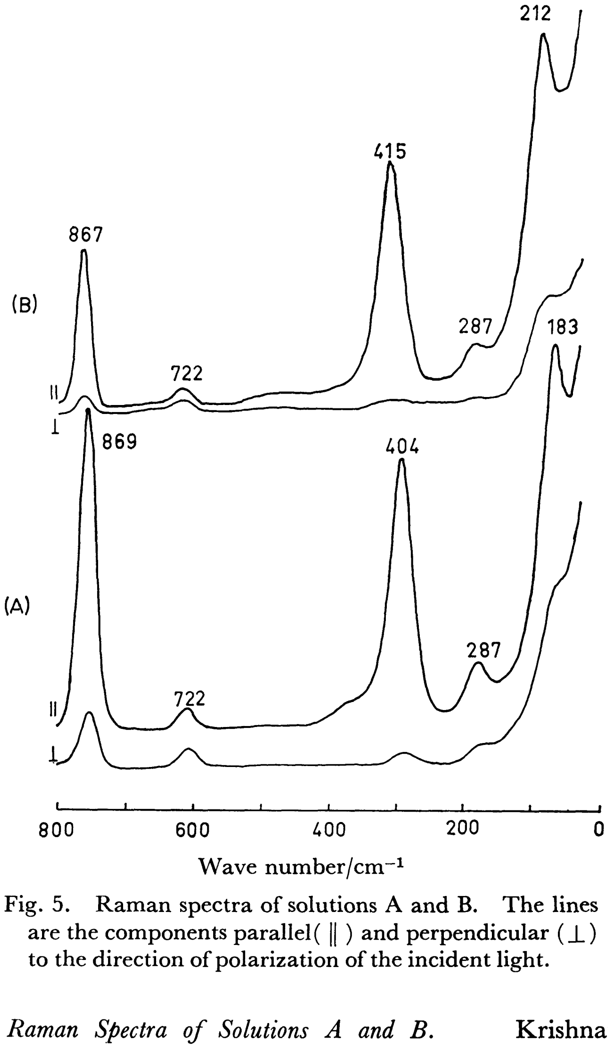

Fig. 5. Raman spectra of solutions A and B. The lines are the components parallel(||) and perpendicular (⊥) to the direction of polarization of the incident light.

Raman Spectra of Solutions A and B. Krishnan and Plane[9] reported Raman spectra of the tris(ethylenediamine)cadmium(II) complex in an aqueous solution and assigned the line at 400 cm^{-1} to the totally symmetric Cd–N stretching vibration of the tris-complex. In solution A in this study we found a strongly polarized band at 404 cm^{-1} (Fig. 5). Another strong line observed at 869 cm^{-1} was ascribed to the CH_2 rocking vibration within ethylenediamine molecules.[10] A weak band at 722 cm^{-1} was assigned to the ν_4-vibration of nitrate ions. Some lines found in the region 170—300 cm^{-1} were not assignable. Krishnan and Plane[9] observed a line at 435 cm^{-1}, which was assigned to the totally symmetric Cd–N stretching for the bis(ethylenediamine)cadmium(II) complex. However, in solution B we found a strongly polarized band at 415 cm^{-1} which might be ascribed to the totally symmetric Cd–N stretching of the bis-complex. The band of the bis-complex shifted by only 11 cm^{-1} to the higher frequency compared with that of the tris-complex. The bands appearing at 722 and 867 cm^{-1} were assignable to the nitrate ν_4 and CH_2 rocking vibrations, respectively.

The difference of the frequencies of the Cd–N stretching of the bis- and tris-complexes was small in contrast to the case of the zinc(II) ethylenediamine complexes.[1] The Cd–N bond distances within the bis-complex was almost the same as that of the tris-complex, whereas in the zinc(II) system the Zn–N bond length within the bis(ethylenediamine)zinc(II) complex was much shorter than that within the tris(ethylenediamine)zinc(II) complex, and the shorter Zn–N bond having a higher frequency within the bis-complex was concluded to be stronger than the longer Zn–N bond with lower frequency within the tris-complex, as described in the preceding paper.[1] In the case of cadmium ethylenediamine complexes, however, strength of the Cd–N bonds within the bis- and tris-complexes may not be appreciably different, because the lengths of the Cd–N bonds within the both complexes are practically the same and the shift of the frequency of the stretching vibration of the Cd–N bond within these complexes by changing their structures was small.

The Cd–N stretching vibration of the $Cd(NH_3)_6^{2+}$ complex appears at 341 cm^{-1},[8] which is lower than that of the tris-complex by about 63 cm^{-1}. The Cd–N bond distances within the hexaamminecadmium(II) and the tris-complexes are not significantly different, however. The higher frequency of the Cd–N stretching of the ethylenediamine complex may be due to coordination of a less freely movable amino group, which is attached to a CH_2 group, to the central metal ion, and the strength of the Cd–N bond within the $Cd(en)_3^{2+}$ and $Cd(NH_3)_6^{2+}$ complexes may be almost identical, because the enthalpy changes of the formation of the tris-complex ($\Delta H^\circ \simeq -84$ kJ mol^{-1}) is essentially the same as that of the hexaamminecadmium(II) complex ($\Delta H^\circ \simeq -88$ kJ mol^{-1}).[11]

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