An X-Ray Diffraction Study on the Structures of Bis- and Tris(ethylenediamine)nickel(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

(Received August 21, 1981)

The structures of nickel(II) complexes with ethylenediamine(en) in solution have been determined by means of X-ray diffraction. The measurements were performed at 25 °C for aqueous ethylenediamine solutions of nickel nitrate, the mole ratios (en/Ni) in the solutions being 3.964, 3.672, 2.071, and 1.892. In the two solutions of the higher en/Ni mole ratio, the tris(ethylenediamine)nickel(II) complex was predominant, whereas in the other solutions the bis(ethylenediamine)nickel(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 ethylenediamine and two oxygen atoms within water molecules were octahedrally coordinated to the central nickel(II) atom, the oxygen atoms being assumed to be axially bonded. The Ni–N bond length within the bis-complex was 2.10 Å, which was almost the same as the length of the Ni–O bonds. The nonbonding Ni···C distance was 2.82(2) Å. In the tris-complex the nickel ion was coordinated with six nitrogen atoms and Ni–N and Ni···C distances were determined to be 2.202(4) Å and 2.88(1) Å, respectively. These parameter values obtained in the experiment were compared with the crystallographic data reported.

The structures of the bis- and tris(ethylenediamine)-zinc(II) and -cadmium(II) complexes have recently been reported.[1,2] In the present study, we have attempted to determine the structures of the bis- and tris(ethylenediamine)nickel(II) complexes in aqueous nitrate solutions in a series of structural studies of chelate complexes of transition metals in solution. The ground state of a nickel(II) octahedral complex is known to have the electronic configuration of $(t_{2g})^6(e_g)^2$ and thus most nickel(II) complexes have the O_h symmetry in the solid state. In a complex of the NiA_4B_2 type (A and B denote ligand atoms) in which B atoms locate along the axis of the octahedron, the symmetry of the complex may be approximated to be D_{4h}. Most of the bis-nickel(II) chelate complexes with bidentate ligands have the symmetry of this type.[3] The distortion of the symmetry of such nickel(II) complexes has been extensively investigated by means of electronic spectra and X-ray diffraction in crystal.[4]

Dorosh and Skryshevskii[5] reported the distorted octahedral structures of $Ni(OH_2)_6^{2+}$ with two different Ni–O bond lengths of 2.0—2.1 and 2.25—2.30 Å by means of X-ray diffraction in solution. However, according to a recent study the $Ni(OH_2)_6^{2+}$ complex has a regularly octahedral structure with the length of Ni–O=2.04 Å.[6]

Many works on the crystal structures of the $Ni(en)_3^{2+}$ complex with various counter anions have been carried out and showed that the $Ni(en)_3^{2+}$ complex has a regularly octahedral structure independent of the counter anions. In the $Ni(en)_3SO_4$ salt, the Ni–N bond length was found to be 2.12 Å.[7] In the structure of $Ni(en)_2(NCS)_2$, on the other hand, the equatorial Ni–N bond distance was 2.10 Å and the Ni–NCS bond length in the axial position was 2.15 Å, the latter being slightly longer than the former. Thus the structure of the $Ni(en)_2(NCS)_2$ complex is distorted octahedral.[8] The structure of the $Ni(en)_2(OH_2)_2^{2+}$ has not been investigated either in the crystalline state or in solution. In this paper, the structural determination of the bis- and tris(ethylenediamine)nickel(II) complexes has been attempted by the X-ray diffraction method in solution.

Experimental

Preparation and Analysis of Sample Solutions. Ethylenediamine was purified by the method previously reported.[1] Nickel(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 nickel(II) nitrate into aqueous ethylenediamine solutions.

The concentration of nickel(II) ions in the test solutions was determined by gravimetry using dimethylglyoxime. The concentration of the nitrate ion was calculated from the stoichiometry of the nickel nitrate. The density of the test solutions was measured pycnometrically. The composition of the test solutions is given in Table 1.

Table 1. Composition of solutions A, B, C, and D (mol/dm^3)

	A	B	C	D
Ni	1.476	1.356	1.717	1.787
N	13.79	13.46	10.54	10.34
C	10.84	10.75	7.113	6.762
O	42.69	42.34	50.13	50.09
H	111.0	111.4	106.1	92.27
$\rho/g\,cm^{-3}$	1.205	1.187	1.227	1.237
$V/Å^3$	1267	1224	967.1	929.2
en/Ni	3.672	3.964	2.071	1.892

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.[6,9] 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 the whole angle range. Corrections and analysis of the scattering data were performed in the same ways to those previously reported.[1,2,6,9,10] 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:

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

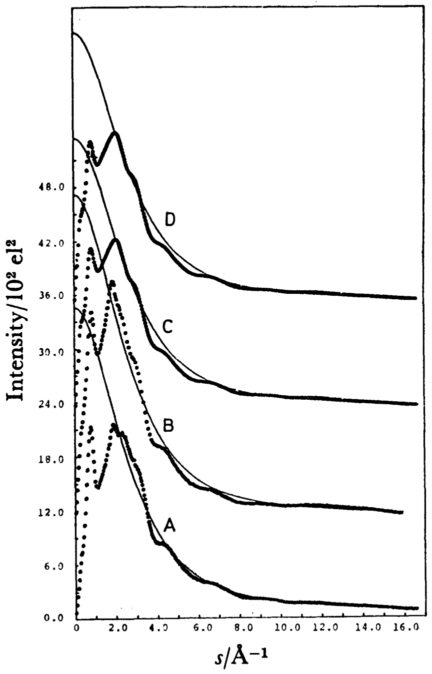

Fig. 1. Coherent scattering intensities of sample solutions A, B, C, and D. Experimentally obtained intensities I^{coh} are shown by circles and calculated values of independent scattering intensities by solid lines.

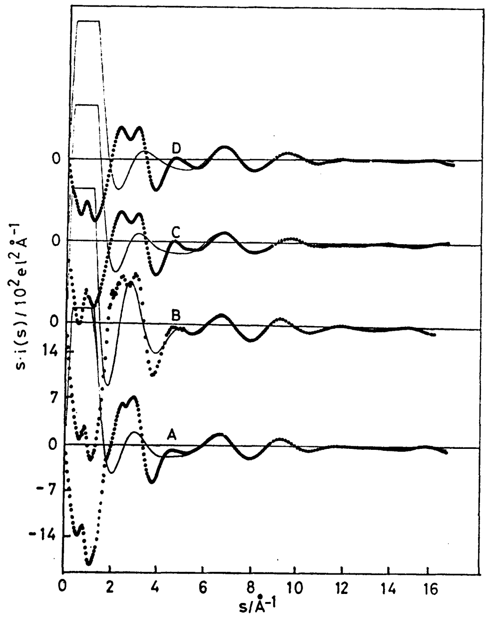

Fig. 2. The reduced intensities multiplied by s for solutions A, B, C, and D. The observed $s\cdot i(s)$ curves are shown by circles and the calculated ones by solid lines.

where ρ_0 is the average scattering density in the stoichiometric volume V of the solution per Ni atom, and s_{max} denotes the maximum s-value attained in the measurements ($s_{\mathrm{max}}=16.7$ Å^{-1}). $M(s)$ represents the modification function[10] and the reduced intensities $i(s)$ are given by

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

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.[11] 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.[6]

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

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

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

All calculations were performed with the electronic computers M-160 and M-180 by means of KURVLR program.[12]

Results and Discussion

According to the formation constants so far reported, sample solutions A and B contain the tris(ethylenediamine)nickel(II) complex as the main species and, on the other hand, sample solutions C and D contain the bis(ethylenediamine)nickel(II) complex as the predominant one.[13] Solutions A and B may contain a little amount of the bis-complex. In solutions C and D, small amounts of the mono- and tris-complexes may coexist with the bis-complex.

Solution A. From the diffraction data after corrections for absorption and polarization[9] (Fig. 1A), the $s\cdot i(s)$ curve (Fig. 2A) was obtained and then, the radial distribution function $D(r)$ was drawn by using the Fourier transformation according to Eq. 1 (Fig. 3a). A broad and small peak at about 1.0—1.3 Å in the $D(r)$ curve 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 as we have pointed out in the previous papers[1,2] (Fig. 3b). The second peak appearing at 2.2 Å is attributed to the Ni–N bond within the metal complex, the O···O pairs within nitrate ions and the C···N interactions within ethylenediamine molecules.

The third peak at about 2.9 Å may be mainly ascribed to nonbonding Ni···C and O···O interactions within the metal complex and in bulk water, respectively. The O···O interactions between nitrate ions and water molecules may contribute to some extent to this peak. In the analysis of the radial distribution curve of solution A which contains a small amount of the bis-complex, the amount of the bis-complex coexisting was assumed to be negligible at the first approach. After subtraction of the theoretical peaks of the intramolecular interactions within ethylenediamine molecules and nitrate ions, the chain line (·—·—·) was obtained as the residual curve, from which we obtained the parameter values of intramolecular interactions of the tris-complex. A successive approximation which has been described in the previous papers[1,2] was employed in order to refine the parameter values thus obtained on the assumption of the existence of the only tris-complex, but assumptions taking into account the coexistence of various amounts of the bis-complex in

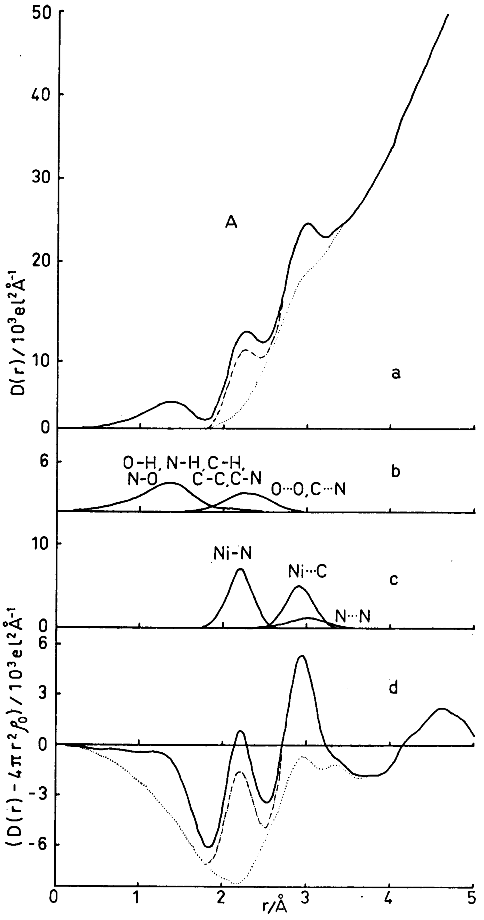

Fig. 3. (a) : $D(r)$ curve for solution A. The chain line (•—•—) shows the residual curve after subtraction of the theoretical peak shapes shown in (b) from the original radial distribution curve represented by the solid line. The dotted line shows the residual curve after subtraction of the theoretical peak shapes shown in (c) from the data represented by the chain line. (b) and (c) : The theoretical peak shapes for atom pairs. (d) : The corresponding $D(r)-4\pi r^2\rho_0$ curve to (a).

solution A did not improve the parameter values of the tris-complex. The lengths of the Ni–N bond and nonbonding Ni···C interaction were found to be 2.20 and 2.90 Å, respectively. The distance of the N···N pair was estimated to be $\sqrt{2}$ times the length of the Ni–N bond. The area under the peak at 2.20 Å corresponded to six Ni–N bonds. The temperature factors of the Ni–N and Ni···C interactions were evaluated to be 0.002—0.003 Å^2 and 0.005—0.007 Å^2, respectively. Subtraction of the peaks of all the intramolecular interactions from the original radial distribution curve led to a smooth background having no appreciable peak over the range <4 Å, expect 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. From the analysis of the radial distribution curve of solution A, the tris(ethylenediamine)nickel(II) complex in the solution was concluded to have an octahedral structure.

Solution B. The atomic composition in solution B was almost the same as that in solution A, and solution B was considered to contain the tris(ethylenediamine)nickel(II) complex as the main species with a very small amount of the bis-complex. The analytical procedure of solution B was the same as that in the case of solution A. The radial distribution curve of solution B showed that the lengths of the Ni–N bond and nonbonding Ni···C interaction were 2.20 Å and 2.90 Å, respectively, which were consistent with the results obtained in solution A. The parameter values of the tris(ethylenediamine)nickel(II) complex are further refined by the least squares method by using the reduced intensity data in the high angle region of the $s\cdot i(s)$.

Solutions C and D. According to the stability constants previously reported, solutions C and D contain a small amount of the tris- and mono-complexes besides the bis-complex as the main species.[10] In the course of the analysis of the radial distribution curve

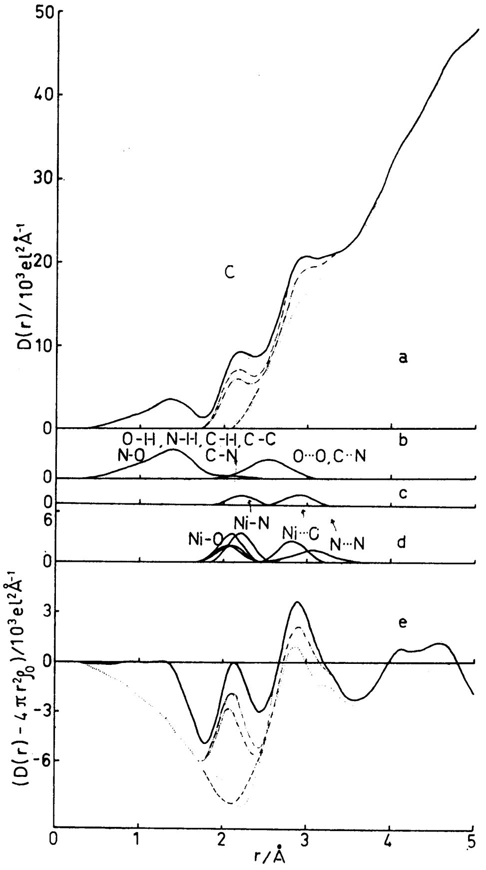

Fig. 4. (a) : $D(r)$ curve for solution C. The chain line (•—•—) shows the residual curve after subtraction of the theoretical peaks in (b). The chain line with double-dots (••—••) is obtained after further subtraction of the theoretical peak shapes due to the tris-complex in (c) from the data represented by the chain line, •—•—. After subtraction of the theoretical peak shapes due to the biscomplex assuming that both the Ni–N and Ni–O bond distances are 2.10 Å, the dashed line is obtained as the residual curve. Assuming that the Ni–O distance is the same as that $Ni(OH_2)_6^{2+}$ and that the Ni–N distance is slightly larger than 2.10 Å, the dotted line is obtained as the residual curve. (b), (c),. and (d) : The theoretical peak shapes for atom pairs. (e) : The corresponding $D(r)-4\pi r^2\rho_0$ curve to (a).

in solution C, the tris-complex was assumed to coexist with the bis-complex, whereas the formation of the mono-complex was neglected.

The analytical procedure of the radial distribution curve of solution C is as follows.

By introducing the parameter values of the tris-complex found from the analysis of solutions A and B, the parameter values of the bis(ethylenediamine)nickel(II) complex was obtained by changing the mole ratio of the bis-/tris-complexes until a smooth background curve was obtained in the residual radial distribution curve. The chain line (·–·–·) in Fig. 4 was obtained after subtraction of the peaks of the intramolecular interactions of ethylenediamine molecules and nitrate ions from the original radial distribution curve, and further subtraction of the theoretical peaks of the tris-complex from the curve led to the chain line with double-dots (··–··–··). The curve (··–··–··) might show the radial distribution curve due to the bis-complex. The area under the peak at 2.10 Å approximately corresponded to six Ni–N pairs. Since the bis-complex has at most four Ni–N bonds within it, the other two pairs must be Ni–O ones, because X-ray scattering due to the Ni–O bond is close to that due to the Ni–N bond as far as the bond lengths of the pairs are practically the same. Thus, we concluded that the bis-complex has four Ni–N bonds and two Ni–O bonds within the complex.

The structure of $Ni(OH_2)_6^{2+}$ in an $Ni(ClO_4)_2$ solution has been determined by X-ray diffraction method and the length of the Ni–O bond has been estimated to be 2.04 Å.[6] Bol, *et al.*[14] reported a slightly longer Ni–O bond length (2.06 Å) in a nickel(II) nitrate solution than that reported by Ohtaki *et al.*[6] However, if we assume that the Ni–O bond length within the $Ni(en)_2(OH_2)_2^{2+}$ was 2.04—2.06 Å, the theoretical radial distribution curve showed descrepancies from the experimental curve, and the radial distribution curve in solution C could be better explained by assuming the Ni–O bond distance within the bis-complex to be about 2.10 Å, which was almost the same length as the Ni–N bond. The results obtained from the studies by means of infrared[15] and electronic[16] spectroscopic analyses suggested that the bis(ethylenediamine)nickel(II) complex has two water molecules at the axial positions. Since the area under the peak at 2.10 Å corresponded to the sum of four Ni–N and two Ni–O bonds, the bis-complex was concluded to be almost regularly octahedral which contained two water molecules at the axial positions, and thus, the residual radial distribution curve of solution C was well analyzed by assuming the bond distances of the Ni–N: 2.10 Å (the frequency factor $n_{\text{Ni–N}}=4$), Ni–O : 2.10 Å ($n_{\text{Ni–O}}=2$), Ni···C : 2.87 Å ($n_{\text{Ni}\cdots\text{C}}=4$), and N···N (or N···O) $=\sqrt{2}\times 2.10$ Å ($n_{\text{N}\cdots\text{N}}+n_{\text{N}\cdots\text{O}}=12$), and no appreciable peak remained on the double-dotted curve over the range <4 Å except for the broad peak at around 3.0 Å, which was attributed to the O···O interactions in bulk water and the hydrated nitrate ions.

Solution D may contain a small amount of the mono-complex and a lesser amount of the tris-complex according to the literature.[13] However, the concentration of the mono-complex is too small to be determined by the present X-ray diffraction method, and thus, the radial distribution curve of solution D could be analyzed assuming the only bis-complex existed in the solution. The essentially same procedure as that used in the analysis of the radial distribution curve of solutions A and B was employed. The parameter values of the bis-complex obtained from the analysis of the radial distribution curve of solution D were almost consistent with those obtained in solution C. The parameter values obtained by analyzing the radial distribution curves of each solution were refined by the least squares method using the intensities $s\cdot i(s)$ in the high angle region ($4\ \text{Å}^{-1}\lesssim s\lesssim 16\ \text{Å}^{-1}$).

Least Squares Refinements. The intensity data in the high angle region ($s>4\ \text{Å}^{-1}$) of the $s\cdot i(s)$ curves of solutions A, B, and C were used for the least squares refinements[17] of the structural parameters of the bis- and tris-complexes. For avoiding errors introduced by neglecting long range intermolecular interactions in the course of least squares calculations, the lowest s-value was varied from 4.5 Å^{-1} to 7 Å^{-1}.

In the A-1 type calculation of the least squares refinement of the intensity data of solution A, the frequency factor (n) of the metal-ligand bond was floated. The frequency factors of the Ni–N and Ni···C interactions of the tris(ethylenediamine)nickel(II) complex were actually six. In the A-2 type calculation, the bond distances and temperature factors were floated, while the frequency factors of the Ni–N and Ni···C interactions were kept constant ($n=6$). The final values of the Ni–N and Ni···C distances were 2.191(3) Å and 2.876(8) Å, respectively (Table 2). The values of the Ni–N and Ni···C distances were practically independent of the type of calculations.

Table 2. Results of the least squares refinements of solution A

Interaction	Parameter	A-1[b]	A-2[b]
O···O(NO_3^-)	r/Å	2.25(2)	2.24(2)
C···N (en)	r/Å	2.46(4)	2.48(3)
N···N (en)	r/Å	2.87(6)	2.92(5)
$Ni(en)_3^{2+}$			
Ni–N	r/Å	2.193(4)	2.191(3)
	b/Å^2	0.0022(3)	0.0025(2)
	n	5.99(9)	6[a]
Ni···C	r/Å	2.87(1)	2.876(8)
	b/Å^2	0.005[a]	0.005[a]
	n	6.2(1)	6[a]

a) Fixed. b) Standard deviations are given in parentheses.

By the same procedure of the least squares refinements of the intensity data of solution B, the Ni–N and Ni···C distances were found to be 2.202(4) Å and 2.88(1) Å, respectively.

In the least squares calculations of solution C, an assumption of two water molecules binding to the central nickel(II) ion within the bis(ethylenediamine)nickel(II) complex was introduced as an initial condition which should be refined in the course of the calcula-

TABLE 3. RESULTS OF THE LEAST SQUARES REFINEMENTS OF SOLUTION C[a)]

Interaction	Parameter	$5.0<s/\text{Å}^{-1}<16.7$	$6.0<s/\text{Å}^{-1}<16.7$
Ni–O	r/Å	2.10(1)	2.10(1)
	b/Å^2	0.0030(7)	0.0029(7)
	n	2.00(7)	2.1(1)
Ni–N	r/Å	2.102(7)	2.099(8)
	b/Å^2	0.0028(4)	0.0027(4)
	n	4.00(9)	4.2(1)
Ni⋯C	r/Å	2.82(2)	2.83(2)
	b/Å^2	0.0046(7)	0.0048(8)
	n	4.1(2)	4.2(2)
N⋯N	r/Å	3.01(5)	3.06(7)

a) The concentration of the tris-complex is assumed to be 20 mol% on the basis of the stability constants reported in the literature. Standard deviations are given in parentheses.

TABLE 4. FINAL VALUES OF THE INTRAMOLECULAR DISTANCES (Å) WITHIN THE BIS- AND TRIS(ETHYLENEDIAMINE)Ni(II)COMPLEXES

	Bis-complex[a)]	Tris-complex[a)]
Ni–N	2.102(7)	2.202(4)
Ni–O	2.10(1)	—
Ni⋯C	2.82(2)	2.88(1)
Structure	Regular octahedron	

a) The values in parentheses are their standard deviations.

tions. The final results showed that the frequency factors of the Ni–O interaction was about two and those of the Ni–N and Ni⋯C interactions within the bis-complex were approximately four (Table 3). In the least squares calculations of the intensity data of solution C, various types of calculation were carried out. In one case, the frequency factors of the Ni–N or Ni⋯C interactions within the bis-complex were held constant at four, other parameter values being refined. In other cases, the frequency factor of the Ni–O bond was fixed at two by assuming the structures of the bis-complex, and other parameters were refined. The s_{min}-value was changed in some cases. All the calculations examined here led to almost the same values of the Ni–N and Ni–O bond lengths. The final results obtained in the calculations were summarized in Table 3, in which the bond lengths, temperature, and frequency factors were floated. The results obtained by the calculations gave almost the same results as listed in Table 3 and the distances of the Ni–N and Ni–O bonds were finally determined to be 2.10 Å. Consequently, the bis(ethylenediamine)nickel(II) complex has almost a regularly octahedral structure with four nitrogen and two oxygen atoms. The parameter values obtained in the analysis of the intensity data of solution D were almost the same as those obtained for solution C. As shown in Fig. 2, the $s\cdot i(s)$ curves calculated from the refined parameters thus obtained well fit the observed $s\cdot i(s)$ curves in the region 5 Å^{-1}<s<16 Å^{-1}. The final parameter values found in this study are summarized in Table 4.

In the X-ray crystal analysis, the Ni–N bond distance within the tris(ethylenediamine)nickel(II) complex has been found to be 2.07—2.17 Å (Table 5). The Ni–N bond distance within the tris-complex in solution found in the present study is 2.20 Å, which is slightly longer than the distances found in crystals. The bis(ethylenediamine)nickel(II) complex in crystals has the Ni–N bond distances of 2.08—2.12 Å, which is almost the same as that in this study (Table 5).

The work has partially been supported by the Grant-in-Aid for Scientific Research No. 343011 from the Ministry of Education, Science and Culture.

References

1) T. Fujita, T. Yamaguchi, and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **52**, 3539 (1979).

2) T. Fujita and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **53**, 930 (1980).

3) K. Ueno, "Kireito Kagaku," Nankodo, Tokyo (1976), Vol. 2.

TABLE 5. THE Ni–N AND Ni–O DISTANCES WITHIN THE BIS- AND TRIS(ETHYLENEDIAMINE)-NICKEL(II) COMPLEXES IN CRYSTAL AND IN SOLUTION

Compound	Ni–N(Ni–O)(Å)	Author
$\text{Ni(en)}_3\text{(NO}_3)_2$	2.120	Swink and Atoji[a)]
$[\text{Ni(en)}_3]\text{Si}_2\text{O}_5\cdot 8.7\text{H}_2\text{O}$	2.066—2.171	Smolin[b)]
$\text{Ni(en)}_3\text{SO}_4$	2.124	Ul-Haque *et al.*[c)]
$[\text{Ni(en)}_3](\text{O}_2\text{C}_2\text{H}_3)_2\cdot 2\text{H}_2\text{O}$	2.104—2.139	Cramer *et al.*[d)]
$[\text{Ni(en)}_3][\text{B(C}_6\text{H}_5)_4]_2\cdot 3(\text{CH}_3)_2\text{SO}$	2.11—2.17	Cramer and Huneke[e)]
$\text{Ni(en)}_2\text{(NCS)}_2$	2.09—2.11	Brown and Lingafelter[f)]
$[\text{Ni(en)}_2(\text{OH}_2)(\text{BF}_4)]\cdot\text{BF}_4$	2.08—2.12(2.19)	Tomlinson *et al.*[g)]
$[\text{Ni(en)(OH}_2)_4](\text{NO}_3)_2$	2.08(2.10)	Komiyama and Lingafelter[h)]
$\text{Ni(en)}_3{}^{2+}$	2.20	This work[i)]
$\text{Ni(en)}_2(\text{OH}_2)_2{}^{2+}$	2.10(2.10)	This work[i)]

a) L. N. Swink and M. Atoji, *Acta Crystallogr.*, **13**, 639 (1960). b) Yu. I. Smolin, *Soviet Phys. Crystallogr.*, **15**, 23 (1970). c) M. Ul-Haque, C. N. Caughlan, and K. Emerson, *Inorg. Chem.*, **9**, 2421(1970). d) R. E. Cramer, W. Van Doorne, and J. T. Huneke, *ibid.*, **15**, 529 (1976). e) R. E. Cramer and J. T. Huneke, *ibid.*, **17**, 365 (1978). f) B. W. Brown and E. C. Lingafelter, *Acta Crystallogr.*, **16**, 753 (1963). g) A. A. G. Tomlinson, M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J. Chem. Soc., Dalton Trans.*, **1972**, 1671. h) Y. Komiyama and E. C. Lingafelter, Reports Faculty Eng. Yamanashi University, **1963**, 5. i) In solution.

4) K. O. Joung, C. J. O'Conner, E. Sinn, and R. L. Carlin, *Inorg. Chem.*, **18**, 804 (1979).

5) A. K. Dorosh and A. F. Skryshevskii, *Zh. Strukt. Khim.*, **8**, 348 (1967).

6) H. Ohtaki, T. Yamaguchi, and M. Maeda, *Bull. Chem. Soc. Jpn.*, **49**, 701 (1976).

7) M. Ul-Haque, C. N. Caughlan, and K. Emerson, *Inorg. Chem.*, **9**, 2421 (1970).

8) B. W. Brown and E. C. Lingafelter, *Acta Crystallogr.*, **16**, 753 (1963).

9) H. Ohtaki and M. Maeda, *Bull. Chem. Soc. Jpn.*, **47**, 2197. (1974); H. Ohtaki, M. Maeda, and S. Ito, *ibid.*, **47**, 2217 (1974).

10) T. Yamaguchi and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **51** 3227 (1978).

11) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965); D. T. Cromer, *J. Chem. Phys.*, **50**, 4857 (1965); D. T. Cromer and D. Liberman, *ibid.*, **53**, 1891 (1970).

12) G. Johansson and M. Sandström, *Chem. Scripta*, **4**, 195 (1973).

13) L. G. Sillén and A. E. Martell, "Stability Constants," ed by The Chemical Society, London, Spec. Publ. No. 17 (1964) and Supplement No. 1 Spec. Publ. No. 25 (1971).

14) W. Bol, G. J. A. Gerrits, and C. L. P. van Eck, *J. Appl. Chem.*, **3**, 140 (1970).

15) R. J. H. Clark and R. E. Hester, "Advances in Infrared and Raman Spectroscopy," Heyden, London (1976), Vol. 1.

16) K. Yamasaki and H. Yamatera, "Mukikagaku Zensho: Suppl., Sakutai," Maruzen, Tokyo (1969), p. 129.

17) J. Waser and V. Schomaker, *Rev. Mod. Phys.*, **25**, 671 (1953); K. Furukawa, *Rep. Prog. Phys.*, **25**, 395 (1962); T. Yamaguchi, Doctor Thesis, Tokyo Institute of Technology (1978).