March, 1982] © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***55***, *817—821 (1982)* 817

# The Structure of Nickel(II) Bromide in Highly Concentrated Aqueous Solution by X-Ray Diffraction Analysis

Hisanobu Wakita,* Mitsuyoshi Ichihashi, Takeharu Mibuchi,**
and Isao Masuda
*Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma, Nishi-ku, Fukuoka 814-01*

(Received August 31, 1981)

An X-ray diffraction analysis of the aqueous nickel(II) bromide solutions with the concentrations of 2.004, 4.064, and 4.845 mol dm$^{-3}$ demonstrated the presence of the complex $[NiBr(H_2O)_5]^+$. This inner-sphere type complex has interatomic distances of 2.52—2.58 Å for Ni–Br and of 2.04—2.05 Å for Ni–$OH_2$. With an increase in the concentration the average number of the Ni–Br contacts per one $Ni^{2+}$ ion increased; it was found to be 0.18, 0.47, and 0.68 in the 2.004, 4.064, and 4.845 mol dm$^{-3}$ solutions, respectively.

The X-ray diffraction investigation by Mizuno[1)] showed that in crystalline $NiCl_2 \cdot 6H_2O$ the nickel ion has a unitary coordination geometry formulated as *trans*-$[NiCl_2(H_2O)_4]$. Caminiti *et al.*[2)] investigated the structure of the aqueous $NiCl_2$ solution by X-ray scattering measurements and showed that the nickel ion existed in the form of the hexaaqua complex $[Ni(H_2O)_6]^{2+}$ even if the concentration was as high as 4 mol dm$^{-3}$. The neutron diffraction measurement on the aqueous 4.41 mol kg$^{-1}$ $NiCl_2$ solution carried out by Soper *et al.*[3)] did not indicate any Ni–Cl interaction, though it confirmed the Ni–$OH_2$ and Cl–$OH_2$ interactions. The EXAFS spectra for the aqueous solutions of $NiCl_2$ (0.5 and 4 mol dm$^{-3}$) and of $NiBr_2$ (0.4 and 4 mol dm$^{-3}$), obtained by Lagarde *et al.*[4)] indicated no contact between $Ni^{2+}$ and halide ions. Sandstrom[5)] also demonstrated the EXAFS spectra of the aqueous $NiCl_2$ solutions of 2.78 and 3.74 mol dm$^{-3}$ indicated the presence of only the hexaaqua complex ion with the Ni–$OH_2$ distance of 2.07 Å.

On the other hand, the $^{17}O$-NMR relaxation rate measurements by Hertz *et al.*,[6,7)] supported the presence of the Ni–halogen bond in the first coordination sphere in the aqueous $NiCl_2$ and $NiBr_2$ solutions. Libuś *et al.*[8,9)] determined the molal-scale stability constant, $\beta_1$, of the halogenonickel(II) complex to be 0.10 for $X=Cl^-$ and 0.05 for $X=Br^-$, in the aqueous 2 mol kg$^{-1}$ $NiX_2$ solutions; however, they proposed that the Ni–Br interaction occurred with an outer-sphere coordination.

In this paper, in order to determine whether the nickel ion could form a halogeno complex of the inner-sphere type, an X-ray diffraction investigation has been carried out with highly concentrated aqueous $NiBr_2$ solutions.

## Experimental and Data Treatment

*Sample Solutions.* Sample solutions were prepared by dissolving $NiBr_2$, which was obtained by recrystallizing commercially available reagent grade nickel(II) bromide twice from water. The nickel and bromide ion concentrations in the solutions were determined by EDTA titration and the Volhard method, respectively. The density of the solutions was determined pycnometrically. The amount of water in the solutions was calculated from the nickel and bromide ion concentrations and the density. The composition of the sample solutions is shown in Table 1 along with the X-ray linear absorption coefficient of the solutions which were used for the absorption correction of X-ray intensity data.

Table 1. Composition and parameter values of sample solutions

| | Solution | | |
|---|---|---|---|
| | A | B | C |
| Ni (mol dm$^{-3}$) | 4.845 | 4.064 | 2.004 |
| Br (mol dm$^{-3}$) | 9.690 | 8.129 | 4.008 |
| O (mol dm$^{-3}$) | 46.48 | 47.95 | 53.02 |
| H (mol dm$^{-3}$) | 92.96 | 95.90 | 106.0 |
| $v$/Å$^3$ | 342.7 | 408.6 | 828.6 |
| $\rho$/g cm$^{-3}$ | 1.896 | 1.752 | 1.393 |
| $\mu$/cm$^{-1}$ | 76.05 | 63.97 | 32.20 |

$v$, Stoichiometric volume per one atom of nickel; $\rho$, density; $\mu$, linear absorption coefficient.

*X-Ray Diffraction Measurements.* The X-ray diffraction intensity data were recorded on a diffractometer by applying the Bragg-Brentano geometry.[10)] A cylindrical quartz-cell with 42 mm in diameter and 21 mm in depth filled with a sample solution was placed in the cell holder. Then the holder was covered with a holder cover which was made of Pyrex-glass and had a double layer Mylar window. The holder was set in a furnace thermostatted by means of circulating water. A Johansson type LiF monochrometer was placed between a receiving slit and a scintillation counter; a pulse height analyzer was used for further effective monochromatization. A Philips Mo X-ray tube ($\lambda=0.7107$ Å) was employed. The diffraction intensities were recorded at about 300 points in the angle range 60—0.5°, which corresponds to the $s$ value range 15.3—0.15 Å$^{-1}$, where $s=4\pi \sin\theta/\lambda$. The time required for accumulating 40000 counts was recorded at every 0.5° to $\theta=36°$, 0.25° to $\theta=18°$, and 0.1° to $\theta=0.5°$. Two sets of divergent and scattering slit combinations, 1°:1° and 1/6°:1/2° were employed. The recording was repeated twice for each sample solution.

*Treatment of Diffraction Intensity Data.* The diffraction intensities recorded by using each set of the slit combinations were corrected for the background scattering recorded for the cell without solution by using the same slit combination. And the intensities for 1°:1° slit combination were normalized to the intensities measured with the 1/6°:1/2° slit combination by using the data in the overlapping angle regions. Moreover, the intensity data were corrected for the polarization and absorption due to the sample solution. The

---

** Present address: Idemitsu Kosan Co. Ltd., Sodegaura-machi, Kimitsu-gun, Chiba 292-01.

scaling to the absolute intensities was made by the conventional high angle region method comparing the data in the high angle region ($\theta>45°$) with the sum of the coherent scattering, and by the method proposed by Norman[11] and Krogh-Moe.[12]

The atomic scattering factors for Ni, Br, and O atoms were cited from Cromer and Waber's paper,[13] and for H atom from the International Tables;[14] the incoherent scattering factors for Ni, Br, and O atoms were obtained from Balyuzi[15] and for H atom from Compton and Allison.[16] The incoherent scattering factors were corrected for the Breit-Dirac effect.[17] The values of the anomalous dispersion for these atoms were taken from Cromer's paper.[18] The reduced intensities *i(s)* due to the combinations of each pair of atoms were evaluated from the scaled intensities $I(s)$ in Eq. 1. In Eq. 1, $s$ represents $4\pi\sin\theta/\lambda$

$$i(s) = I(s) - \sum_{\mathrm{i}} n_{\mathrm{i}}\cdot\{f_{\mathrm{i}}(s)^2+del(s)\cdot I_{\mathrm{i}}^{\mathrm{inco}}(s)\} \qquad (1)$$

($\lambda=0.7107$ Å), $n_{\mathrm{i}}$ the number of atoms i, $f_{\mathrm{i}}(s)$ the atomic scattering factor corrected for the anomalous dispersion; $f_{\mathrm{i}}(s)^2=(f_{\mathrm{i}}^{\circ}(s)+\Delta f_{\mathrm{i}}'(s))^2+(\Delta f_{\mathrm{i}}'')^2$ where $\Delta f_{\mathrm{i}}'$ and $\Delta f_{\mathrm{i}}''$ is the real and imaginary parts of the anomalous dispersion, respectively; *del(s)* is the fraction of the incoherent radiation $I_{\mathrm{i}}^{\mathrm{inco}}(s)$ reaching the counter,[19] and was determined by measuring the resolving power of the monochrometer with the use of a calcite single crystal.[20]

The radial distribution function $D(r)$ was calculated by Eq. 2:

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

where $\rho_0$, given in electron units, is the average scattering density of a sample solution, $s_{\max}$ ($=15.3$ Å) the maximum $s$ value during the measurements; the modification function $M(s)$ given by Eq. 2′ was used in this study.

$$M(s) = \{\sum_{\mathrm{i}} n_{\mathrm{i}}\cdot f_{\mathrm{i}}(0)^2/\sum_{\mathrm{i}} n_{\mathrm{i}}\cdot f_{\mathrm{i}}(s)^2\}\cdot\exp(-0.01s^2) \qquad (2')$$

In the calculated radial distribution curve a small spurious peak appears in the region less than 1 Å where no interatomic interactions besides the O–H interactions in water molecules could be expected to appear. Then the correction for this spurious peak was made with the Fourier inversion method by considering the contribution of the O–H interactions in water molecules.[21] The intensities due to the interatomic interactions were calculated by Eq. 3:

$$i(s)_{\mathrm{calcd}} = \sum_{\mathrm{i}}\sum_{\mathrm{j}}^{\mathrm{i}\neq\mathrm{j}} n_{\mathrm{ij}}\cdot f_{\mathrm{i}}(s)\cdot f_{\mathrm{j}}(s)\frac{\sin(r_{\mathrm{ij}}\cdot s)}{r_{\mathrm{ij}}\cdot s}\exp(-b_{\mathrm{ij}}\cdot s^2), \qquad (3)$$

where $f_{\mathrm{i}}(s)$ and $f_{\mathrm{j}}(s)$ denote the scattering factors of atom i and j, respectively, and $r_{\mathrm{ij}}$ the average distance between atom i and j, $b_{\mathrm{ij}}$ the temperature factor ($=\langle\Delta r_{\mathrm{ij}}^2\rangle/2$; $\langle\Delta r_{\mathrm{ij}}^2\rangle$ is the mean square amplitude of the molecular vibration), and $n_{\mathrm{ij}}$ the frequency factor that were refined to minimize the following function $U$ by a least squares method.

$$U = \sum_{s_{\min}}^{s_{\max}} s^2\cdot[i(s)_{\mathrm{obsd}}-i(s)_{\mathrm{calcd}}]^2 \qquad (4)$$

In Eq. 4, $s_{\max}$ and $s_{\min}$ are the upper and lower limits in the selected $s$ regions. Calculations were carried out on a TOSBAC ACOS-600 computer at our University and on a FACOM M-200 computer at Kyushu University; the KURVLR[19] and NLPLSQ[22] programs were used.

## Results and Discussion

Both $D(r)$ and $D(r)-4\pi r^2\rho_0$ curves, shown in Figs. 1 and 2, exhibit four distinct peaks at 1.0, 2.1, 2.6, and 3.4 Å. As for the solution C, which is more diluted than the other solutions A and B, the peak at 2.6 Å is rather obscure, though the other three peaks are apparent. The distance of the first peak at 1.0 Å is consistent with that of the O–H bond in water molecules.[23] The second peak at 2.1 Å can be ascribed to the Ni–O interaction in the aqua complexes; a similar peak of the $D(r)$ curves has been reported to appear in the aqueous solutions of 2.491 mol dm$^{-3}$ $\mathrm{Ni(ClO_4)_2}$ at 2.04 Å,[22] of 4 mol dm$^{-3}$ $\mathrm{NiCl_2}$ at 2.06 Å,[2] and of 1 mol dm$^{-3}$ $\mathrm{Ni(NO_3)_2}$ at 2.06 Å.[24]

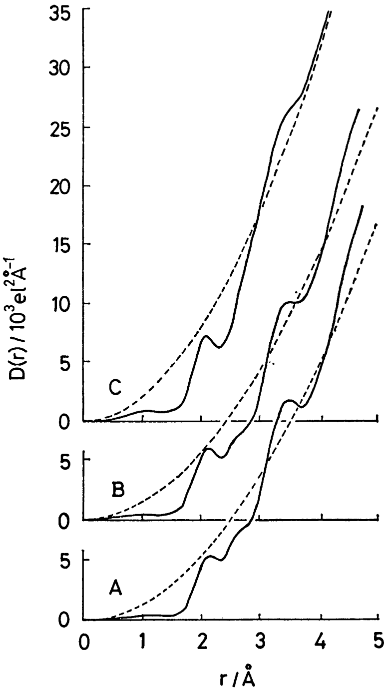

Fig. 1. Radial distribution curves $D(r)$ for the solutions A, B, and C; dashed line shows $4\pi r^2\rho_0$ curve.

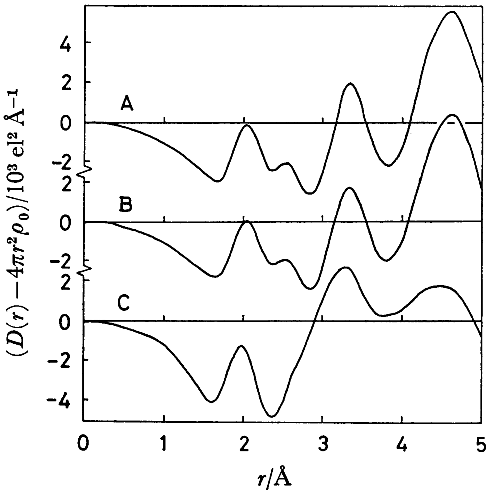

Fig. 2. $D(r)-4\pi r^2\rho_0$ curves for the solutions A, B, and C.

The peak at 2.6 Å may be attributed to the Ni–Br interaction, because the appearance of this peak is reflected by the concentration of $NiBr_2$ and the distance 2.6 Å is very close to the sum of the crystal radii of $Ni^{2+}$ and $Br^-$, *i.e.* 2.65 Å {=0.83 Å ($Ni^{2+}$)+1.82 Å ($Br^-$)}.[25] The solution equilibrium investigations indicated the formation of a monobromo complex. However, the formation constants $\beta_1$ were very small, ranging from 0.05 to 0.95.[26] By taking the datum $\beta_1=0.05$ reported by Libuś *et al.* for the aqueous 2 mol kg$^{-1}$ $NiBr_2$ solution, the monobromo complex presented in our solution C is evaluated to be 16% of the total $Ni^{2+}$ content.

The peak at 3.4 Å can be attributed to the Br–$OH_2$ interaction, because no comparable peak in this region on the radial distribution curve is observed for the aqueous 2.491 mol dm$^{-3}$ $Ni(ClO_4)_2$ solution, while a clear peak due to the Br–$OH_2$ interaction is observed at 3.4 Å for the aqueous 2.5 mol kg$^{-1}$ LiBr solution.[27]

On the basis of the above considerations, refinements of the numerical data on the interatomic distances, and frequency and temperature factors of these interactions have been made by the method of Eq. 4. The final data thus obtained are listed in Table 2. And Fig. 3 shows that the $s \cdot i(s)$ curves calculated from these final data are in good agreement with the observed $s \cdot i(s)$ curves in the region above $s>4$. Moreover, subtracting the calculated curve from the radial distribution curve gives a smooth curve indicating a good reliability of the final data, as seen in Figs. 4, 5, and 6.

TABLE 2. REFINED PARAMETERS OBTAINED FROM THE REDUCED INTENSITY CURVE

| Interaction | Parameter | Solution A | Solution B | Solution C |
|---|---|---|---|---|
| Ni-O | *r* | 2.04 | 2.05 | 2.04 |
| | *b* | 0.003 | 0.004 | 0.004 |
| | *n* | 5.40 | 5.46 | 5.73 |
| Ni-Br | *r* | 2.52 | 2.53 | 2.58 |
| | *b* | 0.007 | 0.008 | 0.008 |
| | *n* | 0.68 | 0.47 | 0.18 |

*r*, Bond distance, Å; *b*, temperature factor, Å$^2$; *n*, frequency factor.

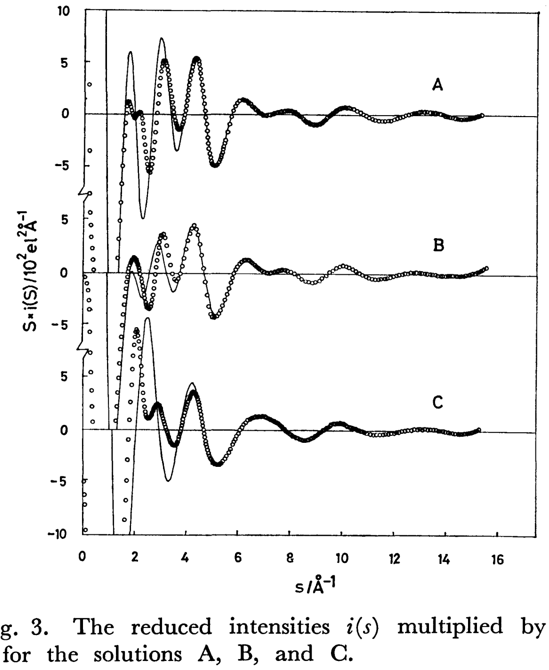

Fig. 3. The reduced intensities $i(s)$ multiplied by $s$ for the solutions A, B, and C.
Observed $s \cdot i(s)$ curve, circles; calculated curve, solid line.

The bond distance of Ni–Br given in Table 2 indicates that the bromo complex is in the inner-sphere type of coordination. Moreover, as seen in the frequency factor, the molar ratio of the bromo complex *vs.* hexaaqua complex increases with an increase in the total $NiBr_2$ concentration. This tendency agrees with the prediction from the stability constant determined by Libuś and Kowalewska.[9] However, they interpreted their formation constant $\beta_1=0.05$ for the 2 mol kg$^{-1}$ solution by proposing a monobromo complex with the outer-sphere type of coordination. In fact, on varying the concentration from 0.86 to 4.27 mol kg$^{-1}$, the ligand field absorption spectra of $NiBr_2$ aqueous solutions changed very little.[28]

For $NiCl_2$ in an aqueous 4 mol dm$^{-3}$ solution, the X-ray investigation was made by Caminiti *et al.*[2] Though they concluded that no chloro complex was formed, a small shoulder is seen around 2.6 Å in their correlation function; this is ascribable to the Ni–Cl

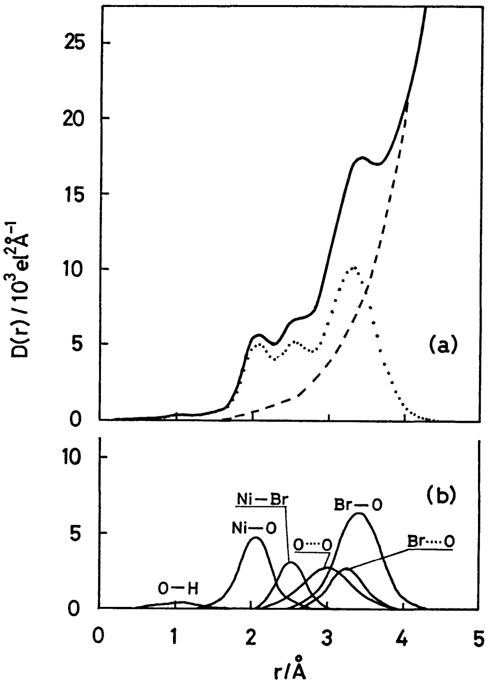

Fig. 4. (a) Radial distribution curve for the solution A. (b) Calculated peak shapes: the O–H interaction is in $H_2O$; the Ni–O and Ni–Br interactions, and the O···O and Br···O contacts are in $[NiBr(H_2O)_5]^+$; the O···O contact is in hydrogen bonded $H_2O$ molecules; and the Br–O interaction is in $[Br(H_2O)_6]^-$. The O···O peak is composed of two interactions, *i.e.*, the O···O contact in $[NiBr(H_2O)_5]^+$, and the O···O contact in hydrogen bonded $H_2O$ molecules.

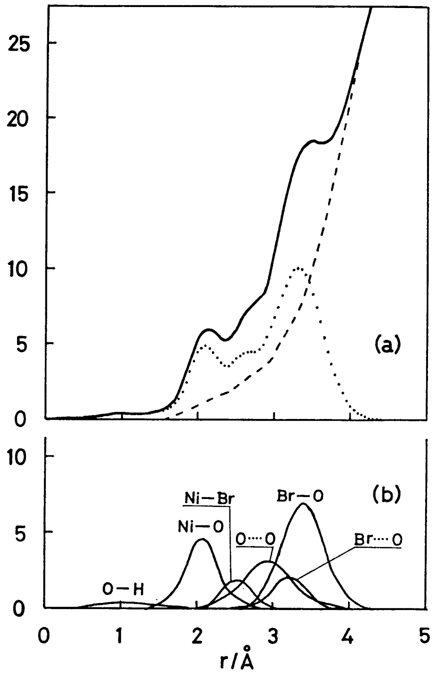

Fig. 5. (a) Radial distribution curve for the solution B. (b) Calculated peak shapes: the O–H interaction is in $H_2O$; the Ni–O and Ni–Br interactions, and the O···O and Br···O contacts are in $[NiBr(H_2O)_5]^+$; the O···O contact is in hydrogen bonded $H_2O$ molecules; and the Br–O interaction is in $[Br(H_2O)_6]^-$. The O···O peak is composed of two interactions, *i.e.*, the O···O contact in $[NiBr(H_2O)_5]^+$, and the O···O contact in hydrogen bonded $H_2O$ molecules.

interaction. Therefore, in our work the larger X-ray scattering factor of the bromine resulted in the appearance of a pronounced peak of the Ni–Br interaction in the radial distribution curve.

Table 2 shows that the refined data of the bond distance of Ni–Br, 2.52 Å, is smaller than the sum of their ionic radii, 2.65 Å as mentioned above, and is rather approximated by the sum of their covalent bond radii, 2.50 Å $\{=1.39$ Å $(Ni^{2+})+1.11$ Å $(Br^-)\}$.[29] The bond distance 2.05±0.01 Å of Ni–$OH_2$ in the bromoaqua complex falls in the same range with those 2.04—2.06 Å of the hexaqua complexes in the aqueous $Ni(ClO_4)_2$[22] and $NiCl_2$[2] solutions. And the temperature factors of the Ni–$OH_2$ bond in both bromoaqua and hexaaqua complexes are also similar.[22] The Ni–$OH_2$ distance of the aqua complexes in the solutions seems to be slightly shorter than that of the crystalline $NiCl_2 \cdot 6H_2O$ (2.10 Å).

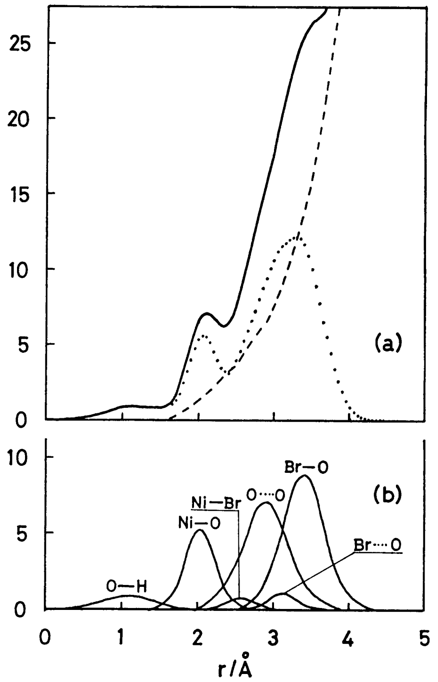

Fig. 6. (a) Radial distribution curve for the solution C. (b) Calculated peak shapes: the O–H interaction is in $H_2O$; the Ni–O and Ni–Br interactions, and the O···O and Br···O contacts are in $[NiBr(H_2O)_5]^+$; the O···O contact is in hydrogen bonded $H_2O$ molecules; and the Br–O interaction is in $[Br(H_2O)_6]^-$. The O···O peak is composed of two interactions, *i.e.*, the O···O contact in $[NiBr(H_2O)_5]^+$, and the O···O contact in hydrogen bonded $H_2O$ molecules.

### References

1) J. Mizuno, *J. Phys. Soc. Jpn.*, **16**, 1574 (1961).

2) R. Caminiti, G. Licheri, G. Piccaluga, and G. Pinna, *Faraday Discuss. Chem. Soc.*, **1977**, 62.

3) A. K. Soper, G. W. Neilson, J. E. Enderby, and R. A. Howe, *J. Phys. C*, **10**, 1793 (1977).

4) P. Lagarde, A. Fontaine, D. Raoux, A. Sadoc, and P. Migliardo, *J. Chem. Phys.*, **72**, 3061 (1980).

5) D. R. Sandstrom, *J. Chem. Phys.*, **71**, 2381 (1979).

6) H. Weingärtner and H. G. Hertz, *J. Chem. Soc., Faraday Trans. 1*, **75**, 2700 (1979).

7) H. Weingärtner, C. Müller, and H. G. Hertz, *J. Chem. Soc., Faraday Trans. 1*, **75**, 2712 (1979).

8) Z. Libuś and H. Tialowska, *J. Solution Chem.*, **4**, 1001 (1975).

9) Z. Libuś and G. Kowalewska, *Pol. J. Chem.*, **52**, 709 (1978).

10) H. Ohtaki, M. Maeda, and S. Ito, *Bull. Chem. Soc. Jpn.*, **47**, 2217 (1974).

11) N. Norman, *Acta Crystallogr.*, **10**, 370 (1957).

12) J. Krogh-Moe, *Acta Crystallogr.*, **9**, 951 (1956).

13) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

14) "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham (1962), Vol. III, pp. 202—203.

15) H. H. M. Balyuzi, *Acta Crystallogr., Sect. A*, **31**, 600 (1975).

16) A. H. Compton and S. K. Allison, "X-Rays in Theory and Experiment," Van Nostrand, New York (1935).

17) S. Miyake, "X-Sen no Kaisetsu," Asakura Shoten, Tokyo (1969), p. 38.

18) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

19) G. Johansson and M. Sandström, *Chemica Scripta*, **4**, 195 (1973).

20) H. Wakita, M. Ichihashi, and I. Masuda, *Fukuoka Univ. Sci. Reports*, **10**, 95 (1980).

21) H. A. Levy, M. D. Danford, and A. H. Narten, "Data Collection and Evaluation with an X-Ray Diffractometer Designed for the Study of Liquid Structure," ORNL-3960 (1966).

22) H. Ohtaki, T. Yamaguchi, and M. Maeda, *Bull.*

*Chem. Soc. Jpn.*, **49**, 701 (1976). The authors are grateful to Prof. H. Ohtaki for the use of this program.

23) A. H. Narten, "X-Ray Diffraction Data on Liquid Water in the Temperature Range 4 °C—200 °C," ORNL-4578 (1970).

24) W. Bol, G. J. A. Gerrits, and C. L. van Panthaleon van Eck, *J. Appl. Crystallogr.*, **3**, 486 (1970).

25) R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976).

26) L. G. Sillén and A. E. Martell, "Stability Constants," The Chemical Society, London (1964), Spec. Publ. No. 17, pp. 321—322.

27) R. M. Lawrence and R. F. Kruh, *J. Chem. Phys.*, **47**, 4758 (1967).

28) Z. Libus, W. Maciejiewski, and G. Kowaleswka, *Pol. J. Chem.*, **52**, 793 (1978).

29) "Kagaku-binran Kiso-hen II," ed by the Chemical Society of Japan, Maruzen, Tokyo (1966), p. 1266.