Formation Constants and Structures of Complexes between Cadmium (II) and Iodide Ions in Aqueous Solution

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The formation constants of complexes between cadmium (II) and iodide ions in an aqueous 4 mol dm⁻³ (Na)ClO₄ solution were determined potentiometrically at 25°C by using both silver-silver iodide and cadmium amalgam electrodes. Only the mononuclear complexes CdI_n⁽²⁻ⁿ⁾⁺ (*n*=1-4) were found over a wide range of the concentrations of Cd²⁺ and I⁻ ions. The X-ray diffraction analysis of a solution containing the moniodocadmium and aquacadmium ions was carried out. The diffraction intensities scattered by the aquacadmium ions in the solution were subtracted from the observed intensities with knowledge of the concentration and the structure of the aquacadmium ion, and the rest of the diffraction data was analyzed for the moniodocadmium ion. The complex ion was found to exist as CdI(OH₂)₆⁺ and the Cd-I and Cd-OH₂ bond lengths within this complex were 2.80 ± 0.05 Å and 2.30 ± 0.05 Å, respectively. These bond lengths were the same as the corresponding ones within the tetrahedral CdI₄²⁻ and octahedral Cd(OH₂)₆²⁺ complexes. The Raman spectra were measured for the cadmium iodide solutions of various $\bar{n}$ values ($\bar{n}$ =average number of iodide ions bonded to Cd²⁺). The Cd-I stretching frequency of the CdI⁺ complex was found at 131 cm⁻¹. With increasing $\bar{n}$ values, the Cd-I stretching frequency gradually decreased to 117 cm⁻¹, which had been assigned to the ν_1 frequency of the tetrahedral CdI₄²⁻ complex. However, the Cd-I stretching frequencies of the CdI₃⁺ and CdI₃⁻ complexes could not be determined because of their small amounts in the solutions. The force constants and temperature factors of atom pairs within CdI⁺ and CdI₄²⁻ complexes were calculated from the frequencies of the fundamental vibrations and bond lengths.

1 Introduction

The analysis of Raman spectral data in aqueous solution indicated that the CdI₄²⁻ complex has a regular tetrahedral structure^{(1), (2)}, and the X-ray diffraction analysis confirmed the structure⁽³⁾. The Cd-I bond length within the complex is 2.79 Å⁽³⁾. The aqua complex, Cd(OH₂)₆²⁺ ion, is known to have a regular octahedral structure having the Cd-OH₂ bond distance of 2.31 Å⁽³⁾. However, the structures of other iodo complexes CdI_n(OH₂)_m⁽²⁻ⁿ⁾⁺ have not been determined yet. The CdI₂ and CdI₃⁻ moieties within the diiodocadmium and triiodocadmiate complexes in organic solvents have been found to have linear and regular-triangular symmetries, respectively, by Raman

spectroscopy⁽⁴⁾, but the configuration of the organic solvent molecules within the complexes has not been known.

In order to determine the structures of complexes in solution, it is essential to know the composition and concentration of each complex in the solution used for the measurements. Although the equilibria between cadmium (II) and iodide ions in aqueous solution have been studied by many investigators⁽⁵⁾, no reliable data have been reported in highly concentrated solutions which are suitable for X-ray diffraction and Raman spectral measurements.

In the present work, therefore, we first aimed at determining by potentiometry the formation constants of iodo complexes in concentrated cadmium iodide solutions at a constant ionic medium of sodium perchlorate. Then, with the aid of the results obtained, X-ray diffraction and Raman spectral data were analyzed to determine the structures of each complex in the

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solutions. The X-ray diffraction analysis of the monoiodocadmium complex $\text{CdI}(\text{OH}_2)_p^+$ was carried out for a solution in which the complex was dominantly present. The X-ray diffraction measurements of $\text{CdI}_2(\text{OH}_2)_q^0$ and $\text{CdI}_2(\text{OH}_2)_r^-$ complexes could not be performed because their amounts in the test solutions prepared were too small to be examined. Raman spectra were measured for cadmium iodide solutions of various $\bar{n}$ values from zero to four, and the fundamental frequencies of each complex were estimated. Force constants and temperature factors of atom pairs within the $\text{CdI}(\text{OH}_2)_p^+$ and CdI_2^{2-} complexes were calculated with knowledge of the fundamental frequencies and bond lengths determined by the Raman spectral and X-ray diffraction analyses, and the temperature factors thus calculated were compared with those estimated from the only X-ray diffraction analysis of these complexes.

2 Experimental

2.1 Reagents and analysis

2.1.1 Cadmium perchlorate solution was prepared by dissolving cadmium oxide (Mitsuwa 99.99% purity) in perchloric acid (Wako super special grade). The concentration of the cadmium ions in the stock solution was determined both by gravimetry as $\text{Cd}_3\text{P}_2\text{O}_7$ and by titration with EDTA. The results obtained by the two methods agreed each other within 0.1%. The concentration of the perchlorate ions was determined by passing an aliquot of the stock solution through a column of cation exchange resin (Dowex 50 W-X12) in the hydrogen form and titrating eluted H^+ ions.

2.1.2 Sodium perchlorate used for the ionic medium was prepared by dissolving recrystallized Na_2CO_3 in HClO_4 and then recrystallized twice from water. The concentration of sodium perchlorate in the stock solution was determined gravimetrically as NaClO_4 by drying an aliquot of the solution at 120°C and finally at 180°C .

2.1.3 Sodium iodide (Merck Suprapur) was used without further purification.

2.1.4 Cadmium iodide (Wako a.g.) was recrystallized from water. The concentration of cadmium ions in the stock solution was deter-

mined by the same procedures as employed for the analysis of the cadmium perchlorate solution.

2.2 Apparatus

2.2.1 A cadmium amalgam electrode was prepared by electrolysis using the apparatus described in Ref. 6. The concentration of cadmium in the amalgam ranged from 0.1 to 2 wt. %.

2.2.2 A silver-silver chloride electrode was prepared by electrolysis as recommended by Brown⁷⁾.

2.2.3 A silver-silver iodide electrode was prepared by the same procedures as for the silver-silver chloride electrode.

2.2.4 A TR-1156 potentiometer from Takeda Riken Co. was used for emf measurements with both the cadmium amalgam and silver-silver iodide electrodes. The cadmium amalgam electrode was stable within ± 0.01 mV. Emf's measured by the silver-silver iodide electrode were reproducible within the error of ± 0.05 mV.

2.2.5 A θ - θ X-ray diffractometer (JEOL Co., Tokyo) set in a room thermostated at $25 \pm 1^\circ\text{C}$ was employed for X-ray scattering measurements. $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) was used for irradiation of the sample solution. Details of measurements are described in a previous paper³⁾.

2.2.6 A JEOL JRS-SI Raman spectrometer (JEOL Co., Tokyo) was used in combination with argon ion and helium-neon lasers with exciting frequencies of 4880 and 5145, and $6328 \text{ \AA}$ at 25°C for Raman spectral measurements of the solutions.

3 Methods of Measurements

3.1 Potentiometric measurements

Equilibria between Cd^{2+} and I^- ions were studied at 25°C in solutions in which the concentration of ClO_4^- ion was kept at 4 mol dm^{-3} . The concentration of hydrogen ions was maintained at about $10^{-5} \text{ mol dm}^{-3}$ in order to suppress the hydrolysis of Cd^{2+} ion. The test solution S had the following composition:

$$S = \begin{cases} B \text{ mol dm}^{-3} \text{ Cd(II)} \\ 10^{-5} \text{ mol dm}^{-3} \text{ H}^+ \\ (4.000 - 2B + A) \text{ mol dm}^{-3} \text{ Na}^+ \\ A \text{ mol dm}^{-3} \text{ I}^- \\ 4.000 \text{ mol dm}^{-3} \text{ ClO}_4^- \end{cases}$$

The B value was changed from 0.005 to 0.5 mol dm⁻³, and the A value up to 0.6 mol dm⁻³.

The concentrations of Cd²⁺ ions b and iodide ions a at equilibrium were measured by the cell assemblies (I) and (II), respectively.

Here Ref stands for the reference half-cell (III) | 4.000 mol dm⁻³ NaClO₄ | 0.010 mol dm⁻³ AgClO₄ and 3.990 mol dm⁻³ NaClO₄ | AgCl-Ag (III)

The emf's of cells (I) and (II) may be expressed by Eqs. 1 and 2, respectively.

$$E_B = E_B^0 + 29.58 \log b + E_j \quad (1)$$

$$E_A = E_A^0 - 59.15 \log a + E_j \quad (2)$$

where E_B^0 and E_A^0 represent constants. E_j is the liquid junction potential arising from the potential difference at the interface between the test solution and the 4 mol dm⁻³ NaClO₄ solution. The liquid junction potential due to replacement of Na⁺ by Cd²⁺ in the test solution and that due to the addition of I⁻ to the test solution were determined by separate titrations by the usual method^{(8),(9)}. It was found that the liquid junction potential is expressed as a linear function of b at the concentration of perchlorate ions of 4 mol dm⁻³, $E_j = (22 \pm 2) b$ mV, and it is practically independent of the concentration of iodide ions in the solution when $a < 0.5$ mol dm⁻³. Thus, Eqs. 1 and 2 can be rewritten as Eqs. 3 and 4, respectively.

$$E_B = E_B^0 + 29.58 \log b + 22 b \quad (3)$$

$$E_A = E_A^0 - 59.15 \log a + 22 b \quad (4)$$

Emf measurements were carried out at constant B with increasing A in the measuring vessel described by Tsukuda *et al.*⁽¹⁰⁾ Under the experimental conditions, the total concentration of the anions may vary with the increase in A , but the increase of the concentration of the anions in the ionic medium may not be so significant, because it is expected that a large part of the iodide ions added are combined with cadmium ions. The test solutions were deaerated by bubbling nitrogen gas free from oxygen which has been successively passed through bottles containing 10% H₂SO₄-VOSO₄·Zn-amalgam, 10% NaOH and 4 mol dm⁻³ NaClO₄ solutions. All the emf measurements were carried out in a paraffin oil thermostat maintained at 25.00 ± 0.02°C which was set in a

dark room thermostated at 25 ± 1°C.

3.2 X-Ray diffraction measurements and treatment of intensity data

In order to determine the structure of the CdI(OH₂)_p⁺ complex, we must resolve the intensity data obtained from the solution containing both Cd(OH₂)₆²⁺ and CdI(OH₂)_p⁺ complexes into those of each species. Therefore, the formation constant of the CdI(OH₂)_p⁺ complex as well as those of other complexes in the same solution as that used for the X-ray diffraction measurements must be known. However, measurements of formation constants of complexes are usually carried out in a solution containing a relatively large amount of a medium salt (in the present case [ClO₄⁻] = 4 mol dm⁻³). On the contrary, one wishes to avoid introducing any foreign salt into sample solutions in X-ray diffraction measurements. Therefore, strictly speaking, no suitable formation constants of complexes are available for X-ray diffraction studies.

Since we attempted to use the formation constants of Cd(II)-I complexes obtained in the 4 mol dm⁻³ (Na)ClO₄ medium for the solution used for the X-ray analysis, the sample solution for the X-ray scattering measurements was prepared so as to have the formal ionic concentration $\{(1/2) \sum c_i z_i^2\}$ where c_i denotes the analytical concentration of i -ion and z_i the charge of the i -ion close to that of the solutions used for potentiometric titrations. By taking into consideration the solubilities of cadmium perchlorate and sodium iodide and of the experimental condition favorable to the determination of the structure of the CdI(OH₂)_p⁺ complex, the solution with the atomic composition listed in Table 1 was used.

The distribution of the iodo complexes calculated from the formation constant in the 4 mol dm⁻³ (Na)ClO₄ ionic medium obtained in this

Table 1 Composition of the sample solution (in g-atom dm⁻³)

Cd	1.265
I	0.917
Cl	2.552
O	58.33
Na	0.917
H	96.27

Fig. 1 The distribution of the iodo complexes as a function on $\bar{n}$

Table 2 The values for the formation constants determined by use of silver-silver iodide and cadmium amalgam electrodes

	Ag-AgI	Cd (Hg)
$\log \beta_1$	2.33 (5)	2.23 (6)
$\log \beta_2$	3.32 (4)	3.39 (4)
$\log \beta_3$	5.71 (15)	5.40 (13)
$\log \beta_4$	7.46 (7)	7.38 (8)

Uncertainties in parentheses were estimated as 3σ , where σ is the standard deviation.

work (Table 2) is shown in Fig. 1. This figure shows that only the $\text{CdI}(\text{OH}_2)_p^+$ complex is dominant in the low $\bar{n}$ region where the X-ray diffraction analysis of the complex is possible. The sample solution of the $\bar{n}$ value of about 0.7 was prepared by mixing the required amounts of the $\text{Cd}(\text{ClO}_4)_2$ solution and NaI crystals. In this solution it is seen that the monoiodocadmium and aquacadmium complexes are present at the approximate ratio of 1 to 1 and the amounts of other iodo complexes are negligible.

The radial distribution function $D(r)$ and the theoretical intensity scattered by atom-pairs were calculated by the usual method⁹⁾. The

values for coherent, incoherent, and anomalous scattering factors of relevant atoms were the same as those used in a previous paper³⁾.

3.3 Raman spectroscopic measurements

Raman spectral measurements were performed in a thermostated room at 25°C for the cadmium iodide solutions of various $\bar{n}$ values from zero to four. The compositions of the sample solutions are tabulated in Table 3. The curved background arising from the Rayleigh scattering of each solution was approximated by the Raman spectrum of a solution containing both NaI and NaClO_4 in which the concentrations of iodide and perchlorate ions were adjusted to those in the sample solution. Overlapped Raman lines due to the iodo complexes coexisting were resolved on the assumption that each line was represented by a Lorentz-Gaussian curve.

4 Results and Calculations

4.1 Compositions and formation constants of complexes between cadmium and iodide ions

The formation curve $\bar{n}(\log a)_B$ obtained from the emf measurements with cell(II) is shown in Fig. 2. The plot was a function of only a and independent of B , and approached 4 as a increased. This fact indicates that only mononuclear complexes are present and the highest complex formed is CdI_4^{2-} .

The formation constants of iodo complexes were estimated by Leden and Fronaeus's method¹¹⁾, and then least-squares method was applied to the refinement of the formation constants by inserting the values graphically estimated into $\bar{n}$ as a first approach. The formation constants β_n were determined by searching the minimum error square sum $U = \sum (1 - \bar{n}/\bar{n}_{\text{calc}})^2$.

Table 3 Compositions of solutions and observed Raman frequencies

$\bar{n}$	Total concentration of cadmium ions (mol dm ⁻³)	Total concentration of iodide ions (mol dm ⁻³)	Total concentration of perchlorate ions (mol dm ⁻³)	Observed frequency (cm ⁻¹)
0	0.46	0	0	360
0.54	0.45	0.25	4.0	131, 360
1.2	0.27	0.32	4.0	125, 360
1.9	0.20	0.40	4.0	122
3.1	0.23	0.71	4.0	42, 118, 145
4.0	0.32	1.21	4.0	34, 46, 117, 142

Fig. 2 $\bar{n}$ as a function of $\log a$

The drawn curve was calculated with the formation constants obtained with the silver-silver iodide electrode which are given in Table 2.

B $\square$ 0.005040 mol dm⁻³, $\triangle$ 0.01245 mol dm⁻³
 $\circ$ 0.1243 mol dm⁻³, $\circ$ 0.4999 mol dm⁻³

Points with the solid symbol $\blacktriangledown$ were obtained by the reverse titrations in which B varied from 0.03112 to 0.1014 mol dm⁻³

$\bar{n}_{\text{calc}}$ denotes $\sum_{n=1}^4 n a^n \beta_n / (1 + \sum_{n=1}^4 a^n \beta_n)$ and $\beta_n = [\text{CdI}_n^{(2-n)+}] / [\text{Cd}^{2+}][\text{I}^-]^n$. The formation constants determined by the least-squares method are given in Table 2.

The (B , A , b) data obtained from the measurements with the amalgam electrode were also analyzed to search for the best set of formation constants by a different least-squares procedure from the preceding one, which was performed to minimize $U = \sum (E_B - E_{B\text{calc}})^2$. The differences between E_B and $E_{B\text{calc}}$ values calculated with the best set of formation constants are shown in Fig. 3 as a function of A/B . The

Fig. 3 The differences between E_B and $E_{B\text{calc}}$ values as a function of A/B

B $\square$ 0.005040 mol dm⁻³, $\circ$ 0.1243 mol dm⁻³
 $\odot$ 0.01025 mol dm⁻³

formation constants thus derived are compared in Table 2 with those obtained from the measurements with the silver-silver iodide electrode. The measurements with the two different kinds of electrodes gave the same result within experimental uncertainties.

4.2 Structures of complexes between cadmium and iodide ions

4.2.1 X-Ray analysis of the structure of the monoiodocadmium ion

Figure 4 shows the radial distribution curve in the form of $D(r) - 4\pi r^2 \rho_0$ for the solution of $\bar{n} = 0.7$ in which monoiodocadmium and aquacadmium complexes were dominantly contained. The curve shows three peaks at around 1.4, 2.3 and 2.8 Å in the range less than $r = 3$ Å. The first peak is ascribed to the Cl-O bond within the ClO_4^- ion³⁾. In order to determine the structure of the $\text{CdI}(\text{OH}_2)_6^{2+}$ complex, the contributions from ClO_4^- and $\text{Cd}(\text{OH}_2)_6^{2+}$ complexes were subtracted from the $D(r)$ curve. The theoretical peak shapes due to the interactions between atoms within the ClO_4^- and $\text{Cd}(\text{OH}_2)_6^{2+}$ ions were calculated by use of the parameter values of the bond length r , the temperature factor b , and the frequency factor n reported in Ref. 3. The mole fraction of the $\text{Cd}(\text{OH}_2)_6^{2+}$ complex was calculated on the basis of the formation constants of the complexes determined in the preceding section. The theoretical peak shapes and the residual radial distribution curve thus calculated are shown by curves b and a in Fig. 5, respectively. A hump at around 2.3 Å in Fig. 5 (curve a) can be attributed to the Cd-OH₂ bond within the monoiodocadmium complex because the peak position is consistent with that of Cd-OH₂ bond within the hexaaqua-

Fig. 4 The $(D(r) - 4\pi r^2 \rho_0)$ curve for the solution of $\bar{n} = 0.7$

Fig. 5 The radial distribution curve of the solution of $\bar{n}=0.7$

Curve a: the residual curve obtained by subtraction of curve b from the $D(r)$ curve. Curve b: theoretical peak shapes for interactions within ClO_4^- and Cd-OH₂ bond within $\text{Cd}(\text{OH}_2)_6^{2+}$. Curve c: theoretical peak shapes for Cd-OH₂ and Cd-I bonds within $\text{CdI}(\text{OH}_2)_5^+$. Curve d: the background curve obtained by subtraction of curve c from curve a

cadmium ion previously determined³¹. The peak at 2.8 Å may be ascribed to the O-O contacts between perchlorate anions and water molecules and between hydrogen-bonded water molecules¹⁵) and also to the Cd-I bond within the monoiodocadmium complex because the bond distance may be similar to the Cd-I bond distance within the CdI_4^{2-} complex³¹). The Cd-OH₂ bond distance and the number of water molecules bonded to the cadmium ion within the monoiodocadmium ion were determined by the method of trial-and-error in such a way that the subtraction of the calculated peaks due to the Cd-OH₂ and Cd-I bonds within the $\text{CdI}(\text{OH}_2)_5^+$ from the peak at 2.3 Å in the residual curve (Fig. 5 (curve a)) results in a smooth background curve with no distinct indication of

the existence of other interatomic distances in the r -range examined^{12,13}).

The hydration number of p from one to five was tested by the method. The assumption of the hydration number of 5, *i.e.*, the $\text{CdI}(\text{OH}_2)_5^+$ as the monoiodocadmium ion, led to the smoothest background curve, which is shown in Fig. 5 (curve d), together with the calculated peak shapes due to the Cd-OH₂ and Cd-I bonds within the $\text{CdI}(\text{OH}_2)_5^+$ (curve c).

From these calculations it was found that five water molecules coordinate to the Cd^{2+} ion within the monoiodocadmium complex and the Cd-OH₂ bond length within the complex is 2.30 ± 0.05 Å. The Cd-I bond length within the $\text{CdI}(\text{OH}_2)_5^+$ species was found to be 2.80 ± 0.05 Å. The hump at around 2.8 Å still remained in the residual curve (curve d) can be ascribed to the O-O contacts between perchlorate anions and water molecules¹⁴) and between hydrogen-bonded water molecules as described previously.

4.2.2 Raman spectral analysis of iodo complexes

The Raman spectra observed for the solutions of various $\bar{n}$ values from zero to four are shown in Fig. 6, along with the resolved bands on the horizontal backgrounds. The positions of the bands are summarized in Table 3. The solution of $\bar{n}=0$, *i.e.* the cadmium perchlorate solution showed only one polarized band at *ca.* 360 cm^{-1} except for the band at *ca.* 460 cm^{-1} which is ascribed to the ClO_4^- ion. The 360 cm^{-1} band may be assigned to the Cd-O stretching vibration within the regular octahedral $\text{Cd}(\text{OH}_2)_6^{2+}$ ion. For the solution of $\bar{n}=0.54$ in which $\text{CdI}(\text{OH}_2)_5^+$ and $\text{Cd}(\text{OH}_2)_6^{2+}$ complexes are contained, two polarized bands were observed at 131 and *ca.* 360 cm^{-1} . The former band can be assigned to the Cd-I stretching vibration within the $\text{CdI}(\text{OH}_2)_5^+$ complex, because the intensity of the band was approximately proportional to the concentration of the $\text{CdI}(\text{OH}_2)_5^+$ complex. The latter band may be ascribed to the Cd-O stretching vibrations within the $\text{CdI}(\text{OH}_2)_5^+$ and $\text{Cd}(\text{OH}_2)_6^{2+}$ complexes. The solution of $\bar{n}=4$ containing only the CdI_4^{2-} complex showed four bands at 34 (ν_2), 46 (ν_4), 117 (ν_1), and 142 (ν_3) cm^{-1} . This result is consistent with that reported by several investigators^{11,2)} who proposed a tetra-

Fig. 6 Raman spectra for solutions with various $\bar{n}$ values, together with resolved bands based on the horizontal background

hedral structure for the complex. The distinct and polarized bands appeared at *ca.* 125, 122 and 118 cm^{-1} in the spectra of solutions of $\bar{n}=1.2$, 1.9 and 3.1 which contain iodo complexes of different compositions, respectively. The bands are asymmetric and the positions shift to the lower frequency region as the $\bar{n}$ value increases. Resolution of the bands into the frequencies of CdI_2 and CdI_3^- with knowledge of the concentration of each species was not successful because of low concentrations of the CdI_2 and CdI_3^- complexes.

4.2.3 Calculations of force constants and temperature factors of atom pairs within iodo complexes The force constants and temperature factors for atom pairs within the

$\text{CdI}(\text{OH}_2)_3^+$ and CdI_4^{2-} complexes were calculated by use of the interatomic distances within these complexes obtained from the X-ray diffraction analysis and the frequencies observed by the Raman spectral measurements. The force constant K for the Cd-I stretching in the moniodocadmium complex was determined on the assumption that the coordinated five water molecules to the Cd^{2+} ion have negligible influence on the Cd-I stretching vibration and the complex can be regarded as a diatomic molecule of CdI^+ . The value of K was calculated to be 0.60 $\text{mdyn}/\text{\AA}$. The force constants for atom pairs within the tetrahedral CdI_4^{2-} complex were calculated on the basis of the modified Urey-Bradley force field. They were as follows: $K=0.58$ $\text{mdyn}/\text{\AA}$, $H=-0.009$ $\text{mdyn}/\text{\AA}$, $F=0.11$ $\text{mdyn}/\text{\AA}$, and $F'=-0.006$ $\text{mdyn}/\text{\AA}$.

The temperature factors for the interatomic interactions within the $\text{CdI}(\text{OH}_2)_3^+$ and CdI_4^{2-} complexes were thus calculated by use of the force constants and the interatomic distances and were compared with those estimated from the X-ray diffraction analysis. These calculations were carried out according to procedures summarized by Cyvin¹⁶⁾. The temperature factor $b_{\text{Cd-I}}$ for the Cd-I bond within the $\text{CdI}(\text{OH}_2)_3^+$ complex was 0.0037 $\text{\AA}^2$. $b_{\text{Cd-I}}$ for the Cd-I bond and $b_{\text{I}\cdots\text{I}}$ for the nonbonded I $\cdots$ I interaction within the CdI_4^{2-} complex were 0.0033 $\text{\AA}^2$ and 0.0050 $\text{\AA}^2$, respectively.

5 Discussion and Conclusion

Although potentiometric measurements were carried out on the system containing the cadmium and iodide ions of high concentrations, no complex other than the mononuclear ones ($\text{CdI}_n^{(2-n)+}$, $n=1-4$) so far reported³⁾ was found.

The X-ray diffraction analysis showed that the moniodocadmium complex has the composition of $\text{CdI}(\text{OH}_2)_3^+$ and that the Cd-OH₂ and Cd-I bond lengths within this complex are 2.30 $\text{\AA}$ and 2.80 $\text{\AA}$, respectively. These Cd-OH₂ and Cd-I bond lengths are almost the same as the corresponding bond lengths within the octahedral $\text{Cd}(\text{OH}_2)_6^{2+}$ and tetrahedral CdI_4^{2-} complexes³⁾ irrespective of the different compositions and structures of the complexes. The

temperature factors for the Cd-OH₂ and Cd-I bonds within the CdI(OH₂)₅⁺ complex were estimated to be 0.002 Å² and 0.004 Å², respectively, which are also in good agreement with those found for the Cd(OH₂)₆²⁺ and CdI₄²⁻ complexes³⁾.

The Raman spectral analysis revealed that the Cd-I stretching band at 131 cm⁻¹ for the CdI(OH₂)₅⁺ complex shifted to 117 cm⁻¹ for the CdI₄²⁻ complex with increasing number of bonded iodide ions. The frequencies could not be determined for the CdI₂ and CdI₃⁻ complexes. The temperature factors for the Cd-I bonds within CdI(OH₂)₅⁺ and CdI₄²⁻ calculated from the bond lengths and fundamental frequencies were in good agreement with those estimated from the X-ray diffraction analysis. However, the temperature factor ($b_{I...I}=0.005$ Å²) for the nonbonded I...I interaction within the CdI₄²⁻ complex evaluated from the force constants and the interatomic distances was much smaller than that ($b_{I...I}=0.025$ Å²) found by the X-ray diffraction analysis. The reason of this discrepancy is not clear at the present stage of investigation.

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