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Calorimetric and Raman Spectroscopic Studies on Formation of Cadmium(II) Thiocyanato Complexes in Aqueous Solution

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Complex formation equilibria between cadmium(II) and thiocyanate ions have been calorimetrically studied at 25 °C in aqueous solution containing $NaClO_4$ in order to keep 3 mol dm^{-3} ionic strength in the test solutions. Calorimetric titration curves thus obtained were well explained in terms of formation of dinuclear $[Cd_2X]^{3+}$ (X=SCN) and mononuclear $[CdX_n]^{(2-n)+}$ (n=1—4) complexes, and their formation constants, enthalpies and entropies were determined. The stepwise enthalpy and entropy values at the third consecutive step were largely positive, indicating that water molecules solvating Cd(II) ion were extensivelyl liberated at this step. It was thus suggested that the coordination symmetry around Cd(II) ion changed from octahedral to tetrahedral at the formation of $[CdX_3]^-$. Raman spectra of the C–S and C–N stretching vibrations of SCN^- ion were measured in cadmium(II) thiocyanate solutions with varying molar ratios of the metal to ligand ions. It was shown that SCN^- ion coordinated to Cd(II) ion through the N atom at the first step of the complex formation, and the S atom at the second, N at the third and then S at the last. The suggested bonding type of SCN^- ion with Cd(II) ion within each cadmium(II) thiocyanato complex was supported by the thermodynamic data.

In a previous paper,[1] we elucidated the structures of the tetrathiocyanato complexes of the Group 2B metal ions, Zn(II), Cd(II), and Hg(II), in aqueous solutions by X-ray scattering, Raman and ^{13}C- and ^{14}N-NMR measurements.

Thiocyanate (SCN^-) ion binds with metal ions through either the sulfur or nitrogen atom depending on the softness or hardness of metal ions. Relatively hard zinc(II) and soft mercury(II) ions are coordinated with the N and S atoms, respectively, of SCN^- ions within $[Zn(NCS)_4]^{2-}$ and $[Hg(SCN)_4]^{2-}$.

On the other hand, cadmium(II) ion shows an intermediate character between Zn(II) and Hg(II) ions. Then, it has been indicated that, within the tetrathiocyanatocadmate(II) ion, cadmium(II) ion is linked to two N and two S atoms of SCN^- ions to form $[Cd(SCN)_2(NCS)_2]^{2-}$ in aqueous solution.

Raman and infrared spectroscopic measurements so far carried out for various cadmium(II) thiocyanate solutions provided evidence of formation of mono- and polynuclear complexes of Cd(II) having different types of bonding of SCN^- ion.[2–6] Recently, Antić-Jovanović et al.[7] reported Raman spectra of the cadmium(II) thiocyanate aqueous solutions and assigned the band at 2132 cm^{-1} to the C–N stretching vibration within $[Cd(SCN)]^+$ and the bands at 2102 and 784 cm^{-1} to the C–N and C–S stretching vibrations within the higher $[Cd(NCS)_n]^{(2-n)+}$ ($n>2$) complexes.

Enthalpies and entropies of formation of thiocyanato complexes of metal ions also afford us useful information on the coordination structures of the complexes. Ahrland and Kullberg[8] indicated that SCN^- ion coordinated to Zn(II) ion through the N atom and to Hg(II) ion through the S atom. However, as to the thiocyanato complexes of Cd(II) in aqueous solution, no reliable data for enthalpies and entropies of formation of the complexes have been obtained yet.

In this study, therefore, we aimed at obtaining thermodynamic quantities of formation of thiocyanato complexes of Cd(II) in aqueous solution by calorimetry at 25 °C. A computer-controlled on-line system for calorimetry was employed.[9] Raman spectral measurements were also carried out in cadmium(II) thiocyanate aqueous solutions with varying ratios of the metal to ligand ions. The coordination structure within each thiocyanato complex of cadmium(II) ion is discussed on the basis of the thermodynamic and Raman spectroscopic data obtained.

Experimetal

Reagents. All chemicals used were of reagent grade. *Cadmium(II) perchlorate* was prepared by dissolving cadmium oxide into perchloric acid of super special grade and recrystallized twice from water. *Sodium thiocyanate* was recrystallized twice from ethanol. *Sodium perchlorate* was purified by the method described elsewhere.[10]

The concentration of metal ions in the cadmium(II) perchlorate stock solution was determined by titration with EDTA.

Calorimetric Measurements. Calorimetric measurements were carried out in a thermostated bath controlled at (25.000±0.007) °C placed in a room at (25.0±0.2) °C.

Cadmium(II) perchlorate solutions with varying concentrations of the metal ion in the range 10—400 mmol dm^{-3} were prepared, all the solutions containing 3 mol dm^{-3} $NaClO_4$ as a constant ionic medium. A 1 mol dm^{-3} NaSCN solution containing 2 mol dm^{-3} $NaClO_4$ as an ionic medium was used as a titrant solution. 100 cm^3 of a cadmium(II) perchlorate solution was placed in a Dewar vessel, and then, was titrated with the 1 mol dm^{-3} NaSCN titrant solution.

Back titration procedures were also employed. Four NaSCN solutions of 1.0, 1.5, 2.0, and 3.0 mol dm^{-3} were prepared, each solution containing $NaClO_4$ in order to adjust its ionic strength to 3 mol dm^{-3}. A 0.25 mol dm^{-3} $Cd(ClO_4)_2$ solution containing 3 mol dm^{-3} $NaClO_4$ was employed as a titrant solution.

Heats of dilution were determined by titrating a 3 mol dm^{-3} $NaClO_4$ solution with each titrant solution used. In each case, heat of dilution at the addition of an aliquot (δv cm^3) of the titrant solution slightly varied with the total volume (v cm^3) of the titrant added. Thus, the heat of dilution was represented as a function of v and δv as follows:

$$q_{\mathrm{dil}} = \int_{v}^{v+\delta v} (a_0 + a_1 u)\mathrm{d}u, \tag{1}$$

where a_0 and a_1 denote constants, which were evaluated by the least-squares method to be −0.365 J cm^{-3} and 2.68×10^{-3} J cm^{-6}, respectively, for the NaSCN titrant solution and −0.317 J cm^{-3} and 1.85×10^{-3} J cm^{-6}, respectively, for the $Cd(ClO_4)_2$ titrant solution.

Heat evolved q_{obsd} at each titration point was thus corrected by knowing the q_{dil} value as follows:

$$q_{\mathrm{corr}} = q_{\mathrm{obsd}} - q_{\mathrm{dil}}, \tag{2}$$

and the q_{corr} values thus obtained were used for the evaluation of formation constants and enthalpies of formation of cadmium(II) thiocyanato complexes in aqueous solution.

The specific heat C_p and the heat transfer coefficient λ of the test solutions, which were used for analyzing a set of temperature changes at each titration point, slightly varied with volumes of the test solution during the titrations, and thus, the C_p and λ values were determined at the addition of every 10 cm^3 of the titrant. The volume of an aliquot of the titrant solution added at each titration point was changed in the range 1—5 cm^3 depending on the extent of heat evolved during the titrations. The whole titration procedure was carried out by using a fully automatic on-line system for calorimetry as described elsewhere.[9]

Raman Spectral Measurements. Raman spectral measurements were carried out in cadmium(II) thiocyanate solutions with varying ratios of the metal to ligand ions as summarized in Table 1. Raman spectra were recorded on a JEOL JRS-S1 spectrometer using 514.5 nm line of NEC GLG-3200 argon ion Laser in a room at (25.0±0.2) °C.

Analysis of Colorimetric Data. The analytical method used for the calorimetric data obtained was similar to that used in a previous paper.[9] However, since titration curves obtained in the present work were not explainable in terms of formation of a series of mononuclear complexes, the formation of polynuclear thiocyanato complexes of Cd(II) was also taken into account.

Results and Discussion

Calorimetric titration curves obtained by titrating cadmium(II) perchlorate solutions having different concentrations of the metal ion with the NaSCN titrant solution are depicted in Fig. 1. Enthalpies ΔH° calculated by $\Delta H^\circ = -q_{\mathrm{corr}}/(\delta v C_{\mathrm{X,tit}})$, where δv and $C_{\mathrm{X,tit}}$ denote the volume of an aliquot of the titrant added and the concentration of NaSCN in the titrant solution, respectively, were plotted against the ratio C_X/C_M in the test solution at each titration point, where C_X and C_M stand for total concentations of SCN^- and Cd(II) ions, respectively, in a solution.

Table 1. Total Concentrations C_M and C_X of Cd^{2+} and SCN^- Ions, Respectively, in Cadmium(II) Thiocyanate Aqueous Solutions Used for Raman Spectroscopic Measurements

Solution	C_M/mol dm^{-3}	C_X/mol dm^{-3}	C_X/C_M
1	0.126	0.590	4.68
2	0.267	0.585	2.19
3	0.357	0.590	1.65
4	0.462	0.587	1.27
5	0.565	0.586	1.04
6	0.897	0.582	0.65
7	0.913	0.0727	0.08
8	2.090	0.0716	0.034

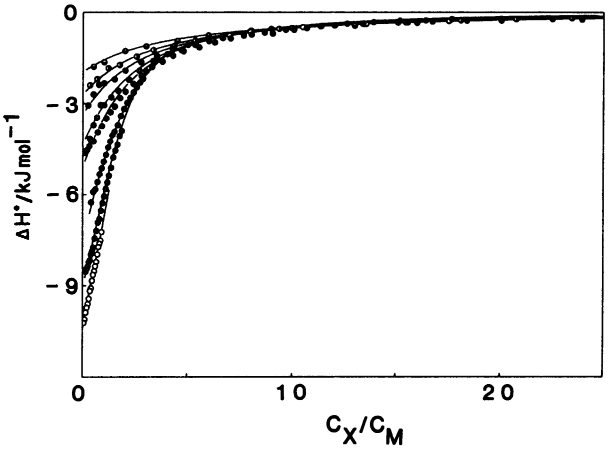

Fig. 1. Calorimetric titration curves of cadmium(II) thiocyanate solutions containing 3 mol dm^{-3} $NaClO_4$ at 25 °C. Initial concentrations of cadmium(II) perchlorate (C_M/mmol dm^{-3}): 10.04(◒), 14.93(◑), 20.02(⊕), 29.96(⦿), 39.96(◉), 100.1(◎), 200.1(●), and 400.1(○). The solid lines show the curves calculated by using the constants of case 2 in Table 2.

The calorimetric data thus obtained were first analyzed by assuming the only formation of mononuclear $[CdX_n]^{(2-n)+}$ (X=SCN and n=1—4) complexes. The formation constants of the third and fourth complexes estimated from the data were rather uncertain. However, as seen in Fig. 2 where the titration curves in Fig. 1 are expanded over the range C_X/C_M= 0—4, we see some deviation of the experimental points from the theoretical curves (the broken lines) calculated by assuming the only formation of $[CdX]^+$ and $[CdX_2]$ at relatively higher concentrations of the metal ion in the range $C_X/C_M<1$. The deviation suggested the formation of polynuclear thiocyanato complexes of Cd(II) in aqueous solution.

Since the formation of $[CdX_3]^-$ and $[CdX_4]^{2-}$ was not conclusive from the data in Fig. 1, titrations of sodium thiocyanate solutions with the 0.25 mol dm^{-3} $Cd(ClO_4)_2$ solution were carried out, where the $[CdX_3]^-$ and $[CdX_4]^{2-}$ complexes were expected to form at the initial stage of the titrations. Calorimetric titration curves thus obtained are illustrated in Fig. 3, in which enthalpies ΔH° ($= -q_{\mathrm{corr}}/(\delta v C_{\mathrm{M,tit}})$ where

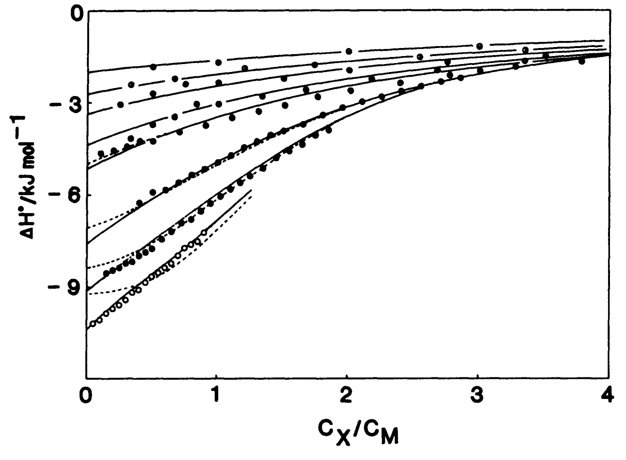

Fig. 2. Calorimetric titration curves of cadmium(II) thiocyanate solution expanded over the range $C_X/C_M=0—4$. Symbols used are the same as those in Fig. 1. The solid lines show the curves calculated by using the constants of case 2 in Table 2. The broken lines show the curves calculated by assuming the formation of the only mononuclear complexes.

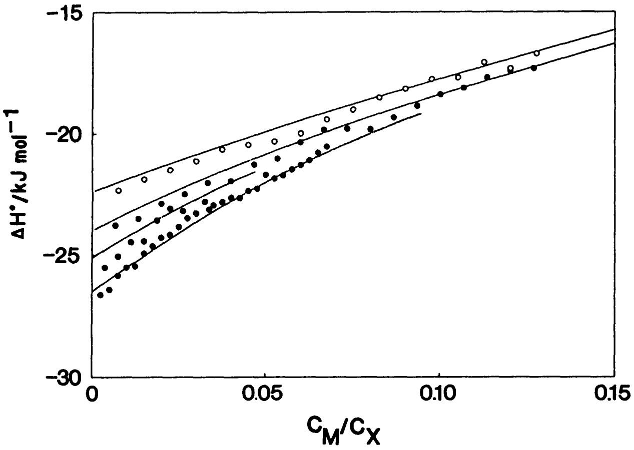

Fig. 3. Calorimetric titration curves obtained by titrating NaSCN solutions with $Cd(ClO_4)_2$ solution. Initial concentrations of sodium thiocyanate (C_X/mol dm^{-3}): 1.0(○), 1.5(●), 2.0(◎), and 3.0(◉). The solid lines show the curves calculated by using the constants of case 2 in Table 2.

Table 2. The Least-Squares Refinement of Formation Constants, β_{pq}/mol$^{-(p+q-1)}$ dm$^{3(p+q-1)}$, and Enthalpies, $\Delta H^\circ_{\beta pq}$/kJ mol^{-1}, of the Reaction, $q\mathrm{Cd}^{2+}+p\mathrm{X}^-=[\mathrm{Cd}_q\mathrm{X}_p]^{(2q-p)+}$ (X=SCN), in Aqueous Solution Containing 3 mol dm^{-3} $NaClO_4$ as a Constant Ionic Medium at 25 °C

	Case 1	Case 2
β_{11}	23.66±0.01	23.48±0.01
β_{21}	79.26±0.01	58.52±0.01
β_{31}	—	65.97±0.01
β_{41}	11.00±0.02	100 ±4
β_{12}	9.4 ±0.9	17.83±0.01
$\Delta H^\circ_{\beta 11}$	−10.39±0.09	−10.19±0.06
$\Delta H^\circ_{\beta 21}$	−24.80±0.07	−30.3 ±0.3
$\Delta H^\circ_{\beta 31}$	—	−7.7 ±0.6
$\Delta H^\circ_{\beta 41}$	−29.6 ±0.2	−30.5 ±0.2
$\Delta H^\circ_{\beta 12}$	−17 ±2	−14.8 ±0.4
NP	241	241
U	8.88	5.67

Uncertainties refer to standard deviations. NP refers to the number of calorimetric data points.

Table 3. Formation Constants $\log(K_n/\mathrm{mol\,dm^{-3}})$ for the Stepwise Reaction, $[\mathrm{MX}_{n-1}]^{(3-n)+}+\mathrm{X}^-=[\mathrm{MX}_n]^{(2-n)+}$ (M=Zn or Cd, X=SCN and n=1—4) in Water and in Dimethyl Sulfoxide at 25 °C

	Cd(II)		Zn(II)	
	Water[a] 3 mol dm^{-3} $NaClO_4$	DMSO[b] 1 mol dm^{-3} NH_4ClO_4	Water[c] 5 mol dm^{-3} $NaClO_4$	DMSO[d] 1 mol dm^{-3} NH_4ClO_4
$\log K_1$	1.378	1.81	0.917	1.38
$\log K_2$	0.396	0.91	0.673	1.40
$\log K_3$	0.052	0.20	0.577	2.43
$\log K_4$	0.180	—	0.347	1.65

a) This work. b) Ref. 11. c) Ref. 9. d) Ref. 12.

$C_{\mathrm{M,tit}}$ denotes the concentration of Cd(II) ion in the titrant), were plotted against the ratio C_M/C_X in the test solution at each titration point.

All the calorimetric data thus obtained were simultaneously analyzed by assuming the formation of mono- and polynuclear thiocyanato complexes of Cd(II) and their formation constants and enthalpies were obtained by the least-squares method. Among various cases examined by assuming the formation of different sets of complexes, two cases gave relatively small error-square sums. The results are summarized in Table 2, in which we assumed the formation of $[\mathrm{Cd}_2\mathrm{X}]^{3+}$ and $[\mathrm{CdX}_n]^{(2-n)+}$ (n=1,2 and 4) in case 1, and the formation of $[\mathrm{Cd}_2\mathrm{X}]^{3+}$ and $[\mathrm{CdX}_n]^{(2-n)+}$ (n=1—4) in case 2. Theoretical curves calculated by using the constants of case 2 in Table 2 are drawn by the solid lines in Figs. 1—3, which well reproduced the experimental points over the whole range of C_X/C_M and C_M/C_X examined here. On the other hand, although the error-square sum U of case 1 was not too large compared with that of case 2, theoretical curves calculated by using the constants of case 1 did not well reproduce the experimental points in Fig. 3. Therefore, we concluded that the formation of $[\mathrm{CdX}_3]^-$ should not be neglected even if the complex was not significantly formed under the present experimental conditions.

The stepwise formation constants $\log(K_n/\mathrm{mol^{-1}\,dm^3})$ of formation of $[\mathrm{CdX}_n]^{(2-n)+}$ (X=SCN and n=1—4) thus obtained are summarized in Table 3, together with those of $[\mathrm{ZnX}_n]^{(2-n)+}$ in water,[9] and $[\mathrm{CdX}_n]^{(2-n)+}$ and $[\mathrm{ZnX}_n]^{(2-n)+}$ in DMSO[11,12] for comparison. The formation constants of $[\mathrm{CdX}_n]^{(2-n)+}$ have also been reported by Gerding[13—15] in aqueous solution containing various ionic media, and the log K_n values in 3 mol dm^{-3} $NaClO_4$ ionic medium are 1.41, 0.83, 0.24, and 0.0 for n=1, 2, 3, and 4, respectively. The log

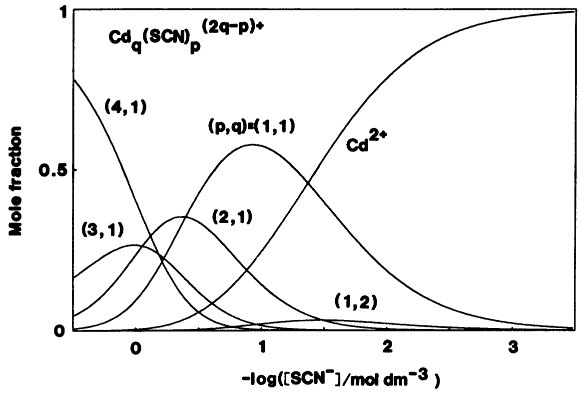

Fig. 4. Distribution of cadmium(II) thiocyanato complexes in 3 mol dm^{-3} NaClO$_4$ aqueous solution containing 0.1mol dm^{-3} Cd(II) ion at 25 °C. (p,q) represents the number of ions within the $[Cd_qX_p]^{(2q-p)+}$ (X=SCN) complex.

K_1 value is in good agreement with ours, but the log K_n (n=2—4) values are appreciably different from the results of the present work. Particularly, the value of log K_2 according to Gerding is remarkably large compared to that obtained in our work.

In Table 3, one finds that the log K_1 value of $[CdX]^+$ is larger than that of $[ZnX]^+$ but stepwise formation constants of the other $[CdX_n]^{(2-n)+}$ complexes were smaller than those of the corresponding zinc(II) complex in water and in DMSO.

We also found the formation of dinuclear $[Cd_2X]^{3+}$ complex in solutions of relatively high concentrations of the metal ion at $C_X/C_M<1$. The log K value for the reaction, $Cd^{2+}+[CdX]^+=[Cd_2X]^{3+}$, was −0.12 and the corresponding $\Delta G°$, $\Delta H°$, and $\Delta S°$ values for the reaction being 0.7 and −4.6 kJ mol^{-1} and −18 J K^{-1} mol^{-1}, respectively.

Distribution of species in cadmium(II) thiocyanate solutions containing 0.1 mol dm^{-3} Cd(II) ions is illustrated in Fig. 4.

Raman Spectra of Cadmium(II) Thiocyanate Solutions. Raman spectra of the C–N and C–S stretching vibrations of SCN$^-$ ion measured in cadmium(II) thiocyanate aqueous solutions with varying ratios of C_X/C_M are shown in Figs. 5 and 6, respectively. The Raman bands observed were assigned by taking into account the distribution of species in each cadmium(II) thiocyanate solution.

The Raman spectra in Fig. 5 show three peaks at ca. 2070, 2105, and 2130 cm^{-1}, the first band being ascribed to the vibration of free SCN$^-$ ion. It was expected from the result of the formation constants obtained that $[CdX]^+$ and $[Cd_2X]^{3+}$ (X=SCN) were formed in cadmium(II) thiocyanate solutions at $C_X/C_M<1$ and the $[Cd_2X]^{3+}$ complex predominated in the solutions with lowering ratio of C_X/C_M and with increasing C_M as examined here. Two peaks at 2105 and 2130 cm^{-1} were observed in the solution of C_X/C_M=0.08, while the former peak disappeared in the solution of C_X/C_M=0.034. Thus the 2105 and 2130 cm^{-1} bands were assigned to the C–N vibration within $[CdX]^+$ and $[Cd_2X]^{3+}$, respectively.

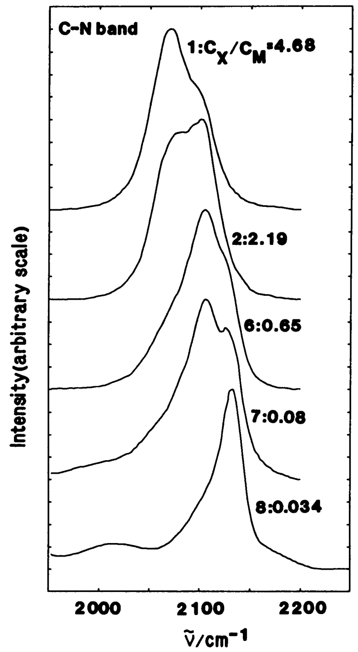

Fig. 5 Raman spectra of the C–N stretching vibration of SCN$^-$ ion measured in various cadmium(II) thiocyanate solutions.

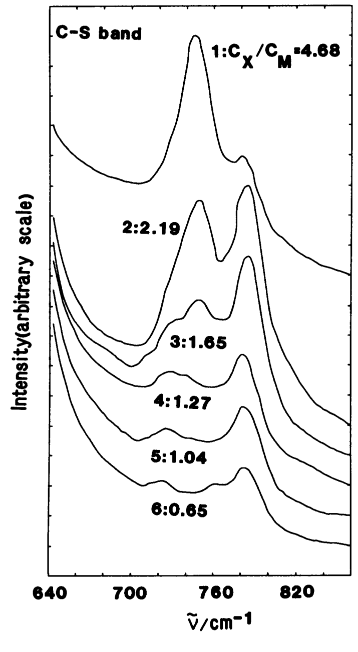

Fig. 6. Raman spectra of the C–S stretching vibration of SCN$^-$ ion measured in various cadmium(II) thiocyanate solutions.

The Raman spectra in Fig. 6 show predominant peaks at ca. 720, 740, and 780 cm^{-1}, the second band being attributable to the vibration of free SCN$^-$ ion. In the solutions of C_X/C_M=0.65—2.19 examined, the intensity of the 780 cm^{-1} band relative to that of the

Table 4. Thermodynamic Quantities, $\log(\beta_{41}/\text{mol}^{-1}\,\text{dm}^3)$, $\Delta G^\circ_{\beta 41}/\text{kJ mol}^{-1}$, $\Delta H^\circ_{\beta 41}/\text{kJ mol}^{-1}$, and $\Delta S^\circ_{\beta 41}/\text{J K}^{-1}\,\text{mol}^{-1}$, for the Overall Reaction, $M^{2+}+4X^- = [MX_4]^{2-}$ (X=SCN and M=Zn, Cd and Hg) in Aqueous Solutions at 25 °C

	Zn(II)[a]	Cd(II)	Hg(II)[b]
$\log\beta_{41}$	2.51	2.00	21.67
$\Delta G^\circ_{\beta 41}$	−14.3	−11.4	−123.7
$\Delta H^\circ_{\beta 41}$	−12.8	−30.5	−141.5
$\Delta S^\circ_{\beta 41}$	5	−64	−60

a) Ref. 12. b) Ref. 18.

720 cm⁻¹ band increased with increasing ratios of C_X/C_M, and thus, these two bands should be assigned to the vibrations of, at least, two different species. Since it was indicated from the distribution of the cadmium(II) thiocyanato complexes in the solutions that $[CdX]^+$ was present as the main species and the concentration of the complex increased with increasing ratios of C_X/C_M in the range 0.65—1.65, the 780 cm⁻¹ band was assigned to the C–N stretching vibration within $[CdX]^+$. Since it was indicated from the thermodynamic data that the $[Cd_2X]^{3+}$ complex was appreciably formed in the solutions of $C_X/C_M=0.65$—1.04 and the $[CdX_2]$ complex in the solutions of $C_X/C_M=1.27$—2.19, a weak band at 720 cm⁻¹ may be ascribed to the C–S stretching vibration of the $[Cd_2X]^{3+}$ and $[CdX_2]$ species.

Thermodynamic Quantities of Formation of Thiocyanato Complexes of Cd(II). Thermodynamic quantities of formation of the tetrathiocyanato complexes of Zn(II), Cd(II), and Hg(II) are summarized in Table 4. The overall formation constant $\log\beta_{41}$ varied in the sequence Zn(II)>Cd(II)<Hg(II), and thus, the formation of $[CdX_4]^{2-}$ (X=SCN) is the least favorable within the metal complex in aqueous solution. The corresponding $\Delta H^\circ_{\beta 41}$ and $\Delta S^\circ_{\beta 41}$ values vary in the sequence, Zn(II)>Cd(II)≫Hg(II) and Zn(II)≫Cd(II)≈Hg(II), respectively. The less favorable formation of $[CdX_4]^{2-}$ than that of $[ZnX_4]^{2-}$ is thus ascribed to the small entropy term, i.e., the $\Delta S^\circ_{\beta 41}$ value of the former complex is largely negative compared to that of the latter.

Among tetrahalogeno complexes of Cd(II) in aqueous solution, $\Delta H^\circ_{\beta 41}$ becomes negative in the only case of the complex with soft iodide ions (−29 kJ mol⁻¹).[16] The fact that the $\Delta H^\circ_{\beta 41}$ value of the tetrathiocyanatocadmate(II) complex was also negative in aqueous solution, therefore, suggests that cadmium(II) ion has some bonds with the soft S atoms within the ligating SCN⁻ ions. However, the $\Delta S^\circ_{\beta 41}$ value of the tetraiodocadmate(II) complex is much more positive (26 J K⁻¹ mol⁻¹)[16] than that of the corresponding thiocyanato complex in aqueous solution. The larger difference in the entropy values may mainly be ascribed to the loss of vibrational and rotational freedoms of triatomic SCN⁻ ion on coordination to Cd(II) ion. Such a difference in the entropies of formation of the halogeno and thiocyanato complexes of Cd(II) has also been observed in DMSO.[11]

Table 5. Thermodynamic Quantities, $\Delta G^\circ_n/\text{kJ mol}^{-1}$, $\Delta H^\circ_n/\text{kJ mol}^{-1}$, and $\Delta S^\circ_n/\text{J K}^{-1}\,\text{mol}^{-1}$, for the Stepwise Reaction, $[MX_{n-1}]^{(3-n)+}+X^- = [MXn]^{(2-n)+}$ (M=Zn or Cd, X=SCN and n=1—4), in Water and in Dimethyl Sulfoxide at 25 °C

	Cd(II)		Zn(II)	
	Water[a] 3 mol dm⁻³ NaClO₄	DMSO[b] 1 mol dm⁻³ NH₄ClO₄	Water[c] 5 mol dm⁻³ NaClO₄	DMSO[d] 1 mol dm⁻³ NH₄ClO₄
ΔG°_1	−7.8	−10.3	−5.2	−7.9
ΔG°_2	−2.3	−5.2	−3.8	−8.1
ΔG°_3	−0.3	−1.2	−3.3	−13.7
ΔG°_4	−1.0	—	−2.0	−9.4
ΔH°_1	−10.2	−3.0	−5.0	5.5
ΔH°_2	−20.1	−2.8	2.9	23.5
ΔH°_3	22.6	4.2	−6.3	−17.8
ΔH°_4	−22.8	—	−4.4	−10.7
ΔS°_1	−8	25	1	45
ΔS°_2	−60	8	23	105
ΔS°_3	77	18	−10	−13
ΔS°_4	−73	—	−8	−4

a) This work. b) Ref. 11. c) Ref. 9. d) Ref. 12.

Coordination Structures of $[Cd_2X]^{3+}$ and $[CdX_n]^{(2-n)+}$ (X=SCN). It has been known that the C–S stretching vibration of SCN⁻ ion shifts toward the higher and lower frequencies, respectively, within metal complexes than that of the free ion as the result of the coordination of SCN⁻ ion to a matal ion through the N and S atoms.[2–7] The Raman bands observed at ca. 720 and 780 cm⁻¹ thus indicated the formation of the complexes having the Cd–S and Cd–N bonds.

Thermodynamic quantities, $\Delta G^\circ_n/\text{kJ mol}^{-1}$, $\Delta H^\circ_n/\text{kJ mol}^{-1}$ and $\Delta S^\circ_n/\text{J K}^{-1}\,\text{mol}^{-1}$, for the stepwise reaction, $[MX_{n-1}]^{(3-n)+}+X^- = [MX_n]^{(2-n)+}$ (M=Zn and Cd, X=SCN and n=1—4), in aqueous solutions are summarized in Table 5, together with those in DMSO for comparison.[11,12] The ΔH°_n and ΔS°_n values for the $[CdX_n]^{(2-n)+}$ complexes in aqueous solution irregularly varied with n and they mostly compensated each other to result in rather smooth changes in ΔG°_n. The irregularities of ΔH°_n and ΔS°_n with n might be correlated to the bonding type of SCN⁻ ions with Cd(II) ion as well as a structural change in the cadmium(II) thiocyanato complexes in aqueous solution.

$[Cd(SCN)Cd]^{3+}$. It is expected that two cadmium(II) ions are bridged by an SCN⁻ ion within the dinuclear complex. A similar bridged structure -[Cd–SCN–Cd]- is found in $Cd(SCN)_2$ crystal. The $[Cd(SCN)Cd]^{3+}$ complex has both Cd–S and Cd–N bonds, and thus, showed the C–S vibrational band at 720 cm⁻¹ which is an indicative of the Cd–S bond formation within the complex.

$[Cd(NCS)]^+$. Since the 780 cm⁻¹ band is assigned to the C–S stretching vibration within the monothiocyanatocadmium(II) complex predominantly formed in the solutions of $C_X/C_M=0.65$—2.19 in Fig. 6, the coordination structure $[Cd(NCS)]^+$ is suggested for the complex. The ΔS_1° value for the formation of the monothiocyanatocadmium(II) complex is comparable with that of $[Zn(NCS)]^+$ in aqueous solution. The result may also support the formation of $[Cd(NCS)]^+$, instead of $[Cd(SCN)]^+$.

[Cd(SCN)(NCS)]. In the cadmium(II) thiocyanate solutions of C_X/C_M=1.27—2.19, the mono- and dithiocyanatocadmium(II) complexes are formed but the formation of the dinuclear complex is negligible. Therefore, the 720 cm^{-1} band still observed in the solutions may arise from the formation of the Cd–S bond within the dithiocyanatocadmium(II) complex. Consequently, the structure [Cd(SCN)(NCS)] having both Cd–S and Cd–N bonds is suggested. The stepwise ΔH_2° and ΔS_2° values for the reaction, $[Cd(NCS)]^+ + SCN^- = [Cd(SCN)(NCS)]$, are largely negative, which is probably due to the formation of a covalent-type bond between moderately soft Cd(II) ion and the soft S atom of SCN^- ion.

$[Cd(SCN)(NCS)_2]^-$. Although there is no evidence on the coordination structure of the trithiocyanatocadmate(II) complex from Raman spectroscopic data, the structure $[Cd(SCN)(NCS)_2]^-$ is suggested, because the tetrathiocyanatocadmate(II) complex may be formed from the trithiocyanato complex with an SCN^- ion by bonding through the S atom as discussed below.

$[Cd(SCN)_2(NCS)_2]^{2-}$. The coordination structure of the tetrathiocyanatocadmate(II) complex has been elucidated by a previous X-ray scattering measurement to be $[Cd(SCN)_2(NCS)_2]^{2-}$. The ΔH_4° and ΔS_4° values were similar to the ΔH_2° and ΔS_2° values, respectively, the result indicating that the Cd–S bond may form at the formation of the tetrathiocyanatocadmate(II) complex in aqueous solution. From this result we concluded that the third complex is $[Cd(SCN)(NCS)_2]^-$, from which an additional Cd–S bond is formed to produce $[Cd(SCN)_2(NCS)_2]^{2-}$.

Change in the Coordination Symmetry around Cd(II). Relatively largely positive ΔH_3° and ΔS_3° values observed at the third consecutive step of formation of $[Cd(SCN)(NCS)_2]^-$ suggest the change in the coordination symmetry around Cd(II) ion from octahedral to tetrahedral.

It is known that cadmium(II) ion is tetrahedrally coordinated with four SCN^- ions and no solvent molecules in the first coordination sphere within the tetrathiocyanatocadmate(II) complex in aqueous solution.[1] On the other hand, aquàcadmium(II) ion is octahedrally coordinated with six water molecules in aqueous solution.[17] Thus, the coordination symmetry around Cd(II) ion changes at a certain step of formation of the thiocyanato complexes of the metal ion. When the symmetry changes from octahedral to tetrahedral, more than one (three in this case) water molecules should be replaced to an entering SCN^- ion. Such an extensive dehydration process should be accompanied with a relatively large entropy gain. At the same time, a large absorption of heat should result due to the rupture of many metal-solvent bonds. As seen in Table 5, the same trend in the variation of ΔH_n° has been observed in the formation of the thiocyanto complexes of Cd(II) in DMSO.[11]

It is noted that the ΔH_2° and ΔS_2° values are largely positive in the complex formation reaction of the zinc(II) thiocyante system in both water[9] and DMSO,[12] and the result suggests that the coordination symmetry around zinc(II) ion may be changed at the second step of the complex formation. The structure change occurring at a different stage of the complex formation in the zinc(II) thiocyanate system from that in the cadmium(II) system may be due to a smaller ionic size of zinc(II) ion than that of cadmium(II) ion.

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