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Calorimetric and Raman Spectroscopic Studies of Cadmium(II) Thiocyanato Complexes in *N,N*-Dimethylformamide

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Formation of thiocyanato complexes of cadmium(II) ion has been calorimetrically studied in *N,N*-dimethylformamide (DMF) at 25 °C. Calorimetric data obtained were well explained in terms of the formation of a series of four mononuclear $[CdX_n]^{(2-n)+}$ (n=1—4, X=SCN) complexes, and their formation constants, enthalpies, and entropies were determined. Raman band shifts for the C–S stretching vibration of SCN^- ion indicated that SCN^- ion binds to cadmium(II) ion only with the N end within the mono- or dithiocyanato complex, $[Cd(NCS)]^+$ or $[Cd(NCS)_2]$. Within the tri- and tetrathiocyanato complexes, thiocyanate ions binds with both the N and S ends, and the coordination modes, $[Cd(NCS)_2(SCN)]^-$ and $[Cd(NCS)_3(SCN)]^{2-}$, were suggested. The coordination modes for the di- and tetrathiocyanato complexes in DMF, $[Cd(NCS)_2]$ and $[Cd(NCS)_3(SCN)]^{2-}$, are different from those in water, $[Cd(NCS)(SCN)]$ and $[Cd(NCS)_2(SCN)_2]^{2-}$.[1] It is thus shown that the N-bonding becomes more favorable in DMF than in water. Such a result may mainly be ascribed to relatively weakened solvation of the SCN^- ion in DMF, especially at the N atom site which is hydrogen-bonded with water molecules but not with DMF.

Thiocyanate ion is capable of bonding through either the hard nitrogen or soft sulfur end with Lewis acids depending on hardness and softness of the Lewis acids. Among thiocyanato complexes of d^{10} metal(II) ions, N-bonding was found in the $[Zn(NCS)_4]^{2-}$ complex that contains a relatively hard zinc(II) ion, while S-bonding was observed in the $[Hg(SCN)_4]^{2-}$ complex of soft mercury(II) ion.[2–4] For cadmium(II) ion, its hardness is weaker than that of zinc(II) ion and its softness is also less than that of mercury(II) ion, thiocyanate ions bind through two N and two S ends to form $[Cd(NCS)_2(SCN)_2]^{2-}$ in water.[2] Furthermore, the coordination of thiocyanate ions in lower complexes has been suggested to be $[Cd(NCS)]^+$ (N-bonding), $[Cd(NCS)(SCN)]$ (N- and S-bondings), and $[Cd(NCS)_2(SCN)]^-$ (two N- and one S-bondings) in water.[1] The result implies that the apparent hard and soft characters of cadmium(II) ion changes in the course of the stepwise complexation with thiocyanate ions. It is thus expected that the binding energies to cadmium(II) ion of the hard N and soft S ends of the SCN^- ion are very close to each other in water. In such a case, solvation of thiocyanate ion might also play an essential role for determining the N- or S-bonding of the ion to cadmium(II) ion.

We therefore aimed at investigating the formation and structure of cadmium(II) thiocyanato complexes in aprotic solvents with different solvating abilities. In this work we report the complexation between cadmium(II) and thiocyanate ions in *N,N*-dimethylformamide (DMF) studied by calorimetry. Raman spectra of cadmium(II) thiocyanate solutions were measured to elucidate the bonding types of SCN^- ion to cadmium(II) ion within the thiocyanato complexes.

Experimental

Reagents. All chemicals used were of reagent grade. Cadmium(II) perchlorate DMF solvate was prepared by dissolving $Cd(ClO_4)_2\cdot6H_2O$ crystals in DMF and then by recrystallizing it three times from DMF. The DMF solvate thus obtained is finally recrystallized from acetone and washed with ether. The cadmium(II) perchlorate DMF solvate thus obtained was dried at about 40 °C in a vacuum oven for several days and kept in a desiccator over P_2O_5. The value of x in the $Cd(ClO_4)_2\cdot x$dmf was found to be 6 from the analysis of the metal concentration by EDTA titration. Tetraethylammonium perchlorate was recrystallized once from water and dried in a vacuum oven at 100 °C. Ammonium perchlorate of reagent grade was dried at 100 °C. Tetraethylammonium thiocyanate and ammonium thiocyanate of reagent grade were used without further purification and dried in vacuum in a desiccator over P_2O_5. *N,N*-Dimethylformamide was dried for several weeks over Molecular Sieve 4A 1/16 and then distilled at 25 °C under reduced pressure and stored over molecular sieve in a dark bottle with a P_2O_5 drying-tube.

Measurements. Calorimetric measurements were carried out in a room thermostated at (25±0.2) °C.[1] Test solutions contained either 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ or 1 mol dm^{-3} NH_4ClO_4 as a constant ionic medium. A cadmium(II) perchlorate solution (50 cm^3) was placed in a stainless steel vessel, the inside wall of which was coated with Teflon. The vessel was inserted into an aluminium block thermostated at (25.0±0.0001) °C in an air-bath. The vessel was filled with dry nitrogen gas and isolated from moisture with a P_2O_5 drying-tube. A $Cd(ClO_4)_2$ solution in the vessel was then titrated with a 0.4 mol dm^{-3} $(C_2H_5)_4NSCN$ or a 1 mol dm^{-3} NH_4SCN DMF solution by using an autoburet (APB-118, Kyoto Electronics). Heats of complexation at each titration point were measured with a certainty of ±0.02 J and were corrected for heat of dilution of the titrant. The heat of dilution had been determined by separate experiments by titrating a 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ (or 1 mol dm^{-3} NH_4ClO_4) DMF solution with a 0.4 mol dm^{-3} $(C_2H_5)_4NSCN$ (or 1 mol dm^{-3} NH_4SCN) DMF solution. The heat of dilution observed in this measurement was found to be very small. Calorimetric measurements were carried out by using a fully automatic on-line system developed in our

Table 1. The Total Concentrations (mol dm^{-3}) of Cd^{2+} and SCN$^-$ Ions in the Various Cadmium(II) Thiocyanate Solutions Used for Raman Spectroscopic Measurements

	Cd^{2+}	SCN$^-$	$\bar{n}$[a)]
A	0.4006	0.4065	1.0
B	0.3997	0.8321	2.0
C	0.3998	1.321	3.0
D	0.3992	4.171	3.9

a) The average number of SCN$^-$ ions bound per cadmium(II) ion calculated by using the formation constants in Table 2 obtained in the 1 mol dm^{-3} NH_4ClO_4 ionic medium at 25 °C.

laboratory.

Raman spectra of cadmium(II) thiocyanate solutions were measured with a JRS-400T Raman spectrometer (JEOL) using 514.5 nm line of an NEC GLG argon ion laser in a room at 25 °C. The composition of solutions for the Raman spectroscopic measurements is listed in Table 1.

Data Analysis. A heat q_i measured at the ith titration point is represented by Eq. 1 using overall formation constants β_n and overall enthalpies $\Delta H^\circ_{\beta n}$ of formation of the $[CdX_n]^{(2-n)+}$ complexes.

$$q_i = -(V_i \sum \beta_n \Delta H^\circ_{\beta n} m_i x_i^n - V_{i-1} \sum \beta_n \Delta H^\circ_{\beta n} m_{i-1} x_{i-1}^n), \tag{1}$$

where V denotes the volume of a test solution, and m and x stand for the concentrations of free cadmium(II) and thiocyanate ions, respectively, which are related to their total concentrations C_M and C_X according to the mass-balance equations:

$$C_{M,i} = \sum \beta_n m_i x_i^n + m_i, \tag{2}$$

$$C_{X,i} = \sum n\beta_n m_i x_i^n + x_i. \tag{3}$$

The formation constants and enthalpies were simultaneously determined by minimizing the error-square sum, $U=\sum(q_{i,\mathrm{obsd}}-q_{i,\mathrm{calcd}})^2$ by using a non-linear least-squares program.

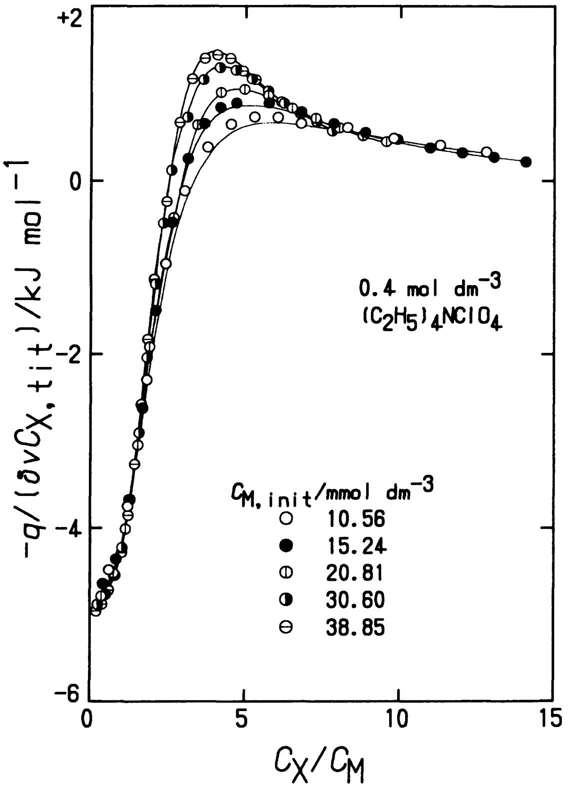

Fig. 1. Calorimetric titration curves of cadmium(II) thiocyanate DMF solutions containing 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C. Concentrations of cadmium(II) ions, $C_{M,init}$/mmol dm^{-3}, in initial test solutions are given. The solid lines show the curves calculated by using the constants of the set (1—4) in the $(C_2H_5)_4NClO_4$ ionic medium in Table 2.

Results and Discussion

Calorimetric titration curves for the complexation of cadmium(II) with thiocyanate ions obtained in the $(C_2H_5)_4NClO_4$ DMF solution are depicted in Fig. 1, in which the values $-q/(\delta v C_{X,tit})$ are plotted against C_X/C_M, where q, δv, $C_{X,tit}$, C_X, and C_M denote the heat evolved and the volume of an aliquot of the titrant added at each titration point, the concentration of $(C_2H_5)_4NSCN$ in the titrant solution, and the total concentrations of SCN$^-$ and Cd^{2+} ions in the test solution, respectively. The calorimetric data were analyzed by assuming the formation of various sets of mononuclear cadmium(II) thiocyanato complexes. Among various sets examined, the set (1—4) assuming the formation of $[CdX]^+$, $[CdX_2]$, $[CdX_3]^-$, and $[CdX_4]^{2-}$ (X=SCN), and the set (1,2,4) eliminating $[CdX_3]^-$ from the set (1—4) gave relatively small Hamilton R factors. The results for these sets are listed in Table 2. Other sets gave significantly large R values. Since both $\log \beta_3$ and $\Delta H^\circ_{\beta 3}$ values were obtained with small standard deviations and they laid within the reasonable range, we concluded that the $[CdX_3]^-$ can not be eliminated, and thus the set (1—4) is the best choice for describing the complexation of cadmium(II) with thiocyanate ions in DMF. In fact, as seen in Fig. 1, the solid lines calculated by using the constants for the set (1—4) in Table 2 well reproduce the experimental points over the whole range of C_X/C_M.

The titration curves obtained in the NH_4ClO_4 DMF solution are shown in Figs. 2 and 3. The data were analyzed by a similar way to that employed for data in the $(C_2H_5)_4NClO_4$ solution. In the NH_4ClO_4 solution, among various sets examined, the sets (1—4) and (1,2,3) gave relatively small R factors as shown in Table 2. Since the R value of the set (1—4) is appreciably smaller than that of the set (1,2,3), we adopted the parameters of the set (1—4) as the final choice.

Distribution of the cadmium(II) thiocyanato com-

Table 2. Least-Squares Refinement of Overall Formation Constants, $\log(\beta_n/\mathrm{mol}^{-n}\,\mathrm{dm}^{3n})$, and Enthalpies, $\Delta H^\circ_{\beta n}/\mathrm{kJ\,mol}^{-1}$, of the Thiocyanato Complexes of Cadmium(II) Ion in *N*,*N*-Dimethylformamide at 25 °C[a)]

	$(C_2H_5)_4NClO_4$[b)]		NH_4ClO_4[c)]	
	(1—4)	(1,2,4)	(1—4)	(1,2,3)
$\log\beta_1$	3.57(0.11)	3.47(0.14)	2.77(0.08)	2.40(0.07)
$\log\beta_2$	5.98(0.15)	5.73(0.17)	4.61(0.11)	3.86(0.07)
$\log\beta_3$	7.59(0.14)	—	5.69(0.12)	4.65(0.07)
$\log\beta_4$	8.81(0.16)	8.39(0.15)	6.55(0.13)	—
$\Delta H^\circ_{\beta 1}$	−4.9(0.04)	−5.0(0.07)	−5.8(0.1)	−6.1(0.2)
$\Delta H^\circ_{\beta 2}$	−9.2(0.2)	−9.1(0.2)	−11.7(0.3)	−15.7(0.8)
$\Delta H^\circ_{\beta 3}$	−7.3(0.2)	—	−11.2(0.4)	−0.4(0.6)
$\Delta H^\circ_{\beta 4}$	2.6(0.4)	−0.2(0.1)	−2.3(0.1)	—
U[d)]	0.045	0.161	0.695	1.49
R[e)]	0.023	0.044	0.034	0.050
N[f)]	88	88	156	156

a) Values in parentheses refer to three standard deviations. b) 0.4 mol dm^{-3}. c) 1 mol dm^{-3}. d) Error-square sum. e) The Hamilton *R* factor. f) The number of calorimetric data points.

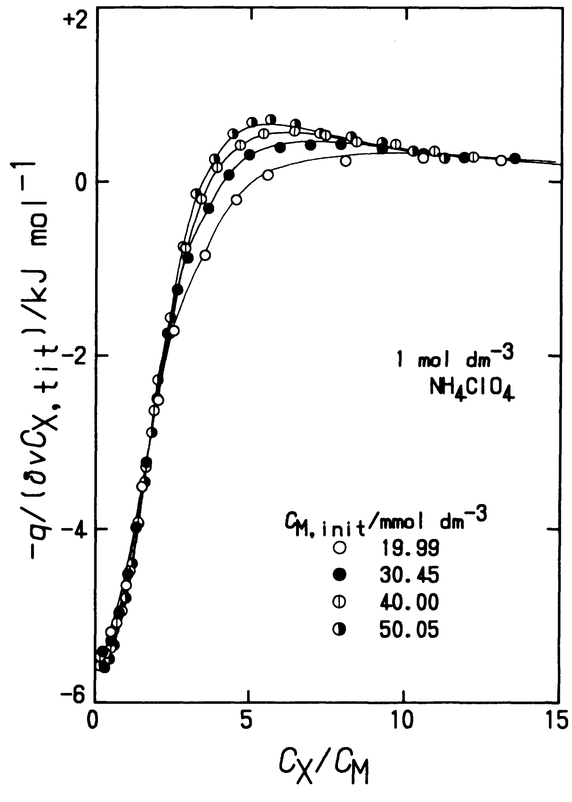

Fig. 2. Calorimetric titration curves of cadmium(II) thiocyanate DMF solutions containing 1 mol dm^{-3} NH_4ClO_4 at 25 °C. Concentrations of cadmium(II) ions, $C_{M,init}$/mmol dm^{-3}, in initial test solutions are given. The solid lines show the curves calculated by using the constants of the set (1—4) in the NH_4ClO_4 ionic medium in Table 2.

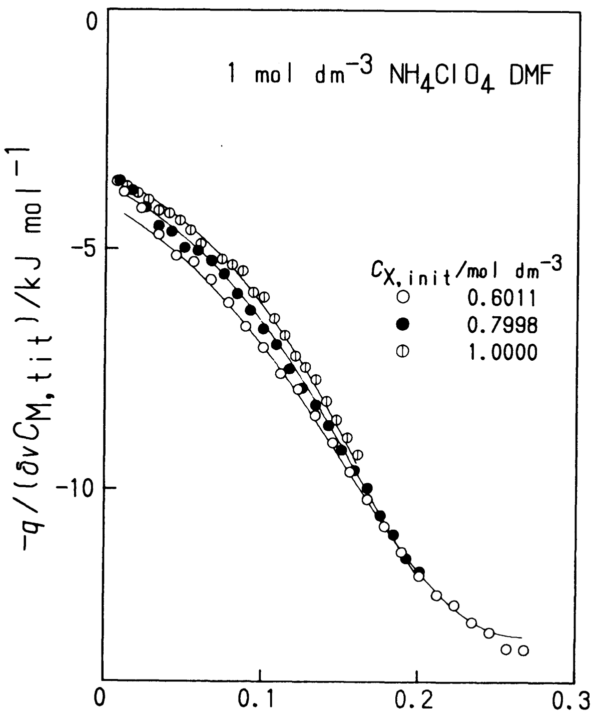

Fig. 3. Calorimetric back titration curves of cadmium(II) thiocyanate DMF solutions containing 1 mol dm^{-3} NH_4ClO_4 at 25 °C. Concentrations of cobalt(II) ions, $C_{X,init}$/mmol dm^{-3}, in initial test solutions are given. The solid lines show the curves calculated by using the constants of the set (1—4) in the NH_4ClO_4 ionic medium in Table 2.

plexes in these $(C_2H_5)_4NClO_4$ and NH_4ClO_4 DMF solutions in shown in Fig. 4, which is calculated by using the formation constants for the sets (1—4) in Table 2. It is demonstrated that the complexation is more favorable in 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ than in 1 mol dm^{-3} NH_4ClO_4 ionic medium. A similar result has been obtained also in the copper(II) bromide system in DMF,[5] where it is suggested that bromide ion forms appreciably ion pairs with NH_4^+ ion, while the ion pair formation of bromide ion with $(C_5H_5)_4N^+$ ions is practically negligible.

Raman Spectra of the Cadmium(II) Thiocyanate Solutions. Raman spectra for the C–S stretching vibrations are shown in Fig. 5. The observed Raman bands were assigned to each complex by taking into

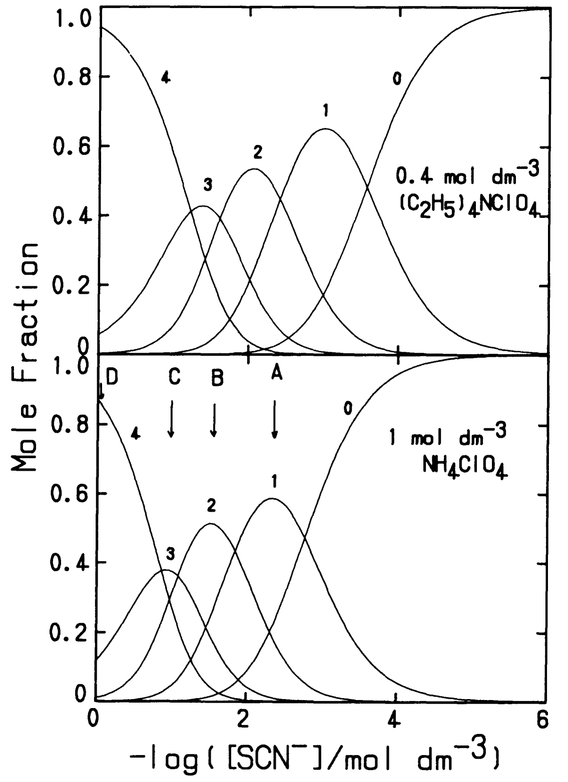

Fig. 4. Distribution of the cadmium(II) thiocyanato complexes in 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ and 1 mol dm^{-3} NH_4ClO_4 DMF solutions. The numbers represent n within the $[CdX_n]^{(2-n)+}$ (X=SCN) complex. Distribution of species in solutions A, B, C, and D used for the Raman spectral measurements is indicated.

account the distribution of the cadmium(II) thiocyanato complexes in the NH_4ClO_4 solution in Fig. 4.

The C–S stretching vibrational band of free SCN^- ion appears at ca. 755 cm^{-1} in DMF. It is known that the band shifts toward higher and lower frequencies when SCN^- ion binds to a metal ion with the N and S ends, respectively.[6–11] Solutions A and B show a sole band at 795 cm^{-1}, which involve the mono- and di(thiocyanato)cadmium(II) complexes, respectively, as the main species. This shift for the C–S stretching band toward a higher frequency from 755 to 795 cm^{-1} evidently indicates that the SCN^- ions bind with the N end to cadmium(II) ion to yield the $[Cd(NCS)]^+$ and $[Cd(NCS)_2]$ complexes. For solution C are observed a band at 795 cm^{-1}, indicative of the Cd–NCS linkage, and a broad one ranging 730—760 cm^{-1}, showing the alternative Cd–SCN bonding, i.e., the tri(thiocyanato)cadmate(II) complex may involve the Cd–SCN linkage suggesting the $[Cd(NCS)_2(SCN)]^-$ coordination. Solution D containing predominantly the tetra(thiocyanato)cadmate(II) complex shows the 795 cm^{-1} band and a weak shoulder at 735 cm^{-1}, indicating that the complex involves both Cd–NCS and Cd–SCN linkages. According to the X-ray diffraction measurement,[12] the four-coordinate tetrahedral $[Cd(NCS)_3(SCN)]^{2-}$ complex with three Cd–N and one Cd–S arrangements is elucidated.

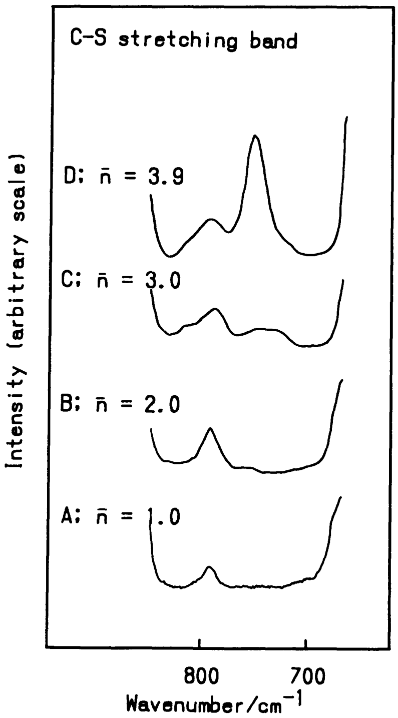

Fig. 5. Raman spectra for the C–S stretching vibration of SCN^- ion in various cadmium(II) thiocyanate DMF solutions.

On the other hand, Raman spectra for the C–N stretching vibration of SCN^- ion show a sole band for all the cadmium(II) thiocyanate solutions examined. No significant shift of the band is observed with the successive complexation. Therefore, it was hard to conclude the binding mode of SCN^- ion to cadmium(II) ion from the C–N stretching vibrational band.

The Coordination Structure Change. In DMF cadmium(II) ion is present as the hexa-solvate $[Cd(dmf)_6]^{2+}$ complex according to the X-ray diffraction measurement.[12] The formation of the four-coordinate $[Cd(NCS)_3(SCN)]^{2-}$ complex thus indicates that the coordination structure changes from octahedral to tetrahedral at a certain step of the complexation between cadmium(II) and thiocyanate ions.

Stepwise thermodynamic quantities of formation of the cadmium(II) thiocyanato complexes in DMF are summarized in Table 3. In any solution examined, the ΔS_4° value is large and positive, even larger than the ΔS_n° (n=1,2,3) values. This result is in contrast to that obtained in the cadmium(II)-halide systems,[13] in which the tri(halogeno)cadmate(II) complexes have a tetrahedral coordination. Such a relatively large and positive ΔS_4° value, together with a relatively large and positive ΔH_4° value for breaking metal-solvent bonds, observed in the cadmium(II) thiocyanate system

Table 3. The Stepwise Formation Constants, $\log(K_n/\mathrm{mol^{-1}\,dm^3})$, Enthalpies, $\Delta H_n^\circ/\mathrm{kJ\,mol^{-1}}$, and Entropies, $\Delta S_n^\circ/\mathrm{J\,K^{-1}\,mol^{-1}}$, for the Cadmium(II)-$SCN^-$ System in *N,N*-Dimethylformamide at 25 °C

	Water $NaClO_4$ a)	*N,N*-Dimethylformamide	
		$(C_2H_5)_4NClO_4$ b)	NH_4ClO_4 c)
$\log K_1$	1.378	3.57	2.77
$\log K_2$	0.396	2.41	1.84
$\log K_3$	0.052	1.61	1.08
$\log K_4$	0.180	1.23	0.86
ΔH_1°	−10.2	−4.9	−5.8
ΔH_2°	−20.1	−4.3	−5.9
ΔH_3°	22.6	1.9	0.5
ΔH_4°	−22.8	9.9	8.9
ΔS_1°	−8	52	33
ΔS_2°	−60	32	16
ΔS_3°	77	37	22
ΔS_4°	−73	56	46
$\Delta G_{\beta 4}^\circ$ d)	−11.4	−50.3	−37.4
$\Delta H_{\beta 4}^\circ$ d)	−30.5	2.6	−2.3
$\Delta S_{\beta 4}^\circ$ d)	−64	178	118

a) Ref. 1, the concentration of ionic medium is $3\,\mathrm{mol\,dm^{-3}}$. b) $0.4\,\mathrm{mol\,dm^{-3}}$. c) $1\,\mathrm{mol\,dm^{-3}}$. d) For the overall reaction, $Cd^{2+}+4X^-=[CdX_4]^{2-}$ (X=SCN).

suggests that an extensive liberation of DMF molecules occurs at the fourth step, i.e., the tri(thiocyanato)cadmate(II) complex is octahedral, and the coordination structure changes from octahedral to tetrahedral at the formation of the tetra(thiocyanato)-cadmate(II) one.14)

In water it was indicated that the corresponding coordination structure change occurs at the formation of the tri(thiocyanato)cadmate(II) complex.1) Consequently, we note that the change in coordination about cadmium(II) ion from octahedral to tetrahedral takes place at the latter step of the complexation in DMF than that in water in the cadmium(II) thiocyanate system. A similar result has been found for the cadmium(II) halide systems in water and in DMSO,15) in which the coordination changes from octahedral to tetrahedral at the second step in water, while at the third one in DMSO.

The Binding Mode Difference of Thiocyanate Ion in Water and in DMF. It is suggested in a previous section that a six-coordination for $[Cd(NCS)]^+$, $[Cd(NCS)_2]$, and $[Cd(NCS)_2(SCN)]^-$, and a four-coordination for $[Cd(NCS)_3(SCN)]^{2-}$ occur in DMF. It is noted that a six-coordination for $[Cd(NCS)]^+$ and $[Cd(NCS)(SCN)]$, and a four-coordination for $[Cd(NCS)_2(SCN)]^-$ and $[Cd(NCS)_2(SCN)_2]^{2-}$ are concluded in water.1,2) These results imply that the apparent hard and soft characters of cadmium(II) ion changes with the stepwise complexation of thiocyanate ions. Furthermore, it is indicated that solvent properties are also responsible for determining the N- or S-bonding of an SCN^- ion to cadmium(II) ion.

Thiocyanate ion binds to cadmium(II) ion through the N end at the first step in both water and DMF, giving a slightly more negative ΔH_1° value in water than that in DMF. At the second step thiocyanate ion ligates to the metal(II) ion through the S end in water, while through the N end in DMF. The difference in the N- or S-bonding of SCN^- ion reflects on the ΔH_2° values. As seen in Table 3 the ΔH_2° value is less negative than the ΔH_1° value in DMF, while the reverse in the case in water. The binding of a soft S atom of SCN^- ion to cadmium(II) ion leads to remarkable exothermicity in water as compared with that of a hard N atom in DMF.

Solvation of SCN^- ion in aprotic DMF solvent may be very different from that in protic water, especially at the hydrogen-bonding N atom site. When the enthalpies are compared, despite the fact that cadmium(II) ion is more strongly solvated by ca. $-63\,\mathrm{kJ\,mol^{-1}}$ in a strong donor solvent DMF than in water,16) the ΔH_1° value for the formation of $[Cd(NCS)]^+$ in the former solvent is only slightly less negative than that in the latter. For the corresponding ΔH_1° values for the halogeno complexes,13) even more negative value in DMF than that in water is in fact observed for chloride ion that is strongly hydrogen-bonded, i.e., strongly solvated in water. The ΔH_1° value is slightly less negative for bromide ion like thiocyanate ion, and much less negative for iodide ion in DMF than in water.17,18) It is thus shown that thiocyanate ion is also hydrogen-bonded at the N atom site in water, although the interaction with water molecules is not so strong as in the case of chloride ion.

Cadmium(II) ion may behave as a harder ion in aprotic DMF solvent than in protic water.15) In fact, the stability of $[CdX]^+$ increases in the sequence Cl<Br<I in water,17,18) i.e. the decreasing order of the hydrogen-bonding abilities of halide ions, while the sequence is reversed in DMF12) and also in DMSO.19) Thiocyanate ion forms hydrogen bonds, especially at

the N atom site, with water molecules but not with DMF. On the other hand, solvation of SCN^- ion at the soft and large S atom site may be weak in both solvents, or even weaker in water than in DMF.[20] Therefore, the reactivity at the N atom site of SCN^- ion may be enhanced in DMF over water. Consequently, thiocyanate ion may favorably bind with cadmium(II) ion through the N end in DMF, while through the S end in water. It is thus reasonably expected that the $[Cd(NCS)_2]$ and $[Cd(NCS)_3(SCN)]^{2-}$ complexes are formed in DMF, while the $[Cd(NCS)(SCN)]$ and $[Cd(NCS)_2(SCN)_2]^{2-}$ ones in water.[1]

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