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An X-Ray Diffraction Study on the Structure of Solvated Cadmium(II) Ion and Tetrathiocyanatocadmate(II) Complex in *N,N*-Dimethylformamide

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The structure of solvated cadmium(II) ion and the tetrathiocyanatocadmate(II) complex in *N,N*-dimethylformamide (DMF) has been determined by means of X-ray diffraction at 25 °C. The radial distribution curve for a cadmium(II) perchlorate DMF solution is well explained in terms of the presence of the octahedral $[Cd(dmf)_6]^{2+}$ complex with the Cd-O bond length of 229.6(4) pm, which is practically the same as that within $[Cd(dmso)_6]^{2+}$ in DMSO and $[Cd(H_2O)_6]^{2+}$ in H_2O. It is also found that the tetrathiocyanatocadmate(II) complex has a tetrahedral structure, $[Cd(NCS)_3(SCN)]^{2-}$, with three Cd-N and one Cd-S bonds, the distances being 223(2) and 257(2) pm, respectively. The coordination structure of the complex in DMF is different from that found in aqueous solution, $[Cd(NCS)_2(SCN)_2]^{2-}$.

Thiocyanate ion binds to metal ions through either the nitrogen or sulfur atom depending on the nature of metal ions. According to the X-ray, Raman, and NMR studies, relatively hard zinc(II) and soft mercury(II) ions form $[Zn(NCS)_4]^{2-}$ and $[Hg(SCN)_4]^{2-}$ in aqueous solution, respectiveiy.[1] Similar coordination geometry has also been reported for the tetrathiocyanato complexes of zinc(II) and mercury(II) ions in dimethyl sulfoxide (DMSO).[2] On the other hand, cadmium(II) ion, which has intermediate hard and soft characters between zinc(II) and mercury(II) ions, forms $[Cd(NCS)_2(SCN)_2]^{2-}$ with coordinating two nitrogen and two sulfur atoms of thiocyanate ions in aqueous solution.[1] It is suggested from Raman spectroscopic and thermodynamic data that the coordination of other thiocyanato complexes of cadmium(II) ion ($[Cd(SCN)_n]^{(2-n)+}$, n=1—3) changes with the number of ligand ions, $[Cd(NCS)]^+$, $[Cd(NCS)(SCN)]$ and $[Cd(NCS)_2(SCN)]^-$, in aqueous solution.[3]

The complex formation between cadmium(II) and thiocyanate ions occurs extensively in *N,N*-dimethylformamide (DMF), and a different coordination mode of thiocyanate ions in the complexes in DMF from that in water has been suggested.[4] However, no direct structural information on the thiocyanato complexes has so far been given in DMF. Therefore, in this work we aimed at determining the structure of the tetrathiocyanatocadmate(II) complex in DMF by the X-ray diffraction method. In aqueous and DMSO solutions cadmium(II) ion is octahedrally coordinated with relevant solvent molecules through oxygen atoms.[5,6] Since the corresponding structure of cadmium(II) DMF solvate has been revealed neither in solution nor in the solid state, we also determined the solvation structure of cadmium(II) ion in DMF.

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Experimental

Preparation of Sample Solutions. All chemicals used were of reagent grade. *Cadmium(II) perchlorate DMF solvate* was prepared by dissolving cadmium(II) perchlorate hydrate crystals in DMF and recrystallized three times from DMF and finally from acetone. Crystals thus obtained were dried at room temperature in a vacuum oven for several days. The analysis of the cadmium(II) perchlorate DMF solvate by EDTA titration showed the composition of $Cd(ClO_4)_2(dmf)_6$. *Cadmium(II) thiocyanate* was obtained by mixing stoichiometric amounts of aqueous cadmium(II) perchlorate and ammonium thiocyanate solutions. Crystals thus obtained were washed by suspending them in hot water and finally dried at 80 °C under atmospheric pressure. *Ammonium thiocyanate* was used without further purification and dried at room temperature in vacuum. *N,N*-Dimethylformamide was purified by the same method as described elsewhere.[4,7]

X-Ray diffraction measurements were performed for three test solutions A, B, and C (Table 1). Solution A was prepared by dissolving cadmium(II) perchlorate DMF solvate crystals in DMF. Solutions B and C were prepared by dissolving suitable amounts of cadmium(II) and ammonium thiocyanates in DMF so as to involve the tetrathiocyanatocadmate(II) complex as the main species in the solutions. Concentrations of cadmium(II) and thiocyanate ions in the sample solutions were determined by EDTA

Table 1. The Composition (mol dm^{-3}), Stoichiometric Volumes V, and Densities ρ of the Sample Solutions

	A	B	C
Cd^{2+}	0.9738	0.9854	0.9433
SCN^-	—	5.009	5.996
NH_4^+	—	3.038	4.110
ClO_4^-	1.948	—	—
DMF	12.28	9.624	8.872
ρ/g cm^{-3}	1.201	1.160	1.160
V/10^9 pm^3	1.705	1.685	1.760
C_{SCN}/C_{Cd}	—	5.083	6.356

titration and by gravimetry as AgSCN, respectively. Densities of the solutions were determined pycnometrically.

X-Ray Diffraction Measurements. X-Ray diffraction data were obtained on a JEOL θ-θ type diffractometer and an Mo tube (λ=71.07 pm) was used as the X-ray source. The observed range of scattering angle 2θ was from 2° to 140° and the data were recorded at least twice over the whole angle range. Corrections for absorption, polarization, and multiple scatterings of X-rays to the observed intensities were made by a usual manner as described elsewhere.[8]

The reduced intensities $i(s)$ are given as

$$i(s)=K\cdot I(s)-\sum_j n_j\cdot f_j^2(s), \quad (1)$$

were K represents a normalization factor of the observed intensities $I(s)$ to the absolute unit, n_j the number of atom j in a stoichiometric volume and $f_j(s)$ the atomic scattering factors of atom j corrected for anomalous dispersion. The reduced intensities multiplied by s ($=4\pi\ \lambda^{-1}\sin\theta$) for the sample solutions are depicted in Fig. 1. The $s\cdot i(s)$ values are converted into the radial distribution function $D(r)$ as

$$D(r)=4\pi r^2\rho_0+\frac{2r}{\pi}\int_0^{s_{max}} s\cdot i(s)\cdot M(s)\cdot\sin(rs)ds. \quad (2)$$

ρ_0 ($=\{\sum n_j\cdot f_j(0)\}^2/V$) stands for the average scattering density in a stoichiometric volume V per cadmium atom of the sample solution and s_{max} the maximum s-value available in the measurement ($s_{max}=16.6\times10^{-2}$ pm^{-1}). The modification function $M(s)$ has the form of $[\sum n_j\cdot f_j^2(0)/\sum n_j\cdot f_j^2(s)]\cdot\exp(-ks^2)$, the damping factor k being chosen as 100 pm^2 in the present case. The radical distribution curves in the form of $D(r)-4\pi r^2\rho_0$ for the test solutions are shown in Fig. 2.

A least-squares refinement for determining the structure parameters was carried out by comparing the observed and theoretical reduced intensities so as to minimize the error-square sum U,

$$U=\sum_{s_{min}}^{s_{max}} s^2\{i(s)_{obsd}-i(s)_{calcd}\}^2. \quad (3)$$

The theoretical intensities $i(s)_{calcd}$ resulting from the interatomic interactions in the solutions are calculated as

$$i(s)_{calcd}=\sum_{p}\sum_{\substack{q\\ p\neq q}} n_{pq}f_p(s)f_q(s)\frac{\sin(r_{pq}s)}{r_{pq}s}\exp(-b_{pq}s^2), \quad (4)$$

where r_{pq}, b_{pq}, and n_{pq} stand for the distance, the temperature factor, and the frequency factor of the atom-pair p-q, respectively.

All calculations were performed by using programs KURVLR[9] and NLPLSQ.[10]

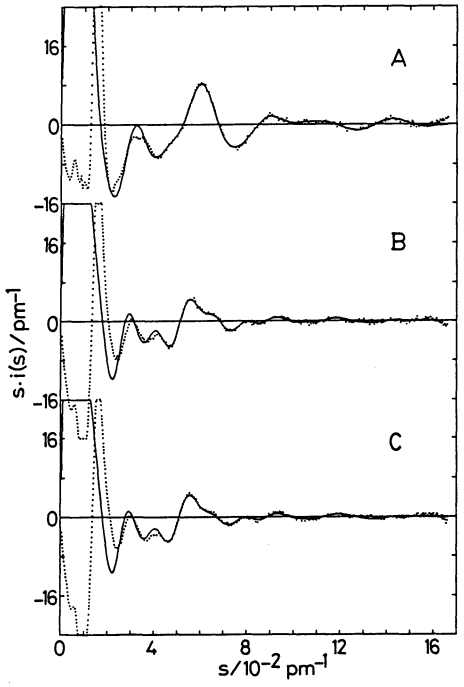

Fig. 1. The reduced intensities multiplied by s for solutions A, B, and C. The observed $s\cdot i(s)$ values are drawn by the dotted lines and calculated ones by the solid lines.

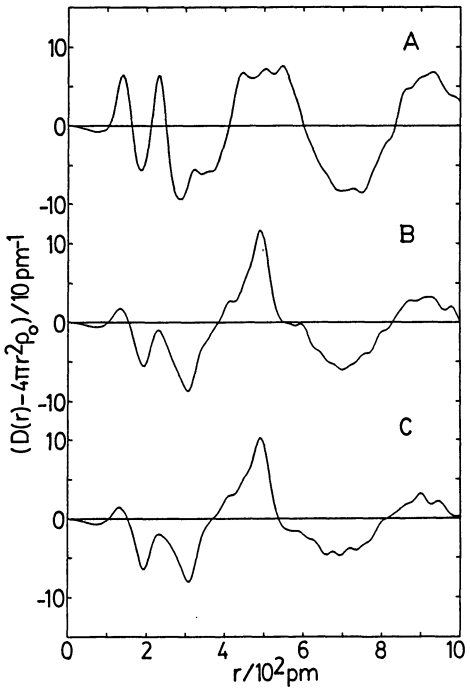

Fig. 2. The radial distribution curves in the form of $D(r)$-$4\pi r^2\rho_0$ for solutions A, B, and C.

Results and Discussion

Structure of Solvated Cadmium(II) Ion. Figure 3 shows the ($D(r)-4\pi r^2\rho_0$) curve of solution A. In the curve six peaks are observed at 140, 230, 320, 440, 500, and 550 pm. The last two peaks are originated from long distant intermolecular interactions which are not analyzed in the present study. The first peak at 140 pm is ascribable to the C-H, C-N, and C=O bonds within DMF molecules and the Cl-O bonds within perchlorate ions. The second peak at 230 pm is expected to be due to the Cd-O(dmf) bond similar to the Cd-O(H_2O) and Cd-O(dmso) bonds within the $[Cd(H_2O)_6]^{2+}$ and $[Cd(dmso)_6]^{2+}$ complexes, respectively.[5,6] The nonbonding C···C, C···O, and N···O interactions within DMF molecules and the O···O contacts within perchlorate ions also contribute to the

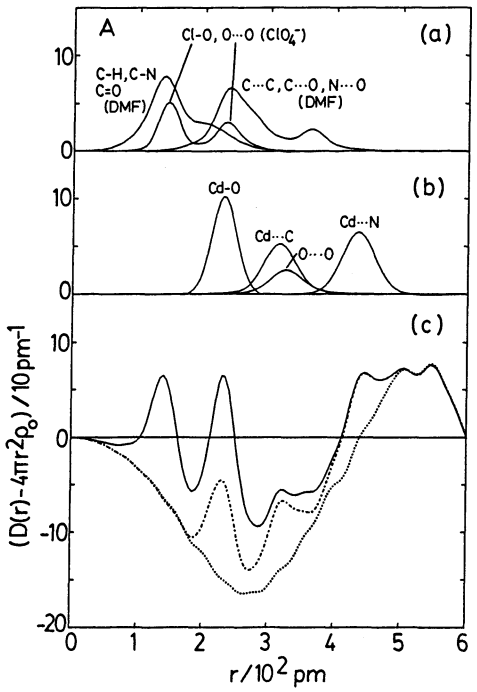

Fig. 3. The $(D(r)-4\pi r^2\rho_o)$ curve for solution A. (a) The theoretical peak shapes for intramolecular interactions within DMF molecule and perchlorate ion. (b) The peak shapes calculated for the Cd-O, Cd···C, O···O, and Cd···N interactions within the $[Cd(dmf)_6]^{2+}$ ion. (c) The chain and dotted lines represent the residual curves after subtraction of the theoretical peaks in (a) and (b), respectively, from the original one (solid line).

peak. The third and fourth peaks at 320 and 440 pm may be attributed to the nonbonding Cd···C(dmf) and Cd···N(dmf) interactions, respectively, the corresponding peaks having also been observed for the solvated copper(II) ion in DMF.[11]

In order to evaluate the structure parameters of the solvated cadmium(II) ion in DMF, the theoretical peak shapes due to the intramolecular interactions within DMF and perchlorate (Fig. 3a) are subtracted from the observed radial distribution function. The parameter values are taken from the literature.[12,13] The residual curve thus obtained (chain line in Fig. 3c) shows a large peak at 230 pm, which is ascribed to the Cd-O bonds within the solvated cadmium(II) ion. The area under the peak corresponds to six Cd-O bonds. Thus the solvated cadmium(II) ion in DMF is concluded to have an octahedral structure. Subtraction of the peaks due to the Cd-O, Cd···C, Cd···N, and O···O interactions based on the octahedral $[Cd(dmf)_6]^{2+}$ structure leads to a smooth background curve (dotted line) with no distinct peak over the range $r<450$ pm.

The least-squares method was applied to the high-angle region of $s\cdot i(s)$ values ($s>4\times10^{-2}$ pm^{-1}) to refine the structure parameters of the $[Cd(dmf)_6]^{2+}$, where the intramolecular interactions within DMF molecule, perchlorate and $[Cd(dmf)_6]^{2+}$ ions mainly contribute to the intensity values. In the course of the refinement, the structure parameters for DMF molecule and perchlorate ion were fixed at the literature values,[12,13] and the interatomic distances and the corresponding temperature factors arising from atom-pairs based on the $[Cd(dmf)_6]^{2+}$ structure were optimized. The interligand O···O distance was calculated from the Cd-O distance. The results thus obtained are summarized in Table 2, together with the structure parameters for the $[Cd(H_2O)_6]^{2+}$ and $[Cd(dmso)_6]^{2+}$ complexes. The Cd-O bond distance within the $[Cd(dmf)_6]^{2+}$ finally determined is 229.6(4) pm, and the Cd···C distance is 315(1) pm. The Cd-O-C bond angle is thus calculated to be 123°.

The structure parameters of the octahedrally solvated cadmium(II) ion in DMF, DMSO, and water in Table 2 show that the Cd-O distance within the solvated ion is not largely different within the limit of experimental uncertainties. However, the observed Cd-O bond length seems to be lengthened in the order Cd-O(H_2O) > Cd-O(dmf) > Cd-O(dmso), i.e., the decreasing order of the solvent donicity DMSO > DMF > water.[14]

Structure of $[Cd(SCN)_4]^{2-}$. According to the formation constants of cadmium(II)-thiocyanato complexes in DMF,[4] the tetrathiocyanatocadmate(II) complex is present as the main species in solutions B and C. The radial distribution curves of solutions B and C depicted in Fig. 2 were analyzed by the similar procedure to that employed for solution A. In the following discussion we describe only the result for solution C because the same conclusion was obtained for solution B. The peaks owing to the C-H, C-N, and C=O bonds within DMF molecule, the C-S and C≡N bonds within thiocyanate ion and the N-H bonds within ammonium ion appear around 100 pm, and those of the nonbonding C···C, C···O, and N···O interactions within DMF molecule and N···S interactions within thiocyanate ion give a composite peak at 200—300

Table 2. Structure Parameters for the Solvated Cadmium(II) Ion in DMF, DMSO, and Water

Interaction	Parameter	DMF	DMSO[a]	Water[b]
Cd-O	r/pm	229.6(4)	229.4	231
	b/10 pm^2	6.3(5)	4.4	2
	n	6[c]	6	6
O···O	r[d]/pm	325	—	—
	b/10 pm^2	10[c]	—	—
	n	12[c]	—	—
Cd···C	r/pm	315(1)	342.2[e]	—
	b/10 pm^2	20(2)	15.4[e]	—
	n	6[c]	6[e]	—
Cd···N	r/pm	434(2)	—	—
	b/10 pm^2	20(2)	—	—
	n	6[c]	—	—

Standard deviations are given in parentheses.
a) Ref. 6. b) Ref. 5. c) The values were kept constant during the calculation. d) $r_{O\cdots O}=\sqrt{2}\,r_{Cd\text{-}O}$. e) Cd···S (dmso) interaction.

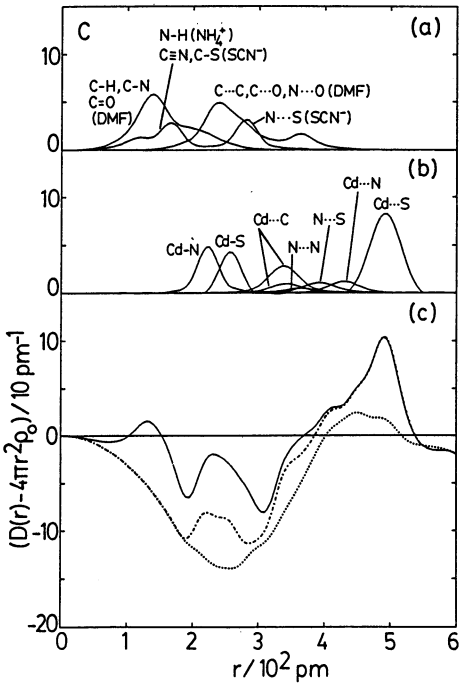

Fig. 4. The $(D(r)-4\pi r^2\rho_0)$ curve for solution C. (a) The theoretical peak shapes calculated for intramolecular interactions within DMF molecule and ammonium and thiocyanate ions. (b) The peak shapes for the intramolecular interactions within the $[Cd(NCS)_3(SCN)]^{2-}$ complex. (c) The chain and dotted lines represent the residual curves after subtracting the theoretical peaks in (a) and (b), respectively, from the original one (solid line).

pm. Subtraction of these peaks leads to the residual curve shown by the chain line in Fig. 4c. The peaks in the curve may mainly be ascribed to the intramolecular interactions within the tetrathiocyanatocadmate(II) complex.

The peak at 200—270 pm is doublet and thus consists of at least two kinds of interactions, probably the Cd-N and Cd-S bonds within the tetrathiocyanatocadmate(II) complex. The hump around 340 pm may be due to the intramolecular Cd···C, Cd···N, N···N, and N···S interactions within the complex. The large peak at about 500 pm is mainly due to the nonbonding Cd···S interaction between cadmium(II) ion and sulfur atom of N-bonding thiocyanate ion which has been seen also in aqueous solution.[1]

In the course of the analysis of the tetrathiocyanatocadmate(II) in DMF, we assumed as a first approximation that the distances of atom-pairs within the complex are the same as those in aqueous solution,[1] and the coordination numbers of cadmium(II) ion with nitrogen and sulfur atoms are searched by analyzing the areas under the doublet peak, the hump and the large and sharp peak at about 500 pm. The best result was obtained when we assumed the coordination numbers of three and one for the Cd-N and Cd-S bonds, respectively (Fig. 4b and c). No solvent molecule coordinates to cadmium(II) ion. Thus, we concluded that the tetrathiocyanatocadmate(II) complex has a four-coordinated tetrahedral structure, $[Cd(NCS)_3(SCN)]^{2-}$.

The structure parameters for the tetrahedral $[Cd(NCS)_3(SCN)]^{2-}$ complex in DMF were finally optimized by the least-squares method using the $s\cdot i(s)$ data in the high-angle region ($s>4\times10^{-2}$ pm^{-1}) at the fixed coordination structure. The interligand N···N and N···S distances are calculated from the Cd-N and Cd-S bond lengths and the tetrahedral structure. Since the contribution of the nonbonding Cd···C and Cd···N interactions arising from the S-bonding thiocyanate ion with cadmium(II) ion to the overall intensity is rather small, the distances are calculated from the Cd-S bond length and the Cd-S-C and Cd-S-N bond angles found in aqueous solution (106°)[1] and no significant error could be introduced by this treatment. The parameter values thus refined are given in Table 3, together with those obtained in aqueous solution.[1]

The Cd-N and Cd-S bond distances are finally determined to be 223(2) and 257(2) pm, respectively.

The tetrathiocyanatocadmate(II) complex has the

Table 3. Structure Parameters for the Tetrathiocyanatocadmate(II) Complex in DMF and Water

Interaction	Parameter	DMF B	DMF C	Water[a]
Cd-N	r/pm	224(1)	222(1)	224.6
	b/10 pm²	4(1)	2(1)	2.5
	n	3[b]	3[b]	2
Cd···C	r/pm	333(3)	337(3)	328
	b/10 pm²	15[b]	15[b]	15
	n	3[b]	3[b]	2
Cd···S	r/pm	491(1)	491(1)	486.7
	b/10 pm²	16(1)	22(2)	18
	n	3[b]	3[b]	2
Cd-S	r/pm	257(2)	256(1)	264.9
	b/10 pm²	18(4)	4(1)	7.7
	n	1[b]	1[b]	2
Cd···C	r/pm	341[c]	340[c]	349
	b/10 pm²	15[b]	15[c]	15
	n	1[b]	1[b]	2
Cd···N	r/pm	429[c]	428[c]	435
	b/10 pm²	15[b]	15[b]	14
	n	1[b]	1[b]	2
N···N	r/pm	360[d]	362[d]	367
	b/10 pm²	8[b]	8[b]	8
	n	3[b]	3[b]	1
S···N	r/pm	388[d]	390[d]	400
	b/10 pm²	15[b]	15[b]	15
	n	3[b]	3[b]	4
S···S	r/pm	—	—	433
	b/10 pm²	—	—	17
	n	—	—	1

Standard deviations are given in parentheses.
a) Ref. 1. b) The values were kept constant during the calculation. c) Assumed ∠Cd-S-C=∠Cd-S-N=106°. d) Assumed ∠N-Cd-N=∠S-Cd-N=109.5°.

different coordination structures of $[Cd(NCS)_3(SCN)]^{2-}$ and $[Cd(NCS)_2(SCN)_2]^{2-}$ in DMF and water, respectively. The difference may be ascribed to different solvation tendency of thiocyanate ion in the two solvents. As discussed in a previous paper,[4] thiocyanate ion is strongly solvated at the hydrogen bonding N-site in water, but much weakly at the S-site. Solvation of the thiocyanate ion is much weaker in aprotic DMF with a smaller acceptor number than water, and the solvation at the N-site may be especially weakened and consequently solvation at the S-site may become even relatively stronger than that at the N-site.[15] Therefore, the formation of the Cd-N bond may become more favorable in DMF than in water and the $[Cd(NCS)_3(SCN)]^{2-}$ structure may be formed in the DMF solutions. The coordination geometry of $[Cd(NCS)_3(SCN)]^{2-}$ may be favorable rather than that of $[Cd(NCS)_2(SCN)_2]^{2-}$ in DMF in the respect of solvation of the complex itself, because the former complex exposes more S atoms of ligating SCN^- ions into the bulk DMF solvent, which may be able to better solvate than the N atoms[15] in the ligand.

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