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X-Ray Diffraction, Raman, and NMR Studies on Tetrathiocyanato Complexes of Zinc(II), Cadmium(II), and Mercury(II) Ions in Aqueous Solution

Toshio YAMAGUCHI, Kiyoshi YAMAMOTO, and Hitoshi OHTAKI*
Department of Electronic Chemistry, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227

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X-Ray scattering, Raman, and ^{13}C- and ^{14}N-NMR measurements were performed on aqueous solutions containing tetrathiocyanato complex ions of Zn(II), Cd(II), and Hg(II). The radial distribution functions revealed that four thiocyanate ions tetrahedrally coordinated to Zn(II) and to Hg(II) ions through the N and S atoms, respectively, while Cd(II) ion was bound to two sulfur and two nitrogen atoms within the coordinated four SCN$^-$ ions. The bond distances and bond angles are as follows: Zn–N 204 pm, Cd–N and Cd–S 225 and 265 pm, respectively, and Hg–S 254 pm, and Zn–N–C 145°, Cd–N–C and Cd–S–C 149° and 106°, respectively, and Hg–S–C 102°. The Raman bands of the C–S vibration within the tetrathiocyanato complexes of Zn(II), Cd(II), and Hg(II) ions in aqueous solutions appeared at 821 and 710 cm^{-1} for the Zn(II) and Hg(II) complexes, respectively, consistent with the values in the literature. The C–S stretching Raman bands of tetrathiocyanatocadmate(II) complex were resolved into two components at 779 and 732 cm^{-1}. The C–S frequency shifted toward the higher frequency side than that (747 cm^{-1}) of the free SCN$^-$ ion in the case of the binding of SCN$^-$ to metal ion *via* the N atom in the Zn(II) and Cd(II) cases, while the C–S bands influenced by the M–S bonding appeared on the lower frequency side in the Cd(II) and Hg(II) complexes. The ^{13}C chemical shifts of the tetrathiocyanato complexes in aqueous solutions showed the downfield and upfield shifts for Zn(II) and Hg(II), respectively, and the intermediate for Cd(II). The nitrogen-14 resonance in $[M(SCN)_4]^{2-}$ in aqueous solutions shifted upfield (−30.8 ppm) for Zn(II), downfield (30.3 ppm) for Hg(II), and in between for Cd(II) (−1.3 ppm). The trend of the ^{13}C- and ^{14}N-chemical shifts supported the different types of binding of ambient SCN$^-$ ion deduced from the X-ray and Raman measurements.

Complex formation between thiocyanate ions and different metal ions has widely been investigated from interesting ambient nature of SCN$^-$ ion, which can bind with metal ions through either the nitrogen or the sulfur atom depending on the central cation involved. Among these studies, thiocyanato complexes of the Group IIb metals are of particular interest,[1–21] since Hg(II) and Zn(II) ions behave as soft and hard acids, respectively, and Cd(II) ion has an intermediate character. From recent X-ray diffraction and Raman spectral studies[21] on the thiocyanate complexes of Zn(II), Cd(II), and Hg(II) ions in combination with the thermodynamic data[7] in dimethyl sulfoxide (DMSO), it has been established that thiocyanate ions coordinate to both Hg(II) and Cd(II) ions through the sulfur atom, but to Zn(II) ion through the nitrogen atom.

Formation of the thiocyanato complexes of Zn(II), Cd(II), and Hg(II) ions in aqueous solution has also been studied by thermodynamic,[1–5] Raman and infrared methods.[8–14] The results obtained from these studies are consistent with the conclusion that thiocyanate ions bind with Hg(II) ion through the sulfur atom, but to Zn(II) ion through the nitrogen atom, giving in both cases mononuclear species up to the tetra-complex. However, the coordination site of thiocyanato groups to Cd(II) ion in aqueous solution is still not conclusive.

Fronaeus and Larsson[9] interpreted two C–N absorption bands at 2098 and 2132 cm^{-1} in terms of the presence of mononuclear and bridged polymer species, respectively, in aqueous solutions having lower molar ratios of thiocyanate to cadmium ions. Taylor *et al.*[11] measured Raman spectra of the tetrathiocyanatocadmate(II) complex in aqueous solutions, suggesting that some SCN$^-$ ions bound to Cd(II) through the N and some through the S atoms in the Cd(II) complex. In a recent Raman spectral measurement of thiocyanato complexes of Cd(II) ion in aqueous solutions, Antić-Jovanović *et al.*[14] assigned the band at 2132 cm^{-1} to the $[Cd(SCN)]^+$ complex, while the bands appearing at 2102 and 784 cm^{-1} were attributed to higher members of the stepwise $[Cd(NCS)_n]^{2-n}$ series. Their conclusion for the binding type of SCN$^-$ to Cd(II) ions is consistent with that by Taylor *et al.*[11]

In crystal of $Cd(SCN)_2$,[18] a cadmium(II) ion is octahedrally surrounded by four sulfur and by two *trans*-nitrogen atoms with a slightly distorted geometry. In β-$Zn(NCS)_2$ crystal,[19] there are two crystallographically different Zn(II) ions, the one surrounded tetrahedrally by four N atoms and the other by four S atoms.

In the present study, we aimed at determining the structure of the tetrathiocyanato complex of Cd(II) ion in aqueous solution to clarify the type of binding of SCN$^-$ ion by the X-ray diffraction, Raman, and NMR methods. The structure of tetrathiocyanato complexes of Zn(II) and Hg(II) ions in aqueous solution has also been determined for comparison.

Experimental

Preparation of Sample Solutions. If not otherwise

TABLE 1. THE COMPOSITION (mol/dm^3), DENSITY d (g/cm^3) AND STOICHIOMETRIC VOLUME V (10^6 pm^3) PER SCN OF THE SAMPLE SOLUTIONS INVESTIGATED

	A	B	C	D
	Hg(II)	Cd(II)	Zn(II)	NH_4^+
M^{2+}	0.979	1.04	1.00	—
NH_4^+	5.02	5.04	5.03	7.12
SCN^-	6.98	7.12	7.03	7.12
H_2O	33.7	34.0	33.4	31.6
d	1.30	1.23	1.17	1.11
V	2.38	2.33	2.36	2.33

stated, all chemicals used were of analytical reagent grade purchased from Wako Pure Chemical Industries, Ltd.

Zinc(II) thiocyanate was prepared by reacting zinc(II) sulfate with a stoichiometric amount of barium(II) thiocyanate which had been recrystallized twice from water. Zinc(II) thiocyanate thus prepared was then recrystallized from water.

Cadmium(II) thiocyanate was prepared from cadmium(II) perchlorate and ammonium thiocyanate, the former reagent having been prepared by dissolving cadmium(II) oxide in an aqueous perchloric acid solution and then recrystallized twice from water. Cadmium(II) thiocyanate thus obtained was recrystallized twice from water.

Mercury(II) thiocyanate commercially available was recrystallized twice from water.

Ammonium thiocyanate purchased was used without further purification.

The sample solutions investigated were prepared by dissolving required amounts of zinc(II), cadmium(II), mercury(II), and ammonium thiocyanates in water so that the tetrathiocyanato species was predominantly formed according to thermodynamic data[1-5] in the literature which were assumed to be valid in relatively concentrated sample solutions. Density of the solutions was determined pycnometrically.

The composition of the solutions used for X-ray diffraction measurements is given in Table 1. The same samples were used for Raman and NMR studies.

X-Ray Data Collection. X-Ray scattering measurements were carried out at 23 °C with a JEOL θ-θ diffractometer by using Mo$K\alpha$ radiation (λ=71.07 pm). The scanning range of the scattering angle (2θ) was 2—140°, corresponding to the scattering vector $3\times10^{-3} < s/\text{pm}^{-1} < 0.16$ ($s=4\pi\sin\theta/\lambda$). Different slit combinations and step angles were used and a total amount of 80000 counts was collected at each angle. Details of the diffractometer and the method of measurements have been described elsewhere.[22,23]

Raman Measurements. Raman spectra of the sample solutions used in the X-ray measurements were recorded at room temperature on a JEOL JRS-Sl spectrometer using the 514.5 nm line of NEC GLG3200 argon ion laser.

NMR Measurements. ^{13}C-NMR spectra of the sample solutions were obtained at room temperature in the pulsed Fourier transform mode at 25.00 MHz on a JEOL FX-100 spectrometer. ^{14}N-NMR spectra were measured at 7.14 MHz. Small amounts of deuterium oxide as the internal lock and DDS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as the internal standard were added to the sample solutions.

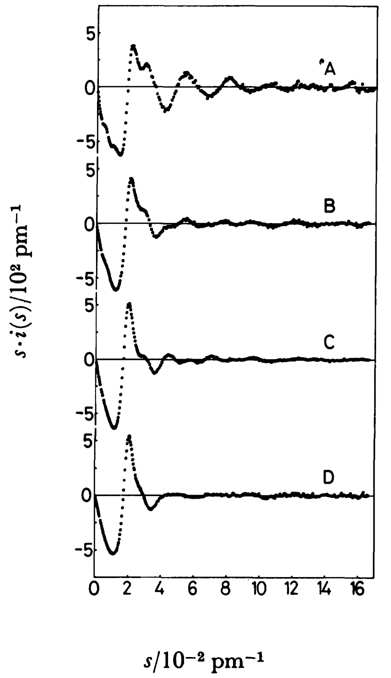

Fig. 1. Experimental structure functions $i(s)$ multiplied by s of aqueous solutions of mercury(II) thiocyanate (A), cadmium(II) thiocyanate (B), zinc(II) thiocyanate (C), and ammonium thiocyanate (D).

X-Ray Data Treatment. Experimental intensities were corrected for background, absorption, polarization, double scattering and Compton scattering and were scaled to absolute units in the usual manners described elsewhere.[22-26] The scattering factors of neutral atoms and the values for the Compton scattering and the anomalous dispersion effect were taken from the same sources previously described.[26]

The structure function $i(s)$ was obtained by

$$i(s) = I(s) - \sum x_j f_j^2(s), \tag{1}$$

where $I(s)$ is the scaled observed intensities, f_j the scattering factor of the jth atom corrected for anomalous dispersion and x_j the number of the jth atom in the stoichiometric volume containing one SCN$^-$ ion. The structure functions of the sample solutions multiplied by s are shown in Fig. 1.

The radial distribution function was calculated by the Fourier transform of the $s\cdot i(s)$ values using the equation,

$$D(r) = 4\pi r^2\rho_0 + (2r/\pi)\int_{s_{\min}}^{s_{\max}} s\cdot i(s)M(s)\sin(rs)\mathrm{d}s. \tag{2}$$

Here, $M(s)$ is the modification function $[\sum x_j f_j(0)^2/\sum x_j f_j(s)^2]\exp(-0.01\ s^2)$, $s_{\min}$ and $s_{\max}$ denote, respectively, the lower and upper limits of the s values available in the experiments. The resulting $D(r)$ values are plotted in Fig. 2. All the calculations were performed by program KURVLR.[27]

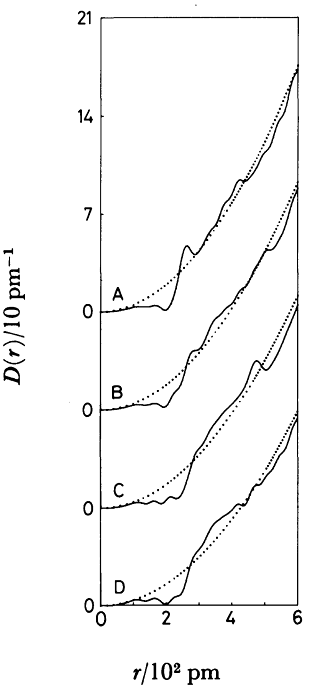

Fig. 2. Radial distribution functions $D(r)$ (solid lines) derived from the curves shown in Fig. 1. Dots show the values of $4\pi r^2\rho_0$.

Results

X-Ray Radial Distribution Functions (RDFs). The total RDFs in the form of $D(r)-4\pi r^2\rho_0$ of Hg(II), Cd(II), Zn(II), and ammonium thiocyanate aqueous solutions of the stoichiometric volume per SCN ion are shown in Fig. 3 (upper figure). The peaks arising from the structure of SCN^- ion should appear at 120 pm (C–N), 165 pm (C–S), and 280 pm (S···N)[18–21] in all the RDFs. As is seen in Fig. 3 A through D, however, the large broad peak at 250—550 pm due to the hydration of SCN^- ion and the bulk water structure is dominant in the RDFs with distinct peaks at 255, 260, and 490 pm, respectively, in the RDFs of Hg(II), Cd(II), and Zn(II) thiocyanate solutions.

In order to extract the peaks originating from Hg(II), Cd(II), and Zn(II) thiocyanato complexes in the solutions, the RDF of NH_4SCN solution (Fig. 3 D) was subtracted from those of the metal thiocyanate solutions. Since an ammonium ion has a similar size as a water molecule and all the sample solutions contain an almost equal amount of SCN^- ions as well as the sum of $[NH_4^+]+[H_2O]$ (see Table 1), the bulk structure and the hydration structure of SCN^- ion may be similar in all the solutions at the first approximation. Thus, in the differences between the total RDFs A, B, or C and D (Fig. 3 lower figures, abbreviated as A-D, B-D, and C-D), the contribution of the bulk water and the SCN^- hydration structure is mostly eliminated and hence the peaks due to the metal thiocyanato complexes in the solutions are emphasized.

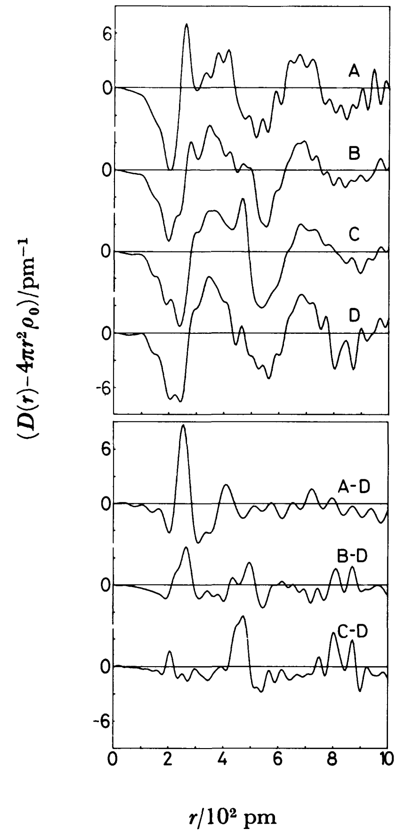

Fig. 3. Radial distribution functions of the form $D(r)-4\pi r^2\rho_0$ derived from the curves in Fig. 1 (above). The figures below are the difference RDFs obtained by subtraction of curve (D) from curves (A), (B), and (C).

In the difference RDF of Hg(II) thiocyanate solution there are two peaks centered at 254 and 415 pm (Fig. 3 A-D). From the sum of the covalent radii of Hg and S (148 and 104 pm,[28] respectively) and the mean Hg–S bond length of 255 pm reported in a structure determination of $[Hg(SCN)_4][Cu(en)_2]$ crystal,[20] the first peak at 254 pm can be assigned to the Hg–S bonds within $[Hg(SCN)_4]^{2-}$. In the crystal structure of $[Hg(SCN)_4][Cu(en)_2]$, nonbonding Hg···N and interligand S···S interactions appear around 400 and 420 pm, respectively, and hence they are possibly responsible for the peak at 415 pm in the difference RDF of the Hg(II) thiocyanate solution.

In the case of Zn(II) thiocyanate solution, the difference RDF shows the distinct peaks at 204 and 462 pm. On the basis of the effective ionic radii of Zn and N atoms (60 and 146 pm[29], respectively) and the knowledge of the mean Zn–N (200 pm) and nonbonding Zn···S lengths (470 pm) within the $[Zn(NCS)_4]^{2-}$ moiety in β-$Zn(SCN)_2$ crystal,[19] the peaks around 204 and 462 pm are assignable to the Zn–N and Zn···S interactions within $[Zn(NCS)_4]^{2-}$, respectively.

The difference RDF of Cd(II) thiocyanate solution is more complex with peaks at 265, 435, and 490 pm with a shoulder at 225 pm. The values of 225 and 265 pm coincide well, respectively, with the sum of the effective ionic radii of Cd and N, and of Cd and S (Cd: 78 pm, N: 146 pm, S: 184 pm[29]). In the crystal structure of $Cd(SCN)_2$ having two Cd–N and four Cd–S bonds,[18] the Cd–N and Cd–S distances have been reported to be 224—225 and 271—280 pm, respectively. On the basis of these facts, it can be concluded that the peak at 265 pm with the shoulder at 225 pm consists of both Cd–S and Cd–N bonds within $[Cd(SCN)_4]^{2-}$ in the aqueous solution.

Model Calculations. A quantitative analysis of the X-ray scattering data was performed by comparing experimental values with theoretical ones calculated by a model both in the difference RDFs and in the difference structure functions.

A theoretical structure function of atom pair "i—j" was calculated by the Debye equation,

$$i(s)_{\text{calcd}} = n_{ij}f_i(s)f_j(s)\sin(sr_{ij})/(sr_{ij})\exp(-b_{ij}s^2), \tag{3}$$

where r_{ij}, b_{ij}, and n_{ij} represent the interatomic distance, the temperature factor and the number of interactions, respectively. The corresponding peak shape is obtained by the Fourier transform of the $s \cdot i(s)_{\text{calcd}}$ values using Eq. 2.

Firstly, the difference RDFs of Zn(II), Cd(II), and Hg(II) thiocyanate solutions were analyzed. In the difference RDF of the Hg(II) system (Fig. 3 A-D), the peak shape calculated for four Hg–S interactions was compared reasonably with the contour of the first peak at 254 pm, suggesting the tetrahedral coordination of four SCN^- ions to Hg(II). On the basis of the tetrahedral geometry of the $[Hg(SCN)_4]^{2-}$ complex, the interligand S···S interaction was estimated to be 415 pm, a corresponding peak appearing at 417 pm in the difference RDF. The nonbonding Hg···N interaction should also appear around 417 pm according to the crystal structure of $[Hg(SCN)_4]$-$[Cu(en)_2]$.[20] The distance of the Hg···C interactions within the $[Hg(SCN)_4]^{2-}$ complex in the solution was also estimated to be 330 pm from the crystal structure data.[20] The peak shapes calculated for these atom pairs are shown in Fig. 4. Subtraction of the sums of the peak shapes from the difference RDF gave the residue shown by dots in Fig. 4. Thus, the difference RDF of the Hg(II) thiocyanate solution was satisfactorily explained by the tetrahedral coordination model of four SCN^- ions to Hg(II) through the S atom.

A similar analysis applied to the difference RDF of the Zn(II) thiocyanate solution resulted in four Zn–N bonds from the area of the first peak at 204 pm. Four Zn···S interactions also explained satisfactorily the distinct peak at 460 pm. On the basis of the Zn–N and Zn···S distances with a linear SCN^- ion, the Zn···C interaction was expected to appear 310 pm, consistent well with the peak at 310 pm in the difference RDF (Fig. 5). The theoretical peak shapes due to the Zn–N, Zn···C, Zn···S, and interligand N···N interactions were calculated for the tetrahedral model of the $[Zn(NCS)_4]^{2-}$ complex and subtracted from the difference RDF. In the resulting residue shown by dots in Fig. 5, a small and broad peak still remains at 350—500 pm, which may be attributable to other interligand interactions such as N···C, N···S, C···S, and S···S. Small ripples left at 200—300 pm may be physically insignificant features judging from uncertainties in the difference RDF.

In the case of the Cd(II) thiocyanato complex, the first peak at 200—300 pm was analyzed by a trial-and-error method assuming various combinations of Cd–N and Cd–S interactions, and the most likely

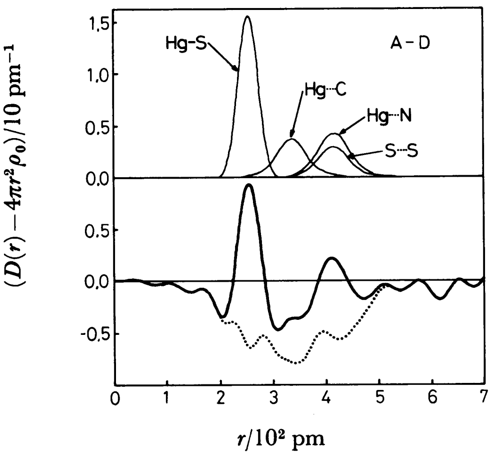

Fig. 4. Difference RDF of aqueous mercury(II) thiocyanate solution (solid line, below) obtained in Fig. 3A, and the residue (dots, below) obtained after subtraction of the peak shapes (solid line, above).

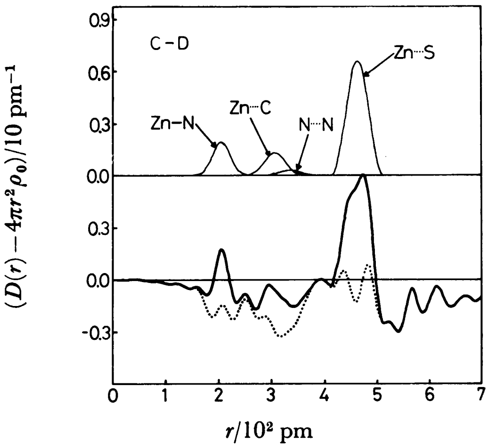

Fig. 5. Difference RDF of aqueous zinc(II) thiocyanate solution (solid line, below) obtained in Fig. 3C, and the residue (dots, below) obtained after subtraction of the peak shapes (solid line, above).

model attained was the one with two Cd–N and two Cd–S bonds per Cd(II). Nonbonding Cd···N and Cd···S interactions were assigned to the peaks at 440 and 490 pm, respectively, from the structural data of $Cd(SCN)_2$ crystal.[18] Cd···C and interligand N···N, S···S, and N···S distances were calculated from the tetrahedral geometry of the $[Cd(SCN)_4]^{2-}$ complex with the linear SCN^- ion coordinated and their peak shapes are shown in Fig. 6. Small peaks at 380—500 pm left after subtraction of the sum of the peak shapes from the difference RDF are probably related to other interligand interactions which were not taken into consideration. Since the X-ray scattering data can give the time- and space-averaged structure of a species, the present X-ray data for the Cd(II) thiocyanate solution could also be explained in terms of an equivalent mixture of $[Cd(SCN)_4]^{2-}$ having four Cd–S bonds and $[Cd(NCS)_4]^{2-}$ having four Cd–N bonds or a statistic mixture of $[Cd(NCS)_{4-n}(SCN)_n]^{2-}$ with the n value of 0 to 4. This problem will be discussed in more detail in a later section.

A direct comparison between experimental and theoretical difference structure functions was also performed by the least-squares method of minimizing the error square sum,

$$U = \sum_{s_{\min}}^{s_{\max}} s^2[\Delta i(s)_{\text{obsd}} - \Delta i(s)_{\text{calcd}}]^2. \tag{4}$$

Here, $\Delta i(s)_{\text{obsd}}$ denotes the difference structure functions experimentally obtained by subtraction of the total $i(s)$ values of NH_4SCN solution from those of metal thiocyanate solutions, $s_{\min}$ and $s_{\max}$ the lower and upper values of the s-range used in the calculations. Program NLPLSQ[30] was used for the calculations.

The model considered had the following characteristics.

(a) Four SCN^- ions coordinate to Zn(II) ion through the N atom, and to Hg(II) ion through the S atom. Cd(II) ion is bound with two SCN^- through the N atom, and the other two through the S atom.

(b) The interactions between atoms directly bonded to metal ion were taken into account by assuming the tetrahedral coordination of the atoms around the metal ion.

(c) The interactions between metal ion and the N or S atoms in SCN^- groups were defined by their interatomic distances, temperature factors, and number of interactions (=4), and the corresponding parameters r_{ij} and b_{ij} were allowed to vary independently with the coordination number fixed to the value of four. Parameters (r and b) due to the nonbonding M···C interactions were also allowed to vary in order to examine the deviation from the linearity of the SCN^- ions.

The final results of important parameters are summarized in Table 2. As shown in Fig. 7, the difference structure functions experimentally obtained are satisfactorily reproduced by the models, except for the data in the s-range less than 0.02 pm^{-1}, to which much longer interactions than those considered in the present models may contribute. On the basis of the M–N, M–C, and M–S distances within $[M(SCN)_4]^{2-}$, we see that the SCN^- ion within the complex has an almost linear structure.

Raman Spectra. Raman bands of the C–N and C–S stretching vibrations in the Zn(II), Cd(II), Hg(II), and ammonium thiocyanate solutions are shown by dots in Figs. 8 and 9, respectively.

A quantitative analysis of the Raman bands was performed by a nonlinear least-squares method by assuming the Lorentzian-Gaussian function expressed by

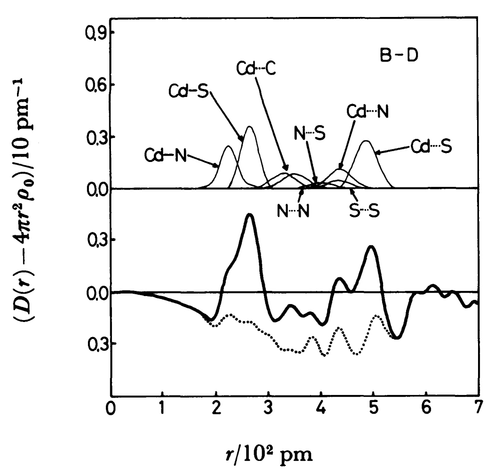

Fig. 6. Difference RDF of aqueous cadmium(II) thiocyanate solution (solid line, below) obtained in Fig. 3B, and the residue (dots, below) obtained after subtraction of the peak shapes (solid line, above).

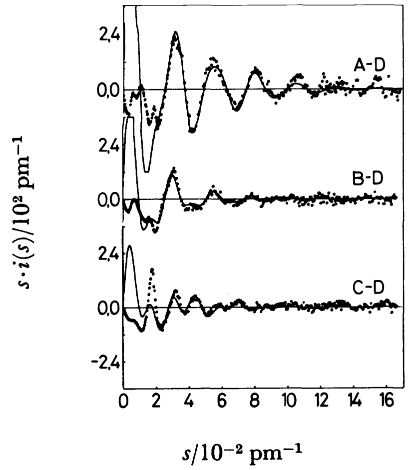

Fig. 7. Comparison between difference structure functions, $\Delta i(s)$, multiplied by s, and calculated values (solid lines) by the model with the parameter values given in Table 2. The symbols of the curves are the same as those used in Fig. 3.

TABLE 2. DISTANCES r (pm), TEMPERATURE FACTORS b (10^2 pm^2), NUMBER OF INTERACTIONS n AND THE BOND ANGLES (ϕ/°) USED IN THE MODEL CALCULATIONS DESCRIBED IN THE TEXT. THE ESTIMATED STANDARD DEVIATIONS ARE GIVEN IN PARENTHESES

		$[Hg(SCN)_4]^{2-}$	$[Cd(NCS)_2(SCN)_2]^{2-}$		$[Zn(NCS)_4]^{2-}$
M-N	r	415(4)	224.6(6)	435(2)	204.1(3)
	b	2.5[a]	0.25(8)	1.4(4)	0.30(5)
	n	4[a]	2[a]	2[a]	4[a]
M-C	r	335(4)	328(2)	349(3)	305[a]
	b	2.0[a]	1.5[a]	1.5[a]	1.0[a]
	n	4[a]	2[a]	2[a]	4[a]
M-S	r	253.5(5)	486.7(3)	264.9(3)	462(1)
	b	0.86(8)	1.8(2)	0.77(5)	1.5[a]
	n	4[a]	2[a]	2[a]	4[a]
N-N	r		367[b]		333[b]
	b		0.8[a]		1.0[a]
	n		1[a]		6[a]
S-S	r	414[b]	433[b]		414[b]
	b	2.5[a]	1.7[a]		2.5[a]
	n	6[a]	1[a]		6[a]
N-S	r		400[b]		
	b		1.5[a]		
	n		4[a]		
∠M-N-C			149(1)		145(1)
∠M-S-C		102(2)		106(1)	

a) Fixed. b) Assumed that ∠N-M-N = ∠N-M-S = ∠S-M-S = 109.5°.

$$I(\nu) = I(\nu_0)[\exp\{-4\ln 2((\nu-\nu_0)/\sigma)^2\}\{1+(\nu-\nu_0)/\sigma\}^{-1}]^{1/2}, \tag{5}$$

where $I(\nu_0)$ denotes the peak height at the peak position ν_0, σ the half width. Parameters $I(\nu_0)$, ν_0, and σ were allowed to vary independently in the optimizing procedure.

Resolved peak components are shown by broken lines in Figs. 8 and 9, respectively, for the C-N and C-S bands. The sum of the components thus calculated is given by solid lines in the figures, which agrees well with the experimental values. The C-S and C-N frequencies thus determined are summarized in Table 3, together with those reported previously by other groups.[11,13,14]

As seen in Fig. 8, the C-N band at 2068 cm^{-1} observed in all the thiocyanate solutions is due to free SCN$^-$ ion on the basis of the spectrum of the NH$_4$SCN solution. The higher C-N frequencies around 2100 cm^{-1} appearing in the metal thiocyanate solutions, the values of which agree well with those reported previously (Table 3),[11,14] are ascribed to SCN$^-$ ions bound to a metal ion. As seen in Table 3, in the case of the bonding between SCN$^-$ ion and a metal ion through the S atom, the C-N band appears at the higher frequency side than that of free SCN$^-$ ion. The C-N frequency also increases when the

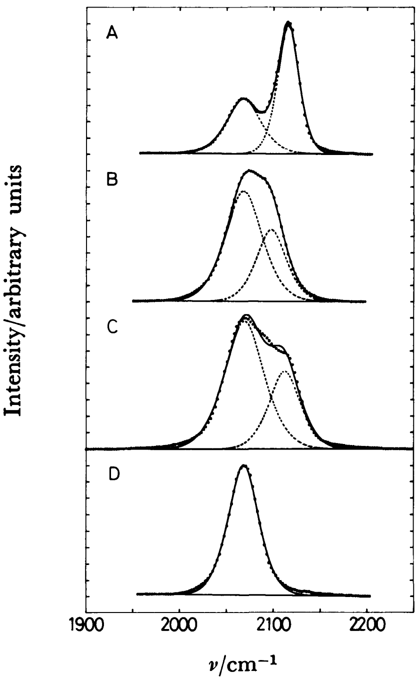

Fig. 8. Raman spectra of the C-N stretching bands of aqueous solutions of mercury(II) thiocyanate (A), cadmium(II) thiocyanate (B), zinc(II) thiocyanate (C), and ammonium thiocyanate (D). Dots represent the observed intensities and the solid line shows the sum of the components (broken lines) obtained by the least-squares fits.

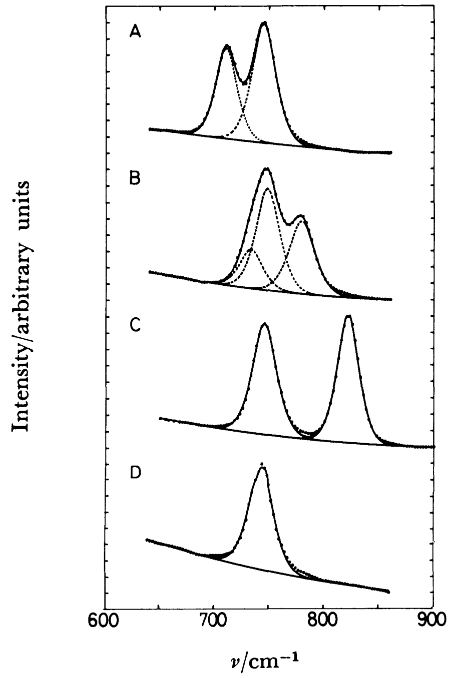

Fig. 9. Raman spectra of the C-S stretching bands of aqueous solutions of mercury(II) thiocyanate (A), cadmium(II) thiocyanate (B), zinc(II) thiocyanate (C), and ammonium thiocyanate (D). Dots represent the observed intensities and the solid line shows the sum of the components (broken lines) obtained by the least-squares fits.

Table 3. Raman frequencies of the C–S and C–N stretching bands of the tetrathiocyanato complexes of Hg(II), Cd(II), and Zn(II) ions in aqueous solutions

	Hg	Cd		Zn		
Binding atom	S	N	S	N	free SCN^- a)	Ref
C–S band	710	779	732	821	747	This work
	717	747		817	747	11)
				823	747	13)
		784			747	14)
C–N band	2117	2105		2114	2068	This work
	2114	2098		2110	2068	11)
		2102			2068	14)

a) Measured value in the present work.

nitrogen atom within SCN^- binds to a metal ion. Tramer[10] and Taylor *et al.*[11] have commented that the increasing C–N frequency on binding of SCN^- ion to a metal ion through the N atom is caused by the removal of repulsive interactions between the lone-pair electrons on the N atom. The shift of the C–N frequency thus is not applicable to specify the end atom of SCN^- bound to a metal ion.

On the other hand, the influence of complex formation between SCN^- and metal ions on the C–S frequency is more distinct (see Fig. 9 and Table 3). As seen in Fig. 9, the C–S frequency of SCN^- ions bound to a metal ion increases for the Zn(II) thiocyanate solution, but decreases for the Hg(II) system, relative to that of free SCN^- ion observed in the NH_4SCN solution. The C–S frequencies determined for the Zn(II) and Hg(II) thiocyanate solutions in the present analysis are in accordance with the previous values[11,13,14] and suggest that SCN^- ions are bound to Zn(II) ion through the N atom, and to Hg(II) ion through the S atom.

In the case of the Cd(II) thiocyanate solution, two C–S bands were observed at around 745 and 780 cm^{-1} (Fig. 9). These C–S frequencies have been reported in Refs. 11 and 14. However, a preliminary analysis of the C–S bands assuming two Lorentzian-Gaussian components failed, but the error square sum decreased significantly in the case of the calculation with three peaks and the whole contour of the C–S bands was satisfactorily reproduced. The final C–S frequencies obtained are given in Table 3 and the corresponding peaks are shown in Fig. 9. The lower and higher C–S frequencies (732 and 779 cm^{-1}) correspond well, respectively, to the presence of both N- and S-bindings to Cd(II) ion, which has been revealed by the X-ray diffraction study of the Cd(II) thiocyanate solution as described in a previous section.

NMR Spectra. The chemical shifts δ of ^{13}C- and ^{14}N-NMR spectra were measured as the internal standards DDS and NH_4^+ ion, respectively, in the Zn(II), Cd(II), Hg(II), and ammonium thiocyanate solutions and are summarized in Table 4. The differences between the chemical shifts for the metal thiocyanate solutions and that for the NH_4SCN solution are also given as $\Delta\delta(SCN^-)$ in Table 4.

Table 4. Chemical shifts (ppm) of Hg(II), Cd(II), Zn(II), and ammonium thiocyanate solutions

	^{13}C-NMR		^{14}N-NMR	
	δ(DSS)	$\Delta\delta(SCN^-)$	$\delta(NH_4^+)$	$\Delta\delta(SCN^-)$
$[Hg(SCN)_4]^{2-}$	130.1	−4.9	215.0	30.8
$[Cd(SCN)_4]^{2-}$	134.3	−0.7	182.9	−1.3
$[Zn(NCS)_4]^{2-}$	136.4	1.4	153.9	−30.3
NH_4SCN	135.0	0.0	184.2	0.0

The $\Delta\delta(SCN^-)$ of the nitrogen-14 resonance shifted downfield in the Zn(II) thiocyanate solution, but upfield in the Hg(II) thiocyanate solution. Howarth *et al.*[15] measured the ^{14}N-chemical shifts of many S- and N-bonding metal thiocyanato complexes in various solvents and have reported that the ^{14}N-resonance shifts downfield in the N-bonding complexes, but upfield in the S-bonding complexes, from that of the free thiocyanate ion. Thus, the present ^{14}N-chemical shifts of the Zn(II) and Hg(II) thiocyanate solutions suggest the coordination of SCN^- ions to Zn(II) ion *via* the N atom, and to Hg(II) ion *via* the S atom. In the Cd(II) thiocyanate solution, the $\Delta\delta(SCN^-)$ value is in between those for Zn(II) and Hg(II) cases. This can be interpreted in terms of the convolution of peaks of downfield and upfield shifts due, respectively, to both N- and S-bonding SCN^- ions for Cd(II) ion, together with the peak of free SCN^- ion.

The $\Delta\delta(SCN^-)$ values of the ^{13}C-resonance of Zn(II), Cd(II), and Hg(II) thiocyanate solutions have shown the downfield shift for Zn(II), the upfield for Hg(II), and the intermediate for Cd(II) (Table 4), the same trend but reverse order of the $\Delta\delta(SCN^-)$ values being found in the ^{14}N-chemical shifts. Thus, ^{13}C-chemical shifts of these solutions also indicate the different types of bonding of SCN^- ions to Zn(II), Cd(II), and Hg(II) ions in the thiocyanate solutions.

Discussion

The structural parameters of Zn(II), Cd(II), and Hg(II) thiocyanato complexes both in aqueous solution and in DMSO are compared in Table 5. The SCN^- ions are bound to Hg(II) through the S atom within the $[Hg(SCN)_4]^{2-}$ complex in both aqueous solution and in DMSO and the Hg–S bond length and the bond angle Hg–S–C are similar in the two solvents within experimental uncertainties.

The Zn–N distance within $[Zn(NCS)_4]^{2-}$ in H_2O is

Table 5. Comparison of interatomic distances (pm) and bond angles ($\phi/^\circ$) within the tetrathiocyanato complexes of Hg(II), Cd(II), and Zn(II) ions in H_2O and in DMSO

	Hg		Cd			Zn	
	H_2O	DMSO	H_2O		DMSO	H_2O	DMSO
Binding atom	S	S	N	S	S	N	N
r (M-N)	415	427	225	435	435[a]	204	193
r (M-C)	335	340	328	349	349[a]	305	308
r (M-S)	254	253	487	265	263[a]	462	473
∠M-N-C						145	180
∠M-S-C	102	108		106	106[a]		

a) The values determined for complex species in a DMSO solution of $\bar{n}=2.3$ in Ref. 21 where $\bar{n}$ denotes the average number of thiocyanato ions bound to the central metal ion.

somewhat longer than the corresponding distance in DMSO. In the analysis of the X-ray scattering data of a DMSO solution of Zn(II) thiocyanate,[21] the Zn–N distance within $[Zn(NCS)_4]^{2-}$ has not been directly determined because of a low Zn(II) concentration and fixed at the value (194 pm) found in β-$Zn(NCS)_2$ crystal, although the structure of the crystal has not been solved with a high precision (the R-value= 0.09[19]). The Zn–N distance obtained in the present study is in good agreement with the value estimated from the effective ionic radii (206 pm[29]). The Zn–N–C bond angle may also be affected from the errors of the same source.

Thus, a relatively hard acceptor Zn(II) ion prefers to bind with the nitrogen atom and a soft acceptor Hg(II) ion combines with the soft sulfur atom within an SCN^- ion in both aqueous and DMSO solutions.

The structural parameters of Cd(II) thiocyanate complex determined in DMSO were those of a mixture of $[Cd(SCN)_2]$ and $[Cd(SCN)_3]^-$ because the structure determination of cadmium(II) thiocyanato complexes in DMSO has been carried out in a solution of $\bar{n}=2.3$ ($\bar{n}$ is the average coordination number of SCN^- ion within the complexes). However, as far as Persson *et al.*[21] have examined, cadmium(II) ion combines with SCN^- ions through the S atoms in DMSO (see Table 5).

On the other hand, cadmium(II) ion binds with both nitrogen and sulfur atoms within SCN^- ions in the $[Cd(SCN)_4]^{2-}$ complex in water. This fact may be related to different donicities of H_2O and DMSO, the latter has a larger donor number than the former (H_2O: 18.0, DMSO: 29.8[31]). The larger electron donation from ligand solvent molecules toward the central metal ion may decrease the fractional charge of the metal ion and thus the metal ion becomes softer. Therefore the metal ion may prefer a soft ligand atom than a hard one in a solvent with a larger donicity. Water molecule having a larger acceptor number than DMSO (H_2O: 54.8, DMSO: 19.3[30]) may preferentially solvate to the sulfur atom than the nitrogen site and thus the N-end within SCN^- tends to bind to Cd(II) ion in H_2O, while the S-end may not be strongly solvated in DMSO. These two factors of different solvating properties of H_2O and DMSO may affect the bonding of SCN^- to Cd(II) ion. The Cd–S bond length and the bond angle Cd–S–C do not differ significantly in the two solutions.

The present X-ray scattering data of the Cd(II) thiocyanate solution have demonstrated the presence of two Cd–N and two Cd–S bonds per Cd(II) on the average within the tetrathiocyanatocadmate(II) ion in aqueous solution. By the X-ray diffraction experiment, however, the result is not distinguishable between the formation of the $[Cd(SCN)_2(NCS)_2]^{2-}$ complex and the statistic mixture of $[Cd(NCS)_{4-n}(SCN)_n]^{2-}$ with n=0—4. Thermodynamic quantities (ΔG°_n, ΔH°_n, and ΔS°_n for the stepwise formation of $[Cd(NCS)_n]^{(2-n)+}$ complexes) and Raman spectra of solutions containing the thiocyanato complexes with low $\bar{n}$ values in aqueous solution, details of which will be described elsewhere,[32] indicated that the first SCN^- ion coordinates to Cd(II) ion through the N atom and the second and third SCN^- ions combine with Cd(II) ion through the S and N atoms, respectively, and then, at the fourth step, the Cd–S bond forms. These results indicate that the X-ray diffraction data obtained for the tetrathiocyanatocadmate(II) solution should be interpreted in terms of the formation of the $[Cd(NCS)_2(SCN)_2]^{2-}$ with two Cd–N and two Cd–S bonds, but not the statistical mixture of $[Cd(NCS)_{4-n}(SCN)_n]^{2-}$ complexes.

The covalency of the metal-ligand bonds within thiocyanato complexes of Zn(II), Cd(II), and Hg(II) may be reflected on their bond lengths. The Zn–N distance (204 pm) is close to the value estimated from the effective ionic radii (206 pm) (*cf.* 201 pm for the sum of the covalent radii of the atoms[28]), while the Hg–S distance (254 pm) agrees well with the sum (252 pm) of covalent radii of the relevant atoms (*cf.* 280 pm for the sum of the ionic radii of Hg^{2+} and S^{2-}). Both Cd–N (225 pm) and Cd–S (265 pm) distances are close to those (224 and 264 pm, respectively) calculated using the effective ionic radii (*cf.* 218 and 252 pm, respectively, for the sum of the covalent radii of the atoms).

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