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An X-Ray Diffraction and Raman Study of Mercury(II), Cadmium(II) and Zinc(II) Thiocyanate Complexes in Dimethylsulfoxide Solution

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X-Ray diffraction and Raman studies of mercury(II), cadmium(II) and zinc(II) thiocyanate complexes in dimethylsulfoxide (DMSO) solution have resulted in the elucidation of the structures of $Hg(SCN)_2$, $Hg(SCN)_3^-$, $Hg(SCN)_4^{2-}$ and $Zn(NCS)_4^{2-}$ and also yielded some information about the complexes $Cd(SCN)_2$ and $Cd(SCN)_3^-$.

In the complexes of the soft acceptor Hg^{2+}, the thiocyanate ions are coordinated *via* S. In $Hg(SCN)_2$, the two Hg–S bonds are not colinear. This complex is also rather strongly solvated, most likely by four DMSO, *via* O. A tetrahedral arrangement is found already in $Hg(SCN)_3^-$, with a DMSO completing the tetrahedron. The saturated complex $Hg(SCN)_4^{2-}$ is regularly tetrahedral. The Hg–S distances increase and the Hg–S stretching frequencies decrease as more thiocyanate ions are coordinated, indicating that the strength of the bonds Hg–S decreases in that order. The angle Hg–S–C is in all these complexes $\simeq 107°$. The complex $HgSCN^+$ is completely disproportionated at the high mercury(II) concentrations used in these structure determinations. Not unexpectedly the thiocyanate complexes behave rather similarly to the analogous halide complexes investigated previously.

The complexes $Cd(SCN)_2$ and $Cd(SCN)_3^-$ are no doubt S-coordinated in DMSO while in water N-coordination presumably occurs. Such switches seem natural for an acceptor like Cd^{2+}, on the borderline between hard and soft. In the complex $Zn(NCS)_4^{2-}$ of the hard acceptor Zn^{2+}, the thiocyanate ions are coordinated *via* N in a regular tetrahedral arrangement, with an angle Zn–N–C $= 180°$.

In the present study, the structures of thiocyanate complexes formed by mercury(II), cadmium(II) and zinc(II) in DMSO solution have been determined, primarily by X-ray diffraction measurements.

Mercury(II) forms a series of mononuclear complexes $Hg(SCN)_j^{2-j}$, $j=1-4$. At least in the dilute solutions (mercury concentration $C_M \leq 20$ mM) used in the stability measurements, the consecutive steps are well separated except for the third one.[1] At the ligand number $\bar{n}=j$, the complex $Hg(SCN)_j^{2-j}$ completely predominates in solution, except for $Hg(SCN)_3^-$ which at $\bar{n}=3$ reaches a maximum share of only 50 %. Such a solution also contains large amounts of $Hg(SCN)_2$ and $Hg(SCN)_4^{2-}$ which would seriously impair the structure determination. The conditions would thus be less favourable than in the mercury(II) halide systems where all steps are well separated in DMSO.[1] Fortunately enough, however, the relative stability of $Hg(SCN)_3^-$ increases very much with C_M. At the fairly high value of C_M ($= 0.8$ M) that has been used in the diffraction measurements at $\bar{n}=3$. $Hg(SCN)_3^-$ is in fact completely predominating, as shown by the Raman spectrum of the solution, *cf.* below.

In DMSO, the fairly high concentrations necessary for a successful structure determination can be reached for all the complexes $Hg(SCN)_j^{2-j}$ $j=2-4$. The neutral complex $Hg(SCN)_2$, slightly soluble in water, is readily soluble in DMSO. As in most of the halide solutions studied, the extra amounts of ligand necessary to form the higher complexes are added as the sodium salt.[2,3] With

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Na^+ as counterion, high concentration of both $Hg(SCN)_3^-$ and $Hg(SCN)_4^{2-}$ can be reached. The conditions for the structure determination of these complexes are thus very favourable.

For the first step the situation is, on the other hand, less favourable. In the halide systems, the structures of the complexes HgX^+ cannot be determined by X-ray diffraction as solutions concentrated enough disproportionate extensively into Hg^{2+} and HgX_2 in the case of chloride and bromide, and into HgI_2 and the dinuclear Hg_2I^{3+} in the case of iodide.[2,4] As will be shown below, a disproportionation analogous to that found for chloride and bromide occurs also in the thiocyanate system as the mercury(II) concentration is increased.

The soft Hg^{2+} should coordinate the ambident ligand SCN^- by its softer donor atom S. Such a coordination has also been inferred in aqueous solution from measurements of the intensities of the band in infrared due to C–N stretching.[5] Also Raman measurements of the shift of the C–S stretching frequency in $Hg(SCN)_4^{2-}$ relative to free SCN^- leads to the same conclusion.[6] The frequency decreases considerably, as expected for a coordination *via* S. For the solids $Hg(SCN)_2$ and $K_2Hg(SCN)_4$, exactly the same downward shift of the C–S frequency has been observed, indicating the same coordination.[7] Later the Hg–S coordination of the complexes $Hg(SCN)_2$ and $Hg(SCN)_4^{2-}$ has been confirmed by complete structure determinations.[8–11]

The cadmium(II) thiocyanate complexes formed in DMSO are fairly weak.[12] At the highest concentration of ligand used, $\bar{n}$ reaches $\simeq 2.3$, implying a beginning formation of the third complex. For the cadmium(II) halides, thermodynamic as well as electrode kinetic measurements indicate a switch of coordination at the formation of the second complex in DMSO, implying that the original octahedral configuration is changed into a tetrahedral one. For thiocyanate such a switch does not occur. Even the third complex is octahedral.[12,36]

The mode of coordination of SCN^- to Cd^{2+} in solution is not well-known. Being an acceptor on the borderline between soft and hard, Cd^{2+} might well act differently in different cases. Also, as the affinities to S and N presumably do not differ very much, polynuclear complexes with thiocyanate bridges might easily be formed.

The infrared spectra of aqueous cadmium(II) thiocyanate solutions suggest that both mononuclear and bridged polynuclear complexes are formed.[5] No conclusion about the mode of coordination in the mononuclear complexes is drawn, however, though the frequency shift of the C–N bond relative to free SCN^- speaks very much in favour of a coordination *via* N. In crystalline $Cd(SCN)_2$, the central ion octahedrally coordinates 2 N and 4 S. The thiocyanate ions thus act as bridges but the bond lengths clearly show that the Cd–N interactions are by far the stronger ones, the distances Cd–S being on the average no less than $\simeq 0.5$ Å longer than the distances Cd–N.[13] An example of pure N-coordination is previded by $Cd(NCS)_2(dpt)$ (dpt = di-(3-aminopropyl)amine.[14] The structure of this compound is composed of discrete molecules. Besides the tridentate amine, two thiocyanate ions are coordinated to the central ion *via* their N atoms, completing a square pyramide. Especially the N atom of the apical thiocyanate ion is very tightly bonded. In this compound, the S atoms do not at all participate in the coordination of Cd^{2+}.

In other thiocyanate complexes, however, the Cd–S interactions are no doubt the stronger ones. This is *e.g.* the case in $Cd(SCN)_2(etu)_2$ (etu = ethylenethiourea), a compound where the cadmium atoms are joined by double thiocyanate bridges.[15]

In the present investigation, the structure of the complexes present in a cadmium thiocyanate DMSO solution of $\bar{n} = 2.3$ have been determined by X-ray diffraction. Subsidiary information has been obtained from the Raman spectrum of this solution, and from the spectrum of crystalline $Cd(SCN)_2$.

Zinc(II) coordinates thiocyanate fairly strongly in DMSO. Finally $Zn(NCS)_4^{2+}$ is formed, most probably of tetrahedral configuration. The thermodynamics indicate that the switch from the octahedral structure of the solvate $Zn(DMSO)_6^{2+}$ occurs already as the second complex is formed.[16]

The hard Zn^{2+} prefers hard donors, and therefore coordinates SCN^- by its harder donor atom N. This mode of coordination has been established in aqueous solution, from measurements of the intensity of the C–N band.[5,6,17] These measurements also show, however, that the Zn–N interaction is quite weak in aqueous solution. This is also compatible with the fairly low stabilities of the zinc thiocyanate complexes in this solvent.[18] Also the increase of the C–S stretching frequency found

Table 1. Concentrations(M) of the solutions investigated. The linear absorption coefficient $\mu(cm^{-1})$ is calculated for Mo$K\alpha$-radiation.

Solution	Hg(II)	Cd(II)	Zn(II)	SCN^-	ClO_4^-	Na^+	DMSO	μ
HGSCN1	0.50			0.50	0.50		13.2	16.7
HGSCN2	0.80			1.60			13.0	23.8
HGSCN3	0.80			2.40		0.80	12.1	23.8
HGSCN4a	0.50			2.26		1.16	12.3	16.8
HGSCN4b	0.30			1.37		0.77	13.2	12.0
CDSCN2		0.30		1.35		0.75	13.2	6.0
ZNNCS4			0.30	1.35		0.75	13.2	6.1

for the complexes relative to free SCN^- by Raman measurements proves that N-coordination takes place.[17] The same upward shift of this frequency has also been observed for solid zinc thiocyanate complexes.[7] In other complexes, however, thiocyanate bridges are formed implying that also S-coordination occurs.[19] This is the case *e.g.* in $Zn(NCS)_2$, where zinc otherwise would not be able to attain a sufficiently high coordination number. In this compound, the zinc atoms are all tetrahedrally coordinated, surprisingly either by 4 N or by 4 S atoms.[20] As in $Cd(SCN)_2$(s), the interaction with N is the stronger one, however, the bonds Zn – S being $\simeq$0.4 Å longer than the bonds Zn – N. The average distance Zn – S = 2.35 Å is in fact almost as long as the distance Hg – S = 2.38 Å in $Hg(SCN)_2$(s) where, on the other hand, the distances Hg – N = 2.81 Å are extremely long.[8]

In the present investigation, the structure of the complex $Zn(NCS)_4^{2-}$ has been determined in DMSO solution. Also the Raman spectra of this solution, and of solid $Zn(NCS)_2$, have been recorded.

EXPERIMENTAL

Preparation of solutions. The solutions investigated were prepared by dissolving in DMSO appropriate amounts of zinc(II), cadmium(II), mercury (II) and sodium thiocyanate, and, in the case of the solution HGSCN1, solvated mercury(II) perchlorate, $Hg(ClO_4)_2 \cdot 4DMSO$.[21] The DMSO was purified as described previously.[22] The composition of the solutions is given in Table 1.

The distribution of the consecutive complexes as a function of the free thiocyanate concentration, as calculated from the stability constants determined.[1] is given in Fig. 1. In this Figure, the compositions of the present solutions are also indicated.

X-Ray data collection. The X-ray scattering of Mo$K\alpha$-radiation (λ = 0.71069 Å) was measured

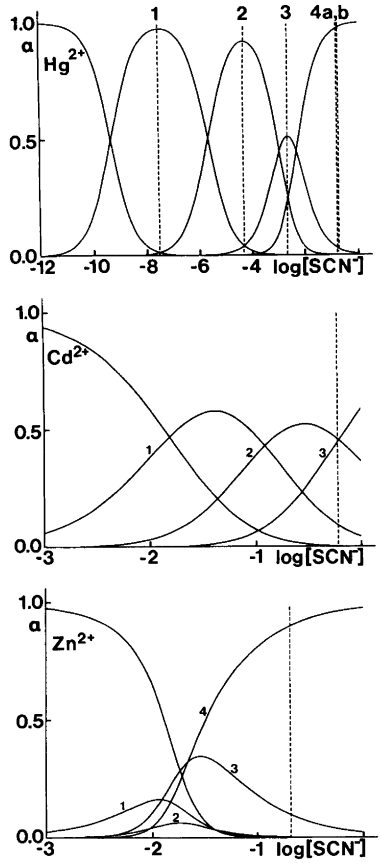

Fig. 1. Distribution of the zinc(II), cadmium(II) and mercury(II) thiocyanate complexes in diluted DMSO solutions as a function of the free thiocyanate ion concentration. The curves have been calculated from stability constants in 1 M NH_4ClO_4 medium. The compositions of the solutions investigated by X-ray diffraction, calculated on the assumption that the same constants are valid, are indicated by vertical lines.

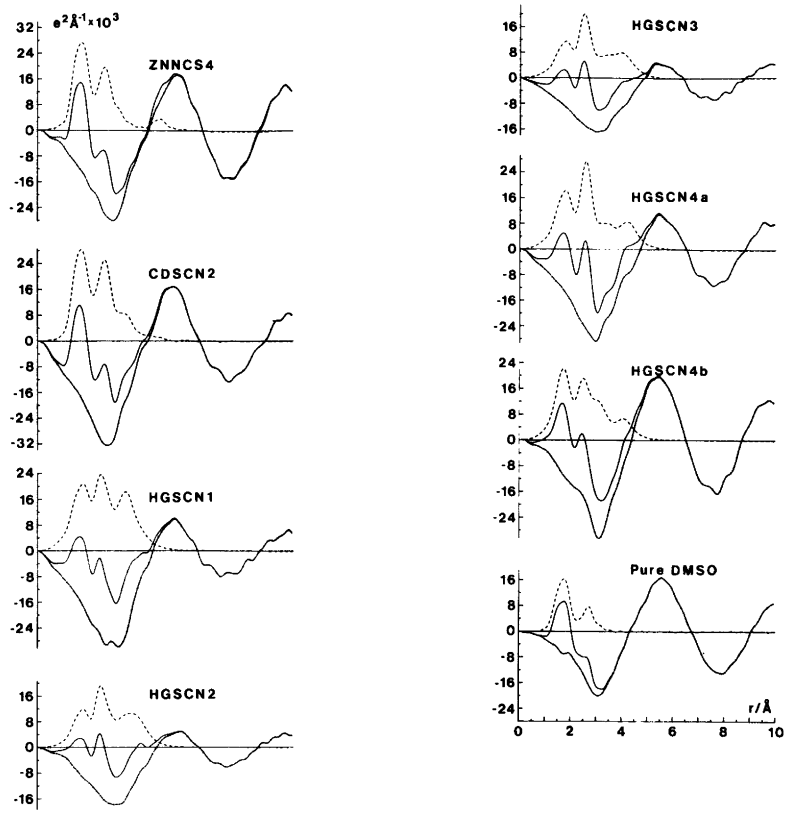

Fig. 2. Functions $D(r)-4\pi r^2\rho_0$ (solid lines) compared with sums of calculated peak shapes of the refined models (dashed lines). The parameter values given in Table 3 have been used. The differences are shown by the dashed-dotted lines.

Table 2. Raman frequencies observed for the solutions listed in Table 1, 0.5 M NH_4SCN in DMSO, and the solids $Hg(SCN)_2$, $Cd(SCN)_2$, $Zn(SCN)_2$, NaSCN.

Solutions	Dominating species	M–N stretch	M–S stretch	S–C[a] stretch	C≡N stretch
NH_4SCN	SCN^-			740	2060
HGSCN1	$Hg(DMSO)_6^{2+}$, $Hg(SCN)_2$		270	[b]	2133
HGSCN2	$Hg(SCN)_2$		266[c]	[b]	2135
HGSCN3	$Hg(SCN)_3^-$		242	[b]	2122
HGSCN4a	$Hg(SCN)_4^{2-}$		235	[b]	2117
CDSCN2	$Cd(SCN)_2(DMSO)_4$			[b]	~2090
ZNNCS4	$Zn(NCS)_4^{2-}$	240		836	2110
Solids	NaSCN			749	2073
	$Hg(SCN)_2$		274	726	2109+(2061)[d]
	$Cd(NCS)_2$	202		763	2148
	$Zn(NCS)_2$	240		790	2163+2182

[a] In thiocyanate. [b] Hidden by the sym. S–C stretch peak of DMSO. [c] A very weak ν_3(Hg–S) frequency at 318 cm^{-1} is also observed. [d] Much weaker than 2109.

from the free surface of the solutions as described elsewhere.[23,24] The apparatus and procedure has also been described previously.[25] The measurements were carried out at 25±1 °C.

Raman measurements. The Raman spectra were recorded in the range 1500 to 100 cm^{-1} with a Cary 82 argon ion laser spectrophotometer as described previously.[21] The spectral measurements were performed at room temperature.

X-RAY DATA TREATMENT

The data reduction was performed as described previously .[26] The experimental intensities were normalized to a stoichiometric unit of volume containing one metal atom, *V*. From the reduced intensity curves, $i_{obs}(s)$, multiplied by *s*, the electronic radial distribution functions (RDF), $D(r)-4\pi r^2\rho_o$, were obtained by a Fourier transformation. The same modification function as before was used.[26] The least squares refinements of distinct intramolecular interactions were performed minimizing the sum $\sum_{s(min)}^{s(max)} w(s)[i_{obs}(s)-i_{calc}(s)]^2$, according to the same procedure as before.[25,26] In these calculations fixed values were introduced for the interatomic distances within the species DMSO, ClO_4^- and SCN^-. These were taken from structure determinations of liquid DMSO[4] and crystalline structures[27,28] of alkali salts, respectively. The RDF's are given in Fig. 2 where the experimental curves are also compared with the peaks calculated from the parameters determined.

RESULTS

Raman measurements. The important Raman frequencies found for the solutions investigated, and for the solid thiocyanates $M(SCN)_2$, M=Zn, Cd, and Hg, are listed in Table 2. For comparison, the bands of the free thiocyante ion, present in ammonium thiocyanate solution and in solid NaSCN, have also been measured.

For solid $Hg(SCN)_2$, the earlier results[7] indicating S-coordination are confirmed. The S–C frequency shifts downwards, the C–N frequency upwards, though not very much. For solid $Cd(NCS)_2$, on the other hand, both frequencies shift upwards, in the case of C–N quite considerably. This indicates that the strongest coordination is *via* N, in conformity with the result of the structure investigation.[13] For solid $Zn(NCS)_2$, the indications of N-coordination are even stronger. Also in this case, the preponderance of the Zn–N interaction is in keeping with the structural data.[20]

As to the DMSO solutions, the S–C stretch frequency is observed only for $Zn(NCS)_4^{2-}$ where the large upward shift confirms that the coordination takes place *via* N, as expected. The downward shifts certainly taking place in the S-coordinated mercury(II) complexes cause their S–C bands to disappear in the intense symmetric S–C stretch frequency of DMSO. The circumstance that no S–C band is found for the cadmium solution suggests that also Cd^{2+} is coordinated *via* S. The mode of coordination in DMSO would thus be different from that in aqueous solution, or solid $Cd(SCN)_2$. Also the small shift in the C–N frequency in DMSO suggests an S-coordination in this solvent. The C–N frequency of the complex $Hg(SCN)_2$ is markedly higher in the solution than in the solid phase. Considering that the auxiliary coordination around mercury is very different in the two cases, this is not surprising. As the number of SCN^- in the complex increases, this frequency decreases, indicating that the C–N bond becomes weaker.

The very intense peaks found around 250 cm^{-1} for the mercury(II) solutions have been assigned to the Hg–S stretching mode. Between the solutions of $C_L/C_M=2$, 3 and 4, the frequency decreases with increasing number of ligands coordinated, as is also found for the corresponding halide complexes.[2] The differences between the solution of $C_L/C_M=1$ and 2 is very small, however, Table 2. In the solution of $C_L/C_M=1$, bands characteristic of the solvate $Hg(DMSO)_6^{2+}$ moreover appear, *viz.* the Hg–O bending and stretching frequencies at 210 and 425 cm^{-1}, respectively.[21] Obviously, the complex $HgSCN^+$ predominating in dilute solutions disproportionates as C_M increases, according to

$$2HgSCN(DMSO)_p^+ + nDMSO \rightleftarrows Hg(DMSO)_6^{2+} + Hg(SCN)_2(DMSO)_q$$

The pattern would thus be the same as for $HgCl^+$ and $HgBr^+$, though the solvation of the complexes might well be fairly different.[4]

The intensity of the band due to $Hg(SCN)_2$ at 270 cm^{-1} is proportional to C_M in the range $0.25 \leq C_M \leq 0.8$ M and the intensity found for the solution of $C_M=0.5$ M is moreover the same as that observed for a genuine $Hg(SCN)_2$ solution of $C_M=0.25$ M. Consequently, the disproportionation is complete in the range stated. For values of $C_M<0.25$ M, the band due to $Hg(SCN)_2$ becomes less intense than warranted by the decrease of C_M, until it

completely disappears at $C_M \simeq 0.05$ M. At that concentration, the reproportionation to $HgSCN^+$ is evidently complete. No band that can be assigned to this complex appears, however. As in the halide complexes HgX^+, the mercury–ligand bond in $HgSCN^+$ is obviously very much less Raman active than in the higher complexes.[4]

In solid $Hg(SCN)_2$, ν_1(Hg–S) is observed at a slightly higher frequency than in DMSO solution, indicating a somewhat stronger bond in the crystalline phase, Table 2. The bond is evidently more weakened by the solvation in solution than by the coordination, *via* N, of four weakly bonded SCN^- in the solid.

The spectrum of $Hg(SCN)_2$ solution has a very weak band at 318 cm^{-1} which is assigned to the vibration ν_3(Hg–S). The complex would thus be bent. This is certainly to be expected if it is still fairly strongly solvated. In the solid where the Hg–S bonds are colinear,[8] this band is neither expected nor observed.

The spectrum of the solution HGSCN3 shows a sharp and intense peak, at 242 cm^{-1}, which should evidently be assigned to $Hg(SCN)_3^-$, Table 2. No traces of the bands due to $Hg(SCN)_2$ or $Hg(SCN)_4^{2-}$ are observed, in spite of the fact that each of these complexes account for $\simeq 25\%$ of the total C_M in the dilute solutions used in the stability measurements, Fig. 1. Evidently, the partial disproportionation of $Hg(SCN)_3^-$ taking place under these conditions does not occur in the concentrated solutions used in the structure determinations. In this respect, the behaviour of $Hg(SCN)_3^-$ is just the opposite to that of $HgSCN^+$.

For the cadmium(II) solution, no band appears that can be assigned to the Cd–S bond. In solid $Cd(SCN)_2$, the Cd–N stretch is at the low wavenumber 202 cm^{-1}, much lower than Hg–S, in spite of the lighter donor atom. This confirms that the Cd–N bond is a fairly weak one. The bond Zn–N is much stronger, in both the tetrahedral structures investigated here, *viz.* $Zn(NCS)_4^{2-}$ in DMSO, and solid $Zn(NCS)_2$. In both instances, ν_1(Zn–N) = 240 cm^{-1}, *i.e.* much higher than ν_1(Cd–N).

Diffraction measurements. For all the solutions investigated, the RDF's have a peak at $\simeq 1.8$ Å, due to the S–O and S–C distances in DMSO. In the solution HgSCN1, Cl–O distances of 1.43 Å in ClO_4^- also contribute to the diffraction in this region. The large and broad peak around 5.5 Å is due to interactions between DMSO molecules, as is evident from the RDF of pure DMSO, Fig. 2. As no precise data exist about the intermolecular structure of liquid DMSO,[4] this peak is not accounted for in the refinements of the structures of the complexes present.

For the mercury(II) thiocyanate solutions, the sharp peak at 2.4 to 2.5 Å corresponds to the Hg–S bond distance. In the solutions HGSCN4 and HGSCN3 shoulders are observed at $\simeq 4.3$ and 4.0 Å, respectively, due to the interligand S–S distances. For the solution HGSCN2 no such shoulder can be discerned. In $Hg(SCN)_2$, the two S atoms are presumably so far apart that the corresponding diffraction disappears in the broad DMSO peak; moreover the intensity of this interaction is low, as it involves only one S–S distance.

The RDF of HGSCN2 shows a small but distinct peak at 3.7 Å which most probably is due to the interaction $Hg-S_D$ between the central ion and the S atoms of coordinated DMSO molecules. The long distance indicates that DMSO is coordinated *via* oxygen, as in $Hg(DMSO)_6^{2+}$. The corresponding Hg–O bond length would be 2.7 Å. The solvate bonds are thus quite weak in comparison with those in $Hg(DMSO)_6^{2+}$ where the Hg–O bond length is only 2.39 Å. Also in the RDF of HGSCN3 an interaction $Hg-S_D$ can be clearly discerned, at $\simeq 3.7$ Å.

As the bond lengths Hg–O in $Hg(DMSO)_6^{2+}$ and Hg–S in $Hg(SCN)_2$ are about the same, the peak due to the coordinate bonds in the RDF of the disproportionated solution HGSCN1 should be in the same position as for HGSCN2. This is also the case, though the peak is less intense in HGSCN1, due to the much lower concentration of $Hg(SCN)_2$ and to the low scattering factor of the oxygen atom in the Hg–O interation. Also in this RDF a diffraction due to the solvation of $Hg(SCN)_2$ can be discerned.

Only in the RDF of HGSCN4a, *i.e.* the most concentrated solution of $Hg(SCN)_4^{2-}$, are the Hg–C distances immediately discerned at $\simeq 3.4$ Å. Also for HGSCN3 and HgSCN2, these interactions are found in the refinements, however.

Only in the RDF of HGSCN3 are the Hg–N distances immediately discerned as a shoulder at 4.3 Å. In the case of HGSCN4, this shoulder evidently merges with that due to the S–S interactions.

In the case of HGSCN1, completely disproportionated into 0.25 M $Hg(DMSO)_6^{2+}$ and 0.25 M $(Hg(SCN)_2$, no refinement of the parameters has been performed. The calculated curves in Figs. 2

Table 3. Results of the least-squares refinements on the reduced intensities. The parameters describing atomic interactions are; d = distance (Å), b = temperature factor coefficient (Å^2) and n = number of distances per metal atom. The refined parameters are those with standard deviations indicated in parentheses. The intramolecular intensity contributions from DMSO, SCN^- and ClO_4^- were held constant during the refinements.

Solution		ZNNCS4	CDSCN2	HGSCN2	HGSCN3	HGSCN4a	HGSCN4b
M–S	*d*	4.73(4)	2.634(11)	2.410(2)	2.464(3)	2.547(4)	2.531(7)
	b	0.020	0.010	0.0006(2)	0.0057(4)	0.0037(6)	0.0098(6)
	n	4	2.3	2	3	4	4.1(1)
M–C	*d*	3.08	3.49	3.287(14)	3.35(4)	3.427(14)	3.40
	b	0.013	0.018	0.005	0.010	0.010	0.012
	n	4	2.3	2	3	4	4
M–N	*d*	1.93	4.35	4.195	4.24	4.30	4.27
	b	0.007	0.025	0.010	0.018	0.018	0.021
	n	4	2.3	2	3	4	4
S–S	*d*				4.0	4.127(16)	4.13
	b				0.004	0.004(2)	0.023
	n				3	6	6
M–O	*d*		2.30	2.655(5)	2.70		
	b		0.012	0.0085(13)	0.012		
M–S_D	*d*		3.43	3.656(5)	3.70		
	b		0.020	0.032(3)	0.022		
M–O and M–S_D	*n*		3.7	3.7(3)	1		

and 3 have been obtained by introducing the parameters determined earlier for $Hg(DMSO)_6^{2+}$ and presently for $Hg(SCN)_2$.

For the other mercury(II) solutions, the results of the refinements are given in Table 3. For those parameters that are possible to refine, the standard deviations are given in parentheses. These of course do not include systematic errors which may be of at least the same order of magnitude. The Hg–S distances can be refined for all solutions, and Hg–C (though with a much larger error) for all except HGSCN4b. The distances S–C and C–N in the linear thiocyanate ion have been determined for several crystalline mercury(II) thiocyanate complexes.[8-11,29] Generally, these distances are close to 1.65 and 1.15 Å, respectively. On the assumption that the distances in solution are not markedly different, the angles Hg–S–C can be calculated, Table 4, and hence also the distance Hg–C in HGSCN4b and all the distances Hg–N, Table 3. For the Hg–S interactions, the values of the temperature factor coefficients b can also be refined while probable values of b have to be introduced for Hg–C and Hg–N interactions. For the most strongly solvated complex $Hg(SCN)_2$ (solution HGSCN2) also the parameters pertaining to the solvation (distances Hg–S_D; number of DMSO coordinated, n) can be refined. Only in the case of HGSCN4a are the interligand S–S interactions prominent enough to be refined. No further refinement is possible for the S–S interaction found at 4.0 Å in the RDF of HGSCN3. This value fits well with a tetrahedral arrangement of the S atoms, however. As moreover an Hg–S_D interaction is indicated in the RDF, one DMSO has been introduced in the fourth tetrahedral position. For this DMSO, an Hg–O distance of 2.7 Å has been calculated from the observed d(Hg–S_D) = 3.7 Å, on the assumption that the angle Hg–O–S is the same as in $Hg(DMSO)_6^{2+}$, *viz.* 120°

In the RDF of the cadmium(II) thiocyanate solution CDSCN2, a peak appears at 2.6 Å. This distance fits to a Cd–S octahedral bond. Such bonds are generally in the range[15,30,31] 2.64 to 2.66

Å. For a Cd–N coordination, on the other hand, a bond length ≃2.3 Å would be expected as the covalent radius of N is 0.34 Å shorter than that of S.[32] Also the interaction Cd–S_D in DMSO is clearly seen in the RDF, at ≃3.4 Å.

For the refinements, a structural model has been assumed where on the average 2.3 SCN are coordinated per Cd, as indicated by the stability measurements. The complexes present are thus mainly $Cd(SCN)_2$ and $Cd(SCN)_3^-$, Fig. 1. As has already been pointed out, these complexes are still octahedral. Therefore 3.7 DMSO have been introduced, coordinated *via* O at the same distance as in $Cd(DMSO)_6^{2+}$. Only the Cd–S distance can be refined. The distances Cd–C and Cd–N have been calculated assuming distances S–C and C–N of 1.65 and 1.15 Å, respectively[13,14] and an angle Cd–S–C=107°, *i.e.* the same value as found for Hg–S–C in DMSO, Table 4. Probable values of *b* have to be introduced for all interactions present. The results are listed in Table 3.

In the RDF of the zinc(II) solution ZNSCN4, the Zn–N interaction of the tetrahedral $Zn(NCS)_4^{2+}$ is expected at 1.9 Å.[33,34] This diffraction is not intense enough to be observed, Fig. 2. The broad DMSO band around 5.5 Å has a marked shoulder at ≃4.7 Å, however. On the reasonable assumption that the Zn–N bond is colinear with the SCN^- ion, which is approximately the case for several solid complexes where coordination takes place *via* N,[20,28] this distance would be a reasonable one for Zn–S. The corresponding Zn–N distance would then be ≃1.9 Å, *i.e.* as expected. The Zn–S distance has been refined under the same assumptions regarding the other parameters introduced that were applied in the calculations of the cadmium system, Table 3.

DISCUSSION

Mercury(II) thiocyanate. Both the Raman and X-ray diffraction studies show that $HgSCN^+$ is completely disproportionated in DMSO solutions concentrated enough for structural studies. On the other hand, $Hg(SCN)_3^-$ which is extensively disproportioned in dilute solutions is completely predominating in concentrated solution of $\bar{n} \simeq C_L/C_M = 3$. The structures of the complexes $Hg(SCN)_j^{2-j}$, $j=2-4$, can therefore be determined. They are all, as expected, S-coordinated. In $Hg(SCN)^2{}_4{}^-$, the S-atoms form a regular tetrahedron. The ratio $d(Hg-S)/d(S-S)$ found is 0.617(3), very close to the theoretical value of 0.612. Structurally, $Hg(SCN)_4^{2-}$ is thus analogous to the halide complexes HgX_4^{2-}, as is certainly expected. Also $Hg(SCN)_3^-$ is approximately tetrahedral, with a DMSO in the fourth position. This structure is very similar to that found[3] for HgI_3^-. In $HgBr_3^-$, the trigonal pyramide is already flattened considerably and in $HgCl_3^-$, the arrangement is trigonally planar[2] (presumably with two DMSO completing a bipyramide).

Like HgI_2, $HgBr_2$ and, presumably, also $HgCl_2$, the complex $Hg(SCN)_2$ is bent in DMSO. In the case of the two latter complexes, the Cl–Cl and S–S diffractions are not intense enough, however, to allow the determination of the deviations from linearity. The neutral complexes are rather extensively solvated, presumably by four DMSO. To judge from the Hg–O bond lengths found, generally ≃2.6 Å, the solvate bonds are of much the same strength in $Hg(SCN)_2$ as in the halide complexes.[2] As might be expected, the bonds are considerably longer, and hence weaker, than in the solvate[21] $Hg(DMSO)_6^{2+}$ where $d(Hg-O)=2.39$ Å. In the case of the halides, the large difference in solvate bond strength between HgX_2 and $Hg(DMSO)_6^{2+}$ has also been directly proved by determinations of the respective solvation enthalpies.[35]

To judge from the entropy changes ΔS_j° found for the consecutive steps in the systems discussed, $Hg(SCN)_2$ should be more strongly solvated than

Table 4. Hg–S bond lengths (Å), Hg–S–C angles (degress) and ν_1 (Hg–S) Raman frequencies (cm^{-1}) for mercury(II) thiocyanate complexes in DMSO solution. For comparison, Hg–S bond lengths in solids containing the entities $Hg(SCN)_2$ and $Hg(SCN)_4^{2-}$.

Complex	Hg–S (solution)	Hg–S (solids)	Hg–S–C	ν_1(Hg–S)
$Hg(SCN)_2$	2.410	2.381[b]	107	266[a]
$Hg(SCN)_3^-$	2.464		107	242
$Hg(SCN)_4^{2-}$	2.547	2.55[c] 2.53[d]	108	235

[a] ν_3(Hg–S) at 318 cm^{-1}. [b] Ref. 8. [c] $[Cu(en)_2][Hg(SCN)_4]$; average of Hg–S varying between 2.49 and 2.61 Å, Ref. 9. [d] $[Ph_4P]_2[Hg(SCN)_4]$; average of Hg–S varying between 2.491(3) and 2.575(4) Å, Ref. 10.

the halide complexes[1] HgX_2. In the concentrated solution used in the present structure investigation, this is seemingly not the case, however. That such a difference exists between solutions of so very different concentrations ($C_M \leq 20$ mM in the thermodynamic measurements) is not surprising. Similar differences are of course implied in the destabilization of $HgSCN^+$, and the stabilization of $Hg(SCN)_3^-$ already discussed.

An important reason for these changes is no doubt that the structure of the solvent changes drastically with C_M. At sufficiently high concentrations, the unstructured bulk solvent is bound to disappear.[4] Consequently, the huge entropy gains accompanying the break-up of an ordered solvate in dilute solution will also largely disappear. This means that complexes which are highly entropy stabilized in dilute solution will be destabilized with increasing C_M, as is in fact found for both $HgSCN^+$ and all the halide complexes HgX^+.

The bond length Hg–S increases with the number of ligands coordinated, implying a weakening of the bond in the same order, Table 4. This weakening is also reflected in the decrease of the ν_1(Hg–S) frequency, Table 4. In all the halide systems, completely analogous changes of bond length and bond strength also occur.[2] Naturally enough, the bonds become weaker as the bonding capacity of the central ion has to be divided between more ligands.

The bond length Hg–S in $Hg(SCN)_4^{2-}$ is close to those found in solids containing this entity,[9,10] Table 4. Also in the bispyridine adduct of cobalt(II) mercury(II) tetrathiocyanate, SCN is tetrahedrally coordinated to Hg *via* S, at much the same distance, in spite of the fact that all SCN^- serve as bridges to Co.[11]

The angle Hg–S–C is in all the complexes $\simeq 107°$, Table 4. An angle of this magnitude is the rule for thiocyanate complexes coordinated *via* S.[8,9,11,20,28] For complexes coordinated *via* N, on the other hand, the angle M–N–C is generally not far from 180°.[11,20,28]

As to *cadmium(II)*, the present results confirm the inference that for this borderline acceptor small changes of the conditions are sufficient to change the coordination of an ambident ligand as SCN^-. In DMSO, S-coordination no doubt prevails while in aqueous solution the opposite is presumably the case. In solids, both modes evidently exist, and bridged compounds where they are used simultaneously are common, as might be expected.

For *zinc(II)*, the preference for N over S is evident. This does not preclude however, that in solids S-coordination often occurs in order to create a favourable coordination polyhedron.

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