An X-Ray Diffraction and Raman Study of Mercury(II) Chloride, Bromide and Iodide Complexes in Dimethylsulfoxide Solution

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Dimethylsulfoxide solutions containing mercury(II) and halide in equimolar amounts have been investigated by Raman and X-ray diffraction measurements. The complexes HgX^+ which are very stable in dilute solutions are found to disproportionate completely as the concentration increases. In the chloride and bromide systems, the simple reaction $2HgX^+ \rightleftharpoons Hg^{2+} + HgX_2$ takes place. The disproportionation of $HgCl^+$ is practically complete at $C_M \simeq 0.5$ M, but at still higher values of C_M further reactions take place. The disproportionation of $HgBr^+$ is complete already at $C_M \simeq 0.1$ M and remains so to saturated solution. In the iodide system, Hg^{2+} is not formed, but instead the dinuclear complex Hg_2I^{3+} most probably is, according to $3HgI^+ \rightleftharpoons Hg_2I^{3+} + HgI_2$. This reaction is complete at $C_M \simeq 0.2$ M and no further reactions take place at higher values of C_M. Evidently, the strong entropy stabilization which makes the species HgX^+ very prominent in dilute solutions completely disappears as C_M increases. The reason for this is discussed.

The structures of the tetrahedral complexes $HgCl_4^{2-}$ and $HgBr_4^{2-}$ finally formed as the halide concentration is increased have been determined by X-ray diffraction.

As in the protic solvent water, mercury(II) forms in the aprotic solvent dimethylsulfoxide (DMSO) a series of four mononuclear complexes HgX_j^{2-j} with chloride, bromide and iodide.[1,2] Of the intermediate steps only the neutral complexes HgX_2 are very prominent in water.[1] In DMSO, on the other hand, all these steps are well separated in all the systems, at least at the mercury(II) concentrations covered by the stability measurements[2] ($C_M \lesssim 20$ mM). The

maximum share of C_M reached by each complex (which occurs at the ligand number $\bar{n} = j$) is well over 90%, except for $HgCl_3^-$ which, however, still exceeds 80%. The stabilization of the complexes HgX^+ in DMSO relative to water is exclusively an entropy effect.[2] Both enthalpy and entropy changes contribute, on the other hand, to the stabilization of the complexes HgX_3^- in DMSO.

Another striking difference between the two solvents is that the neutral complexes HgX_2 are all very soluble in DMSO,[3,4] while in water their solubility varies[5] from fair ($HgCl_2$) to very slight (HgI_2).

The fact that the mercury(II) halide complexes are so well separated in DMSO, in combination with their high solubility, makes it possible to determine their structures in solution by X-ray diffraction technique. In water such measurements are possible only for the final complexes[6,7] HgX_4^{2-}, and, to a certain extent,[6] for $HgBr_3^-$ and HgI_3^-. Studies recently performed in DMSO have also successfully elucidated the structures of all complexes HgX_2, HgX_3^- and HgX_4^{2-} (except for $HgCl_4^{2-}$ which was not investigated).[3,4] In these measurements, the mercury(II) concentration has varied between 0.55 and 4.4 M, most solutions measured have been between 1 and 2 M. The values of C_M have thus been about 100 times higher than in the stability measurements. In spite of this, the distribution between the complexes mentioned seems to be much the same as found in the dilute solutions. For ligand concentrations C_L chosen so that $C_L/C_M = 2, 3$ and 4.5, the results of the diffraction studies are compatible with a strong predominance of the complexes HgX_2, HgX_3^- and HgX_4^{2-}, respectively.

The Hg−X bond distances calculated increase regularly in the order $HgX_2 < HgX_3^- < HgX_4^{2-}$, and the values are moreover close to those found for crystalline compounds containing these entities, Table 6. Evidently, the strength of the bonds Hg−X decreases as more ligands are coordinated.

The Raman spectra of the solutions are also consistent with these results.[4] For all the halides, the frequency of the prominent band due to the Hg−X stretching mode (v_1) decreases markedly in the order $HgX_2 > HgX_3^- > HgX_4^{2-}$, which directly indicates the weakening of the bond Hg−X as further ligands are coordinated to the central ion.

The complexes HgX^+, predominating at $C_L/C_M = 1$ in dilute solutions, behave in a manner very different to that of the higher complexes, however. At the values of C_M necessary for structure determinations, they have mainly disappeared, evidently due to disproportionation reactions.[4] The large increase of the concentration thus brings about very considerable changes of the relative stabilities of the complexes involved.

These changes were first indicated by the presence in the Raman spectra of concentrated solutions[4] with $C_L/C_M = 1$ of $v_1(Hg−X)$ frequencies characteristic of the complexes HgX_2. In the chloride and bromide systems the well-established Hg−O bending and stretching frequencies of the solvate[8] $Hg(DMSO)_6^{2+}$ were also found. In conformity with this, the bond lengths Hg−X calculated from X-ray diffraction studies of the solutions were close to those found for solutions with $C_L/C_M = 2$. Seemingly the same halide complexes HgX_2 predominated at both the ratios investigated.

The present investigation was undertaken primarily in order to study more closely the conditions prevailing in DMSO solutions containing halide and mercury(II) in the molar ratio 1:1. The first question is how the disproportionation depends upon the concentration in the various systems studied. To find this, Raman spectra of 1:1 solutions of widely varying C_M have been recorded. Secondly, solutions of $C_M = 0.8$ M have been studied by X-ray diffraction, and the results compared with those calculated from previous measurements[4] involving solutions of higher C_M.

In addition, the structure of the complex $HgCl_4^{2-}$, missing in the earlier study, has been determined. Finally, a redetermination of the structure of $HgBr_4^{2-}$ was undertaken, in order to ensure that the instrumental setup used in the present investigation yielded the same result as that used for the study of all the other mercury(II) halide complexes in DMSO solution.

EXPERIMENTAL

Preparation of solutions. The solutions were prepared by dissolving weighed amounts of mercury(II) halide (p.a.) and $Hg(ClO_4)_2.4DMSO$ or lithium halides (p.a.) in DMSO. The compositions of the solutions used in the X-ray diffraction measurements are given in Table 1. In this Table, the compositions of the solutions investigated previously[4] (denoted HGCLMS, etc.) are stated.

The solvate $Hg(ClO_4)_2.4$ DMSO was prepared and analyzed as described previously.[8] The mercury(II) halides (p.a.) were recrystallized,[9] and then carefully dried and stored in a vacuum desiccator at about 100 °C. The lithium halides (p.a.)

Table 1. Concentrations/M of the solutions investigated by X-ray diffraction. The linear absorption coefficient μ/cm^{-1} is calculated for MoKα-radiation.

Solution	Hg(II)	X⁻	ClO_4^-	Li⁺	DMSO	μ
HGCL	0.80	0.80	0.80		13.0	24.0
HGCLMS	1.30	1.30	1.30		13.0	35.5
HGCL4	0.40	1.80		1.00	13.6	14.8
HGBR	0.80	0.80	0.80		13.1	27.8
HGBRMS	1.54	1.47	1.61		12.3	49.2
HGBR4	0.40	1.80		1.00	13.8	22.8
HGI	0.80	0.80	0.80		13.4	27.5
HGIMS	1.27	1.27	1.27		12.7	39.9
Pure DMSO					14.0	4.9

were recrystallized from water, dried and stored as the mercury(II) halides.

Raman measurements. The Raman spectra were recorded, in the wavelength range 100 to 600 cm^{-1}, with a Cary 82 argon ion laser spectrophotometer using the 4880 Å line. Glass tubes with a diameter of 1 mm were used as sample holders for the solutions. The measurements were carried out at room temperature.

Diffraction measurements. The X-ray scattering from the free surface of the solution was measured in $\theta - \theta$ diffractometer of the same type as the one used by Johansson.[6,10,11] The sample holder was a teflon container enclosed in an air-tight shield. Mo$K\alpha$-radiation ($\lambda = 0.71069$ Å) was used with a lithium fluoride single crystal placed between the sample and the scintillation counter as monochromator. The amount of incoherently scattered radiation reaching the counter was estimated and checked as described before.[3] The intensity of the diffracted radiation was measured at discrete points separated by 0.1° and 0.25° in the ranges $1° \leq \theta \leq 30°$ and $30 \leq \theta \leq 63°$, respectively. For each point, 40 000 counts were recorded twice. The data of Sandström[4] recalculated for the present study are based on $2 \times 100\,000$ counts per point. The corresponding statistical errors are 0.35 and 0.22 ‰, respectively.

Treatment of diffraction data. The same data reduction procedure and corrections as described previously were applied.[6,12] The experimental intensities were normalized to a stoichiometric unit of volume containing one mercury atom. The scattering factors, corrections for anomalous dispersion and values for incoherent scattering were the same as used before.[6] The reduced intensity curves, $i_{obs}(s)$ multiplied by s, where $s = 4\pi\lambda^{-1}\sin\theta$, are given in Figs. 3 and 6. The corresponding electronic radial distribution functions (RDF), $D(r) - 4\pi r^2 \rho_0$, were obtained by Fourier transformation, Figs. 2 and 5. The same modification function as described previously was used.[6] Spurious peaks below 1.5 Å which could not be related to interatomic distances within the DMSO molecule or the perchlorate ion have been removed by a Fourier transformation procedure.[10]

All calculations were carried out on the UNIVAC 1100/80 computer of the University of Lund by means of the programs KURVLR and PUTSLR.[13]

RAMAN MEASUREMENTS

Raman spectra have been recorded for solutions of varying C_M, all with $C_L/C_M = 1$. The stretching modes v_1 (Hg$-$X) were found at 303, 195 and 145 cm^{-1} for X = Cl, Br and I, respectively, *i.e.* within the

limits of error at the same wavenumbers as reported by Sandström[4] both for solutions of HgX$_2$ ($C_L/C_M = 2$) and for solutions of the present ratio $C_L/C_M = 1$. The chloride and bromide spectra also show the Hg$-$O bending and stretching modes at 210 and 425 cm^{-1} which are characteristic[8] of the solvate Hg(DMSO)$_6^{2+}$. In the iodide spectra these bands are absent, but a relatively strong band appears instead at 173 cm^{-1}. In concentrated aqueous solutions (2 M $\leq C_M \leq 4$ M) an analogous band has been found, at 168 cm^{-1}, which has been assigned to the dinuclear complex[14] Hg$_2$I^{3+}. Very plausibly such a complex also exists in DMSO. If so, it should be especially prominent in concentrated solutions containing a large excess of mercury(II). In fact, in the spectrum of a solution of $C_M = 1$ M and $C_L/C_M = 0.4$, the peak assigned to Hg$_2$I^{3+} persists, while that assigned to HgI$_2$ almost vanishes.[15] No bands that can be assigned to HgX$^+$ are found in any of the investigated solutions.

The chloride band at 303 cm^{-1} cannot be resolved from a fairly intense DMSO band[8] at 308 cm^{-1}. The contribution from this band was corrected for by comparing the total height of the peak found at $\simeq 305$ cm^{-1} with that of the DMSO peak at $\simeq 335$ cm^{-1} which is not disturbed by the mercury complexes present. The correction becomes, of course, more uncertain the lower the value of C_M. For the solutions measured here, with $C_M \gtrsim 0.3$ M, it should be adequate, however. No interference occurs with the bromide band at 195 cm^{-1}, so for this system the lower limit of C_M can be chosen at $\simeq 0.035$ M. The iodide band at 145 cm^{-1} is on the edge of an intense band. In this case, the lower limit of C_M must therefore again be chosen somewhat higher, at $\simeq 0.07$ M. The upper limits of C_M have been the saturated solutions, with values of $C_M = 1.3$, 1.5 and 1.3 M for chloride, bromide and iodide, respectively.

In concentrated DMSO solutions, the complexes HgCl$^+$ and HgBr$^+$ thus seem to disproportionate according to the simple mononuclear reaction 2 HgX(DMSO)$_p^+$ + n DMSO $\rightleftharpoons$ HgX$_2$(DMSO)$_q$ + Hg(DMSO)$_6^{2+}$ with the constant given by eqn. (1),

$$K_{HgX}[\text{DMSO}]^n = \frac{[\text{HgX}_2][\text{Hg(DMSO)}_6^{2+}]}{[\text{HgX}^+]^2} \qquad (1)$$

while the disproportionation of HgI$^+$ most probably occurs according to

$$3\,\text{HgI(DMSO)}_p^+ + n\,\text{DMSO} \rightleftharpoons$$
$$\text{HgI}_2(\text{DMSO})_q + \text{Hg}_2\text{I(DMSO)}_r^{3+}$$
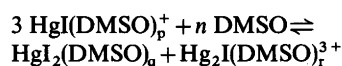
with the equilibrium constant given by eqn. (2).

$$K_{HgI}[DMSO]^n = \frac{[HgI_2][Hg_2I^{3+}]}{[HgI^+]^3} \qquad (2)$$

To determine how far the disproportionation has proceeded at a certain C_M, the ratio h/C_M is formed where h is the (corrected) height of the $v_1(Hg-X)$ peak (in arbitrary units). As h is proportional to $[HgX_2]$, this ratio is proportional to $[HgX_2]/C_M$. For this quantity, the expressions (1a) and (2a) can be deduced from eqns. (1) and (2), referring to chloride and bromide (1a), and to iodide (2a).

$$\frac{[HgX_2]}{C_M} = \frac{1}{(K_{HgX}[DMSO]^n)^{-1/2} + 2} \qquad (1a)$$

$$\frac{[HgI_2]}{C_M} = \frac{1}{([HgI_2]K_{HgI}[DMSO]^n)^{-1/3} + 3} \qquad (2a)$$

As expressed by eqn. (1a), a simple disproportionation of the type (1) should *per se* be independent of C_M. From the ratios h/C_M plotted in Fig. 1a, b it is obvious that this is not the case. As already found in the stability measurements,[2] no disproportionation occurs at low C_M. With increasing C_M, however, the disproportionation rather suddenly becomes prominent. In the case of chloride, h/C_M slowly decreases after having passed a maximum at $C_M \simeq 0.5$ M, Fig. 1a. In the case of bromide, on the other hand, the high values of h/C_M reached already at $C_M \simeq 0.1$ M stays constant as C_M is further increased, Fig. 1b.

In the chloride system, the peak height h for a solution of $C_M = 0.5$ M is the same as that found for a 0.25 M solution of $HgCl_2$. At the maximum value of h/C_M, the disproportionation according to eqn. (1) is thus complete. The following decrease of the ratio might be interpreted as indicating a partial reproportionation to $HgCl^+$, though such a reaction is admittedly fairly unexpected. The low value of the bond distance $Hg-Cl$ found[4] in the saturated solution of $C_M = 1.3$ M nevertheless speaks in favour of such an interpretation (cf. Table 4). Another possibility would be that a dinuclear complex Hg_2Cl^{3+}, analogous to Hg_2I^{3+}, is formed. Low concentrations of such a complex have been found to be quite important for the electrode kinetics of the mercury electrode in DMSO.[16] Even in the concentrated solution used here the dimerization cannot be very extensive, however, as
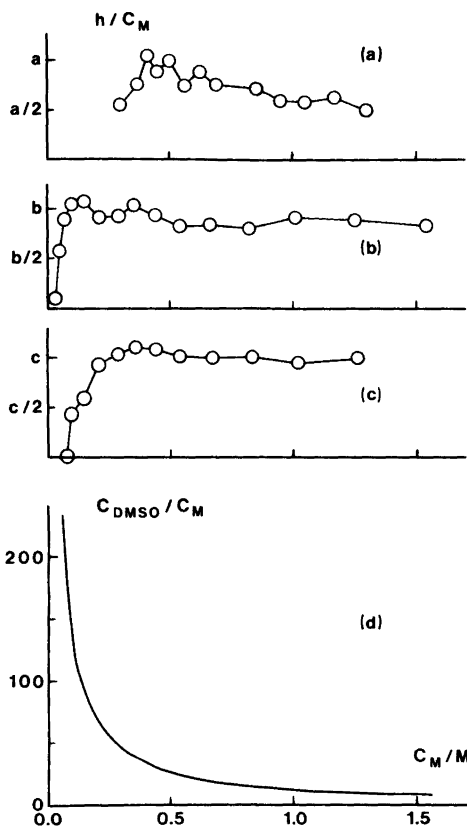

Fig. 1. a − c. Ratios h/C_M between the peak heights of the $v_1(Hg-X)$ bands of the HgX_2 complexes formed by disproportionation in solutions of $C_L/C_M = 1$, and the total mercury(II) concentration. The values of h/C_M are on an arbitrary scale. The figures refer to the chloride (*a*), bromide (*b*) and iodide (*c*) solutions, measured at 303, 195 and 145 cm^{-1}, respectively. *d.* Number of DMSO per mercury atom as a function of C_M.

the band due to the $Hg-O$ bending mode at 210 cm^{-1}, characteristic of the solvate $Hg(DMSO)_6^{2+}$, persists strongly all the way to the saturated solution. It is moreover not easy to understand why a complex Hg_2Cl^{3+}, analogous to Hg_2I^{3+}, should exist in fair amounts in a concentration range where a complex Hg_2Br^{3+} certainly does not.

It should finally be remembered that, on account of the interference from the DMSO band, the precision as well as the accuracy of the chloride data is limited, and lower than for the data pertaining to the bromide and iodide systems. Even for these, the

random errors, mostly due to the difficulty in defining the base line, are fairly large, especially at low values of C_M. Errors around 10 % are quite probable in these cases; for the chloride system they might be considerably larger.

The constant value of h/C_M found for $C_M \gtrsim 0.1$ M in the bromide system *per se* strongly suggests that complete disproportionation takes place in this region. That this is indeed the case has been proved by measuring the value of h/C_M for a 0.25 M solution of $HgBr_2$. This value is twice as large as that of the plateau in Fig. 1b, just as expected if within the whole of this region a complete disproportionation takes place according to eqn. (1).

In the case of the more complicated disproportionation proposed for the iodide system, $[HgI_2]/C_M$, and hence h/C_M, should depend upon C_M until $([HgI_2]K_{HgI}[DMSO]^n)^{-1/3} \ll 3$, *cf.* eqn. (2a). When this condition is met, $[HgI_2]/C_M = 1/3$, *i.e.* a disproportionation taking place according to eqn.

(2) is then complete. The constant value of h/C_M found for $C_M \gtrsim 0.2$ M, Fig. 1c, thus strongly indicates that the disproportionation is complete in this region. The final proof is the fact that an 1 M HgI_2 solution has a value of h/C_M three times higher than that of the plateau in Fig. 1c, *i.e.* just as expected if the disproportionation takes place according to eqn. (2).

The addition of even large amounts of ammonium perchlorate, used to provide an ionic medium in the stability measurements, does not influence the disproportionation of HgI^+. Thus solutions of 0.1 M $\leq C_M \leq 0.3$ M, containing ammonium perchlorate to a total ionic strength of 1.2 M, have the same Raman spectra as solutions with no salt added.

X-RAY DIFFRACTION MEASUREMENTS

Pure DMSO. In the present diffraction measurements, the values of C_M were lower than previously, and more precise corrections for the
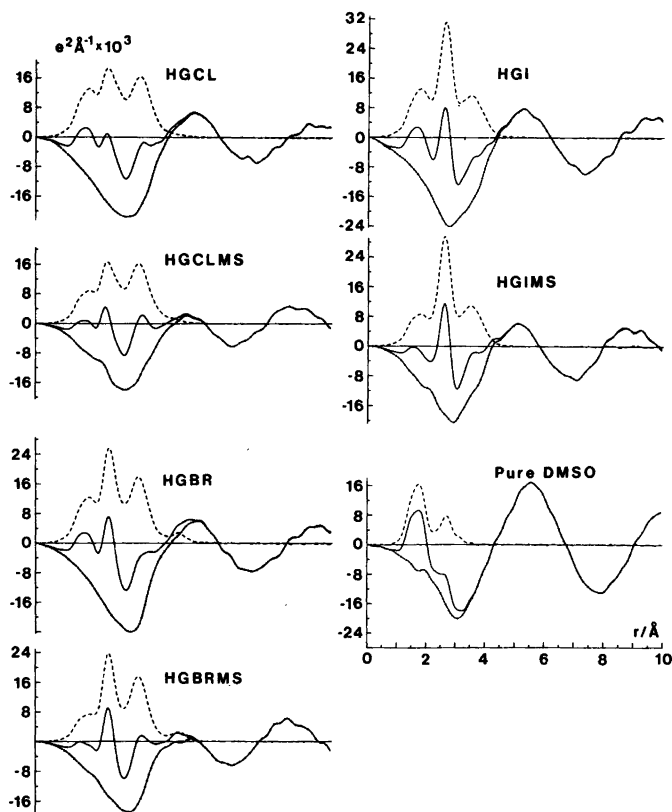

Fig. 2. $D(r) - 4\pi r^2 \rho_0$ functions of the solutions of $C_L/C_M = 1$ (solid lines) compared with sums of calculated peak shapes (dashed lines). The differences are shown by dashed-dotted lines.

contributions from DMSO were needed. The data previously recorded for liquid DMSO have therefore been refined.

The RDF function for pure DMSO has a peak at about 1.8 Å and a marked shoulder at about 1.5 Å, corresponding to S−C and S−O bond distances, respectively. A prominent shoulder at about 2.7 Å corresponds to the O−C and C−C interactions, Fig. 2. The very broad peaks at $\simeq 5.5$ and 10 Å are certainly due to intermolecular interactions between S atoms. For solid DMSO whose structure is well known,[17,18] the distances between the S atoms of neighbour molecules can be computed. These are (at 5°[17]) 4.2, 5.0, 5.3 and 6.0 Å. The S−S distances preferred in liquid DMSO are evidently within the same range giving rise to the broad peak at $\simeq 5.5$ Å. The peak at $\simeq 10$ Å would thus reflect the S−S distances of the second sphere.

In the final refinements of the intramolecular parameters, the numbers of the various atomic distances per sulfur atom, n, have been fixed as they are, of course, well known for pure DMSO. The values of the distances d (Å) and temperature coefficients b (Å^2) resulting from these refinements are given in Table 2. The distances determined for liquid DMSO are quite close to those found previously for the solid[17,18] and gaseous[19] states.

The intramolecular bond distances and angles in the three states of aggregation are given in Table 3.

Formal HgXClO$_4$ solutions. The disproportionation of the HgX$^+$ complexes results in three or, when the disproportionation is complete, two different mercury(II) species in the solution. In neither case, however, is a refinement of all the parameters of the individual complexes possible. In the iodide solutions, the distances Hg−I in the complex formed, Hg$_2$I^{3+} and HgI$_2$, are not different enough to be resolved. In the bromide and chloride solutions, the same applies to the distances Hg−O in the solvate Hg(DMSO)$_6^{2+}$ and Hg−X in the complexes HgX$_2$. In the latter cases, however, most parameters of the species involved are well known from previous studies of solutions where these species predominate.[4,8] Only the number of DMSO coordinated to HgX$_2$ is somewhat uncertain. A probable number is 4, however.[4] In the iodide case, on the other hand, only the parameters referring to the Hg−I bonds in HgI$_2$ are well known.[3,4] Hardly any data exist about the solvation of this complex. As to the postulated dinuclear complex Hg$_2$I^{3+}, no structural data are known at all.

For the chloride and bromide solutions, the parameter values reported in Ref. 4 for the solutions Cl2A and Br2A, both of $C_M = 1.00$ M, and those

Table 2. Least-squares refinements on the reduced intensities for pure DMSO. The distances d (Å) and temperature coefficients b (Å) are calculated from the range $5.5 \leq s \leq 16$ Å, with standard deviations in parentheses. The numbers of interactions per sulfur atom, n, have been fixed.

Interaction →	S−O	S−C	O−C	C−C
d	1.496(4)	1.805(4)	2.661(8)	2.774(10)
b	0.0006(5)	0.0020(3)	0.000(1)	0.0006(2)
n	1	2	2	1

Table 3. Interatomic distances (Å) and angles (degrees) in gaseous, liquid and solid DMSO.

	Gaseous[19]	Liquid[a]	Solid[17,b]	Solid[18,c]
S−O distance	1.47	1.496(4)	1.531	1.471(8)
S−C distance	1.82	1.805(4)	1.775	1.801(10)
			1.821	1.812(14)
C−S−O angle	107(5)	107.0(9)	106.7	107.4(5)
			106.8	107.0(6)
C−S−C angle	100(5)	100.4(8)	97.4	97.9(5)

[a] This work. [b] At 5 °C. [c] At −60 °C.

reported in Ref. 8 for the perchlorate solution of C_M = 0.93 M, have been used to calculate the RDF:s. On the assumption of complete disproportionation, smooth differences $(D(r)_{obs} - D(r)_{calc})$ of much the same shape as for pure DMSO are found for the bromide solutions HGBR and HGBRMS, and also for the chloride solution HGCL, Fig. 2. For HGCLMS, however, a marked shoulder in the RDF difference at $\simeq 2.3$ Å implies that the parameter values do not fit quite well. This is not surprising if further reactions have occurred in this solution, as indicated by the lower intensity of the Raman v_1(Hg —Cl) band for solutions of such high concentrations, Fig. 1.

Least square refinements of the parameters d and b of the Hg—Cl and Hg—Br interactions were performed in the range $6 \leq s \leq 16$ Å^{-1}. All other parameters were fixed at the values indicated above, and complete disproportionation of HgX$^+$ was assumed. The values found for HGCL, and for both bromide solutions, agree well with those found previously for the complexes HgCl$_2$ and HgBr$_2$, respectively, Table 4. For HGCLMS, on the other hand, the values are again significantly different. Most probably, therefore, the first three solutions are indeed completely disproportionated according to eqn. (1) while HGCLMS is not. The satisfactory overall fit of the model is also demonstrated in Fig. 3.

In the RDF's of the iodide solutions, Fig. 2, the intense peak at about 2.6 Å corresponds to Hg—I

Table 4. Least squares refinements on the reduced intensities for DMSO solutions of equal mercury(II) and halide concentrations. Distances d (Å) and temperature coefficients b (Å^2) are calculated for the Hg—X interactions, from the range $6 < s < 16$ Å^{-1}, and compared with the values previously reported[4] for solutions (Cl2A, Br2A, I2A) of the complexes HgX$_2$. Standard deviations in parentheses.

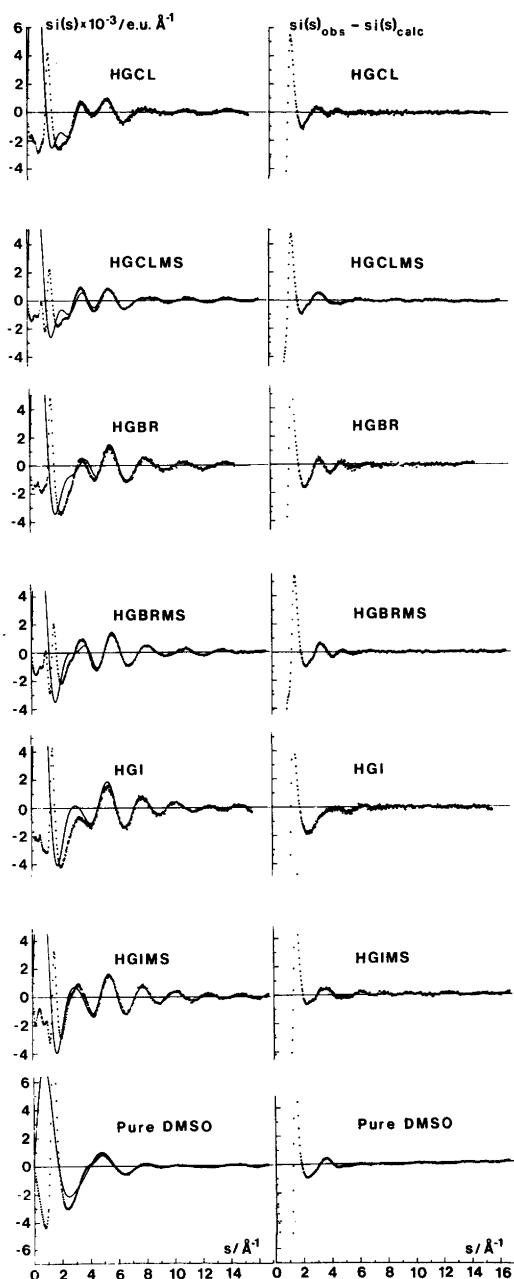| Interaction	Solution	d	b
Hg—Cl	HGCL	2.363(6)	0.0014(7)
	HGCLMS	2.300(3)	0.0018(5)
	Cl2A	2.350(3)	0.0013(3)
Hg—Br	HGBR	2.469(4)	0.0032(5)
	HGBRMS	2.455(3)	0.0021(2)
	Br2A	2.452(2)	0.0015(2)
Hg—I	HGI	2.621(2)	0.0058(3)
	HGIMS	2.607(2)	0.0053(2)
	I2A	2.620(2)	0.0037(4)

Fig. 3. Reduced intensities multiplied by s for pure DMSO and for the solutions of $C_L/C_M = 1$. To the left, experimental values are denoted by dots, values calculated for the refined model (with the parameter values of Tables 2 and 4) by solid lines. To the right, differences between experimental and calculated functions are represented by dots.

interactions. The sharpness of this peak indicates that the distances $Hg-I$ must be almost the same in the complexes HgI_2 and Hg_2I^{3+} postulated to be present. The shoulder at $\simeq 3.7$ Å is very likely in part due to the $Hg-Hg$ interaction in Hg_2I^{3+}. Also the interactions between Hg and the S atoms of the DMSO molecules coordinated (via their O atoms) certainly contribute to this diffraction, however. With $d(Hg-I)=2.6$ Å and $d(Hg-Hg)=3.7$ Å, the angle $Hg-I-Hg$ in Hg_2I^{3+} would be $\simeq 90°$. This fits nicely with the fact that the endless chains present[20] in solid $(HgI)_2TiF_6$ have $d(Hg-I)=2.62$ Å and angles $Hg-I-Hg$ not far from 90° (89 and 97°).

No more than three DMSO can be coordinated to each mercury atom in the strongly bent Hg_2I^{3+}, as is evident from a molecular model. A complete disproportionation according to the formula assumed thus means that the frequency factor n of the $Hg-O$ and $Hg-S$ interactions of Hg_2I^+ cannot exceed 2 when referred to the total mercury(II) concentration. In the following calculations $n=2$ has been used. The lower coordination number of Hg in Hg_2I^{3+} as compared with $Hg(DMSO)_6^{2+}$ will presumably shorten the distances $Hg-O$ and $Hg-S$. Because of the less regular coordination, the b values of these interactions will presumably be larger in Hg_2I^{3+} than in $Hg(DMSO)_6^{2+}$. On the basis of these considerations, the following parameter values have been assumed: $d(Hg-O)=2.35$ Å, $d(Hg-S)=3.35$ Å; $b(Hg-O)=0.015$ Å^2, $b(Hg-S)=0.025$ Å^2. The contribution to the $si(s)$ function from such an $Hg-S$ interaction is shown in Fig. 4a.

From a recent Raman investigation, it has been concluded that two DMSO molecules are coordinated to HgI_2 in DMSO solution.[21] If so, the frequency factors of the $Hg-O$ and $Hg-S$ interactions of HgI_2 are 2/3 in the present solutions, where 1/3 of the mercury is present as HgI_2. To judge from the data reported for $HgCl_2$ and $HgBr_2$, Table 4, the $Hg-O$ and $Hg-S$ distances are probably $\simeq 2.6$ and $\simeq 3.7$ Å, respectively, and the b parameters around 0.03 Å^2.

With these models for the solvation of HgI_2 and Hg_2I^{3+}, an attempt was made to refine the parameters d and b of the $Hg-I$ interactions, and of the interaction $Hg-Hg$ in Hg_2I^{3+}. Complete disproportionation was assumed which implies frequency factors of 4/3 and 1/3 for the $Hg-I$ and $Hg-Hg$ interactions, respectively. No significant values of the $Hg-Hg$ parameters could be obtained,
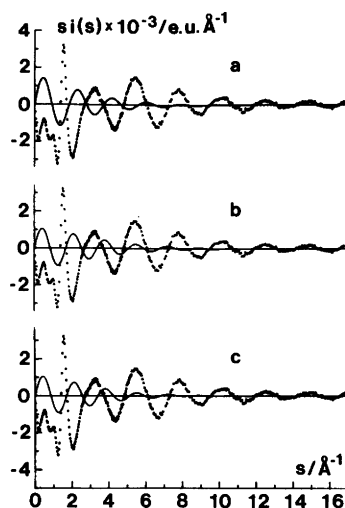

Fig. 4. The calculated contribution (solid lines) to the function $si(s)$ of the HGIMS solution from an $Hg-S$ interaction with $d=3.35$ Å, $b=0.025$ Å^2 and $n=2$ (a); from an $Hg-Hg$ interaction with $d=3.70$ Å, $b=0.02$ Å^2 and $n=0.33$ (b); and from an $Hg-Hg$ interaction with the same values of d and n but with $b=0.03$ Å^2 (c).

however, evidently on account of the high temperature coefficient. It was found that a value of $b \gtrsim 0.02$ Å^2 means that the $Hg-Hg$ interaction does not contribute significantly to the $si(s)$ function for values of $s \gtrsim 5$ Å^{-1}, Fig. 4, b and c. When the values $d=3.70$ Å and $b=0.03$ Å^2 are introduced for the $Hg-Hg$ interaction, a least squares refinement of the $Hg-I$ interaction resulted in the parameter values listed in Table 4. Those were constant within ± 0.01 Å for d and ± 0.001 Å^2 for b when the lower limit of the s-range was varied between 5 and 7 Å. No significant differences were found between the two solutions studied. As seen from Figs. 2 and 3, the model adopted fits very well to the experimental data.

The value of $b=0.03$ Å^2 for the $Hg-Hg$ interaction corresponds to a root mean square variation of 0.24 Å in the average $Hg-Hg$ distance. This in turn corresponds to a variation of $\pm 6°$ in the angle $Hg-I-Hg$ which seems to be a reasonable flexibility.

HgX_4^{2-} solutions. The stability measurements[2] indicate that $HgCl_4^{2-}$ and $HgBr_4^{2-}$ should be the predominating complexes in the solutions HGCL4 and HGBR4, respectively. Their Raman spectra
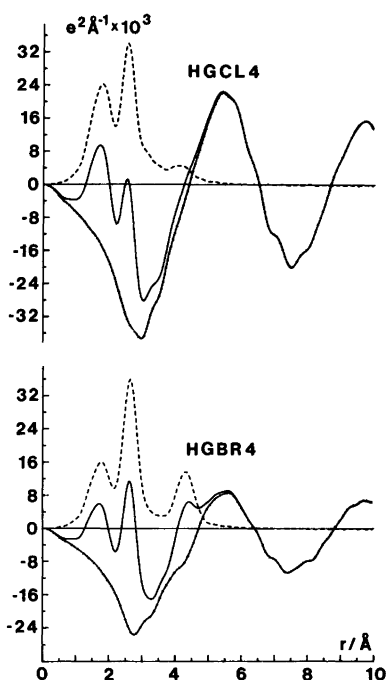
Fig. 5. $D(r) - 4\pi r^2 \rho_0$ functions for the HgX_4^{2-} solutions (solid lines) compared with sums of calculated peak shapes (dashed lines). The differences are shown by dashed-dotted lines.

confirm that this is indeed the case. The v_1 (Hg—X) bands are found just at the wavenumbers expected,[4] 260 cm^{-1} for $HgCl_4^{2-}$ and 164 cm^{-1} for $HgBr_4^{2-}$, and no bands exist that can be assigned to other complexes.

Besides the peaks due to interactions within DMSO, and between DMSO molecules, only two peaks, or shoulders, are present in the RDF's, Fig. 5. The intense peaks at $\simeq 2.5$ Å in HGCL4 and $\simeq 2.6$ Å in HGBR4 correspond to Hg—X bond distances. The diffuse shoulder at $\simeq 4$ Å in HGCL4 and the small peak at $\simeq 4.3$ Å in HGBR4 correspond to X—X distances.

Least squares refinements were performed of the parameters d and b of the Hg—X and X—X distances, and also of the number of the Hg—X bonds. The number of X—X distances were fixed at 6. The parameters found are listed in Table 5. The good fit obtained is demonstrated in Fig. 6.

The distances show beyond doubt that the complexes $HgCl_4^{2-}$ and $HgBr_4^{2-}$ are regular tetrahedrons. The ratios $d(Hg-X)/d(X-X)$ are 0.612(7) and 0.612(2), respectively, *i.e.* not distinguishable from the tetrahedral value of 0.6124. The number of Hg—X distances is also consistent with this structure. The result found for $HgBr_4^{2-}$ also agrees well with that previously reported, Table 6.
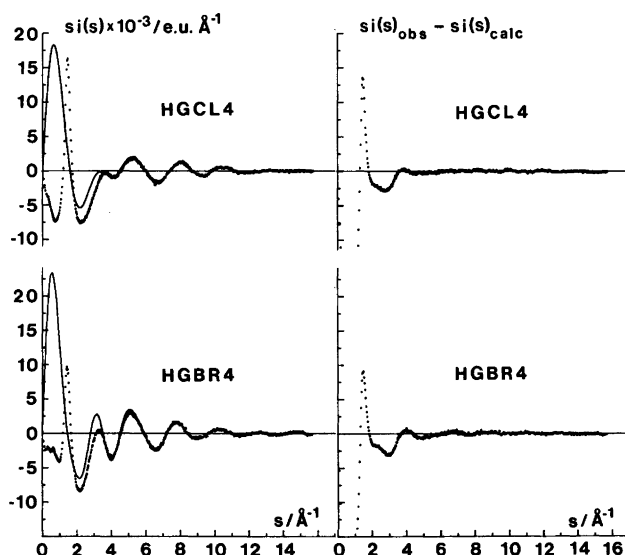

Fig. 6. Reduced intensities multiplied by s for investigated HgX_4^{2-} solutions, plotted according to the scheme given in the legend of Fig. 3.

Table 5. Least squares refinements on the reduced intensities for DMSO solutions of the complexes $HgCl_4^{2-}$ and $HgBr_4^{2-}$. From the ranges $5 < s < 14.5$ Å^{-1} and $6 < s < 15.5$ Å^{-1}, respectively, distances d (Å) and temperature coefficients b (Å^2) are calculated for the $Hg-X$ and $X-X$ interactions. For $Hg-X$, also the number of interactions n has been refined, while for $X-X$ this value has been fixed at $n = 6$. The results found for $HgBr_4^{2-}$ are compared with those of an earlier investigation.[4] Standard deviations are given in parentheses.

Solution	Interaction	d	b	n
HGCL4[a]	Hg−Cl	2.532(2)	0.0013(4)	3.7(1)
	Cl−Cl	4.14(4)	0.0025(6)	6
HGBR4[a]	Hg−Br	2.628(3)	0.0076(2)	4.0(1)
	Br−Br	4.293(13)	0.0152(4)	6
Br4[4]	Hg−Br	2.628(2)	0.0058(4)	4.1(2)
	Br−Br	4.31(1)	0.0026(8)	6(2)

[a] This work.

Table 6. Distances $Hg-X$ (Å) in HgX_2, HgX_3^- and HgX_4^{2-}, $X = Cl$, Br and I, in DMSO solution and in solid phases; for HgX_4^{2-} also in aqueous solution.

	HgX_2	HgX_3^-	HgX_4^{2-}	
Cl				
solid	2.291(9)[22]	2.432(3)[23]	2.495(10),[24]	2.438−2.540(1)[25]
DMSO	2.350(3)[4]	2.434(3)[4]	2.532(2)[a]	
aq			2.47(1)[7]	
Br				
solid	2.428(5)[26,b]	2.483−2.56(3)[27]	2.587(4)[28]	
DMSO	2.455(2)[4]	2.547(3)[4]	2.628(2)[a,4]	
aq			2.610(5)[6]	
I				
solid	2.618(6)[29,c]	2.72(1)[30]	2.77(1),[31]	2.783(2)[29,d]
DMSO	2.624(8)[4]	2.733(3)[3]	2.796(3)[3]	
aq			2.785(3)[6]	

[a] This work. [b] $3HgBr_2 \cdot CH_3CN$, longest d. [c] Yellow HgI_2. [d] Red HgI_2, no discrete ions.

CONCLUSIONS

The disproportionation reactions inferred from the Raman data of solutions containing mercury(II) and halide in equimolar amounts are compatible with the results of the diffraction measurements. For chloride and bromide, the reaction thus occurs according to eqn. (1), for iodide according to eqn. (2), with the formation of a dinuclear complex. For chloride, further reactions occur at high values of C_M, for bromide and iodide the disproportionation stays complete up to saturated solution.

In the potentiometric and calorimetric measure-ments[2] where $C_M \leq 20$ mM, the number of DMSO per mercury is always very large, Fig. 1d. Under these conditions, HgX^+ is, as mentioned earlier, exceptionally stable towards disproportionation. Such reactions begin as C_{DMSO}/C_M decreases, and the disproportionation is complete for the approximate ratios 30, 150 and 75 for chloride, bromide and iodide, respectively. Evidently these changes are enough to destroy that entropy stabilization which renders the complex HgX^+ so very stable. This would mean that once C_{DMSO}/C_M are down to these

values, a really unstructured bulk solvent no longer exists. It is not easy to rationalize, however, why the disproportionation becomes prominent at such different values of C_{DMSO}/C_M for the various halides. The easy formation of dimers, and generally polymers in iodide solutions, as compared with chloride or bromide solutions, is well known.

On the other hand, it is rather surprising that the ordering effect exterted by ammonium ions does not affect the degree of disproportionation.

In all the complexes HgX_4^{2-} the bonds $Hg-X$ are somewhat longer in DMSO than in water, Table 6. This lengthening indicates that the complexes are more strongly solvated by DMSO than by water. In conformity with this, the bonds $Hg-X$ are even shorter in solids containing these complexes. Also in the complexes HgX_2 and HgX_3^-, the $Hg-X$ bonds are generally shorter in solid phases than in DMSO solutions, Table 6.

In the solvates $Hg(H_2O)_6^{2+}$ and $Hg(DMSO)_6^{2+}$ the bond distance $Hg-O$ can be precisely measured.[8] Much the same value of $d(Hg-O)$ has been found in both cases, viz. 2.39 and 2.40 Å. In the pure solvates, the bonds $Hg-O$ are therefore of much the same strength.

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