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# The Structure of Mercury(II) Iodide Complexes in DMSO and DMF Solutions

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X-Ray scattering measurements have been made on concentrated solutions of mercury(II) iodide and sodium or cadmium iodide in dimethylsulphoxide (DMSO) and in *N,N'*-dimethylformamide (DMF). The I:Hg ratio was varied from 4.25 to 2. The scattering curves can be interpreted assuming the formation of the complexes $HgI_4^{2-}$, $HgI_3^-$, and $HgI_2$. $HgI_4^{2-}$ is tetrahedral with a Hg–I bond length of 2.80 Å, $HgI_3^-$ is pyramidal with Hg–I 2.73 Å and $HgI_2$ is approximately linear with Hg–I 2.60 Å. No polynuclear complexes seem to occur.

Mercury(II) forms with halogenide ions in aqueous solutions the complexes $HgX^+$, $HgX_2$, $HgX_3^-$, and $HgX_4^{2-}$. The stability constants[1] indicate that solutions can be prepared in which each of these complexes is dominating, although the ranges of stability are largest for $HgX_2$ and $HgX_4^{2-}$. Spectrophotometric and conductometric measurements of mercury(II) iodide complexes dissolved in dimethylsulfoxide (DMSO) or dimethylformamide (DMF) indicate similar complexing in these solvents.[2,3] The stability constants of $HgI_3^-$ and $HgI_4^{2-}$ in DMF solution have been estimated from polarographic measurements and were found to have the same order of magnitude as the stability constants for the complexes in aqueous solutions.[4]

Ultracentrifugation experiments on 0.01 M solutions of $HgI_2$ in DMF have shown that the molecular weight of the mercury (II) iodide is 1040 ± 12 %, roughly corresponding to a dimeric species.[5] Results from spectrophotometric and conductometric measurements have indicated that the iodides of some transition elements, for example cadmium, when added to a solution of $HgI_2$ in DMF or DMSO, might cause the formation of heteropolynuclear complexes.

The large solubility of $HgI_2$ in DMF and DMSO and the high atomic numbers of Hg and I would seem to make it possible to obtain further informa-

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tion about these complexes by measuring the X-ray scattering from solutions. The present work gives the results of measurements on solutions of $HgI_2$ and NaI in concentrations corresponding to the formation of $HgI_2$, $HgI_3^-$, and $HgI_4^{2-}$ complexes. A solution in which NaI was replaced by $CdI_2$ has also been investigated to determine if heteropolynuclear complexes are formed.

## EXPERIMENTAL

*Preparation of solutions.* Weighed amounts of mercury(II) iodide (Mallinckrodt, analytical reagent) and sodium iodide (Coleman & Bell, c.p.) or cadmium iodide (Baker's, analysed) were dissolved in DMSO or DMF and the solutions were diluted to 50 ml. The solvents (Mallinckrodt, analytical reagent) were used without further purification. The compositions of the solutions are given in Table 1.

*Table 1.* Compositions of the solutions (moles/l).

| | DMSO solutions | | | | |
|---|---|---|---|---|---|
| Solution No. | 1 | 2 | 3 | 4 | 5 |
| $HgI_2$ | 0.87 | 1.14 | 1.67 | 1.33 | 2.50 |
| NaI | 1.96 | 2.27 | 1.67 | — | — |
| $CdI_2$ | — | — | — | 0.67 | — |
| DMSO | 12.07 | 11.13 | 10.77 | 12.00 | 11.25 |

| | DMF solutions | | |
|---|---|---|---|
| Solution No. | 6 | 7 | 8 |
| $HgI_2$ | 1.00 | 1.33 | 2.00 |
| NaI | 2.00 | 1.33 | — |
| DMF | 11.16 | 10.95 | 10.91 |

*X-Ray measurements.* The X-ray scattering was measured in a diffractometer described in a previous paper.[6] The X-ray tube and the scintillation counter fixed at equal distances from a point on the surface of the solution, were rotated in a plane perpendicular to the solution surface, such that the incident and reflected angles were always equal. Mo$K\alpha$ radiation was used. Slit openings with widths of 1/12°, 1/4°, and 1° were used to limit the primary X-ray beam. A LiF focusing monochromator was placed between the receiving slit and the scintillation counter. A further monochromatization was obtained by a pulse-height discriminator. The intensity of the scattered radiation was measured at discrete values of the scattering angle ($\theta$) with intervals of 0.1° for the lowest and 0.25° or 0.5° for the largest angles. About 40 000 counts were taken for each point, which corresponds to a statistical error of 0.5 %. To detect and correct for long-time variations in the counting and the X-ray equipment the measurements for each slit opening were repeated using larger intervals. The required corrections did not exceed 1 %. All data were recalculated to the same slit width using measurements in overlapping regions.

The amount of incoherent radiation reaching the counter was estimated in a semi-empirical way from the spectrum of the X-ray tube and the resolving power of the monochromator. For the largest scattering angles the amount of incoherent radiation could be directly determined by a comparison of the intensity of the scattered radiation when measured with a Zr filter between the X-ray tube and the sample and between the sample and the detector.

## TREATMENT OF THE DATA

After correction for polarization in the sample and in the monochromator and subtraction of the incoherent radiation the observed intensity values were scaled by comparison with the independent coherent scattering ($\sum n_i f_i^2$) in the high-angle region ($\theta > 45°$) of the scattering curves. All calculations were referred to a stoichiometric unit of solution, which was chosen to be the volume containing one mercury atom. Scaling factors calculated using

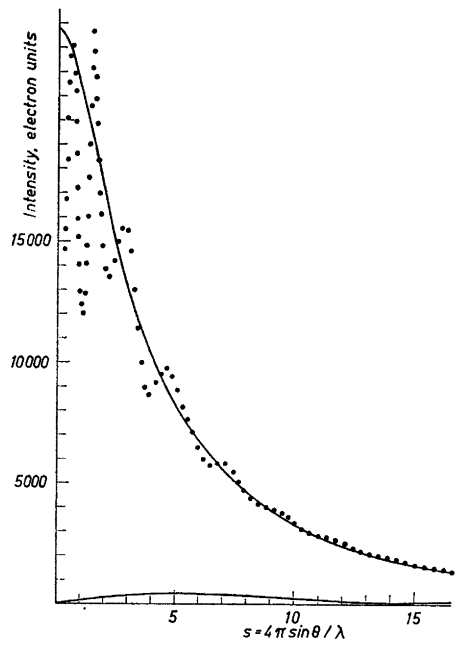


*Fig. 1.* Survey of the intensity measurements for one of the solutions (1 M $HgI_2$ +2.25 M NaI in DMSO). The measured intensities, indicated by dots, are given after scaling and correction for incoherent radiation. The upper full-drawn curve represents the independent coherent scattering ($\sum n_i f_i^2$), the lower curve that part of the incoherent scattering, which reaches the counter. About one third of the measured points, chosen at random, are given.

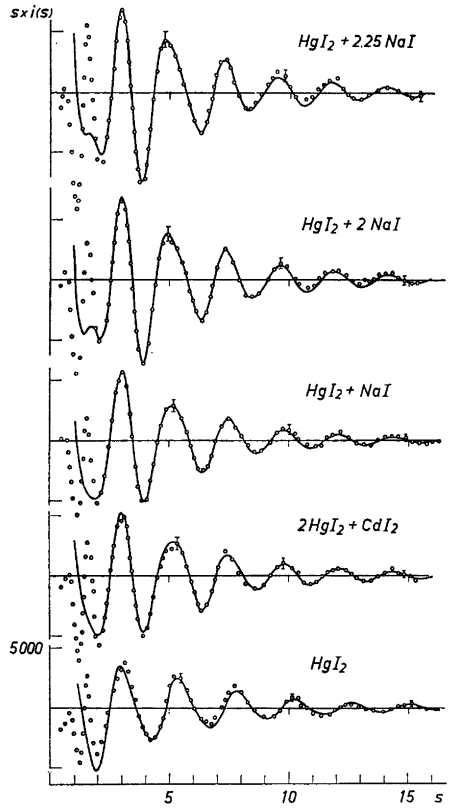


*Fig. 2.* The values $s \cdot i(s)$ as a function of $s$ for mercury(II) iodide complexes in DMSO (referred to a stoichiometric unit of solution containing one mercury atom). Observed values are indicated by open circles, calculated values by the full-drawn curves. I gives the magnitude of three times the standard deviation in the intensity measurements. Between one third and one half of the number of observed values, chosen at random, are given.

the method of Norman [7] and Krogh-Moe [8] lead to the same results with deviations less than 1 %.

The scattering factors given by Cromer and Waber [9] for the neutral atoms were used. Anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) according to Cromer [10] were applied to Hg, I, Cd, and S. The amount of incoherent radiation was obtained for Na, O, C, and N from the *International Tables*,[11] for H from the values given by Compton and Allison [12] and for the remaining atoms from the formula given by Bewilogua.[13]

The reduced intensity function, $i(s)$, was calculated according to the formula:

$$i(s) = k \cdot I - \sum n_i f_i^2$$

Here $s$ is $4\pi \sin\theta/\lambda$ ($\lambda$=0.7107 Å), $k$ is the scaling factor, $I$ the observed intensity values after correction for polarization and incoherent radiation, $n_i$ the number of atoms of kind "$i$" in a stoichiometric unit of solution, and $f_i$ the scattering factors. The procedure is illustrated in Fig. 1 for one of the solutions. After multiplication by $s$ the $i(s)$ curves for the DMSO solutions are shown in Fig. 2.

The radial distribution curves, $D(r)$, were calculated from:

$$D(r) = 4\pi r^2 \varrho_0 + \frac{2r}{\pi} \int_0^{s_{max}} s \cdot i(s) \cdot f(s) \cdot \sin(rs) \cdot ds$$

The modification function $f(s)$ is given by $f(s)=[f_{Hg}^0/f_{Hg}(s)]^2 \cdot \exp(-as^2)$ with $f_{Hg}^0$=the value of the scattering factor of Hg at $s$=0.[14] A value of 0.008 was used for $a$. The average scattering density, $\varrho_0$, is given by the square of the number of electrons per unit volume. The experimental $i(s)$ and $s$ values were used without modification for the Fourier summations and for all the following calculations except that a small number of $i(s)$ values (usually 5 to 10 of the 200 to 300 observed values), which seemed to be definitely outside the estimated limits of error, were excluded from the calculations.

Pair interaction functions were calculated from

$$i_{nm}(s) = f_n f_m \sin r_{nm} s / r_{nm} s \exp(-bs^2)$$

Here $r_{nm}$ is the distance between the atoms, $f_n$ and $f_m$ are the scattering factors and $b$ is a temperature factor.

The least-squares refinements used to get the best fit between calculated and observed $i(s)$ values were made with the "Leta-grop" program. The minimum was sought for the function $\sum(|s \cdot i_{obs}| - |s \cdot i_{calc}|)^2$.

All calculations were carried out on the computer Trask with the use of specially written programs.[15]

## INTERPRETATION OF THE SCATTERING CURVES

Radial distribution curves are shown in Figs. 3 and 4. They all contain three main peaks. One, which occurs below 2 Å, can be related to the intramolecular distances in the DMSO or DMF molecules. The peak at about 2.7 Å occurs at a distance expected for a Hg—I bond and the peaks at 4.5 Å (Fig. 3)

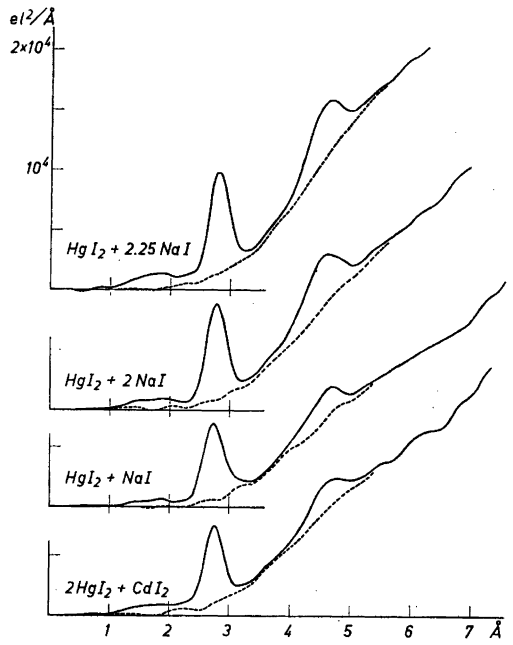


*Fig. 3.* Radial distribution functions for the mercury iodide complexes in DMSO solutions. The full-drawn curves are calculated from the observed intensities. The dashed curves are obtained after subtracting the peaks calculated from the parameters in Table 2.

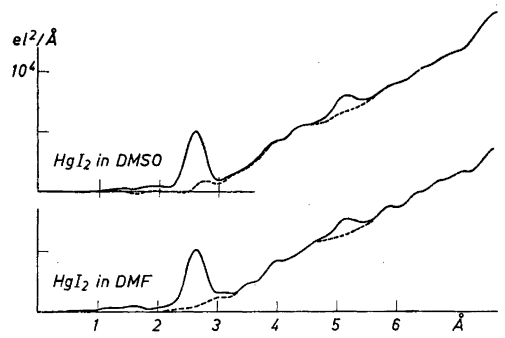


*Fig. 4.* Radial distribution curves. The full-drawn and dashed curves have the same meanings as in Fig. 3.

or 5.2 Å (Fig. 4) are likely to be I—I distances within the mercury(II) iodide complexes.

A more quantitative analysis of the results was made by fitting calculated to observed intensity values by means of a least squares procedure. If discrete

Hg—I complexes occur in the solutions with a random distribution of the complexes among the solvent molecules, the contributions to the $i(s)$ curves from the intermolecular interactions can be shown to be negligible compared to those from the intramolecular interactions except for the smaller $s$ values ($s < \sim 2$). A completely random distribution of the complexes is, of course, an approximation. The presence of the sodium ions, for example, will probably cause some ordering of the negative Hg—I complexes, but the resulting contributions to the $i(s)$ curves may be expected to be highly damped compared to those from the intramolecular distances in the Hg—I complexes and the solvent molecules.

On this assumption, that the intermolecular interactions may be neglected except for the smaller $s$ values, theoretical $i(s)$ curves were calculated including contributions only from intramolecular distances in the DMSO or DMF molecules and from Hg—I and I—I distances within the mercury iodide complexes. For the solvent molecules the bond lengths were taken from literature values. For the mercury iodide complexes the Hg—I and I—I distances, their frequencies and corresponding temperature factors, altogether six parameters, were refined in a least squares procedure until the best fit to the experimental $i(s)$ curves was obtained. Only $i(s)$ values for $s > 2.5$ were included. The number of experimental $i(s)$ values used in the refinements varied between 140 and 230 for the different solutions.

In the course of the refinements it was found that in the low angle region the observed $i(s)$ curves were slightly too low, when the previously determined scaling factors were used. It was assumed that this was caused by small errors in the measured intensities or in the scattering factors in the high-angle region of the data. A 2—3 % decrease of the observed intensities or a corresponding increase in the calculated coherent scattering in the high-angle region was required to eliminate the discrepancy. The corrections, which were applied to the experimental values and led to a 2—3 % increase in the scaling factors, have no significant influence on the results. The main effects are a reduction of spurious peaks below 1 Å in the radial distribution curves and a slight increase in the number of interactions at a particular distance compared with that calculated using the original scaling factors. The resulting increases in the frequencies of the Hg—I and I—I distances (Table 2) will be of the same order of magnitude as the estimated standard deviations.

The results of the refinements are given in Table 2a for the DMSO solutions and in Table 2b for the DMF solutions. Because of experimental difficulties the measurements on the DMF solutions are not as accurate as those on the DMSO solutions, but they are included for comparison.

The calculated $s \cdot i(s)$ curves for the DMSO solutions are compared with the experimental curves in Fig. 2.

The standard deviations given in Table 2 are those calculated in the least-squares program. They are correct if the refined model is correct. Since in this case the calculations have been based on a simplified model for the solution, the actual inaccuracies in the parameters may be larger than the standard deviations would seem to indicate. Possible sources of error could be contributions from Na—I, Cd—I or intermolecular I—I distances. The results of the refinements seem to indicate, however, that these errors cannot be

*Table 2.* Results of the least-squares refinements. (Standard deviations are given within brackets).

Table 2a. DMSO Solutions

| Solution No. | | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| Hg—I | distance | 2.808 (0.002) | 2.784 (0.003) | 2.733 (0.002) | 2.732 (0.003) | 2.599 (0.005) |
| | temp.factor | 0.0037 (0.0004) | 0.0039 (0.0005) | 0.0057 (0.0005) | 0.0037 (0.0006) | 0.0025 (0.0009) |
| | frequency | 3.82 (0.06) | 3.69 (0.06) | 3.10 (0.04) | 2.91 (0.05) | 2.00 (0.06) |
| I—I | distance | 4.549 (0.008) | 4.536 (0.009) | 4.526 (0.011) | 4.582 (0.013) | 5.13 (0.04) |
| | temp.factor | 0.025 (0.003) | 0.031 (0.004) | 0.029 (0.004) | 0.022 (0.005) | — |
| | frequency | 5.52 (0.28) | 5.32 (0.28) | 2.91 (0.18) | 2.64 (0.21) | — |

Table 2b. DMF solutions

| Solution No. | | 6 | 7 | 8 |
|---|---|---|---|---|
| Hg—I | distance | 2.799 (0.004) | 2.752 (0.005) | 2.623 (0.004) |
| | temp.factor | 0.0032 (0.0007) | 0.0047 (0.0011) | 0.002 |
| | frequency | 3.78 (0.09) | 3.11 (0.10) | 2.03 (0.04) |
| I—I | distance | 4.562 (0.011) | 4.577 (0.021) | 5.12 |
| | temp.factor | 0.033 (0.005) | 0.032 (0.006) | — |
| | frequency | 7.2 (0.5) | 3.9 (0.4) | — |

large and that the standard deviations give a relatively realistic estimate of the actual errors.

For each solution the $i(s)$ values, calculated from the parameters in Table 2, were used for a Fourier inversion to give the calculated peak shapes. These were then subtracted from the radial distribution curves calculated from the experimental $i(s)$ values. The resulting difference curves were used to determine if the assumed model had been sufficient for explaining the main peaks (Fig. 3).

### The $HgI_4^{2-}$ complex

For solutions 1, 2, and 6 in Table 2 the number of iodine atoms per mercury atom is sufficient for the formation of a $HgI_4^{2-}$ complex. Solution 1 contains a slight excess of iodide.

For a regular tetrahedral complex the I—I distance should be related to the Hg—I distance by a factor of $\sqrt{8/3}$ and for a stoichiometric unit of solution, that is, for the volume containing one mercury atom, the frequencies should be four for the Hg—I and six for the I—I distances. The results from the least-squares refinements, Table 2, are in agreement with these expected values for a tetrahedral model. The observed Hg—I distances, which vary between 2.784 Å and 2.808 Å, lead to calculated I—I distances of 4.546 to 4.585 Å. Those observed are 4.54 Å to 4.56 Å. The number of Hg—I distances is only slightly less than the expected value and the same is true for the number of I—I interactions. Subtraction of the calculated peaks from the radial distribution curves lead to essentially even background curves (Fig. 3) without any pronounced unexplained peaks.

### The $HgI_3^-$ complex

Solutions 3, 4, and 7 contain three I atoms per Hg atom. For a regular pyramidal or triangular complex one would expect three Hg—I and three I—I distances per Hg atom and the results from the least-squares refinements do not differ significantly from these expected values (Table 2a). The ratio between the Hg—I and the I—I distances indicate an approximately tetrahedral structure with the Hg atom in the center and the I atoms in three of the four corners of the tetrahedron. The resulting pyramid is slightly flattened, however, and the height of the mercury atom over the base plane is smaller than expected for a tetrahedron. Subtraction of the calculated peaks from the radial distribution curves leads to approximately even background curves (Fig. 3). No significant changes in the results are observed when the sodium iodide is replaced by cadmium iodide.

### The $HgI_2$ complex

For a linear $HgI_2$ complex the I—I distance should be twice the length of the Hg—I bond and this is in approximate agreement with the radial distribution curves and the results of the least squares refinements.

The small contributions to the $i(s)$ curves from the I—I interactions did not allow an independent refinement of all the six parameters as was done for the previous solutions. Only the four parameters indicated in Table 2a could therefore be refined and a constant ratio of 1:2 was assumed for the numbers of I—I to Hg—I distances. According to the least squares results and the peak positions in the radial distribution curves, the I—I distance, 5.13 Å, is slightly shorter than twice the Hg—I bond length, 5.20 Å. In view of the standard deviations the difference is hardly significant, but it occurs for both the DMSO and the DMF solutions. It would correspond to an angle between the two Hg—I bonds of 165° rather than the expected 180°. A large vibrational movement perpendicular to the Hg—I bonds, which may be expected for a linear $HgI_2$ molecule, could probably cause an effect like this. A small back-

ground peak in the 5 Å region could have the same effect. Thus the deviation from a linear molecule, indicated by the results, seems too small to be interpreted as being significant.

In the difference curve for the DMSO solution obtained by subtracting the calculated peaks from the radial distribution curve, there are still two minor peaks at about 3.9 and 4.3 Å and probably a peak at about 2.8 Å. These peaks might be explained by assuming a coordination of DMSO molecules to the approximately linear $HgI_2$ complexes. If the Hg—O distance is 2.8 Å the Hg—S distance should be 1.5 Å longer, that is 4.3 Å, and the I—O distance should occur at about 3.9 Å in agreement with the peak positions in the difference curve. This interpretation seems to get support from the results on the DMF solution in which the more intensely scattering S atom is replaced by a C atom. Here the 4.3 Å peak has largely disappeared but the other peaks still seem to be present. As a consequence a coordination of this kind could cause some deformation of the I—I peak towards too low values.

The coordination of the solvent molecules is probably rather loose. The corresponding peaks are small and a calculation shows that the observed size is only about half that expected for a coordination of four DMSO to each $HgI_2$. The data are not sufficient for a more detailed interpretation.

The difference curves (Fig. 4) show no peaks which can be related to the formation of polynuclear complexes.

## DISCUSSION OF THE RESULTS

The scattering curves and the corresponding radial distribution curves can all be satisfactorily explained by assuming the occurrence of only one type of Hg—I and one type of I—I intramolecular distances in each solution. This excludes the formation of any considerable amount of polynuclear complexes in any of the solutions, including the one containing $CdI_2$. The results also indicate that the dominating complexes in the solutions are $HgI_2$, $HgI_3^-$, and $HgI_4^{2-}$ when the I:Hg ratio is 2, 3, and 4, respectively.

The $HgI_4^{2-}$ complex is tetrahedral with a Hg—I bond length of 2.80 Å. This is in agreement with values found in crystal structures containing $HgI_4$-tetrahedra, for example, 2.783 Å in $HgI_2$,[16] 2.77—2.80 Å in $\beta$-$Ag_2HgI_4$ [17] and $\beta$-$Cu_2HgI_4$ and 2.68—2.80 Å in $((CH_3)_3S)_2HgI_4$.[18] For $HgI_4^{2-}$ in water solution the Hg—I bond length has been found to be 2.78 Å from X-ray scattering measurements.[19]

A small amount of $HgI_3^-$ complexes may still be present in the solutions with a I:Hg ratio of 4, as the numbers of Hg—I and I—I interactions are slightly smaller — although not significantly so in view of the standard deviations — than the expected values for a $HgI_4^{2-}$ complex (Table 2). A knowledge of the stability constants would be of value and therefore an accurate determination [20] using emf methods has been started for the mercury iodide complexes in DMSO solution.

In the $HgI_3^-$ complexes the Hg—I distance is 2.73 Å (Table 2). If the iodide atoms occupy the corners of a regular triangle with the Hg atom in the same plane, the expected I—I distance would be $2.73\sqrt{3}=4.73$ Å, but if the $HgI_3^-$ complex is derived from the tetrahedral $HgI_4^{2-}$ complex by merely

removing one of the I atoms, the I—I distance would be $2.73\sqrt{8/3}=4.46$ Å. The observed distance is 4.53 Å (4.58 Å in the presence of $CdI_4$), which shows that the arrangement is more closely tetrahedral than planar trigonal. It seems likely that a solvent molecule occupies the fourth corner of the somewhat flattened tetrahedron, although its contribution to the scattering curves is too small to be observed. An $HgI_3^-$ complex has been found in crystals of $(CH_3)_3SHgI_3$. The structure determination shows that the $HgI_3^-$ complex here is planar trigonal with Hg—I distances 2.69 Å to 2.72 Å.[21]

The $HgI_2$ complexes are approximately linear (see discussion above) with Hg—I distances of 2.60 Å. Electron diffraction measurements on $HgI_2$ vapour[22] have shown the molecules to be linear with Hg—I distances of 2.60 Å. In crystals of the yellow modification of $HgI_2$ a distance of 2.62 Å has been found within the approximately linear $HgI_2$ groups.[16]

In the DMSO and the DMF solutions solvent molecules are coordinated to the $HgI_2$ molecules but their small contributions to the scattering curves do not allow an accurate determination of the coordination number.

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