

## An X-Ray Investigation of the Structure of the $\text{Hg}_2^{2+}$ Ion in Solution

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The X-ray scattering from solutions of mercury(I)perchlorate with concentrations ranging from 2.8 M to 0.6 M in  $\text{Hg}_2^{2+}$  has been investigated. The Hg—Hg bond length was found to be 2.52 Å ( $\sigma = 0.01$  Å) independent of concentration. A preliminary crystal structure determination of  $\text{Hg}_2(\text{ClO}_4)_2(\text{H}_2\text{O})_4$  has given the value 2.50 Å ( $\sigma = 0.01$  Å) for the Hg—Hg distance in the solid. In both the solid and the solutions each mercury atom has one oxygen more closely bonded than the others.

The known crystal structures of mercury(I)compounds are limited to the halogenides,  $\text{Hg}_2\text{X}_2$ ,<sup>1-3</sup> and the nitrate,  $\text{Hg}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ .<sup>4</sup> In all of these structures the mercury(I)ions occur as linear molecules  $(\text{X}-\text{Hg}-\text{Hg}-\text{X})^{2+}$  with X a halogen atom or — in the nitrate — a water molecule. The Hg—Hg distance varies from 2.43 Å in  $\text{Hg}_2\text{F}_2$  to 2.69 Å in  $\text{Hg}_2\text{I}_2$ . In an attempt to determine if similar species exist in solution an X-ray investigation has now been made of mercury(I)perchlorate solutions of various concentrations. The main reason for choosing this problem has been to get experience with the X-ray method before applying it to the investigation of solutions with more complex equilibria.

The measurement of the X-ray scattering was made in a specially built diffractometer applying the Bragg-Brentano parafofocusing geometry. The scattering angle is changed by moving the X-ray tube and the counter symmetrically in opposite directions around the horizontal axis through the sample. The container with the liquid can therefore always be left in the same horizontal position during the measurements. This modification of previously used methods for measuring the X-ray scattering from liquids was introduced some years ago by several research groups independently.<sup>5-8</sup> Its main advantages besides larger intensities are that the free surface of the liquid can be used without the need for any cover and that the absorption is independent of the scattering angle when all scattered radiation reaches the counter.

## EXPERIMENTAL

*Preparation of solutions.* The mercury(I)perchlorate was prepared according to the method of Pugh<sup>9</sup> by shaking mercury(II)oxide with an excess of perchloric acid in the presence of metallic mercury. A stock solution was prepared which was about 3 M in  $\text{Hg}_2^{2+}$  and about 0.5 M in  $\text{H}^+$ . For the analysis  $\text{Hg}_2^{2+}$  was precipitated as  $\text{Hg}_2\text{Cl}_2$  with a slight excess of NaCl. The concentration of  $\text{H}^+$  was determined by titrating the filtrate with NaOH. The compositions of the solutions investigated are given in Table 1.

Table 1. Composition of solutions.

Solution No.	Hg	mole/l Cl	O	H
1	5.60	6.09	62.9	77.6
2	3.94	4.44	62.0	88.9
3	2.28	2.77	58.9	96.0
4	1.12	1.61	57.7	102.9

*Measurements of the X-ray scattering.* A container with a diameter of 40 mm and a depth of 5 mm was used to hold the solution. It was enclosed in an airtight plexiglass cylinder coaxial with the spectrometer axis and with an opening for the X-rays covered by a thin Mylar window.

MoK-radiation was used for all the measurements. A focusing LiF monochromator was placed between the sample and the counter. A further monochromatization was obtained by means of a pulse height discriminator.

1/12°, 1/4°, 1°, 2°, and 4° opening slits were used. Scaling factors to convert all measured data to the same opening slit were obtained from measurements in overlapping regions. Points were measured at intervals in  $\theta$  of 0.25° up to  $\theta = 23^\circ$ , 0.5° to  $\theta = 50^\circ$ , and 1° to  $\theta = 70^\circ$ , the largest angle obtainable. At least 32 000 counts were taken for each point. A number of points were measured repeatedly in order to detect and to correct for any long-time variations in the counting equipment. A Philips PW 1010 X-ray unit with stabilized high voltage and tube current was used. For the determination of the background radiation the receiving slit was covered by a lead plate.

## TREATMENT OF DATA

After subtraction of the background radiation and conversion to a common opening slit, the measured intensities were corrected for polarization by dividing by the factor  $(1 + \cos^2 2\alpha \cos^2 2\theta)/(1 + \cos^2 2\alpha)$  where  $2\alpha$  is the diffraction angle at the monochromator. An absolute scale was established by comparing the high-angle portion ( $\theta > 45^\circ$ ) of the scattering data with the sum of the coherent scattering ( $\sum n_i f_i^2$ ) and the incoherent scattering, or by means of the method suggested by Norman<sup>10</sup> and Krogh-Moe.<sup>11</sup> The two methods agreed within 0.5% except for the 2.80 M solution where the difference was 1.5%. The scattering factors ( $f_i$ ) used were those given by Berghuis *et al.*<sup>12</sup> for O, by Dawson<sup>13</sup> for Cl and by Thomas and Umeda<sup>14</sup> for Hg. For H the calculated values were used.<sup>15</sup> The Hg scattering factor was corrected for anomalous dispersion according to Templeton.<sup>15</sup> For O and Cl the incoherent scattering was taken from the *International Tables*,<sup>15</sup> for Hg it was calculated according to the formula given by Bewilogua<sup>16</sup> and for H it was obtained from the values given

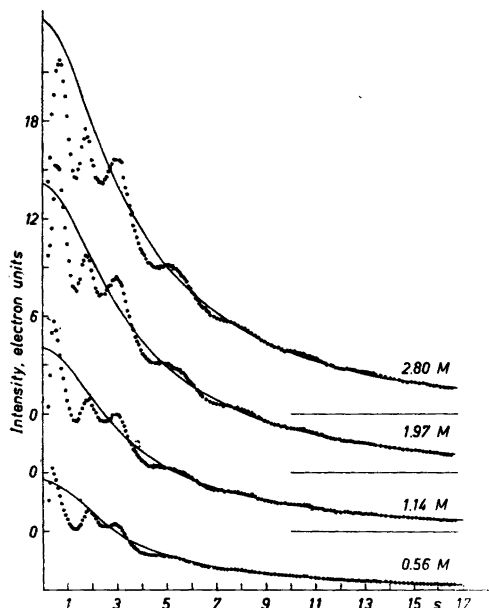


Fig. 1. Scattering curves for mercury(I) perchlorate solutions. Observed values are indicated by dots. The full-drawn curves represent the sum of the coherent and the incoherent scattering.

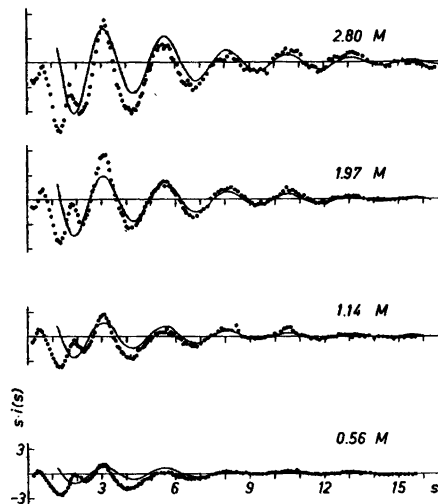


Fig. 2. Observed values  $s \cdot i(s)$  as a function of  $s = 4\pi \sin\theta/\lambda$ . The full-drawn curves represent the calculated  $s \cdot i(s)$  values for the Hg-Hg bond and the  $\text{ClO}_4$  group.

by Compton and Allison.<sup>17</sup> The amount of incoherent scattering reaching the counter was estimated in a semi-empirical way on the basis of the appearance of the spectrum of the X-ray tube.

The scaled intensity values for the four different solutions are shown in Fig. 1 as a function of  $s = 4\pi \sin\theta/\lambda$ . Fig. 2 shows the functions  $s \cdot i(s)$ , where  $i(s)$  is the difference between the observed intensity value and the sum of the independent coherent scattering and the incoherent scattering. The radial distribution function,  $D(r)$ , was calculated according to the formula:

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

where  $\rho_0$  is the average scattering density of the sample in electron units and  $f(s) = (f_{\text{Hg}}^\circ / f_{\text{Hg}}(s))^2 \exp(-bs^2)$

Here  $f_{\text{Hg}}^\circ$  is the scattering factor of the mercury atom at  $\theta = 0$ . The exponential factor  $\exp(-bs^2)$  with  $b = 0.01$  was introduced in order to assure the convergence of the Fourier integral. The observed  $s \cdot i(s)$  values were used for the integration and no attempt was made to draw a smooth curve through the experimental points. All calculations were carried out on the Besk and Facit EDB computers by means of special programs written in Algol. As the upper integration limit  $s = 15.0$  was used.

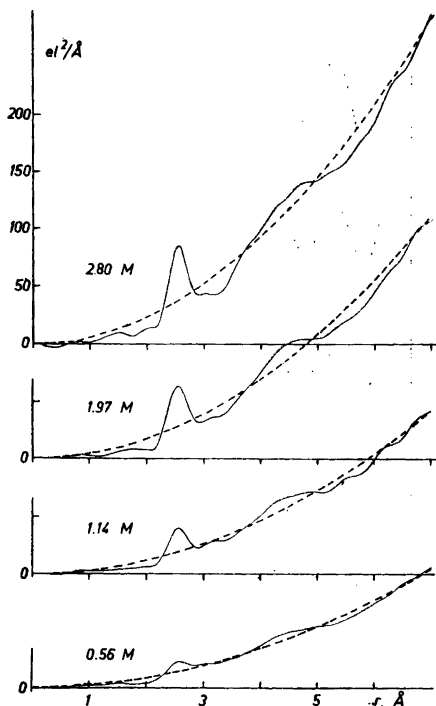


Fig. 3. Radial distribution functions calculated from the observed intensity values. Dashed lines represent  $4\pi r^2 \rho_0$ .

#### DISCUSSION OF THE RESULTS

The first peak in the radial distribution functions (Fig. 3) appears at 1.5 Å and corresponds to the Cl—O distance in the perchlorate ions. The peak at 2.5 Å occurs in the region expected for the Hg—Hg distance in the  $\text{Hg}_2^{2+}$  ion. The area under this peak is larger than would correspond to that of a single Hg—Hg interaction, which is to be expected since water molecules in contact with the mercury atoms should make a substantial contribution to the same peak. Therefore, a very accurate value for the Hg—Hg distance cannot be obtained from the position of the peak. A more reliable value should be obtainable by comparing theoretical scattering curves for the  $\text{Hg}_2^{2+}$  ion with the high-angle portions of the  $s \cdot i(s)$ -curves (Fig. 2), to which the Hg—O bonds may be expected to contribute very little in comparison with the Hg—Hg bonds because of the looser bonding of the oxygen atoms and the more rapidly decreasing scattering factor of oxygen compared to that of mercury.

The theoretical scattering curves were calculated according to the formula

$$\sum_{i \neq j} \sum_j f_i f_j \exp(-Bs^2) \sin(sr_{ij})/sr_{ij}$$

$r_{ij}$  is the distance between the atoms  $i$  and  $j$ ,  $f_i$  and  $f_j$  are the scattering factors and  $B$  is a temperature factor. The contributions from the perchlorate ions, which were assumed to form regular tetrahedra with a Cl—O bond length

of 1.45 Å, were included together with those from the  $\text{Hg}_2^{2+}$  ion. Starting values of 2.54 Å for the Hg—Hg bond length and 0.003 for the temperature factor were refined by means of the general least-squares program "Letagrop"<sup>18</sup> by comparing calculated and observed  $s \cdot i(s)$  values for  $8 < s < 16$ . The statistical errors in the experimental  $s \cdot i(s)$  values are approximately constant over the whole range of  $s$  (Fig. 2) which makes them suitable for a least-squares refinement. The final  $r$  and  $B$  values for the Hg—Hg bond and the corresponding standard deviations are given in Table 2. The previously obtained scaling factors were also refined leading to maximal corrections of about 1 %. Within the standard deviations identical results were obtained when the lower  $s$  limit used in the refinement was varied from  $s = 5.0$  to  $s = 10.0$ , which gives support for the assumption that in this range of the scattering curves the Hg—Hg interaction is not disturbed by other frequencies.

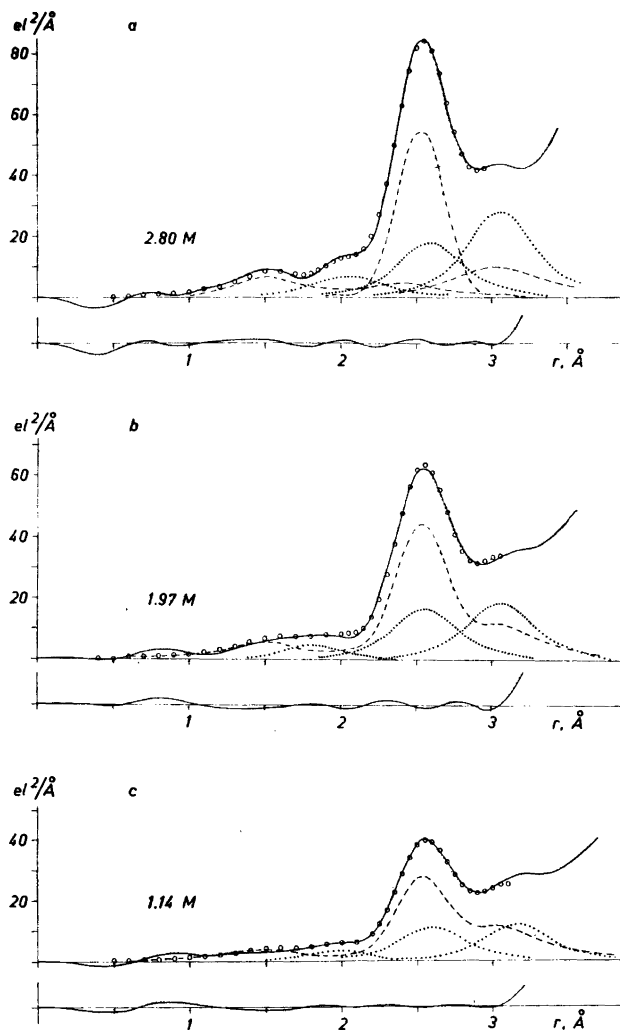
As there seem to be no significant deviations between the different solutions, average values of 2.52 Å for the Hg—Hg bond length and 0.002 for its temperature factor have been used throughout the following calculations.

Table 2. The results of the least squares refinement of the Hg—Hg bond.

Conc. mole $\text{Hg}_2^{2+}$ /l	$r_{\text{Hg-Hg}}$	$\sigma_r$	$B_{\text{Hg-Hg}}$	$\sigma_B$
2.80	2.520	0.010	0.0013	0.0009
1.97	2.518	0.010	0.0020	0.0008
1.14	2.530	0.011	0.0008	0.0009
0.56	2.528	0.017	0.0030	0.0027

If the calculated Hg—Hg peak is subtracted from the corresponding peak in the experimental  $D(r)$  curve (Fig. 3) the remaining area is a measure of the hydration number of the  $\text{Hg}_2^{2+}$  ion. The peak is not, however, well defined towards larger  $r$ -values because the light-atom interactions will contribute in this region and, presumably, because the Hg—O distances in the hydration shell around the Hg atoms do not have a sharp upper limit. In order to get a more detailed picture of the coordination around the mercury atoms an analysis of the region 1.5 Å to 3.1 Å of the radial distribution curves can be made in terms of the expected peak shapes<sup>20,21</sup> for the various interatomic distances in this region.

To a calculated  $D(r)$  curve including the contributions from the  $\text{ClO}_4$  and the Hg—Hg groups were added three mercury-oxygen peaks at those positions where the experimental  $D(r)$  curves indicated a high concentration of Hg—O interactions namely at 2.0, 2.5, and 3.0 Å. By means of the "Letagrop" least-squares program the positions of the peaks, the number of interactions and an exponential factor corresponding to a temperature factor were changed until the best fit to the experimental  $D(r)$  curve was obtained. In order to make a rough estimate of the light atom interactions in this region each oxygen atom was assumed to have four nearest neighbors at about 3.0 Å. This model was capable of a refinement to an agreement between observed and calculated curves which was as good as, or better



*Fig. 4.* Observed (full-drawn) and calculated (open circles)  $D(r)$ -curves for the mercury(I) perchlorate solutions. Dashed lines represent calculated curves which include contributions from Hg—Hg (2.52 Å),  $\text{ClO}_4$  (1.47 and 2.40 Å), O—O (3.0 Å), and O—H (1.0 Å). Dotted lines are the calculated values for the assumed Hg—O distances. The difference between observed and calculated  $D(r)$  values is shown by a separate curve. a) The 2.80 M solution; b) The 1.97 M solution; c) The 1.14 M solution.

than one would expect on the basis of the estimated experimental accuracy. The final values for the peak positions and the number of interactions are given in Table 3. The resulting curves are illustrated in Fig. 4.

The results indicate that each mercury atom has approximately one oxygen at a distance of about 2 Å. The positions of the corresponding peaks are highly

Table 3. Results of the least squares refinement of the region 1.5 Å to 3.1 Å of the radial distribution functions.  $n$  = number of Hg—O distances for each Hg atom.

Conc. mole $\text{Hg}_2^{2+}$ /l	$r_{\text{Hg-O}}$	$n$	$r_{\text{Hg-O}}$	$n$	$r_{\text{Hg-O}}$	$n$
2.80	2.02 Å	1.0	2.57 Å	2.4	3.04 Å	3.9
1.97	1.82 »	0.8	2.54 »	3.3	3.05 »	3.7
1.14	1.90 »	1.0	2.59 »	3.7	3.13 »	4.1

sensitive to small errors in the  $D(r)$  curves which probably explains the rather large deviations in position between the different solutions. About three more oxygens occur at a distance of 2.5 to 2.6 Å. In order to explain the experimental curves there is obviously no need to assume any Hg—O distance between the two values 2 and 2.5 Å. The third peak, at 3 Å, is of little significance since the light-atom interactions are probably underestimated in this region and peaks from larger Hg—O distances have not been included.

#### THE CRYSTAL STRUCTURE OF MERCURY(I)PERCHLORATE

Two hydrates of  $\text{Hg}(\text{I})\text{ClO}_4$  have been described in the literature, one with 2  $\text{H}_2\text{O}$  and the other with 4  $\text{H}_2\text{O}$ .<sup>19</sup> By room temperature evaporation of the solutions investigated, the tetrahydrate could be obtained as large rod-like

Table 4. Powder photograph of  $\text{Hg}_2(\text{ClO}_4)_2(\text{H}_2\text{O})_4$  taken with  $\text{CuK}\alpha$ -radiation in a Guinier camera.  $\text{KCl}$  ( $a = 6.293$  Å) was used as internal standard.

$h k l$	$(\sin^2 A)_{\text{calc}}$	$(\sin^2 A)_{\text{obs}}$	$I_{\text{obs}}$
0 2 0	0.0058	0.0058	m
0 1 1	0.0118	0.0118	w
1 0 1	0.0207	0.0207	s
0 4 0	0.0231		
0 3 1	0.0234	0.0233	w
1 2 1	0.0265	0.0264	s
2 0 0	0.0411	0.0421	m
0 0 2	0.0416	0.0417	m
1 4 1	0.0437	0.0438	w
2 2 0	0.0469	0.0469	m
0 2 2	0.0473	0.0473	m
0 6 0	0.0519	0.0519	w
1 1 2	0.0533	0.0534	s
2 3 1	0.0645		
0 4 2	0.0647	0.0648	vvw
1 3 2	0.0648		
1 6 1	0.0726	0.0725	vvw
2 0 2	0.0827	0.0827	vs
2 2 2	0.0885	0.0886	w
0 8 0	0.0922	0.0924	vvw
2 6 0	0.0930		
0 6 2	0.0935	0.0933	vw
0 1 3	0.0950	0.0950	w

crystals. A preliminary crystal structure determination has been carried out for this salt in order to compare the dimensions of the  $\text{Hg}_2^{2+}$  ion in the solid with those found in the solution.

*Structure determination.* The crystals are unstable and had to be enclosed in a capillary during the X-ray exposure. They also seemed to be slowly decomposed by X-rays. The unit cell was found to be orthorhombic with  $a = 7.59_7$  Å,  $b = 20.29$  Å, and  $c = 7.55_4$  Å. The first lines on the powder photograph are given in Table 4. An almost cylindrical crystal with a diameter of about 0.06 mm and extended along the  $a$  axis was used to record the  $0kl$ ,  $1kl$ ,  $2kl$ ,  $3kl$ , and  $4kl$  layer lines in a Weissenberg camera by means of  $\text{CuK}\alpha$ -radiation. The  $h0l$  and  $hk0$  reflections were obtained with a precession camera.

$hkl$ -Reflections with  $h + k + l$  odd and  $hk0$ -reflections with  $h$  odd are systematically absent which is characteristic for the space groups No. 46:  $Im2a$  and No. 74:  $Imma$ . A Patterson function was calculated with the use of all the 300 observed reflections. The Hg—Hg peaks could be explained by assuming the mercury atoms to occupy position 8(h) in space group  $Imma$  with  $y \approx 0.188$  and  $z \approx 0.048$ . These parameters as well as the scaling factors between the different layer lines were refined by a number of least squares cycles which reduced the  $R$  factor for all observed reflections to 0.26. With the use of the positions of the mercury atoms the signs of the structure factors were determined and an electron density function with the Hg atoms subtracted was calculated. Despite the incomplete set of three-dimensional data all the light atoms were clearly and unambiguously indicated with the exception of one of the oxygens,  $\text{O}_3$ , of the  $\text{ClO}_4$  group which was obscured by diffraction effects from the mercury atoms. A number of least-squares cycles with all atoms included reduced the  $R$  factor to 0.16. No corrections for absorption or extinction were made in this preliminary refinement. The parameters are given in Table 5.

Table 5. Atomic positions for  $\text{Hg}_2(\text{ClO}_4)_2(\text{H}_2\text{O})_4$ . Space group No. 74:  $Imma$ .

8 Hg in	8(h) with		$y = 0.1884$	$z = 0.0465$
8 Cl	8(h)		$y = 0.135$	$z = 0.530$
16 $\text{O}_1$	16(j)	$x = 0.154$	$y = 0.158$	$z = 0.424$
8 $\text{O}_2$	8(h)		$y = 0.067$	$z = 0.567$
8 $\text{O}_3$	8(h)		$y = 0.180$	$z = 0.685$
8 $\text{O}_4$	8(h)		$y = 0.083$	$z = 0.056$
8 $\text{O}_5$	8(g)		$y = 0.010$	

A projection of the structure along the  $a$  axis is shown in Fig. 5. It is built up from  $\text{H}_2\text{O}-\text{Hg}-\text{Hg}-\text{OH}_2$  groups which are linear within the accuracy of the structure determination. The Hg—Hg distance is  $2.50_0$  Å and the Hg—O distance is  $2.1_4$  Å with estimated standard deviations of 0.01 Å and 0.1 Å, respectively. Each mercury atom has three more oxygen neighbours ( $\text{O}_1$ ,  $\text{O}_1$ , and  $\text{O}_3$ ) belonging to  $\text{ClO}_4$  groups, at 2.7 Å and two ( $\text{O}_1$ ) at 3.1 Å. No other oxygens occur at distances below 3.8 Å. The arrangement is similar to that



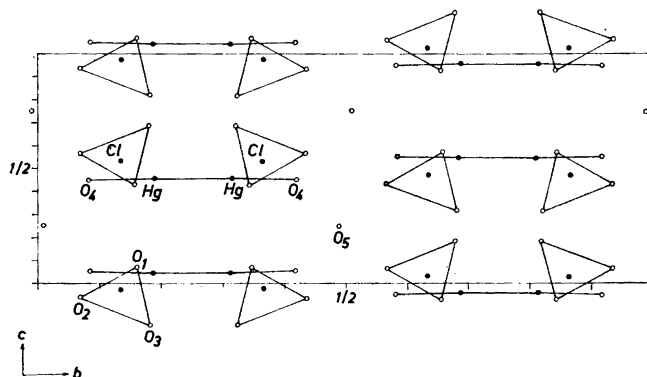


Fig. 5. Projection of the structure of  $\text{Hg}_2(\text{ClO}_4)_2(\text{H}_2\text{O})_4$  along the  $a$  axis.

suggested for  $\text{Hg}_2(\text{NO}_3)_2(\text{H}_2\text{O})_4$  which is built up from  $\text{H}_2\text{O}-\text{Hg}-\text{Hg}-\text{OH}_2$  groups with  $\text{Hg}-\text{Hg}$  2.54 Å and  $\text{Hg}-\text{O}$  about 2.15 Å. Other  $\text{Hg}-\text{O}$  distances seem to be larger than about 2.4 Å.

The other hydrate of mercury(I) perchlorate,  $\text{Hg}_2(\text{ClO}_4)_2(\text{H}_2\text{O})_2$ , contains similar  $\text{H}_2\text{O}-\text{Hg}-\text{Hg}-\text{OH}_2$  groups with  $\text{Hg}-\text{Hg}$  2.48<sub>1</sub> Å and  $\text{Hg}-\text{O}$  2.1<sub>0</sub> Å.<sup>22</sup>

### CONCLUSIONS

In view of the standard deviations there is no significant difference between the  $\text{Hg}-\text{Hg}$  bond length of 2.52 Å in perchlorate solutions and 2.50 Å in crystals of mercury(I)perchlorate. The  $\text{H}_2\text{O}-\text{Hg}-\text{Hg}-\text{OH}_2$  groups in the solid seem to occur also in solution as indicated by the short  $\text{Hg}-\text{O}$  distance of about 2 Å. In the solid there are three more  $\text{Hg}-\text{O}$  contacts at 2.7 Å and approximately the same number of oxygen atoms occur at about 2.6 Å in solution.

It is not easy to estimate the errors in the determination of the number and positions of  $\text{Hg}-\text{O}$  distances in the solutions as these errors are, to a large extent, of a systematic nature. Besides the normal errors in the intensity measurements, inaccuracies in the corrections of the intensity curves for incoherent scattering, uncertainties in the number of background peaks in the radial distribution functions, errors in the scaling factors, and errors in the intensity measurements in the low-angle region will all influence the results to some extent. The variations in the results between the different solutions as shown in Table 3 therefore probably reflect errors in the experimental data and inadequacies in the treatment of the data rather than any significant differences between the solutions.

In the region around 4 Å in the radial distribution curves (Fig. 3) another relatively pronounced peak occurs. A large part of the contributions to this peak is likely to come from interactions between mercury atoms and their next nearest oxygen neighbours. According to the crystal structure determina-

tion, mercury-chlorine distances may also fall in this region. Variations in concentration of the solutions do not noticeably affect the peaks and this makes it likely that Hg—Hg interactions are not involved. The large number of possible distances which occur in this region does not allow a more detailed analysis of the peak.

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A drawing of the X-ray diffractometer for investigation of liquids in use at the Oak Ridge National Laboratory, sent to us by Dr. H A Levy when we contemplated the building of our own apparatus, is gratefully acknowledged. The diffractometer was built in cooperation with Dr. Peder Kierkegaard at the University of Stockholm. The construction work was skillfully done by Mr. K. E. Johansson. I also wish to thank Professor Lars Gunnar Sillén and Professor Georg Lundgren for discussions in connection with the work and Mr. Peter Holm and Miss Sissel Dahl for technical assistance. Dr. David Hume kindly corrected the English of the manuscript.

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