

electrostatic forces. The repulsions terms amount to about 10–15% of the lattice energy and cannot be neglected. It should be pointed out the variation of the oxygen parameter has not been taken into account as has already been done by Verwey, de Boer & van Santen (1948), who already give the energy values for 1 and 2.

This paper is part of an investigation of the cation distribution in mixed crystals. We thank the Deutsche

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## The Structure of Mercuri-iodide Ions. I. Trimethylsulphonium Mercuritriiodide $(\text{CH}_3)_3\text{SHgI}_3$

BY RUTH H. FENN\*

*Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London, W. 1, England*

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Trimethylsulphonium mercuritriiodide,  $(\text{CH}_3)_3\text{SHgI}_3$ , crystallizes in spacegroup  $P2_1/c$  with cell dimensions  $a = 8.51 \pm 0.03$ ,  $b = 15.57 \pm 0.05$ ,  $c = 11.69 \pm 0.12$  Å,  $\beta = 128.0^\circ \pm 0.4^\circ$  and four molecules per cell. Intensity data were collected with an Arndt & Phillips automatic linear diffractometer and  $\text{Mo K}\alpha$  radiation and the structure was solved by Patterson and Fourier syntheses with least-squares refinement. The  $\text{HgI}_3^-$  ion is planar trigonal and the  $(\text{CH}_3)_3\text{S}^+$  ion is pyramidal.

### Introduction

In the analysis of the structures of proteins by the isomorphous replacement method, it is required to introduce a heavy atom into the crystal structure without displacing the protein molecules in any way. One of the most successful heavy atom groups to be used with a number of proteins is an ion derived from  $\text{K}_2\text{HgI}_4$ . At low resolution the precise nature of the complex is not important but the use of these derivatives at a resolution higher than 6 Å has been hampered by lack of knowledge of the nature of the heavy atom group. Sillen (1949) has investigated the nature of the mercuri-iodide ions present in solution as a function of the concentration of iodine and has shown that at any one concentration of iodine a number of different ions can be present.

Bluhm, Bodo, Dintzis & Kendrew (1958) have investigated the probable nature of the ion included in the derivative of sperm-whale myoglobin by a titration experiment carried out in the same conditions as those used in crystallization and obtained results suggesting that the complex included is  $\text{HgI}_3$ . Furthermore, they discovered that a mercuri-iodide group is incorporated in the myoglobin molecule at two sites and, following the work of Smiles (1900) on complexes of mercuric

iodide and methyl sulphide, they speculated that the two methionine residues in sperm-whale myoglobin might be involved in the complex formation. Kendrew, Watson, Strandberg, Dickerson, Phillips & Shore (1961) have since shown, however, by locating the methionine residues, that they are not involved in the complex formation and very recently Scouloudi (1965) has shown that most of the mercuri-iodide in the complex with seal myoglobin is present in the form of a roughly planar  $\text{HgI}_3$  group.

Rây & Adhikary (1930) had already shown that one of the compounds of Smiles was composed of two singly charged ions,  $(\text{CH}_3)_3\text{S}^+$  and  $\text{HgI}_3^-$ , and that another consisted of two singly charged positive ions and one doubly charged negative ion, namely  $2(\text{CH}_3)_3\text{S}^+$  and  $\text{HgI}_4^{2-}$ . These general conclusions have been confirmed and the configurations of the mercuri-iodide ions have been determined in the studies of these two compounds that are reported in this and the following paper. A preliminary account of the work has already been published (Fenn, Oldham & Phillips, 1963).

### Experimental

The compound was prepared by the method of Rây & Adhikary (1930). Needle-shaped crystals were grown from a solution of  $(\text{CH}_3)_3\text{SHgI}_3$  in acetone, and from oscillation, Weissenberg and precession photographs it was established that the crystal system is mono-

\* Present address: Physics Department, College of Technology, Park Road, Portsmouth, Hants., England.



The density was determined by flotation in a mixture of Rohrbach's solution and alcohol. The crystal reacted with this solution after a short time so that only an approximate density of  $3.5 \text{ g.cm}^{-3}$  could be determined. Thus there are four molecules per cell, giving a calculated density of  $3.58 \pm 0.04 \text{ g.cm}^{-3}$ .

### Data collection

Three-dimensional X-ray diffraction data were collected with the automatic linear diffractometer (Arndt & Phillips, 1961). Initially Cu  $K\alpha$  radiation was used to investigate the absorption variation as the crystal was rotated about  $a^*$ . From the positions of the peaks in the relative transmission curve, the indices of the planes forming the faces of the crystal were identified. The three-dimensional reflexion data were then measured with the use of Cu  $K\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ , to the limit of the instrument at  $\theta = 30^\circ$ , two quadrants of data being measured on each level. A second set of data was obtained with Mo  $K\alpha$  radiation,  $\lambda = 0.7107 \text{ \AA}$ . The output from the diffractometer was processed as described by North (1964) and Lp factors were applied.

The linear absorption coefficients of the crystal for the two radiations used are  $\mu_{\text{Cu}} = 863 \pm 10 \text{ cm}^{-1}$  and  $\mu_{\text{Mo}} = 206 \pm 2 \text{ cm}^{-1}$ . The crystal cross-section was  $0.0090 \pm 0.0005 \text{ cm}$  by  $0.0052 \pm 0.0005 \text{ cm}$  where the crystal faces are (011) and (010) respectively. It was attempted to correct for absorption in both sets of data by using the methods described by Howells (1950) and Grdenić (1952, 1956). The formulae given by Grdenić were extended to include both limits of the integral for the molybdenum data as is necessary for the lower absorption coefficient.

The criterion adopted to establish whether the proper absorption factors were being obtained was that a plot of a sample of corrected Cu  $K\alpha$  data against corrected Mo  $K\alpha$  data should approach a straight line. It was found that the corrected data were in no better agreement than the uncorrected data. It was thus decided to use the molybdenum data to investigate the crystal structure without applying any absorption corrections, for in these data they will be far less serious than in the copper data. However the accuracy of the final atomic parameters is limited by the presence of absorption errors in the data.

### Structure determination

The approximate positions of the mercury and iodine atoms were determined from a three-dimensional Patterson synthesis. The positions and anisotropic temperature factors of the four atoms and the scale factor between observed and calculated structure factors were refined by a least-squares method for four cycles, at the end of which the residual had fallen to 0.16. A difference Fourier synthesis contained one dominant peak which was taken to be the sulphur atom and this was then included in the refinement process for three further cycles. A second difference Fourier synthesis

contained three round peaks within  $2.5 \text{ \AA}$  of the sulphur, and these were taken to be the carbon atoms although they were not significantly above the background level of the map. They were included in the refinement process for three further cycles when the residual fell to 0.12. A list of observed and calculated structure factors is given in Table 1. The atomic coordinates obtained were

	$x/a$	$y/b$	$z/c$
Hg	0.310	0.022	0.067
I(1)	0.400	0.869	0.008
I(2)	0.515	0.089	0.333
I(3)	0.033	0.908	0.169
S	0.203	0.369	0.080
C(1)	0.054	0.367	0.913
C(2)	0.438	0.311	0.106
C(3)	0.074	0.274	0.089

The standard deviations for these coordinates were obtained from the least-squares totals though it is to be expected that these values will be an underestimate of the true errors. The average values obtained for the different species of atom are

	$\sigma$
Hg	0.007 $\text{ \AA}$
I	0.011
S	0.043
C	0.124

The refinement included anisotropic temperature factors for all atoms, but it is expected that the values obtained are seriously affected by the absorption errors known to exist in the data.

### Description of structure

The structure is illustrated in Fig. 1 by a clinographic projection. The bond lengths and angles within the ions are

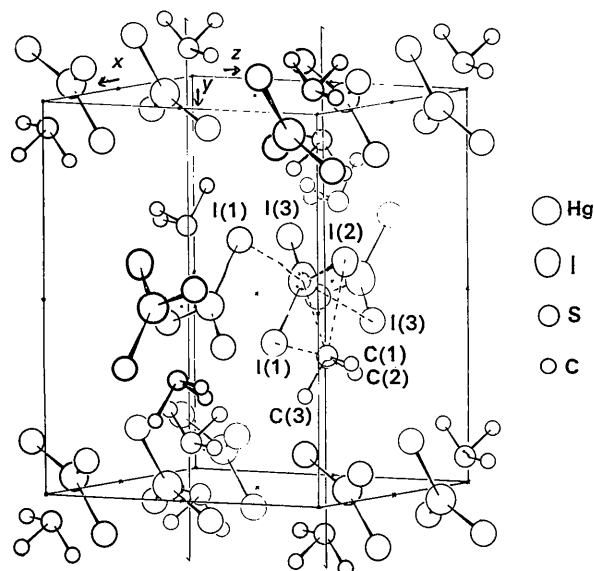


Fig. 1. Clinographic projection of structure.

HgI <sub>3</sub> <sup>-</sup> ion	Hg-I(1)	2.72 Å	I(1)-Hg-I(2)	124°
	Hg-I(2)	2.69	I(1)-Hg-I(3)	113
	Hg-I(3)	2.72	I(2)-Hg-I(3)	123
(CH <sub>3</sub> ) <sub>3</sub> S <sup>+</sup>	S-C(1)	1.54	C(1)-S-C(2)	98
	S-C(2)	2.04	C(1)-S-C(3)	90
	S-C(3)	1.80	C(2)-S-C(3)	101

The coordinates of the atoms were expressed in Å and transformed to an orthogonal set of axes  $X$ ,  $Y$ ,  $Z$  where  $X=xa+zc \cos \beta$ ,  $Y=yb$  and  $Z=zc \sin \beta$ . Taking the standard deviations of the atomic coordinates to be those given above, the constants of the equation of the plane through the iodine atoms,  $AX+BY+CZ+D=0$ , were calculated to be  $A=-16.0 \pm 0.3$ ,  $B=9.4 \pm 0.3$ ,  $C=3.5 \pm 0.3$ ,  $D=-113 \pm 4$ .

The distance of the mercury atom from this plane is  $0.08 \pm 0.3$  Å and so to within the accuracy of the atomic positions the mercury lies in the plane of the three iodines.

There are no distances between the mercuritriiodide and sulphonium ions which are significantly less than 4 Å, which is approximately the sum of the van der Waals radii of iodine and sulphur, and iodine and a methyl group (Pauling, 1960). However, on either side of the mercuritriiodide ion, there are iodine atoms in the groups related by centres of symmetry making contacts Hg-I(1) equal to 3.52 Å and Hg-I(3) equal to 3.69 Å. These iodine atoms lie on a straight line through the mercury perpendicular to the planar trigonal group, and so there are five iodine atoms around each mercury atom forming a trigonal bipyramid. Thus there are chains of mercuritriiodide ions running through the structure linked by these two interactions.

This arrangement may be contrasted with that of the mercuritribromide ions reported by White (1963) in the description of the structure of tetramethyl ammonium mercuritribromide. In the latter structure there is a short distance of 2.93 Å between the mercury of one anion and a bromine atom of the next anion on one side only causing a deviation of the ion from planarity of 0.31 Å. White found that there are chains of

mercuritribromide ions running through the structure linked by the one inter-ionic interaction.

Lopez-Castro & Truter (1964) have determined the structure of the sulphonium ion to be pyramidal with C-S-C angles 102°, 103°, 105°, each  $\pm 1^\circ$ , and bond lengths S-C(methyl) 1.81 and 1.83 Å, and S-C(phenyl) 1.82 Å, each  $\pm 0.02$  Å. In the presence of the mercury and iodine atoms in this structure, the dimensions of the sulphonium ion are not well determined but the results are consistent with the above dimensions.

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