

267. *The Hg-Hg Bond Length in the Mercurous Ion. Part II.**
The Crystal Structure of Mercurous Fluoride.

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The crystal structure of mercurous fluoride has been determined by the use of *X*-ray methods. The value 2.43 ± 0.04 Å has been obtained for the Hg-Hg bond length. It is proved that the Hg-Hg bond length in mercurous halides depends upon the nature of the halogen, decreasing in passing from the iodide *via* the bromide and chloride to the fluoride. The Hg-F distance is 2.13 ± 0.05 Å.

THE crystal structures of mercurous chloride, bromide and iodide^{1,2,3,4} have been previously determined, but the values for the atomic parameters given by Havighurst² are probably the most accurate, since they were obtained from Fourier series. All bond-lengths quoted in this paper are therefore based on Havighurst's data. According to them the Hg-Hg bond length in the mercurous ion increases on passing from calomel to mercurous bromide and iodide. The electronegativity of the halogens decreases as the series is ascended and therefore the mercury atoms would be expected to have smaller positive charges. On this simple conception the Hg-Hg bond length would be expected to decrease as the series is ascended. In fact it increases from fluoride to iodide.

To complete the series of Hg-Hg bond lengths for the mercurous halides it is necessary to determine the structure of mercurous fluoride. If the relation discussed above between the Hg-Hg bond length values and the nature of the anion is valid, the Hg-Hg distance in mercurous fluoride should be the shortest.

Ebert and Voitinek⁵ have reported an examination of mercurous fluoride powder by *X*-ray-diffraction methods. They found that crystals of mercurous fluoride were tetragonal, with the space group $D_{4h}^{17} - I4/mmm$, and that the unit cell, of dimensions $a = 3.66$, $c = 10.90$ Å, contained two molecules. They concluded that mercurous fluoride was isostructural with the other mercurous halides.

EXPERIMENTAL

Preparation of the Specimen.—Mercurous fluoride was prepared by dissolving mercurous carbonate in hydrofluoric acid.⁶ Attempts to obtain suitable single crystals from hydrofluoric acid solution failed. Thus all data were obtained from powder diffraction photographs. The specimen was prepared by sealing the well-ground material in a 0.3 mm. quartz capillary.

X-Ray Data.—The powder photographs were taken with a Unicam vacuum camera of 19 cm. diameter, with nickel-filtered Cu-*K* radiation. The unit cell and space group determined previously⁵ were confirmed.

* Part I, preceding paper.

¹ Mauguin, *Compt. rend.*, 1925, **178**, 15.

² Havighurst, *J. Amer. Chem. Soc.*, 1926, **48**, 2113.

³ Huggins and Magill, *ibid.*, 1927, **49**, 2357.

⁴ Hylleraas, *Z. Physik*, 1926, **36**, 859.

⁵ Ebert and Voitinek, *Z. anorg. Chem.*, 1933, **210**, 269.

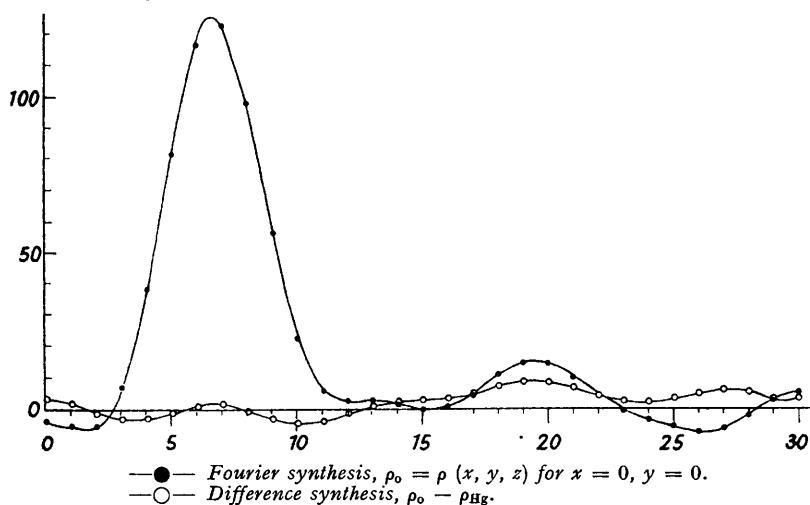
⁶ Henne and Renoll, *J. Amer. Chem. Soc.*, 1938, **60**, 1060.

Intensity Measurements.—The optical density of the diffraction lines was measured with a recording microdensitometer, and the relative intensities of the reflexions obtained from the characteristic curve of the film. These intensities were corrected in the usual way for multiplicity and Lorentz and polarization factors. The correction for absorption was carried according to the absorption-factor tables for a cylindrical specimen.⁷ The absorption coefficient, μ , calculated from these tables, was 2030 cm.⁻¹.

Fifty-two possible reflexions gave only 38 diffraction lines on the photograph, because of the overlapping of several reflexions having nearly equal Bragg angles. The intensities of the integral reflexions in such cases were evaluated by division of the total observed intensity in the ratio of the calculated intensities. The inaccuracy introduced by such an estimation probably influenced the fluorine parameter only, whereas it should have no significant effect on the mercury parameter.

Determination of the Atomic Parameters.—The mercury and fluorine atoms are located in special positions having symmetry 4 mm, the co-ordinates being $0, 0, \bar{z}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z$; $0, 0, z$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z$. Consequently only two parameters, z_{Hg} and z_{F} had to be determined. The preliminary z_{Hg} co-ordinate was obtained by the usual trial-and-error methods and by means of a Patterson

Electron-density distribution along [001] in the crystal structure of mercurous fluoride



The values of the function in e.Å⁻³ are given at 1/60 of the c-period.

line synthesis. The signs of all observed structure factors, $F_o(hkl)$, were computed by neglecting the contributions of the fluorine atom. The three-dimensional electron-density distribution was calculated for the line $(0, 0, z)$ in intervals of 1/60 of the c -axis, with Beever-Lipson strips. The result of the summation is shown in the Figure. The parameters are: $z_{\text{Hg}} = 0.111$; $z_{\text{F}} = 0.322$. The fluorine-atom peak has appeared although influenced by diffraction effects from the mercury atom. The value of z_{Hg} differs only slightly from that obtained by trial-and-error methods. The absolute scale of the structure factors and temperature factor were determined by Wilson's method, and the observed structure factors were corrected accordingly.

To refine the fluorine co-ordinate a difference synthesis with $(F_o - F_{\text{Hg}})$ as coefficients was computed. F_{Hg} was calculated by using f_{Hg} values from the "Internationale Tabellen,"⁸ multiplied by a temperature factor with $B = 5.5 \text{ \AA}^2$. The result is shown in the Figure, together with the F_o synthesis. The slope of $\rho_o - \rho_c(\text{Hg})$ is zero at the point $z = z_{\text{Hg}}$. The fluorine-atom peak appeared without significant change at $z_{\text{F}} = 0.323$.

Observed and calculated structure factors obtained in this way are given in Table 1. The agreement is satisfactory and the reliability index $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ is 0.10.

Accuracy of Atomic Co-ordinates.—Cruickshank's method⁹ for the determination of the

⁷ "Internationale Tabellen zur Bestimmung der Kristallstrukturen," Borntreager, Berlin, 1935, Vol. II., p. 583.

⁸ *Op. cit.*, p. 571.

⁹ Cruickshank, *Acta Cryst.*, 1949, 2, 65.

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standard deviation, $\sigma(z)$, was applied. The result is $\sigma(z) = 0.02 \text{ \AA}$ for the mercury and 0.03 \AA for the fluorine-atom co-ordinate. This gives a standard deviation of 0.04 \AA for the Hg-Hg bond length.

Final atomic co-ordinates are for Hg $z = 0.111$, and for F $z = 0.323$.

TABLE I. *Observed and calculated values of the structure factors.*

$\sin^2 \theta_{\text{obs.}}$	hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$	$\sin^2 \theta_{\text{obs.}}$	hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$	$\sin^2 \theta_{\text{obs.}}$	hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$
0.049	101	154	181	0.438	310	63	66				
0.080	004	246	-205		303	25	-26	0.748	400	31	31
0.088	110	218	229	0.448	109	81	62	0.756	411	16	19
	103	78	83	0.462	312	10	8	0.781	318	22	17
0.168	114	142	-152	0.466	217	10	8	0.788	404	21	-22
	105	157	-166	0.493	208	37	34	0.788	330	23	24
0.175	200	153	168		0,0,10	48	44	0.798	413	9	-10
	006	67	-74	0.518	314	48	-45	0.806	309	20	23
0.225	121	87	98		305	51	-48	0.853	1,1,12	10	-9
0.255	204	106	106	0.574	321	35	31	0.869	2,2,10	13	15
0.263	213	51	-47	0.587	11,1,0	37	32		334	15	-16
0.288	116	46	-50	0.624	323	18	-15	0.887	415	16	-17
0.319	008	60	62		316	20	-17		406	9	-9
0.343	215	95	-87		129	42	36	0.938	1,0,13	16	-17
0.349	220	78	90	0.672	228	22	20	0.957	3,1,10	11	12
0.398	301	46	54		2,0,10	28	25	0.970	424	10	-13
0.407	118	56	47	0.695	325	30	-29	0.980	336	7	-7
0.429	224	51	-59						0,0,14	13	-13

DISCUSSION

From the above parameters the Hg-Hg bond length in mercurous fluoride is $2.43 \pm 0.05 \text{ \AA}$, and as can be seen from Table 2, this fits well into the series of Hg-Hg bond length values for mercurous halides.

TABLE 2. *Comparison of the Hg-Hg bond lengths in mercurous halides (in \AA).*

Hg ₂ F ₂	2.43 ± 0.04	Present authors
Hg ₂ Cl ₂	2.53	Havighurst ²
Hg ₂ Br ₂	2.58	"
Hg ₂ I ₂	2.69	"

It is certain that the degree of ionic character of the mercury-halogen bond decreases from fluoride to iodide, and this can be roughly estimated from the differences in the corresponding electronegativities.¹⁰ It seems therefore that the bond length in mercurous halides is related to the electronegativity of the halogen. It may be concluded that, in spite of the positive charge on both mercury atoms, the mercurous ion is relatively more stable than a covalently bonded mercurous group. This conclusion is supported by the fact that it has so far proved impossible to prepare organic mercurous compounds. The only problem is whether the mercurous ion can occur as a free ion at all, since, as shown in the preceding paper, the mercurous ion in the crystal of Hg₂(NO₃)₂·2H₂O is co-ordinated with water molecules, and it is very likely that this co-ordination persists in aqueous solutions. A simplified model may be suggested in which the structure of mercurous fluoride is explained in terms of mercurous Hg-Hg²⁺ and F⁻ ions, and the structure of mercurous iodide in terms of dimerized HgI radicals. Mercurous chloride and bromide can be considered as intermediate in character. Nevertheless still more data on the properties of mercurous compounds are necessary before the nature of bonds in these compounds can be fully understood.

The Hg-F distance, 2.31 \AA , is smaller than the sum of the corresponding ionic radii (Hg 1.10 \AA , F 1.36 \AA), and is larger than the sum of the covalent radii (Hg 1.48 \AA , F 0.72 \AA), the value for the radii being taken from Wells's book.¹¹ The remarkably large fluorine-fluorine distance in the [001] direction should be mentioned. It is 3.85 \AA and shows that here, in contrast to the other mercurous halide structures, there is no contact between the halogen atoms in this direction. This is presumably due to the small ionic radius of fluorine

¹⁰ Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 1940, p. 41.

¹¹ Wells, "Structural Inorganic Chemistry, 2nd Edn., Oxford, 1950, pp. 50, 58, 70.

compared with that of chlorine, which changes the packing conditions very markedly in passing from mercurous chloride to the fluoride. It is interesting that this change is shown only in a shortening of the *a* dimension (from 4.47 Å for calomel to 3.66 Å for mercurous fluoride) while the *c* dimension remains practically the same (10.89 Å for calomel and 10.90 Å for mercurous fluoride). In consequence there is a close approach of 2.70 Å between the mercury and the fluorine atom of neighbouring molecules and this prevents a closer approach in the [001] direction.

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