Intermetallic Distances in Mercury(I) Halides Hg_2F_2, Hg_2Cl_2, and Hg_2Br_2

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Summary The structures of Hg_2F_2, Hg_2Cl_2, and Hg_2Br_2 have been reinvestigated on the basis of single crystal data; the intermetallic distances differ from those earlier reported and show no correlation with the electronegativity of the halogen.

THE Hg–Hg distance in the mercury(I) halides has been reported to vary considerably from fluoride to iodide. It has been suggested that the variation in published distances: 2·43 Å[1] Hg_2Cl_2 2·53[2] or 2·45 Å,[3] Hg_2Br_2 2·58 or 2·50 Å,[3] Hg_2I_2 Hg_2F_2 2·69 Å,[2] is related to the electronegativity of the ligand in the linear groups X-Hg-Hg-X existing in these compounds. All these structure determinations were based essentially on powder diffraction data. Since the accuracy of the inter-atomic distances thus determined must be low, single crystal refinements have been carried out to test the validity of this relationship.

Precipitated samples of the halides are microcrystalline. To prepare single crystals suitable for *X*-ray work such samples of Hg_2F_2 and Hg_2Cl_2 were sealed in platinum capsules and subjected to a pressure of 2 kbars at elevated temperature. Hg_2F_2 crystallized at 300 °C. Hg_2Cl_2 crystallized at the same temperature when a minute amount of water was added. Crystals of Hg_2Br_2 obtained through reduction of $HgBr_2$ with 2,2′-bisbenzimidazole were supplied by Professor Bengt Aurivillius at The Lund Institute of Technology. The shape and size of the crystals selected for *X*-ray work were such as to allow a rather high degree of accuracy to be reached in the absorption correction. Data for Hg_2F_2 were collected with a Pailred diffractometer using Mo-K_α radiation. Data for the other two compounds were obtained with an integrating Weissenberg camera using Cu-K_α radiation; the intensities were measured with a photometric Saab film scanner. Least squares refinements were carried out, with the assumption of anisotropically vibrating Hg atoms. No deviation from the previously assumed space group *I*4/*mmm* could be detected, but the resulting interatomic distances differ considerably from those given in earlier reports and

only show small differences among themselves. The Table summarizes the results of the present investigation.

The Hg–Hg distance found in the fluoride is very close to the corresponding distance found in several oxo-salts containing mercury doublets with oxygen ligands.[4–9] There is no obvious trend in the Hg–Hg distances among the halides; the difference in bond length between Hg_2Br_2 and Hg_2F_2 is not significant. Thus, no correlation exists between the electronegativity of the ligand and the Hg–Hg bond length.

A single crystal investigation of Hg_2I_2 is in progress, also a refinement of Hg_2Br_2 structure on the basis of diffractometer data.

TABLE

Compound	Hg_2F_2	Hg_2Cl_2	Hg_2Br_2
Cell dimensions			
a/Å	3·673 ± 1	4·482 ± 2	4·663 ± 1
c/Å	10·884 ± 2	10·910 ± 3	11·133 ± 2
Number of independent reflections used	202	56	48
Point position in space group $I4/mmm$		$\pm(0,0,z)$, $\pm(\frac{1}{2},\frac{1}{2},\frac{1}{2}+z)$	
Parameters (X = halide)			
z(Hg)	0·11518 ± 4	0·1158 ± 3	0·1118 ± 5
z(X)	0·3120 ± 10	0·338 ± 4	0·355 ± 1
Temp. factors			
β_{11}(Hg)	0·0309 ± 3	0·027 ± 3	0·034 ± 2
β_{33}(Hg)	0·00138 ± 3	0·0019 ± 5	0·0028 ± 3
B(X)/Å^2	1·6 ± 1	3·6 ± 7	2·1 ± 3
Distances			
Hg–Hg/Å	2·507 ± 1	2·526 ± 6	2·49 ± 1
Two short Hg–X/Å	2·14 ± 2	2·43 ± 4	2·71 ± 2
Four longer Hg–X/Å	2·715 ± 5	3·209 ± 6	3·32 ± 1
Root mean square deviations for Hg			
$r(a)$/Å	0·145 ± 1	0·164 ± 7	0·193 ± 4
$r(c)$/Å	0·091 ± 2	0·107 ± 11	0·132 ± 6
R-Factor	0·036	0·080	0·065

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[1] D. Grdenić and C. Djordjević, *J. Chem. Soc.*, 1956, 1316.
[2] R. J. Havighurst, *J. Amer. Chem. Soc.*, 1926, **48**, 2113.
[3] N. V. Belov and V. I. Mokeeva, *Trudy Inst. Krist. Akad. Nauk S.S.S.R.*, 1949, **5**, 13. *C.A.*, **47**, 3648i.
[4] D. Grdenić, *J. Chem. Soc.*, 1956, 1312.
[5] G. Johansson, *Acta Chem. Scand.*, 1966, **20**, 553.
[6] E. Dorm, *Acta Chem. Scand.*, 1967, **21**, 2834.
[7] B. Lindh, *Acta Chem. Scand.*, 1967, **21**, 2745.
[8] R. C. Elder, I. Halpern, and J. S. Pond, *J. Amer. Chem. Soc.*, 1967, **89**, 6877.
[9] E. Dorm, *Acta Chem. Scand.*, 1969, **23**, 1607.