PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The Preparation and Structure of Chain and Sheet Mercury Compounds [and Discussion]

R. J. Gillespie, I. D. Brown, W. R. Datars, K. R. Morgan, Z. Tun, P. K. Ummat and A. G. MacDiarmid

Phil. Trans. R. Soc. Lond. A 1985 **314**, 105-114
doi: 10.1098/rsta.1985.0011

Phil. Trans. R. Soc. Lond. A **314**, 105–114 (1985) [105]
Printed in Great Britain

The preparation and structure of chain and sheet mercury compounds

By R. J. Gillespie, F.R.S., I. D. Brown, W. R. Datars, K. R. Morgan,
Z. Tun and P. K. Ummat

Departments of Chemistry and Physics, McMaster University, 1280 *Main Street West,*
Hamilton, Ontario, L8S 4*M*1, *Canada*

This paper is a review of the preparation and structures of the polymercury cations Hg_3^{2+} and Hg_4^{2+}, the mercury chain compounds, $Hg_{3-\delta}AsF_6$, $Hg_{3-\delta}SbF_6$, $Hg_{3-\delta}NbF_6$ and $Hg_{3-\delta}TaF_6$, and the mercury layer compounds Hg_3NbF_6 and Hg_3TaF_6. The chain compounds $Hg_{3-\delta}MF_6$ are hard, golden yellow insoluble crystals with a shiny metallic appearance that have linear chains of mercury atoms parallel to the *a* and *b* axes of a tetragonal cell. They are non-stoichiometric because the Hg–Hg distance is not commensurate with the tetragonal lattice of AsF_6^- octahedra. The layer compounds have a silver colour with a distinct metallic lustre, but they are quite soft. They have sheets of hexagonally close-packed mercury atoms separated by a layer of NbF_6^- or TaF_6^- octahedra. In contrast to the chain compounds the layer compounds are stoichiometric. The interconversion of the chain and layer compounds is described and discussed.

The anisotropic metallic compounds $Hg_{3-\delta}AsF_6$ and $Hg_{3-\delta}SbF_6$ were first prepared over ten years ago. They have a golden metallic lustre and have structures containing chains of mercury atoms in two mutually perpendicular directions. Their remarkable electronic and structural properties have aroused considerable interest among chemists and physicists studying the solid state. Recently, two new examples of compounds of this type have been prepared, namely $Hg_{3-\delta}NbF_6$ and $Hg_{3-\delta}TaF_6$. Moreover, these compounds are not stable in contact with liquid SO_2; they are transformed into another type of anisotropic metallic compound which forms soft thin silvery crystals containing sheets, rather than chains, of mercury atoms.

In this paper we first describe the preparation of the polymercury cations Hg_3^{2+} and Hg_4^{2+}, because it was during the preparation of salts of these ions in solution in SO_2 that the formation of the insoluble golden metallic compounds $Hg_{3-\delta}AsF_6$ was first noticed. We then describe the preparation and properties of the four compounds $Hg_{3-\delta}MF_6$ (M = As, Sb, Nb and Ta). Finally we discuss the transformation of the niobium and tantalum compounds to the silver compounds and the layer structure of these compounds.

FINITE POLYMERCURY CATIONS

Covalent metal–metal bonds have become a fashionable and popular area of investigation in inorganic chemistry. The first such bond to be recognized – the mercury–mercury bond – had been known for a very long time in the mercurous ion Hg_2^{2+}, and in various covalent mercury(I) compounds such as mercury(I) chloride, Cl–Hg–Hg–Cl. However, it was not until 1971 that longer chains of mercury atoms were first made. At that time it was shown that the oxidation of mercury with AsF_5 and SbF_5 in solution in SO_2 gave the ions Hg_3^{2+} and Hg_4^{2+} (Davies *et* *al.* 1971; Cutforth *et al.* 1973*a, b*; Cutforth & Gillespie 1979). These were isolated as the crystalline AsF_6^- and $Sb_2F_{11}^-$ salts. The reactions may be represented by equations such as

$$3Hg + 3AsF_5 \rightarrow Hg_3(AsF_6)_2 + AsF_3,$$

$$4Hg + 3AsF_5 \rightarrow Hg_4(AsF_6)_2 + AsF_3.$$

At almost the same time Ellison *et al.* (1972) prepared $Hg_3(AlCl_4)_2$ by the reaction of mercury with a molten mixture of $HgCl_2$ and $AlCl_3$. Recently this method has been extended,

$$Hg + HgCl_2 + 2AlCl_3 \rightarrow Hg_3(AlCl_4)_2,$$

to the preparation of fluoroanion salts of mercury cations by using liquid SO_2 as a solvent (Gillespie *et al.* 1984, unpublished work). For example, $Hg_3(NbF_6)_2$ has been prepared by the reaction

$$2Hg + Hg(NbF_6)_2 \rightarrow Hg_3(NbF_6)_2$$

and $Hg_3(Ta_2F_{11})_2$ by the reaction

$$2Hg + Hg(Ta_2F_{11})_2 \rightarrow Hg_3(TaF_{11})_2.$$

The appropriate $Hg(MF_6)_2$ salt or $Hg(M_2F_{11})_2$ salt can be prepared by the reaction of HgF_2 with the pentafluoride MF_5 in solution in SO_2. In some cases the reaction can be effected in one step, that is, by the reaction of the appropriate amounts of HgF_2, MF_5 and Hg in SO_2. For example, $Hg_4(Ta_2F_{11})_2$ can be prepared by the reaction

$$HgF_2 + 4TaF_5 + 3Hg \rightarrow Hg_4(Ta_2F_{11})_2.$$

This has proved to be a more general and a more versatile method for the preparation of polymercury cation salts than the reaction of mercury with pentafluorides because it appears that very few pentafluorides are capable of oxidizing mercury to polymercury cations.

TABLE 1. Hg_3^{2+} SALTS

	d(Hg–Hg)/Å†	ν(Hg–Hg)/cm^{-1}
$Hg_3(AsF_6)_2$	2.55	140
$Hg_3(Sb_2F_{11})_2$	—	133
$Hg_3(AlCl_4)_2$	2.56	123
$Hg_3(NbF_6)_2$	—	125
$Hg_3(Ta_2F_{11})_2$	—	128
$Hg_3(NbCl_6)_2$	—	130

† 1 Å = 10^{-1} nm = 10^{-10} m.

The reactions involved in the preparation of polymercury cation salts from an Hg(II) salt and mercury are, however, more complex than indicated by the simple equations given above. In the preparation of an Hg_4^{2+} salt a mixture of soluble Hg_3^{2+} and Hg_4^{2+} salts is normally obtained together with a small amount of the insoluble golden metallic compound of composition $Hg_{3-\delta}MF_6$. When the solution is removed from the insoluble 'gold' compound and then crystallized, a mixture of a yellow Hg_3^{2+} salt and a deep red-black Hg_4^{2+} salt is obtained. These crystals must then be separated by hand. The known Hg_3^{2+} and Hg_4^{2+} salts are listed in tables 1 and 2. The MF_6^- salts, with the exception of the AsF_6^- salts, are generally insoluble in SO_2, whereas the $M_2F_{11}^-$ salts are generally very soluble. None of these salts is stable in aqueous

TABLE 2. Hg_4^{2+} SALTS

	d(Hg–Hg)/Å	ν(Hg–Hg)/cm^{-1}
$Hg_4(AsF_6)_2$	2.59, 2.62	80, 104
$Hg_4(Sb_2F_{11})_2$	—	116
$Hg_4(Nb_2F_{11})_2$	—	120

solution or even in the atmosphere as they disproportionate very rapidly to the element and Hg_2^{2+} salts. The preparations were therefore made in dry SO_2 as solvent and the crystals can only be handled in a very dry atmosphere.

Structures of Hg_3^{2+} *and* Hg_4^{2+}

Determination of the crystal structures of $Hg_3(AsF_6)_2$ and $Hg_3(AlCl_4)_2$ has shown that the Hg_3^{2+} ion has a linear, or very nearly linear, structure with two Hg–Hg bonds of equal length (figure 1) (Ellison *et al.* 1972; Cutforth *et al.* 1973*a*, *b*).

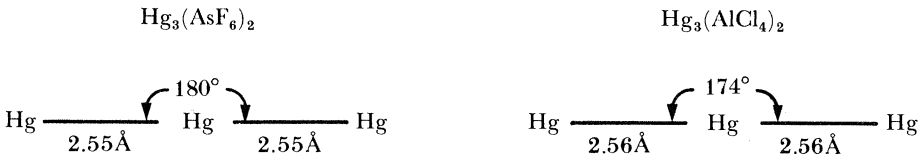


FIGURE 1. The structure of Hg_3^{2+}.

The structure of the Hg_4^{2+} ion has been determined in the compound $Hg_4(AsF_6)_2$ (Cutforth *et al.* 1983*a*, *b*). It has an almost linear structure. The terminal Hg–Hg bonds are slightly longer than the central Hg–Hg bond and both bonds are slightly longer than in Hg_3^{2+} (figure 2).

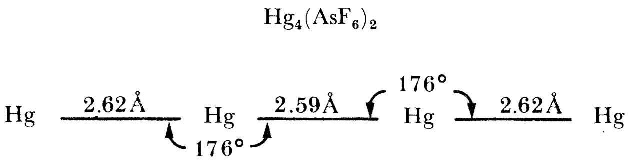


FIGURE 2. The structure of Hg_4^{2+}.

Although the structure can be approximately described as consisting of independent Hg_4^{2+} and $(AsF_6^-$ ions the distance between two adjacent Hg_4^{2+} ions (2.99 Å) is close to the shortest Hg---Hg distance in metallic mercury. Thus the Hg_4^{2+} ions may be considered to be associated together in long zigzag chains. No evidence has been obtained for soluble compounds containing chains of more than four mercury atoms.

INFINITE MERCURY CHAIN COMPOUNDS

In the reactions of mercury with AsF_5, SbF_5 and $Hg(MF_6)_2$ golden crystals with a shiny metallic appearance appear on the surface of the liquid mercury within 10–15 min (Gillespie & Ummat 1971). Some time later the SO_2 solution becomes yellow or orange-red in colour as Hg_3^{2+} and Hg_4^{2+} are formed. In the presence of sufficient oxidizing agent the golden crystals are completely converted to Hg_3^{2+}, but with less oxidizing agent some of the insoluble golden crystals remain at the end of the reaction and can be isolated. Like the Hg_3^{2+} and Hg_4^{2+} salts these compounds are not stable in the presence of even a trace of moisture.

Room temperature structure

X-ray precession photographs of the golden crystals isolated from the reaction of mercury with AsF_5 showed unusual sheets of diffuse intensity perpendicular to the a and b axes of a tetragonal crystal (figure 3) (Brown *et al.* 1974). These arise from non-intersecting chains of mercury atoms running in two mutually perpendicular directions through tunnels in a body-centred tetragonal array of AsF_6^- octahedra (figure 4). The mercury–mercury distance in the chains of 2.67 Å is not commensurate with the tetragonal AsF_6^- lattice, which has $a = b = 7.54$ Å. Thus the compound has the non-stoichiometric formula $Hg_{2.92}AsF_6$. The structure has been confirmed by a detailed neutron diffraction study (Schultz *et al.* 1978). The reaction of SbF_5 with mercury gave the analogous compound $Hg_{2.90}SbF_6$, and very recently from the reaction of $Hg(MF_6)_2$ with mercury we have obtained the new compounds $Hg_{2.88}NbF_6$ and $Hg_{2.88}TaF_6$ (Tun *et al.* 1984). All three compounds have the same golden metallic appearance as $Hg_{2.82}AsF_6$ and X-ray determination of their structures has shown that they have essentially the same structure as the AsF_6^- compound (table 3) (Tun & Brown 1982; Tun *et al.* 1984). Because the anions have slightly different sizes the corresponding lattice dimensions differ slightly and since the Hg–Hg distance is 2.67 Å in all three compounds their compositions differ slightly from that of the AsF_6^- compound. Because of some uncertainty regarding the exact stoichiometry of these compounds, which we refer to later, they are usually designated by the general formula $Hg_{3-\delta}MF_6$.

TABLE 3. SELECTED STRUCTURAL DATA FOR $Hg_{3-\delta}MF_6$ SALTS

	$Hg_{3-\delta}AsF_6$	$Hg_{3-\delta}SbF_6$	$Hg_{3-\delta}NbF_6$	$Hg_{3-\delta}TaF_6$
space group	$I4_1/amd$	$I4_1/amd$	$I4_1/amd$	$I4_1/amd$
$(a = b)$/Å	7.534	7.11	7.692	7.711
c/Å	12.395	12.641	12.679	12.714
V_{cell}/Å^3	703.6	751.6	750.2	756.0
δ	0.178(6)	0.10(2)	0.119	0.116
Hg–Hg separation/Å	2.670(5)	2.66(2)	2.670(3)	2.674(4)

The lack of structure in the diffuse sheets of diffracted intensity at room temperature shows that there is no correlation between the positions of the Hg atoms in one chain an those in another chain; in other words there is complete disorder between the positions of the mercury atoms in one chain and those in another chain. The chains can be regarded as one-dimensional liquids that can move freely in the tunnels in which they are accommodated.

An infinite covalently bonded chain of mercury atoms could, in principle, be built up from neutral mercury atoms

$$\text{Hg–Hg–Hg–Hg–Hg–Hg–Hg–Hg–Hg–Hg–Hg–Hg.}$$

The bonding in such a chain may be conveniently described in terms of two collinear 6s6p hybrid orbitals on each mercury atom. However, in the mercury chain compounds each mercury atom carries a positive charge of $1/(3-\delta)$ or approximately $+0.33$. This deficiency

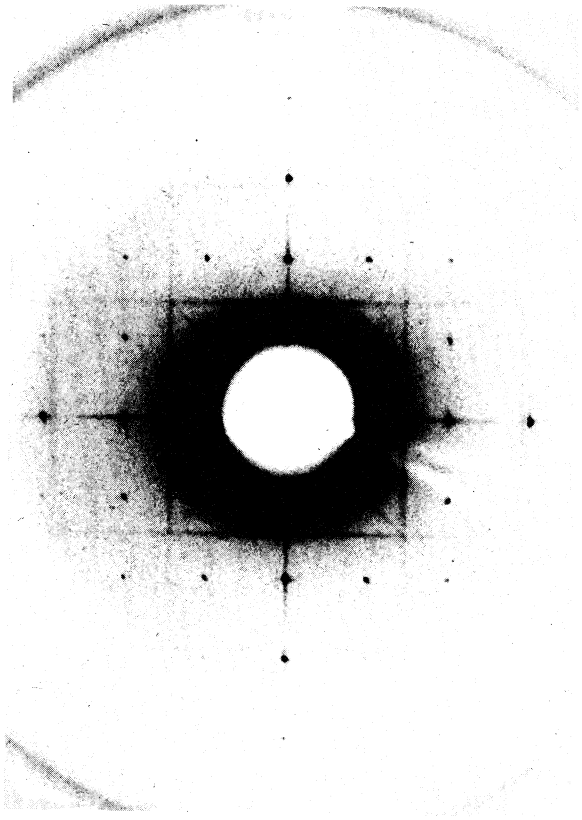


FIGURE 3. X-ray precession photograph of the ($kh0$) plane of Hg_3SbF_6. The lattice of Bragg peaks is associated with the SbF_6^- lattice, the lines with the Hg chains.

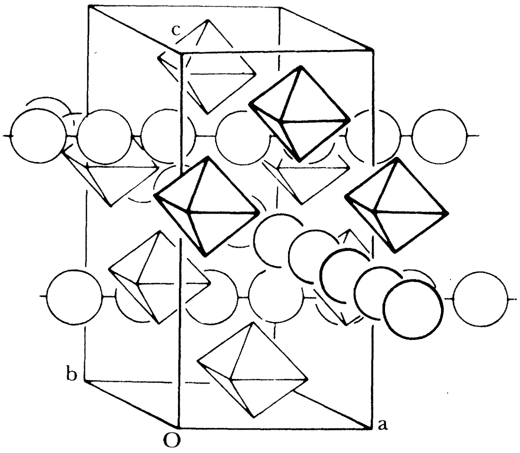


FIGURE 4. The structure of the chain compounds Hg_3MF_6 (M = As, Sb, Nb, Ta). The octahedra represent the MF_6^- anions and the circles the Hg atoms.

of electrons implies that the bonding in the chain is metallic rather than covalent and each chain can be regarded as a one dimensional metal. The crystals exhibit metallic conductivity which, as expected, is considerably greater in the *ab* plane than in the *c* direction.

An interesting feature of all four structures is that the chains are not exactly straight but they undulate with a periodicity equal to the lattice spacing of the host lattice. The undulation is such as to slightly increase the contact distance between the chains where they cross so that this distance becomes 3.22–3.24 Å in all four compounds. The maximum displacement of the chain from the straight configuration is largest for the AsF_6^- compound (0.07 Å) and smallest for the NbF_6^- compound (0.026 Å).

Low-temperature structures

Because of the incommensurability between the Hg–Hg distance in the chains of the MF_6^- lattice, it is impossible for the chains to order relative to the AsF_6^- host lattice; the Hg atoms will necessarily occupy different positions in each unit cell. However, it is possible for the chains to order relative to each other.

From the width of the diffuse sheets it can be shown that there is long-range ordering within the chains that extends over more than 400 Å or 150 Hg–Hg spacings. However, there is very little, if any, ordering between the chains at room temperature. Figure 5 shows that as the temperature is decreased some modulation of the sheets of uniform intensity is observed and broad peaks grow in intensity and become sharper with decreasing temperature. These observations indicate an onset of a short-range ordering between parallel chains.

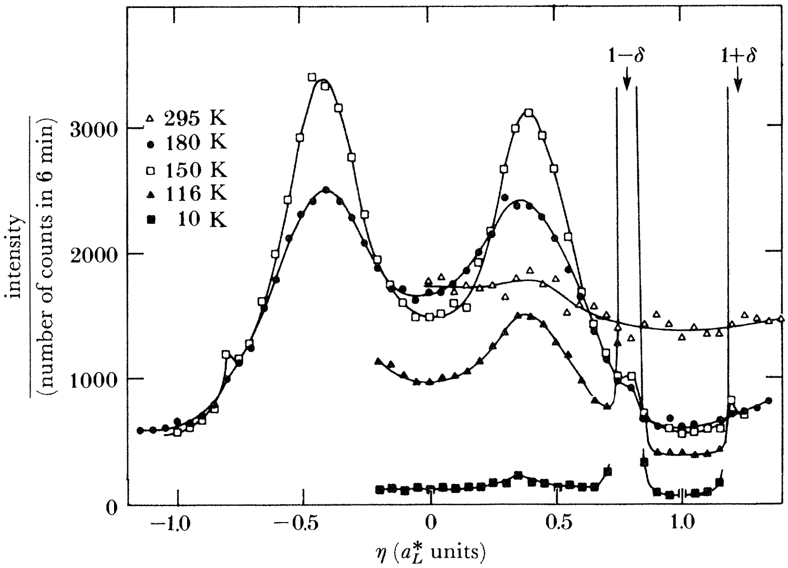


FIGURE 5. Neutron diffraction scans at various temperatures along the line $(3-\delta, \eta, 0)$ in the plane of the diffuse scattering (from reference 14) for $Hg_{3-\delta}AsF_6$.

Between 125 and 120 K the intensities of the broad peaks diminish rapidly and are replaced by a new set of Bragg reflections (figure 5). These arise because interactions between perpendicular chains cause the [100] chains to form an ordered monoclinic lattice and the [010] chains to form another monoclinic lattice sharing a common dimension in the (110) direction. These scatter X-rays and neutrons like a normal crystal. The mercury atom lattices are still, however, incommensurate with the AsF_6^- lattice. Thus the fully ordered phase consists of three interpenetrating lattices: the tetragonal host lattice and the two monoclinic mercury chain lattices. All four compounds show similar ordering phenomena, but the long-range ordering occurs at slightly higher temperatures than for the $Hg_{3-\delta}AsF_6$.

Composition

A particularly interesting feature of these compounds is that although the MF_6^- lattice contracts with decreasing temperature by 1 % between room temperature and 10 K, the Hg–Hg distance remains constant (Pouget *et al.* 1978). This would appear to imply that the composition of these compounds changes with temperature, the percentage of mercury decreasing slightly (table 4). For $Hg_{3-\delta}AsF_6$ the parameter δ decreases from 0.18 at room temperature to 0.21 at 80 K. Presumably mercury must be eliminated from the structure with decreasing temperature. In a few experiments the formation of a very small amount of mercury has been observed on the surface of the crystal when it is cooled to low temperature, but this could always be due to slight sample decomposition. However, it has been found in differential thermal analysis experiments (Datars *et al.* 1978) that if a crystal is cooled below a certain threshold temperature and then warmed to room temperature an endotherm at 235 K is observed corresponding to the melting of solid mercury. The threshold temperature varied somewhat from sample to sample but was normally in the range 200–210 K. It appears that on cooling a crystal below 200–210 K some solid mercury separates from the crystal and on warming this mercury melts and is reabsorbed by the crystal. The cooling–warming cycle can be repeated with the same results. It is not clear, however, why no mercury is formed above 200–210 K.

TABLE 4. TEMPERATURE DEPENDENCE OF THE STRUCTURE OF $Hg_{3-\delta}AsF_6$

	293 K	0 K
$(a = b)/\text{Å}$	7.534(7)	7.44
$c/\text{Å}$	12.395(8)	12.248
$V/\text{Å}^3$	703.6	678.0
Hg–Hg separation/Å	2.670(5)	2.267(5)
δ	0.178(6)	0.210(4) (80 K)

TABLE 5. DENSITY OF $Hg_{3-\delta}As^{18}F_6$

	density/(g cm^{-3})
observed	7.07
calculated for:	
$Hg_{2.82}AsF_6$	7.16
$Hg_3AsF_6 (Hg_{2.82}AsF_6 + 0.18\ Hg)$	7.49
$Hg_{2.82}(AsF_6)_{0.94}$	7.05

Another problem with respect to the composition is that chemical analysis gives a composition that is much closer to the stoichiometric value Hg_3AsF_6 than that obtained from the crystal structure (Gillespie & Ummat 1971; Miro *et al.* 1978). It appears that either the crystal contains additional mercury or it has a deficiency of anions. The latter explanation is more consistent with the observed density of the crystals (table 5). The measured density (Miro *et al.* 1978) is 7.06 g cm^{-3}, which compares with a calculated value of 7.16 g cm^{-3} for $Hg_{2.82}AsF_6$ and

7.49 g cm^{-3} for Hg_3AsF_6; that is, $Hg_{2.82}AsF_6 + 0.18$ Hg in interstitial sites. However, if there are 6% anion vacancies to give the composition $Hg_{2.82}(AsF_6)_{0.94}$, the calculated density is 7.05 g cm^{-3}. These anion vacancies provide sites that could accommodate mercury that is extruded from the structure as the temperature is decreased. Only after all or a certain fraction of these sites have been filled with mercury, presumably at around 200 K, can bulk mercury be detected in d.t.a. experiments.

Infinite mercury sheet compounds

The recent preparation of the golden chain compounds $Hg_{3-\delta}NbF_6$ and $Hg_{3-\delta}TaF_6$ led also to the discovery of an entirely new type of mercury compound containing sheets of mercury atoms. If the golden crystals of $Hg_{3-\delta}NbF_6$ and $Hg_{3-\delta}TaF_6$ are not removed from the reaction mixture, which contains unreacted mercury and the ions Hg_3^{2+} and Hg_4^{2+} in solution, they are transformed in a few hours to thin flexible silvery plates that resemble aluminium foil (Brown *et al.* 1984). If the reaction is effected at −35 °C no golden crystals are observed and the silver crystals appear to be formed directly. These crystals have a completely different diffraction pattern from the golden crystals. Precession photographs show hexagonal symmetry (figure 6).

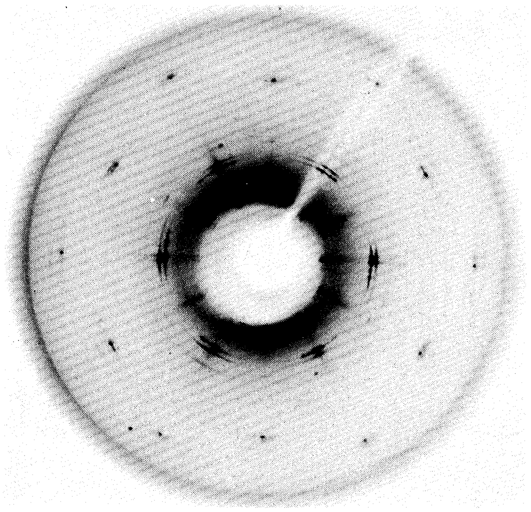


Figure 6. The *hk*0 precession photograph of Hg_3NbF_6.

The principal features of the X-ray diffraction pattern can be explained by a model in space group $P\bar{3}1m$ (table 6 and figure 7) in which layers of close-packed NbF_6^- octahedra are separated by sheets of mercury atoms arranged on a hexagonal net. Each mercury atom has six mercury neighbours at 2.90 Å separation within the sheet and three fluorine neighbours from each of the adjacent NbF_6^- layers at distances of 3.2 Å. The mercury and fluorine atoms form a cubic close-packed lattice with niobium atoms occupying one-third of the octahedral holes between fluorine atoms. In some samples the Nb atoms randomly occupy different positions in different layers. The Hg–Hg distance in these sheets is larger than in the chains in which each mercury atom is bonded to two others but is smaller than in metallic mercury in which each mercury atom has ten or twelve neighbours.

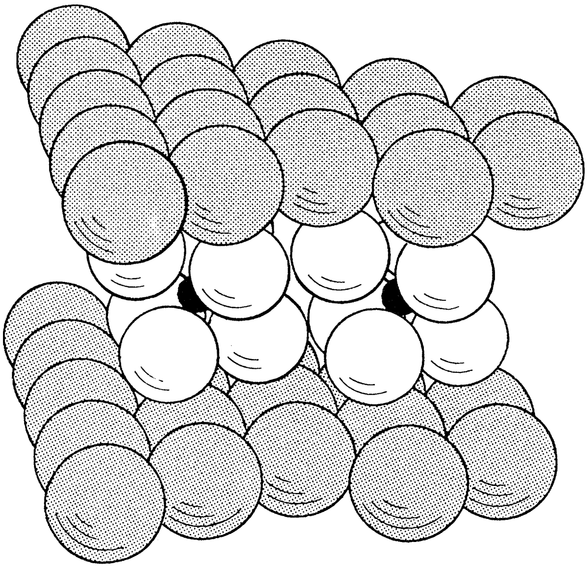


FIGURE 7. The structure of Hg_3NbF_6. The Hg, F and Nb atoms are represented by grey, white and black atoms respectively.

TABLE 6. PROPOSED MODEL FOR Hg_3NbF_6

(Hg_3NbF_6, $M_r = 808.67$, trigonal, space group $P\bar{3}1m$, $Z = 1$, $a = 5.02(1)$ Å, $c = 7.68(7)$ Å, $D_x = 8.0(1)$ Mg m^{-3}.)

		atomic coordinates		
atom	site	*x*	*y*	*z*
Hg(1)	1 b	0	0	1/2
Hg(2)	2 d	1/3	2/3	1/2
Nb	1 a⁽¹⁾	0	0	0
F	6k	0.309⁽²⁾	0	0.143⁽²⁾

(1) In some samples the Nb atom is disordered over the three sites 1 a and 2 c (1/3, 2/3, 0; 2/3, 1/3, 0).
(2) Calculated assuming an undistorted NbF_6 octahedron with Nb–F distance = 1.90 Å.

Unlike the golden crystals from which they are formed the silver crystals have the exact stoichiometric composition Hg_3MF_6 that is determined by the close-packed structure.

Transformations between the chain and sheet compounds

If the silver crystals are heated to 120 °C they are rapidly transformed to the golden crystals (Brown *et al.* 1984). This transformation can easily be observed visually and it was confirmed by X-ray powder photographs. However, the golden crystals can be cooled to room temperature and below without reverting back to the silver form. But if the golden crystals are cooled to room temperature or below in the presence of liquid SO_2 they are transformed back to the silver form. The role played by the liquid SO_2 in this transformation is not clear since both the golden and silver forms are completely insoluble in SO_2. Perhaps the transformation proceeds via the formation of small amounts of Hg_3^{2+} and Hg_4^{2+}.

It appears that the silver form is the thermodynamically stable form of Hg_3NbF_6 and Hg_3TaF_6 but no silver form of either $Hg_{3-\delta}AsF_6$ or $Hg_{3-\delta}SbF_6$ has yet been obtained. The fact that the golden and silver forms of Hg_3NbF_6 and Hg_3TaF_6 are so readily interconverted despite that fact that they apparently have different compositions, and the mercury is not observed to be formed in the transformation of the silver to the golden form again raises the question of the composition of the golden form. This facile interconversion lends some support to the suggestion that the Hg:M ratio is in fact 3:1 and that the apparent non-stoichiometry indicated by the X-ray crystal structure is compensated by an appropriate number of anion deficiencies.

REFERENCES

Brown, I. D., Cutforth, B. D., Davies, C. G., Gillespie, R. J., Ireland, P. R. & Vekris, J. E. 1974 *Can. J. Chem.* **791**, 51.

Brown, I. D., Gillespie, R. J., Morgan, K. R., Tun, Z. & Ummat, P. K. 1984 *Inorg. Chem.* **23**, 4506.

Cutforth, B. D., Davies, C. G., Dean, P. A. W., Gillespie, R. J., Ireland, P. R. & Ummat, P. K. 1973*a* *Inorg. Chem.* **12**, 1343.

Cutforth, B. D., Davies, C. G., Dean, P. A. W., Gillespie, R. J., Ireland, P. R. & Ummat, P. K. 1983*a* *Inorg. Chem.* **22**, 1343–1347.

Cutforth, B. D. & Gillespie, R. J. 1979 In *Inorganic synthesis*, vol. 19 (ed. D. F. Shriver), pp. 22–27. New York: Wiley.

Cutforth, B. D., Gillespie, R. J., Ireland, P. R., Sawyer, J. F. & Ummat, P. K. 1973*b* *Inorg. Chem.* **12**, 1344–1347.

Cutforth, B. D., Gillespie, R. J., Ireland, P. R., Sawyer, J. F. & Ummat, P. K. 1983*b* *Inorg. Chem.* **22**, 1344.

Datars, W. R., Van Schyndel, A., Eass, J. S., Chartier, D. & Gillespie, R. J. 1978 *Phys. Rev. Lett.* **40**, 1184.

Davies, C. G., Dean, P. A. W., Gillespie, R. J. & Ummat, P. K. 1971 *Chem. Commun.* 782.

Ellison, R. D., Levy, H. A. & Fung, K. W. 1972 *Inorg. Chem.* **11**, 833.

Gillespie, R. J. & Ummat, P. J. 1971 *J. chem. Soc. chem. Commun.* 1168.

Miro, N. D., MacDiarmid, A. G., Heeger, A. H., Garito, A. F., Chiang, C. K., Schultz, A. J. & Williams, J. M. J. 1978 *Inorg. nucl. Chem.* **40**, 1351.

Pouget, J. P., Shirane, G., Hastings, J. M., Heeger, A. J., Miro, N. D. & MacDiarmid, A. G. 1978 *Phys. Rev.* B**18**, 3645.

Schultz, A. J., Williams, J. M., Miro, N. D., MacDiarmid, A. G. & Weeger, A. J. 1978 *Inorg. Chem.* **17**, 646.

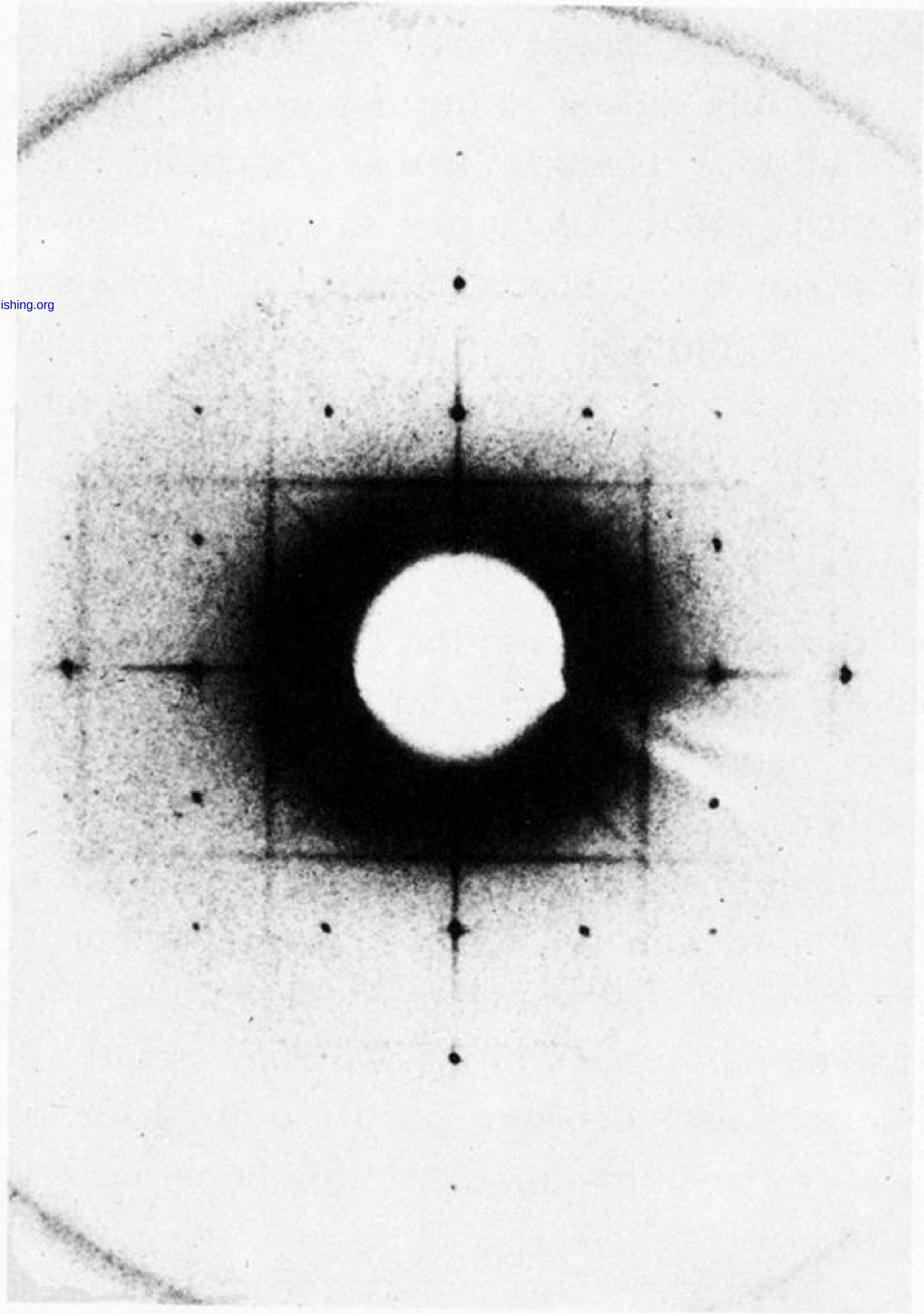
Tun, Z. & Brown, I. D. 1982 *Acta crystallogr.* B**38**, 2321.

Tun, Z., Brown, I. D. & Ummat, P. K. 1984 *Acta crystallogr.* C**40**, 1301.

Discussion

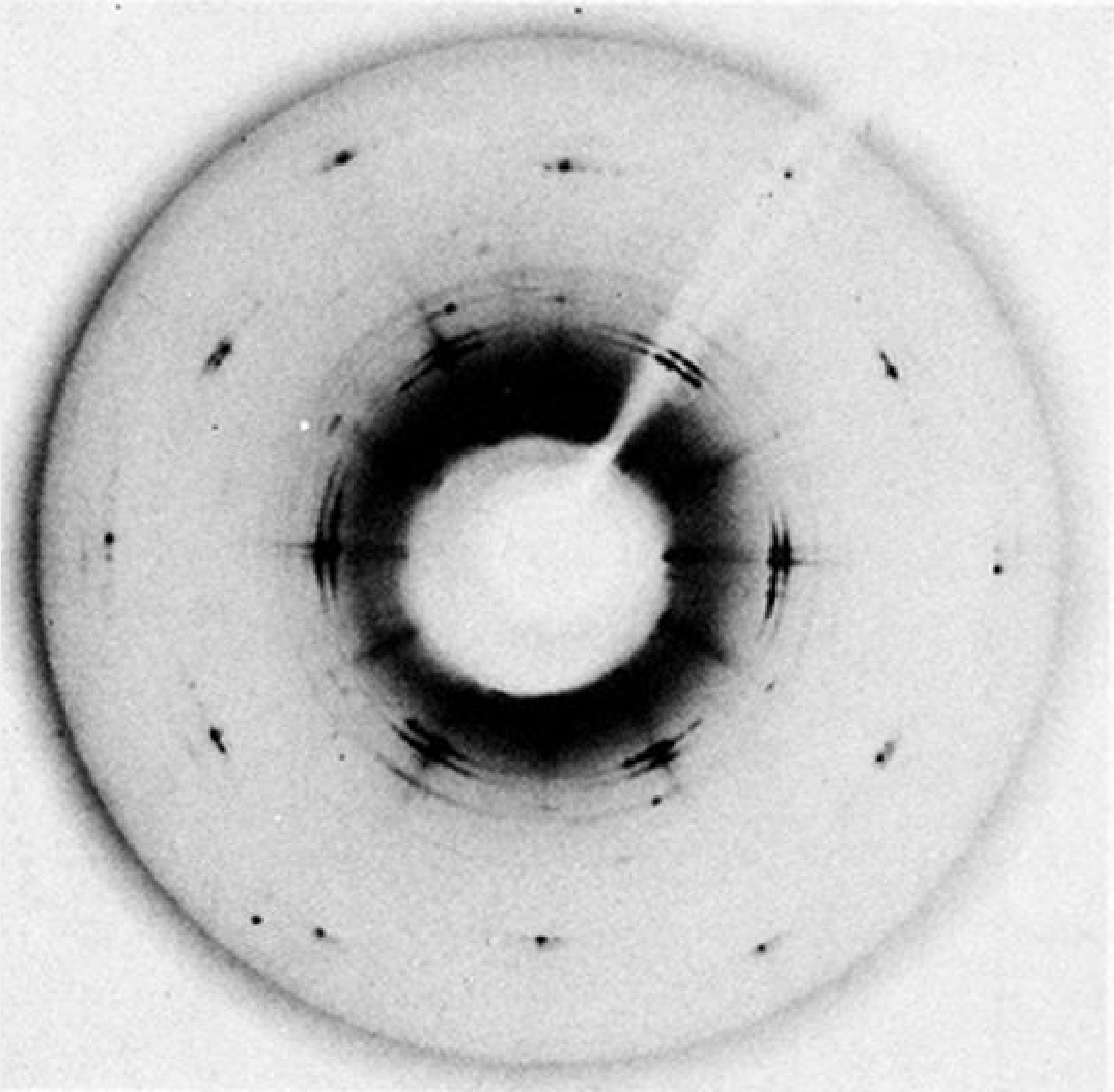
A. G. MacDiarmid (*Department of Chemistry, University of Pennsylvania, Philadelphia, U.S.A.*). Does Professor Gillespie have elemental analyses of the very interesting new compounds he has reported? To rationalize the difference in composition of $Hg_{3-\delta}AsF_6$ as determined by elemental analyses (Hg_3AsF_6), and by neutron diffraction studies ($Hg_{2.82}AsF_6$), we have combined the results of these studies with density measurements and have come to the conclusion, as Professor Gillespie noted, that these apparently different compositions can be understood if one assumes AsF_6^- defect sites in the crystal lattice. To ascertain the generality of this lattice defect phenomena it would appear desirable to make similar studies on the fascinating $Hg_{3-\delta}MF_6$ (M = Nb, Ta, Sb) compounds he has described.

R. J. Gillespie, F.R.S. The analytical and density measurements that you suggest are clearly very desirable as they would almost certainly increase our understanding of these compounds. We have recently commenced such studies, but they have not yet been completed.



IGURE 3. X-ray precession photograph of the $(kh0)$ plane of Hg_3SbF_6. The lattice of Bragg peaks is associated with the SbF_6^- lattice, the lines with the Hg chains.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES



GURE 6. The *hk*0 precession photograph of Hg_3NbF_6.