

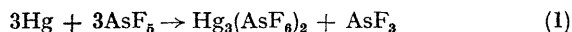
## Preparation and Crystal Structure of the $\text{Hg}_3^{2+}$ Ion

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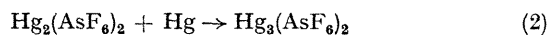
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**Summary** The new compound  $\text{Hg}_3^{2+}(\text{AsF}_6^-)_2$  containing mercury in the oxidation state of  $+\frac{2}{3}$  has been obtained by the reaction of mercury with arsenic pentafluoride in liquid  $\text{SO}_2$ ; the  $\text{Hg}_3^{2+}$  ion which is shown, by X-ray methods, to be linear and symmetrical is also obtained when mercury is dissolved in fluorosulphuric acid.

When mercury in liquid  $\text{SO}_2$  is treated with an equimolar amount of  $\text{AsF}_5$  golden crystals are immediately formed which react further giving a pale yellow solution in  $\text{SO}_2$ . On removal of volatile material a light yellow solid (**1**), for which analytical data give the composition  $\text{Hg}_3(\text{AsF}_6)_2$ , is obtained [see equation (1)]. Further oxidation of (**1**) with  $\text{AsF}_5$  in  $\text{SO}_2$  gives white  $\text{Hg}_2(\text{AsF}_6)_2$ . (**1**) can also be



prepared by treating  $\text{Hg}_2(\text{AsF}_6)_2$  dissolved in  $\text{SO}_2$  with an equimolar amount of elemental mercury when the initially colourless solution gradually becomes pale yellow and on removal of  $\text{SO}_2$  (**1**) is obtained [equation (2)]. The room temperature  $^{19}\text{F}$  n.m.r. spectrum of (**1**) in acetone, with



which some reaction occurs, showed at  $\phi + 63.5$ , the characteristic 1:1:1:1 quartet of the  $\text{AsF}_6^-$  anion ( $J$  ca. 930 Hz). In the i.r. spectrum of a Nujol mull of (**1**) a strong band was observed at  $699\text{ cm}^{-1}$  which can be assigned as the  $\nu_3$  vibration of  $\text{AsF}_6^-$ . The Raman spectrum of (**1**) showed bands at 373, 570, and  $674\text{ cm}^{-1}$  which may be assigned to  $\nu_5$ ,  $\nu_2$ , and  $\nu_1$  vibrations of  $\text{AsF}_6^-$ . We conclude that (**1**) should be formulated as the ionic compound  $\text{Hg}_3^{2+}(\text{AsF}_6^-)_2$ . A solution of (**1**) in  $\text{SO}_2$  shows a single strong polarised band at  $118\text{ cm}^{-1}$  which must be assigned as a Hg-Hg stretch indicating that the  $\text{Hg}_3^{2+}$  cation is linear with the structure  $^+\text{Hg}-\text{Hg}-\text{Hg}^+$ . We have observed the stretching frequency of the  $\text{Hg}_3^{2+}$  ion at  $182\text{ cm}^{-1}$  in an aqueous solution of  $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ . A value of  $169\text{ cm}^{-1}$  has been previously reported for this solution.<sup>1</sup>

Mercury has been previously found to dissolve slowly in fluorosulphuric acid at room temperature.<sup>2</sup> We find that a yellow solution is produced the Raman spectrum of which shows a strong polarised band at  $113\text{ cm}^{-1}$  indicating the presence of the  $\text{Hg}_3^{2+}$  ion. The yellow solution is very slowly further oxidised to give the colourless  $\text{Hg}_2^{2+}$  cation. The absorption spectra of a solution of (**1**) in  $\text{HSO}_3\text{F}$  and of Hg in  $\text{HSO}_3\text{F}$  are identical having a strong peak at 248 nm, the tail of which extends into the visible region.

X-Ray diffraction studies on a single crystal obtained from  $\text{SO}_2$  solution gave the following results:  $\text{Hg}_3(\text{AsF}_6)_2$ ,  $M = 979.6$ , monoclinic,  $a = 5.97$ ,  $b = 8.84$ ,  $c = 11.21\text{ \AA}$ ,  $\beta = 90.0^\circ$ ,  $U = 591.1\text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 5.50$ ; space group  $P2_1/c$ . Integration of precession photographs gave preliminary intensity measurements for 45  $h0l$  and 34  $hkl$  reflections and these were used to calculate two Patterson projections from which the co-ordinates of the mercury atoms were obtained. Calculation of electron density projections using these co-ordinates enabled the position of the arsenic atoms to be found. With two cycles of least-squares refinement with isotropic temperature factors for mercury and arsenic, the conventional agreement index was reduced to 0.11 for 60 observed reflections and to 0.13 for the complete data set. Since the space group is centrosymmetric and since two of the six mercury atoms are situated at special positions ( $000, 0\frac{1}{2}\frac{1}{2}$ ) the  $\text{Hg}_3^{2+}$  ion must be linear and symmetric. The Hg-Hg bond length is  $2.55 \pm 0.01\text{ \AA}$ . The Hg-Hg bond length has been found to vary from  $2.43\text{ \AA}$  in  $\text{Hg}_2\text{F}_2$  to  $2.69\text{ \AA}$  in  $\text{HgI}_2$ .

*Added in proof.* Since this communication was submitted we have become aware of the work of Torsi and Mamantov<sup>3</sup> who have obtained evidence for  $\text{Hg}_3^{2+}$  from studies of the absorption spectra and polarography of solutions obtained when mercury is added to an  $\text{AlCl}_3$ -NaCl melt containing  $\text{Hg}_2\text{Cl}_2$ .

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<sup>1</sup> L. A. Woodward, *Phil. Mag.*, 1934, **18**, 823.

<sup>2</sup> J. Meyer and G. Schramm, *Z. anorg. Chem.*, 1932, **206**, 24.

<sup>3</sup> G. Torsi and G. Mamantov, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 843.