

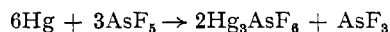
## The $+\frac{1}{3}$ Oxidation State of Mercury

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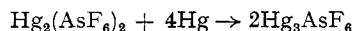
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**Summary** The new compound  $\text{Hg}_6^{2+}(\text{AsF}_6^-)_2$  containing mercury in the previously unknown oxidation state of  $+\frac{1}{3}$  has been obtained by the reaction of mercury with arsenic pentafluoride in liquid  $\text{SO}_2$ .

When mercury in  $\text{SO}_2$  is treated with  $\text{AsF}_5$  in the mole ratio 2:1 for a period of about 1 h, a golden coloured crystalline solid (1) is obtained on removal of volatiles. Analytical data for the three elements were in excellent agreement with the composition  $\text{Hg}_3\text{AsF}_6$ . Further oxidation of (1) with  $\text{AsF}_5$  gave  $\text{Hg}_3^{2+}(\text{AsF}_6^-)_2$ .<sup>1</sup> The reaction producing (1) can be represented:



(1) can also be prepared by treating  $\text{Hg}_2(\text{AsF}_6)_2$  dissolved in  $\text{SO}_2$  with Hg in the mole ratio 1:4

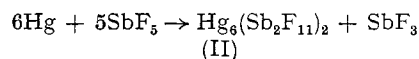


The gold compound reacts with  $10^{-4}$  molar aqueous  $\text{HNO}_3$  to give elemental mercury and  $\text{Hg}_2^{2+}$  in solution. The oxidation state of the golden coloured material is further confirmed by this disproportionation reaction which was found to occur according to the equation,



The room-temperature  $^{19}\text{F}$  n.m.r. spectrum of (1) in acetone, with which some reaction occurs, showed at  $\delta + 63.5$ , the characteristic 1:1:1:1 quartet of the  $\text{AsF}_6^-$  anion ( $J$  ca. 930 Hz). The i.r. spectrum of (1) had a strong band at  $699\text{ cm}^{-1}$  which can be assigned as the  $\nu_3$  vibration of  $\text{AsF}_6^-$ . We conclude that (1) should be formulated as the ionic compound  $\text{Hg}_3^{n+}(\text{AsF}_6^-)_n$ . As it was found to be diamagnetic, odd values of  $n$  can be eliminated and the smallest possible value is  $n = 2$ , i.e.,  $\text{Hg}_6^{2+}(\text{AsF}_6^-)_2$ . It is insoluble in  $\text{SO}_2$  and reacts with  $\text{HSO}_3\text{F}$  to give a pale yellow solution which has been shown to contain  $\text{Hg}_3^{2+}$ . The reflectance spectrum of (1) showed a broad band at approximately 360 nm.

$\text{Hg}(+\frac{1}{3})$  can also be produced by oxidising mercury in  $\text{SO}_2$  with the stoichiometric amount of  $\text{SbF}_5$  according to the equation



The reflectance spectrum of (II) was identical with that of  $\text{Hg}_6(\text{AsF}_6)_2$  both solids having an absorption at approximately 360 nm. However (II) could not be obtained pure as it is insoluble in  $\text{SO}_2$  and could not therefore be separated from the  $\text{SbF}_3$ .

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<sup>1</sup> C. G. Davies, P. A. W. Dean, R. J. Gillespie, and P. K. Ummat, *Chem. Comm.*, 1971, 782.