Preparation and Crystal Structure of the Hg_3^{2+} Ion

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Summary The new compound $Hg_3^{2+}(AsF_6^-)_2$ containing mercury in the oxidation state of $+\frac{2}{3}$ has been obtained by the reaction of mercury with arsenic pentafluoride in liquid SO_2; the 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 SO_2 is treated with an equimolar amount of AsF_5 golden crystals are immediately formed which react further giving a pale yellow solution in SO_2. On removal of volatile material a light yellow solid (**1**), for which analytical data give the composition $Hg_3(AsF_6)_2$, is obtained [see equation (1)]. Further oxidation of (**1**) with AsF_5 in SO_2 gives white $Hg_2(AsF_6)_2$. (**1**) can also be

$$3Hg + 3AsF_5 \rightarrow Hg_3(AsF_6)_2 + AsF_3 \quad (1)$$

prepared by treating $Hg_2(AsF_6)_2$ dissolved in SO_2 with an equimolar amount of elemental mercury when the initially colourless solution gradually becomes pale yellow and on removal of SO_2 (**1**) is obtained [equation (2)]. The room temperature ^{19}F n.m.r. spectrum of (**1**) in acetone, with

$$Hg_2(AsF_6)_2 + Hg \rightarrow Hg_3(AsF_6)_2 \quad (2)$$

which some reaction occurs, showed at ϕ +63·5, the characteristic 1:1:1:1 quartet of the 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 cm^{-1} which can be assigned as the ν_3 vibration of AsF_6^-. The Raman spectrum of (**1**) showed bands at 373, 570, and 674 cm^{-1} which may be assigned to ν_5, ν_2, and ν_1 vibrations of AsF_6^-. We conclude that (**1**) should be formulated as the ionic compound $Hg_3^{2+}(AsF_6^-)_2$. A solution of (**1**) in SO_2 shows a single strong polarised band at 118 cm^{-1} which must be assigned as a Hg–Hg stretch indicating that the Hg_3^{2+} cation is linear with the structure $^+Hg–Hg–Hg^+$. We have observed the stretching frequency of the Hg_2^{2+} ion at 182 cm^{-1} in an aqueous solution of $Hg_2(NO_3)_2,2H_2O$. A value of 169 cm^{-1} has been previously reported for this solution.[1]

Mercury has been previously found to dissolve slowly in fluorosulphuric acid at room temperature.[2] We find that a yellow solution is produced the Raman spectrum of which shows a strong polarised band at 113 cm^{-1} indicating the presence of the Hg_3^{2+} ion. The yellow solution is very slowly further oxidised to give the colourless Hg_2^{2+} cation. The absorption spectra of a solution of (**1**) in HSO_3F and of Hg in HSO_3F 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 SO_2 solution gave the following results: $Hg_3(AsF_6)_2$, M = 979·6, monoclinic, a = 5·9 7,b = 8·84, c = 11·21Å, β = 90·0°, U = 591·1 Å^3, Z = 2, D_c = 5·50; space group $P2_1/c$. Integration of precession photographs gave preliminary intensity measurements for 45 *h*0*l* and 34 *hk*0 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 Hg_3^{2+} ion must be linear and symmetric. The Hg–Hg bond length is 2·55 ± 0·01 Å. The Hg–Hg bond length has been found to vary from 2·43 Å in Hg_2F_2 to 2·69 Å in HgI_2.

Added in proof. Since this communication was submitted we have become aware of the work of Torsi and Mamantov[3] who have obtained evidence for Hg_3^{2+} from studies of the absorption spectra and polarography of solutions obtained when mercury is added to an $AlCl_3$–NaCl melt containing Hg_2Cl_2.

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