Preparation and Crystal Structure of the Hg_4^{2+} Ion

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Summary The compound $Hg_4(AsF_6)_2$ containing mercury in the oxidation state of $+\frac{1}{2}$ has been obtained from the reaction of mercury with arsenic pentafluoride in liquid SO_2; the Hg_4^{2+} ion is shown by *X*-ray methods to be very nearly linear with Hg–Hg distances of 2·57 and 2·70 Å.

It has recently been shown that mercury exists in lower oxidation states than +1. The Hg_3^{2+} ion may be prepared by oxidizing mercury with an equimolar amount of AsF_5[1] or by the reduction of Hg_2Cl_2 by molten $AlCl_3$–NaCl.[2] A crystallographic study of $Hg_3(AsF_6)_2$[3] has shown a linear Hg_3^{2+} ion with an Hg–Hg distance of 2·55 Å while $Hg_3(AlCl_4)_2$ is slightly bent ($<$ Hg–Hg–Hg = 174°) with an Hg–Hg distance of 2·56 Å.

When mercury is treated with AsF_5 in liquid sulphur dioxide at room temperature, the liquid mercury reacts quite rapidly to yield a pale golden crystalline compound. A crystal structure determination has shown that this compound may be formulated as $Hg_{2\cdot85}AsF_6$[5] and that it has a novel structure containing infinite cationic mercury chains. On further reaction with AsF_5, a deep red solution is obtained as well as the insoluble gold compound. Very slow crystallization of this red solution yields two distinct types of crystals, one of which may be identified as $Hg_3(AsF_6)_2$ by Raman and u.v.-visible spectra. The other compound, which crystallizes as red-black needles, is diamagnetic and the analysis is in excellent agreement with formulation $Hg_4(AsF_6)_2$. Contrary to what one would expect, this compound cannot be prepared in the absence of $Hg_3(AsF_6)_2$ and $Hg_{2\cdot85}AsF_6$ and the interesting equilibria among these compounds in the SO_2 solvent system is currently under investigation.

The Raman spectrum of the red solution shows, in addition to the peak at 113 cm^{-1} due to ν_1 of the Hg_3^{2+} ion, two peaks at 95 cm^{-1} and 79 cm^{-1}. For a linear tetratomic molecule with $C_{\infty v}$ symmetry five normal modes of vibration are expected. Three of these, ν_1, ν_2 and ν_4 are active only in the Raman spectrum and the other two, ν_3 and ν_5 are active only in the i.r. spectrum. The two observed bands may be attributed to the two stretching vibrations ν_1 and ν_2. The bending vibration, ν_4, is presumably at much lower frequency and is obscured by the exciting line. The u.v. visible spectrum of the red solution in SO_2 shows peaks at 326 nm, due to the Hg_3^{2+} ion, and at 380 nm which may be assigned to the Hg_4^{2+} ion.

X-ray diffraction studies on a single crystal of $Hg_4(AsF_6)_2$ gave the following results: $Hg_4(AsF_6)_2$, $M = 1180{\cdot}2$, monoclinic, $a = 5{\cdot}485(3)$, $b = 11{\cdot}623(8)$, $c = 9{\cdot}835(5)$ Å, $\beta = 92{\cdot}11(5)°$, $U = 626{\cdot}58$ Å^3, $Z = 2$, $D_c = 6{\cdot}26$. Precession photographs showed absences consistent with the space group $P2_1/c$. Data collected on a four-circle autodiffractometer with Mo-K_α radiation was used to calculate a three-dimensional Patterson function from which the co-ordinates of the mercury atoms were obtained. These co-ordinates were used to calculate a three-dimensional electron density map from which the arsenic and fluorine atoms could be located. Three cycles of least-squares refinement with anisotropic temperature factors for mercury and isotropic temperature factors for arsenic and fluorine reduced the conventional agreement index to 0·13 for 213 observed reflections. Because the crystal had very poorly defined faces, a spherical absorption correction was used. The Hg_4^{2+} group is very nearly linear with an Hg–Hg–Hg bond angle of 176° and with a *trans* configuration. The terminal Hg–Hg distance is 2·57(1) Å while the central Hg–Hg distance is 2·70(1) Å. The average bond length of 2·61 Å follows the observation that the Hg–Hg bond length increases with decreasing charge in the series Hg_2^{2+}, Hg_3^{2+}, Hg_4^{2+}, $Hg_{2\cdot85}$. The structure may be described as nearly linear Hg_4^{2+} cations lying in planes perpendicular to the *a* axis, with the AsF_6^- octahedra lying in alternating planes half the unit cell edge above.

(*Received*, 12*th July* 1973; *Com.* 993.)

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