The Structures of the $Hg_2Br_6^{2-}$ Ion and a Novel Triphenylarsine Oxide Derivative Containing a Short Hydrogen Bond

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IN a recent Paper[1] we reported the preparation of several hydroxytriphenylarsonium salts, including $[Ph_3AsOH^+]_2HgHal_4^{2-}$ (Hal = Br or Cl) and $[Ph_3AsOH^+]ClO_4^-$. We have now demonstrated that by the general reaction:

$$2Ph_3AsO,H_2O + 2HHal + HgHal_2 \rightarrow [Ph_3AsOH^+]_2HgHal_4^{2-} + 2H_2O$$

in aqueous solution, the same tetrachloromercurate(II) derivative is isolated whereas an entirely different bromo-compound is obtained. The new bromo-compound is a white crystalline substance, m.p. 146—147° [*cf.* 156–158° of the expected $(Ph_3AsOH^+)_2HgBr_4^{2-}$] and the high value of specific conductance of its solutions in methyl cyanide points to an ionic formulation. In the infrared spectrum of the solid, however, the strong broad absorption in the region 2800—3000 cm.$^{-1}$, characteristic of the Ph_3AsOH^+ ion (OH stretching), is totally absent. These facts and the results of elemental analysis led us to consider the formulation

$$[\mathrm{Ph_3As^+OAs(Ph_3)OAs(Ph_3)OAs^+Ph_3}][\mathrm{HgBr_3}^-]_2,$$

$\{[\mathrm{A}]^+.[\mathrm{HgBr_3}^-]_2$ for short$\}$ as a possible one. A condensed dipositive ion of this type, although unusual, did not seem improbable and the analytical, spectral, and conductance data of several other compounds obtained[1] in a similar fashion from aqueous media also accorded with a formulation involving this cation *e.g.*, $\mathrm{A^{2+}(ClO_4^-)_2, A^{2+}(I_3^-)_2, A^{2+}PtCl_6^{2-}}$. However, in view of the novelty and uncertainty of the structure of the postulated species $[\mathrm{A^{2+}}]$, an *X*-ray crystal structure analysis has been carried out in Kuala Lumpur and Glasgow.

Crystals of the complex proved to be monoclinic, space group $C2/c$ with four formula units in a cell of dimensions: a = 25·18, b = 11·68, c = 25·41 Å, β = 90·3°. Ion symmetry $\bar{1}$ and/or 2 is thus demanded. For the *X*-ray data collection, Cu-K_α radiation and equi-inclination Weissenberg methods were used with a small crystal rotating about b. The co-ordinates of one mercury atom, four bromine atoms, and two arsenic atoms were obtained from a detailed examination of the three-dimensional Patterson function and completely explained it. An electron-density distribution prepared with the observed amplitudes and heavy-atom phases revealed all thirty-eight remaining non-hydrogen atoms. The atomic parameters have been improved by Fourier and full-matrix least-square methods. R is now 9% and refinement is continuing.†

Our atomic co-ordinates reveal that the compound must be reformulated as

$$(\mathrm{Ph_3As}\overset{\cdots}{-}\mathrm{O}\cdots\overset{+}{\mathrm{H}}\cdots\mathrm{O}\overset{\cdots}{-}\mathrm{AsPh_3})_2\mathrm{Hg_2Br_6}^{2-},$$

$$\{(\mathrm{B^+})_2\mathrm{Hg_2Br_6}^{2-} \text{ for short}\}.$$

Views of the anion and cation are shown in Figures 1a and 1b, respectively.

The anions are discrete $[\mathrm{Hg_2Br_6}]^{2-}$ units with a precise crystallographic 2-fold symmetry. Each mercury atom is bonded approximately tetrahedrally to four bromine atoms, two of which lie on a diad axis and act as bridges linking the mercury atoms. Some distances and angles are shown in Figure 1a.

The cations possess no crystallographic symmetry but pairs of cations separated by van der Waals distances are situated around centres of symmetry. The arsenic–oxygen distances in the cation are virtually identical with a mean value 1·68 ± 0·02 Å. In triphenylarsine oxide monohydrate[2] the As=O distance is 1·64 ± 0·02 Å, while in the 1 : 1 complex of triphenylarsine oxide with mercuric chloride[3] the As=O distance is 1·66 ± 0·02 Å. In *o*-phenylenediarsine oxychloride[4] the As–O distance is 1·69 Å.

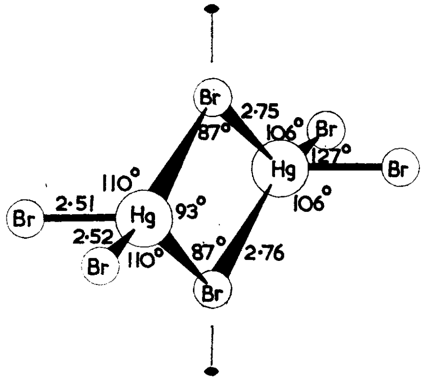

FIGURE 1a. *Bond lengths and angles in the* $\mathrm{Hg_2Br_6}^{2-}$ *ion.*

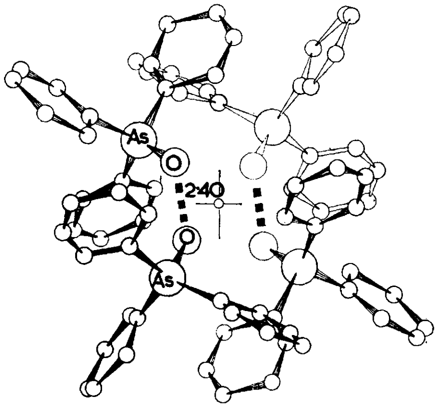

FIGURE 1b. *The arrangement of the*
$[\mathrm{Ph_3As\text{–}O\cdots H\cdots O\text{–}AsPh_3}]^+$
ions around the centre of symmetry at (¼, ¼, 0).

The similarity of the As–O bond lengths in the present case can only be explained if each arsenic atom in the ion shares the unipositive charge and each As–O bond has a 0·5 π-bond order. The hydrogen atom, which must be present to maintain charge balance in the complex, links the two oxygen atoms in a hydrogen bond. From the shortness of this bond (2·40 ± 0·03 Å) and the essentially similar nature of the $\mathrm{Ph_3AsO}$ moieties

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† Using programmes devised by the Glasgow Crystallography Group.

it is likely that the hydrogen atom is midway between the two oxygen atoms, although in this structure the possibility of finding it by *X*-ray methods is remote.

Identification of the cation as

$$[Ph_3AsO\cdots H\cdots OAsPh_3]^+$$

is supported by certain features of the infrared spectrum of the compound: (1) the absence of an observable OH stretching frequency above **1700** cm.$^{-1}$; (2) the presence of strong broad absorption in the range 1600—600 cm.$^{-1}$; (3) the presence of a transmission window at *ca.* 890 cm.$^{-1}$, the As=O stretching frequency in Ph_3AsO. These features correspond closely to those described by Hadži *et al.* as being characteristic of strongly hydrogen-bonded species with nearly symmetrical H-bonds, and on very similar spectral evidence Hadži assigned[5] the structure

$$[C_6H_7N{\rightarrow}O\cdots H\cdots O{\leftarrow}NC_6H_7]^+Br^-$$

to the 2 : 1 adduct of 2-picoline-*N*-oxide with HBr and this has been confirmed[6] by Mills and Speakman's crystal structure analysis.

Since the other compounds which were at first formulated as derivatives of the A^{2+} cation have closely similar i.r. spectra it seems likely that their correct description involves the B^+ cation, *viz.*, $B^+ClO_4^-$,$B^+I_3^-$, and $(B^+)_2PtCl_6^{2-}$. On this basis their analytical and conductance properties are equally well (in fact marginally better) explained.

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