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Preliminary Communication

The preparation and structures of $\text{Ph}_3\text{AsGaI}_3$ and $[\text{Ph}_3\text{AsI}][\text{GaI}_4]$

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Abstract

Colourless crystals of $\text{Ph}_3\text{AsGaI}_3$ (1) have been prepared by reaction of triphenylarsine with $\text{GaI}_3 \cdot \text{OEt}_2$ in diethyl ether. The structure of 1, in which the length of the As–Ga donor–acceptor bond is 2.490(2) Å, has been determined by an X-ray diffraction study. In contact with the solvent phase, 1 is transformed into yellow crystals of $[\text{Ph}_3\text{AsI}][\text{GaI}_4]$, 2 which has been structurally characterised by Raman spectroscopy (As–I stretching at 196 cm^{-1}) and by X-ray diffraction. The salt 2 is the first arsenic(V) iodo complex to have been examined crystallographically; the As–I bond distance is 2.485(1) Å.

Key words: Gallium; Arsenic; Lewis acid–base adduct; Donor–acceptor

The gallium–arsenic bond attracts particular attention, not only in the context of gallium arsenide and single-source precursors for GaAs films [1,2], but also because it is present in monomeric compounds of the $\text{Ga}(\text{AsR}_2)_3$ type (containing suitable bulky ligands) and in a variety of four- and six-membered ring structures [2–4]. Despite this wide interest, which has included recent *ab initio* calculations of the structures of H_3GaAsH_3 [5] and $(\text{CH}_3)_3\text{GaAsH}_3$ [6], there seems to have been no experimental determination of the Ga–As distance in any Lewis acid–base adduct containing this bond.

To this end we prepared the compound $\text{Ph}_3\text{AsGaI}_3$ by adding the stoichiometric amount of triphenylarsine to the etherate $\text{GaI}_3 \cdot \text{OEt}_2$, made by the direct reaction of iodine with gallium metal in dry diethyl ether [7]. Colourless crystals were formed initially, but changed on standing for several days into another

crystalline solid which was yellow. Both products were investigated spectroscopically and by X-ray diffraction. The colourless crystals have the expected structure $\text{Ph}_3\text{AsGaI}_3$ which is shown in Fig. 1 [8*]. Coordination about both the As and Ga atoms is pyramidal, with bond angles $\text{C–As–C} = 105.5^\circ$ and $\text{I–Ga–I} = 115.1^\circ$. The Ga–As bond distance of 2.490(2) Å is much shorter than the value, of 2.82 Å, recently calculated for H_3GaAsH_3 [5], or 3.08 Å for $(\text{CH}_3)_3\text{GaAsH}_3$ [6]. Gallium–arsenic bond distances in four-membered Ga_2As_2 or six-membered Ga_3As_3 rings range from 2.45 to 2.59 Å [2]. The shortest Ga–As bond lengths recorded to date are 2.36 Å in the electron-rich Zintl anion $[\text{Ga}_2\text{As}_4]^{6-}$ [9] and 2.40 Å in $\text{PhAs}\{\text{Ga}(\text{Trip})_2\}_2$ (Trip = 2,4,6- $\text{iPr}_3\text{C}_6\text{H}_2$) [4], which may involve some π -bonding, whereas the donor–acceptor link of $\text{Ph}_3\text{AsGaI}_3$ can be viewed as a simple σ bond. The phenyl groups are partly staggered with respect to the iodine atoms, and this arrangement is probably due to crystal packing effects. The Raman spectrum [10*] of $\text{Ph}_3\text{AsGaI}_3$ displays a strong band at 141 cm^{-1} due to Ga–I stretching, although it may be better described as an in-phase stretching mode of Ga–As and Ga–I bonds since no separate band can be assigned to $\nu(\text{Ga–As})$. We have also observed the $\text{Ph}_3\text{AsGaI}_3$ adduct in solution by NMR spectroscopy [11*], the ^{71}Ga signal ap-

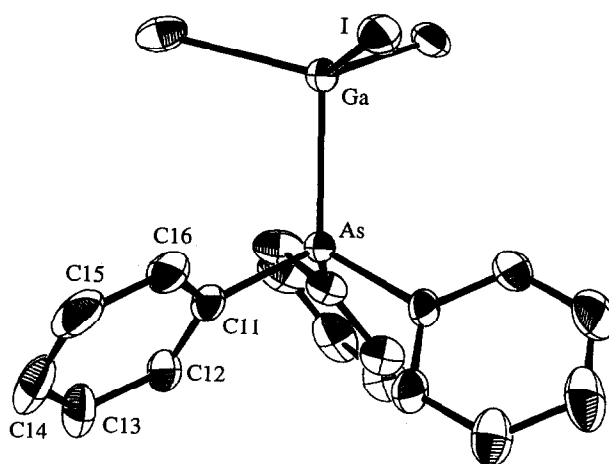


Fig. 1. View (ORTEP) of $\text{Ph}_3\text{AsGaI}_3$. Important bond distances (Å) and angles ($^\circ$): As1–Ga1 2.489(2), Ga1–I1 2.509(1), As1–C1 1.919(2), I1–Ga1–I1 115.11(1), C1–As–C1 105.49(8) torsion angle I–Ga–As–C1 81.6(1).

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* Reference number with asterisk indicates a note in the list of references.

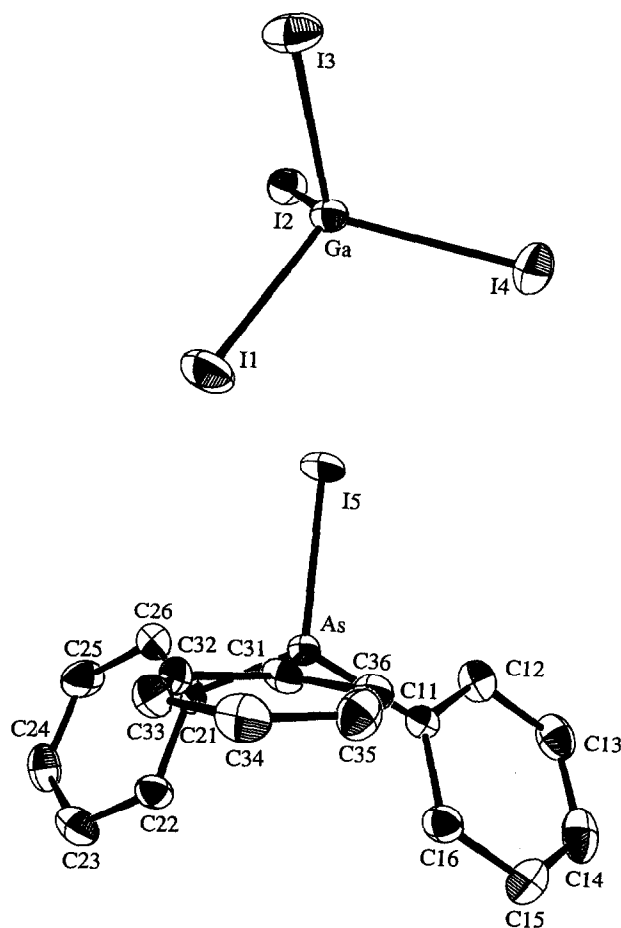


Fig. 2. View (ORTEP) of Ph_3AsI^+ and GaI_4^- . Important bond distances (Å): Ga–I 2.547(1) (average), As–I 2.485(1), As–C 1.914(8) (average).

pearing at -216 ppm, whereas that of the etherate $\text{GaI}_3 \cdot \text{OEt}_2$ appears at -225 ppm [12].

The structure of the yellow product, shown in Fig. 2 [13*], is that of an ionic complex $[\text{Ph}_3\text{AsI}][\text{GaI}_4]$. The arsenic atom of the $[\text{Ph}_3\text{AsI}]^+$ cation has very nearly regular tetrahedral coordination. The As–I distance is 2.485(1) Å, and this appears to be the first measurement of this bond length in an arsenic(V) compound. Although the salt $[\text{AsI}_4][\text{AlCl}_4]$ has been isolated previously, it was highly unstable and it was characterised only by Raman spectroscopy at -110°C [14]. The bond length in the AsI_3 molecule is 2.577 Å and in solid arsenic triiodide (a layer-lattice) it is 2.59 Å [15]. Group 15 cations closely akin to $[\text{Ph}_3\text{AsI}]^+$ are $[\text{Ph}_3\text{PI}]^+$ and $[\text{Ph}_3\text{SbI}]^+$ [16]. The P–I bond length in $[\text{Ph}_3\text{PI}]^+$ is 2.38 Å, which is 0.10 Å less than the As–I distance of $[\text{Ph}_3\text{AsI}]^+$, and this difference matches that between the covalent radii of P and As atoms [17]. Likewise, the As–C (phenyl) distance is 1.915 Å while that of P–C is 1.83 Å. The Raman spectrum [10*] of $[\text{Ph}_3\text{AsI}][\text{GaI}_4]$

reveals, in addition to the characteristic bands of the $[\text{GaI}_4]^-$ complex anion [18], including symmetric Ga–I stretching at 144 cm^{-1} , an additional intense band at 196 cm^{-1} . This can be attributed to As–I stretching, and its frequency agrees satisfactorily with that of 202 cm^{-1} assigned to this mode in the spectrum of the compound $[\text{Ph}_3\text{AsI}][\text{AsF}_6]$ in liquid SO_2 solution [19].

The dimensions of the $[\text{GaI}_4]^-$ ion have been measured once before, in the “diiodide” $[\text{Ga}][\text{GaI}_4]$, in which crystal packing effects and the influence of the Ga^+ counterion cause the anion to be severely distorted and to display unequal Ga–I bonds, three of 2.54 Å and one of 2.61 Å [20]. The Ga–I distance of 2.55 Å in $[\text{Ph}_3\text{AsI}][\text{GaI}_4]$ is close to the average of these values.

The cation $[\text{Ph}_3\text{AsI}]^+$ (stabilised here in the solid state by the accompanying $[\text{GaI}_4]^-$ ion, and in an earlier example [19] by $[\text{AsF}_6]^-$) is notable as a species in which arsenic in the +5 oxidation state bears iodine as a ligand. The existence of such salts prompts comparison with the iodine adducts of triphenyl arsine, $\text{Ph}_3\text{As} \cdot \text{I}_2$ and $\text{Ph}_3\text{As} \cdot \text{I}_4$, which long known [21] have only recently been elucidated by structural methods, with unexpected results [22–24]. Thus $\text{Ph}_3\text{As} \cdot \text{I}_2$ is a molecular complex with a structure based on a linear As–I–I shaft in which the As–I distance of 2.64 Å is considerably longer than the 2.485(1) Å found in $[\text{Ph}_3\text{AsI}]^+$. The compound $\text{Ph}_3\text{As} \cdot \text{I}_4$ is believed to be isostructural with $\text{Ph}_3\text{P} \cdot \text{I}_4$, and to be of the form $[(\text{Ph}_3\text{PI})_2\text{I}_3]^+ \text{I}_3^-$ [24], with significant interaction between the iodoarsonium ion and the triiodide ion.

The mechanism of formation of $[\text{Ph}_3\text{AsI}][\text{GaI}_4]$ from $\text{Ph}_3\text{AsGaI}_3$ is unclear. It may be related to the susceptibility of the Ga–As bond to cleavage by iodine and other halogens, and perhaps also by milder reagents, and this aspect merits further investigation.

References and notes

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