The First Gallium–Arsenic Compound containing a Single Ga_3As Unit: Isolation and Crystal Structure of $[(thf)Br_2Ga]_3As$ (thf = tetrahydrofuran)

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$[(thf)Br_2Ga]_3As$ (thf = tetrahydrofuran), isolated from the products of the reaction of $(Me_3Si)_3As$ with $GaBr_3$, has been shown by *X*-ray crystallographic analysis to be the first example of a compound containing a single Ga_3As unit.

Prior to 1986, there were no published examples of gallium–arsenic compounds containing a single As_3Ga or Ga_3As unit. However, during that year two compounds of the first type having three-co-ordinate Ga and three-co-ordinate As were reported, $(R_2As)_3Ga$ (R = mesityl[1] or Bu^t[2]). We now report the isolation and structure of a compound of the second type having, in this initial case, four-co-ordinate Ga and three-co-ordinate As, $[(thf)Br_2Ga]_3As$ (thf = tetrahydrofuran) (**1**). The reaction of $(Me_3Si)_3As$[3] with $GaBr_3$, which affords the $(Br_2Ga)_3As$ species found in (**1**), appears to be the first reported of a tri(silyl)arsine being utilized to form the Ga–As linkage, and it further demonstrates the importance of silylarsines in the area of preparative gallium–arsenic chemistry.[4]

A toluene solution of $(Me_3Si)_3As$ (1.39 mmol), cooled to −15 °C, was added† to a toluene solution of $GaBr_3$ (4.18 mmol) at −15 °C. After 15 h at −15 °C, stirring at room temperature for 24 h, and removal of solvent and Me_3SiBr (100% yield) *in vacuo*, a yellow powder was obtained. A thf

† All manipulations were performed under a dry nitrogen atmosphere.

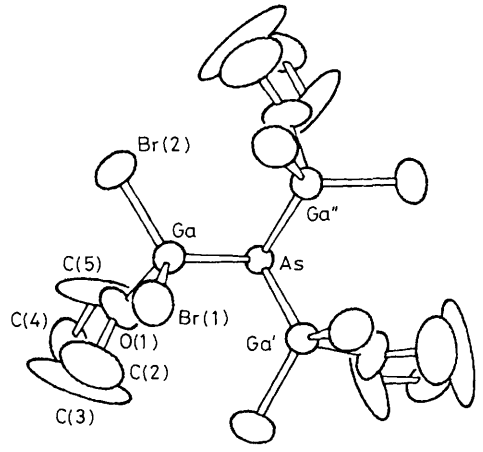

Figure 1. ORTEP plot of $[(thf)Br_2Ga]_3As$ (**1**). Selected distances (Å) and angles (°): Ga–As 2.401(4), Ga–Br(1) 2.321(5), Ga–Br(2) 2.341(7), Ga–O(1) 1.99(2), Ga–As–Ga' 94.4(1), As–Ga–Br(1) 124.0(2), As–Ga–Br(2) 115.4(2), As–Ga–O(1) 102.5(7), Br(1)–Ga–Br(2) 110.5(2), Br(1)–Ga–O(1) 99.2(6), Br(2)–Ga–O(1) 100.1(9).

solution of the powder at −15 °C afforded, after several days, $[(thf)Br_2Ga]_3As$ (**1**) as pale yellow crystals (0.37 g, 27% yield).‡

The structure of (**1**) is illustrated in Figure 1.§ The As atom lies on a crystallographic C_3 axis and, with a Ga–As–Ga′ angle of 94.4(1)°, the Ga_3As skeleton is pyramidal. At Ga, the geometry is distorted from tetrahedral in response to the different steric demands of the substituents. Thus, the three smallest bond angles (mean 100.6°) all involve the thf oxygen atom while the larger of the significantly different As–Ga–Br angles [As–Ga–Br(1) 124.0(2)°, As–Ga–Br(2) 115.4(2)°] is associated with the Ga–Br bond which more nearly eclipses an As–Ga bond [dihedral angles: Br(1)–Ga–As–Ga′ 16.5°, Br(2)–Ga–As–Ga″ 63.7°]. The Ga–As bond length, 2.404(4) Å, is the shortest distance yet recorded for a bond between a four-co-ordinate Ga and a three-co-ordinate As. It is significantly smaller than that of 2.437(1) Å in $\{[(Me_3SiCH_2)_2As]_2GaBr\}_2$ (previously the shortest recorded)[4b] and much shorter than the shortest [2.475(1) Å] of the two corresponding lengths in the cluster $[(PhAsH)(R_2Ga)(PhAs)_6(RGa)_4]$ ($R = Me_3SiCH_2$)[5] as well as the shortest [2.470(1) Å] of four such distances in $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$.[6] Interestingly, the Ga–As bond length in (**1**) is also smaller than the shortest Ga–As distance [2.470(1) Å] in $(Mes_2As)_3Ga$[1] which contains three-co-ordinate Ga and three-co-ordinate As.

Finally, it should be noted that thus far we have been unsuccessful in our attempts to isolate a monomeric compound containing a Ga_3As unit having three-co-ordinate Ga and As; however, it is expected that with the appropriate substituents on Ga this should be possible.

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‡ Compound (**1**) m.p. 125—145 °C (decomp.). A satisfactory elemental analysis was obtained (C, H, and Br).

§ *Crystal data*: $C_{12}H_{24}AsBr_6Ga_3O_3$ (**1**), $M = 979.86$, trigonal, space group $R3c$, $a = b = c = 11.765(1)$ Å, $\alpha = \beta = \gamma = 107.04(1)°$, $U = 1354.7$ Å^3, $Z = 2$, $D_c = 2.402$ g cm^{-3}, μ(Cu-K_α radiation, $\lambda = 1.5418$ Å = 154.7 cm^{-1}. Crystal dimensions: 0.20 × 0.30 × 0.30 mm (sealed inside a thin-walled glass capillary). Intensity data (660 independent reflections) were recorded on an Enraf–Nonius CAD-4 diffractometer (Cu-K_α radiation, incident-beam graphite monochromator; ω–2θ scans, $\theta_{max.} = 55°$). The crystal structure was solved by direct methods. Full-matrix least-squares refinement [375 absorption-corrected reflections with $I > 3.0\sigma(I)$] of non-hydrogen atom positional and anisotropic thermal parameters converged at $R = 0.056$ [$R_w = 0.071$, $w = 1/\sigma^2(|F_o|)$]. Atomic co-ordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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