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THE FIRST GALLIUM-ARSENIC COMPOUND CONTAINING A SINGLE
GASAS UNIT ISOLAT (U) DUKE UNIV DURHAM NC DEPT OF
CHEMISTRY R L WELLS ET AL 28 OCT 87 N00014-83-k-0572

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The First Gallium-Arsenic Compound Containing
a Single Ga₃As Unit: Isolation and Characterization
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by

R. L. Wells, S. Shafieezad,
A. T. McPhail, and C. G. Pitt

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Department of Chemistry
Durham, NC 27706

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**The First Gallium-Arsenic Compound Containing
a Single Ga₃As Unit: Isolation and Crystal Structure
of [(thf)Br₂Ga]₃As (thf = tetrahydrofuran)**

**Richard L. Wells*, Soheila Shafieezad, Andrew T. McPhail,
and Colin G. Pitt***

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University,
Durham, NC 27706 U.S.A.

[(thf)Br₂Ga]₃As, isolated from the products of the reaction of (Me₃Si)₃As with GaBr₃, has been shown by X-ray crystallographic analysis to be the first example of a compound containing a single Ga₃As 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-coordinate Ga and three-coordinate As were reported, (R[□]₂As)[□]₃Ga (R = Mes⁽¹⁾_□, Bu^(t 2)_□). We now report the isolation and structure of a compound of the second type having, in this initial case, four-coordinate Ga and three-coordinate As, [(thf)Br[□]₂Ga][□]₃As (thf = tetrahydrofuran) (1). The reaction of (Me[□]₃Si)[□]₃As³ 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

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it further demonstrates the importance of silylarsines in the area of preparative gallium^{4a} arsenic chemistry. (Keywords: Gallium, Arsenic) ←

A toluene solution of $(\text{Me}_3\text{Si})_3\text{As}$ (0.41 g, 1.39 mmol), cooled to -15°C , was added† to a toluene solution of GaBr_3 (1.29 g, 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 (4.18 mmol, 100% yield) under vacuum, a yellow powder was obtained. A thf solution of the powder at -15°C afforded, after several days, $[(\text{thf})\text{Br}_2\text{Ga}]_3\text{As}$ (1) as pale yellow crystals (0.37 g, 27% yield).‡

The structure of (1) is illustrated in Figure 1.5 The As atom lies on a crystallographic \underline{C}_3 axis and, with a Ga-As-Ga' angle of $94.4(1)^\circ$, 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) $124.0(2)^\circ$, As-Ga-Br(2) $115.4(2)^\circ$] 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 at $2.404(4) \text{ \AA}$ is the shortest distance yet recorded for a bond between a four-coordinate Ga and a three-coordinate As. It is significantly smaller than that of $2.437(1) \text{ \AA}$ in $\{[(\text{Me}_3\text{SiCH}_2)_2\text{As}]_2\text{GaBr}\}_2$ (previously the shortest recorded)^{4b} and much less than the shortest [$2.475(1) \text{ \AA}$] of the two corresponding lengths in the cluster $[(\text{PhAsH})(\text{R}_2\text{Ga})(\text{PhAs})_6(\text{RGa})_4]$ ($\text{R} = \text{Me}_3\text{SiCH}_2$)⁵ as well as the shortest [$2.470(1) \text{ \AA}$] of four such distances in $\{[(\text{Me}_3\text{SiCH}_2)_2\text{As}]_3\text{Ga}\}_2$.⁶

Interestingly, the Ga-As bond length in (1) is also smaller than the shortest Ga-As distance [2.470(1) Å] in $(\text{Mes}_2\text{As})_3\text{Ga}^1$ which contains three-coordinate Ga and three-coordinate 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-coordinate Ga and As; however, it is anticipated that with the appropriate substituents on Ga this should be possible.

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Footnotes

† All manipulations were performed under a dry nitrogen atmosphere.

‡ 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 $R\bar{3}c$, $a = b = c = 11.765(1) \text{ \AA}$, $\alpha = \beta = \gamma = 107.04(1)^\circ$, $V = 1354.7 \text{ \AA}^3$, $Z = 2$, $D_c = 2.402 \text{ g cm}^{-3}$, $\mu(\text{Cu-K}\alpha \text{ radiation}, \lambda = 1.5418 \text{ \AA}) = 154.7 \text{ cm}^{-1}$. Crystal dimensions: 0.20 x 0.30 x 0.30 mm (sealed inside a thin-walled glass capillary). Intensity data (660 independent forms) were recorded on an Enraf-Nonius CAD-4 diffractometer (Cu-K α radiation, incident-beam graphite monochromator; ω -2 θ scans, $\theta_{\text{max.}} = 55^\circ$). 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, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Legend For Figure

Figure 1. ORTEP plot of $[(\text{thf})\text{Br}_2\text{Ga}]_3\text{As}$ (1). Selected distances (\AA) and angles ($^\circ$): 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).

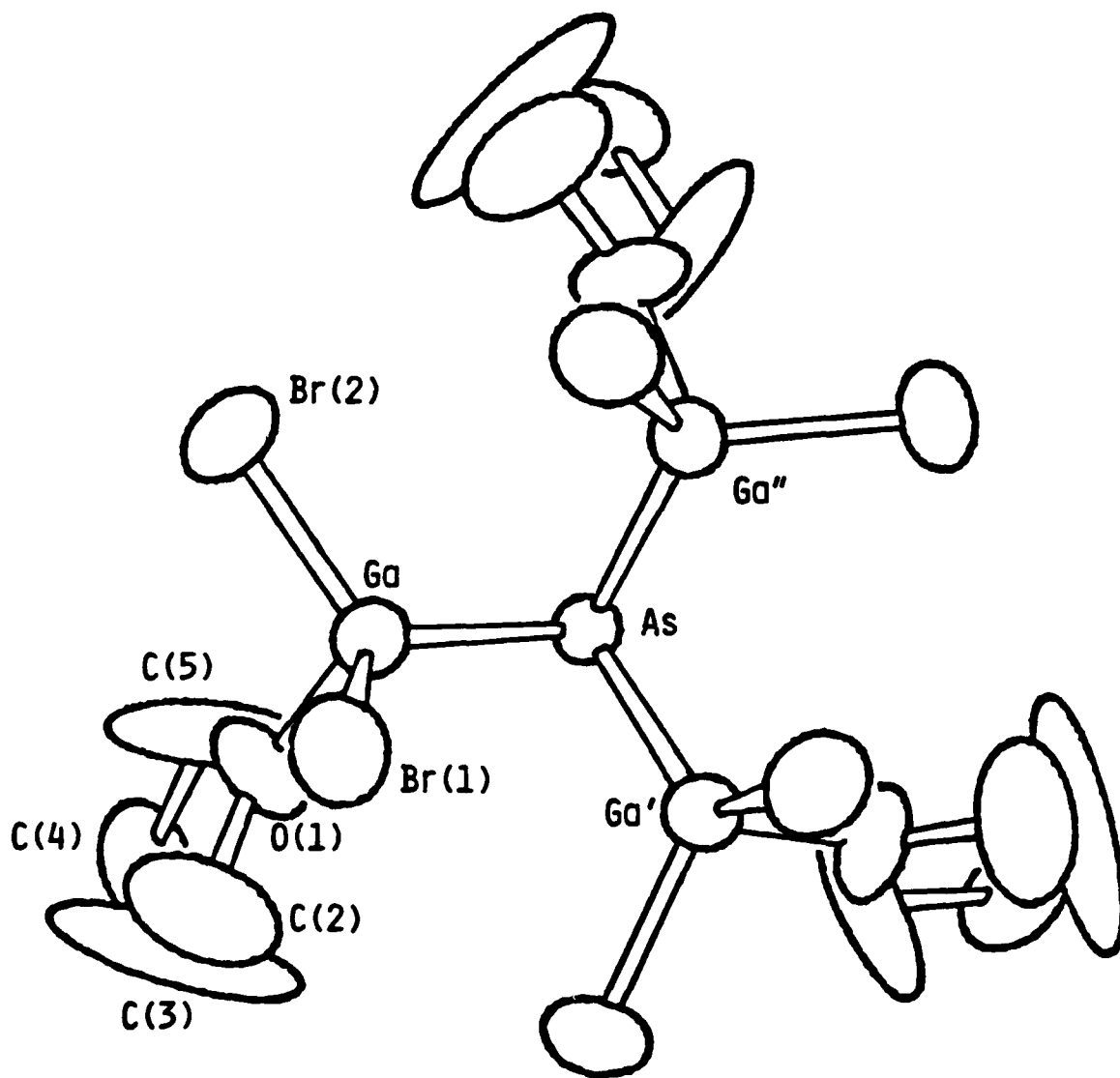


Figure 1

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