

Arachno-2-Gallatetraborane(10), H₂GaB₃H₈: Synthesis, Properties and Structure of the Gaseous Molecule as determined by Electron Diffraction

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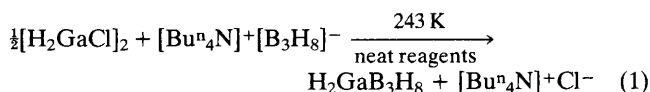
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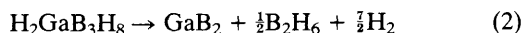
The novel hydride *arachno*-2-gallatetraborane(10), H₂GaB₃H₈, synthesised by metathesis involving monochlorogallane and tetra-*n*-butylammonium octahydridotriborate, is characterised by its spectroscopic and chemical properties; electron diffraction confirms the tetraborane(10)-like structure of the gaseous molecule.

As noted elsewhere,¹ monochlorogallane, [H₂GaCl]₂, is important as a potential source of other gallium hydrides. Thus, the reaction with LiGaH₄ at 243 K gives rise to the elusive binary hydride [GaH₃]_n,² and that with LiBH₄ at 250 K yields the mixed hydride gallaborane, GaBH₆.³

In addition, we find that monochlorogallane reacts with freshly recrystallised [Buⁿ₄N]⁺[B₃H₈]⁻ *in vacuo* at 243 K and in the absence of a solvent to yield a highly volatile product shown to be *arachno*-2-gallatetraborane(10), H₂GaB₃H₈, typically in yields of *ca.* 90% based on eqn. (1). Operations were performed at pressures <10⁻⁴ mmHg (1 mmHg ≈ 13.6 × 9.8 Pa) in all-glass apparatus, which had been preconditioned by heating under continuous pumping, with short distillation paths, and the maintenance of all glassware to which the compound had access at temperatures <283 K. 2-Gallatetraborane(10) condenses as a colourless, glassy solid which melts at *ca.* 178 K and has a vapour pressure at 210 K of *ca.* 1 mmHg.



In the condensed phases 2-gallatetraborane(10) decomposes rapidly at temperatures >283 K to produce metallic gallium, dihydrogen and tetraborane(10). At room temperature and a pressure of *ca.* 100 mmHg, the vapour has a half-life of *ca.* 30 min; the decomposition products are now diborane, dihydrogen, and a grey solid with the composition GaB₂ in the stoichiometric proportions required by eqn. (2), providing a means of chemical analysis.



The vibrational spectra of the compound imply the presence of a molecular unit common to the vapour, matrix-isolated and solid states. Reference to the vibrational spectra of compounds containing terminal GaH₂ units¹⁻³ and dihydrogen-bridged octahydridotriborate groups, *e.g.* Me₂GaB₃H₈⁴ and Me₂AlB₃H₈,⁴ points to a derivative of tetraborane(10), B₄H₁₀, with gallium replacing boron at the 2-position.

At temperatures of 193–273 K, solutions of the hydride in C₆D₅CD₃ display two ¹¹B magnetic resonances with relative intensities = 2 : 1. The response of the corresponding ¹H NMR spectrum to broad-band and selective ¹¹B decoupling is illustrated in Fig. 1. The high-frequency AB-type signal must be associated with the *exo*- and *endo*-protons of the GaH₂ unit; the corresponding doublet at δ_H 2.78–2.09 originates in the apical BH₂ unit; the resonance at δ_H 1.16 is due to the terminal protons at B(1) and B(3); and the resonances at δ_H -0.80 and -1.49 belong to the four bridging hydrogens in the molecule. Unlike Me₂GaB₃H₈,⁴ 2-gallatetraborane(10) does not appear to undergo rapid exchange of hydrogens, at least in the temperature regime studied.

The mass spectrum of the vapour is consistent with the presence of the GaB₃H₁₀ unit (⁷¹Ga¹¹B₃H₁₀ parent ion *m/z* = 114). The electron scattering of the vapour was recorded photographically on the Edinburgh apparatus,⁵ using an all-glass inlet system with the sample at 248 K and nozzle at 273 K. Despite problems of fogging caused by reaction of the vapour with the photographic emulsion, processing and analysis of the pattern were successfully accomplished by the procedures described previously.⁵⁻⁷ The scattering can be satisfactorily interpreted, like the spectroscopic properties, on

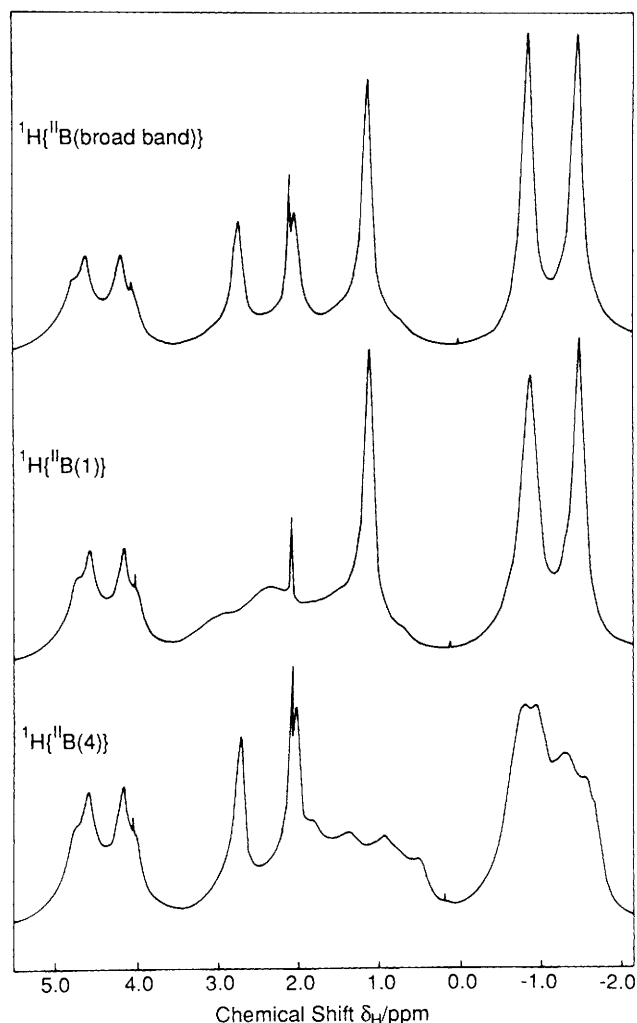


Fig. 1 ¹H NMR spectra of *arachno*-2-gallatetraborane(10) in C₆D₅CD₃ solution at 213 K measured at 300 MHz and showing the effects of broad-band and selective ¹¹B decoupling (the sharp resonance near δ_H 2.0 is due to the solvent)

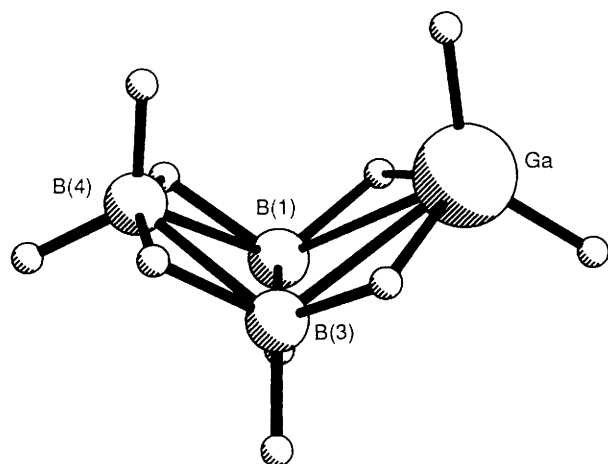


Fig. 2 Perspective view of *arachno*-2-gallatetraborane(10), $\text{H}_2\text{GaB}_3\text{H}_8$, according to the model used to simulate the electron-diffraction pattern of the gaseous molecule

the basis of the tetraborane(10)-like structure illustrated in Fig. 2. With the results derived from two nozzle-to-plate distances (*ca.* 200 and 260 mm), the structure has so far been refined to give $R_G = 0.09$. Parameters of interest (r_a) are $r[\text{Ga}-\text{B}(1)] = 231.2(0.5)$; $r[\text{B}(1)-\text{B}(4)] = 184.2(1.7)$; $r[\text{Ga}-\text{H}_a] = 144.5(1.2)$; $r[\text{Ga}-\text{H}_b] = 178.3(3.2)$ pm; and $114.8(0.8)^\circ$ for the dihedral angle between the planes $\text{GaB}(1)\text{B}(3)$ and $\text{B}(1)\text{B}(3)\text{B}(4)$. These are concordant with the dimensions (*i*) of the related species $\text{H}_2\text{Ga}(\mu\text{-H})_2\text{BH}_2$,³ $\text{Me}_2\text{GaB}_3\text{H}_8$,⁸ $\text{Me}_2\text{AlB}_3\text{H}_8$,⁸ B_4H_{10} ,⁹ and $\text{Cu}(\text{B}_3\text{H}_8)(\text{PPh}_3)_2$,¹⁰ and (*ii*) of 2- $\text{GaB}_3\text{H}_{10}$ as reproduced by recent *ab initio* molecular orbital studies.¹¹

The chemistry of 2-gallatetraborane(10) is now being explored. With ammonia it yields a white solid stable at room temperature, which on the evidence of its IR spectrum is most aptly formulated as $[\text{H}_2\text{Ga}(\text{NH}_3)_2]^+[\text{B}_3\text{H}_8]^-$.¹²

We thank Mr Paul T. Brain for assistance in recording the NMR spectra and the SERC both for a studentship (to C. R. P.) and for financial support of the Edinburgh electron-diffraction service (including a research assistantship to H. E. R.).

Received, 1st August 1990; Com. 0/03534C

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