Gallaborane, $H_2Ga(\mu\text{-}H)_2BH_2$: Synthesis, Properties, and Structure of the Gaseous Molecule as determined by Electron Diffraction

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The novel hydride gallaborane, $GaBH_6$, synthesised by metathesis involving monochlorogallane and lithium tetrahydridoborate, has been characterised by its spectroscopic and chemical properties; electron diffraction confirms that the gaseous molecule has a diborane-like structure, $H_2Ga(\mu\text{-}H)_2BH_2$.

As noted elsewhere,[1] monochlorogallane, $[H_2GaCl]_2$, conveniently synthesised by the reaction of Ga_2Cl_6 with an excess of Me_3SiH, represents an important precursor to other gallium hydrides. Thus, the reaction with $LiGaH_4$ at 243 K has revealed the elusive binary hydride $[GaH_3]_x$,[2] the vapour of which shows IR absorptions and electron-scattering[3] consistent only with the diborane-like molecule $H_2Ga(\mu\text{-}H)_2GaH_2$. Here we outline the synthesis and physical and chemical characterisation of the mixed hydride gallaborane, $GaBH_6$.

Monochlorogallane reacts with freshly recrystallised $LiBH_4$ *in vacuo* at 250 K and in the absence of a solvent to yield, in addition to small amounts of H_2 and B_2H_6, a highly volatile product shown to be gallaborane, typically in yields of *ca.* 80% based on equation (1). Operations were carried out at pressures $<10^{-4}$ mmHg (1 mmHg $\approx 13.6 \times 9.8$ 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 gallaborane had access at temperatures <263 K. Gallaborane condenses as a white solid which melts at *ca.* 228 K and has a vapour pressure at 195 K of *ca.* 1 mmHg.

$$1/2[H_2GaCl]_2 + LiBH_4 \xrightarrow[\text{neat reagents}]{250\,K} GaBH_6 + LiCl \quad (1)$$

In the condensed phases, gallaborane decomposes at temperatures exceeding 238 K (at a pressure of *ca.* 100 mmHg, the vapour has a half-life at room temperature in the order of 2 min), and the resulting quantitative formation of elemental gallium, diborane, and dihydrogen in the stoicheiometric proportions required by equation (2) provides a means of chemical analysis.

$$2GaBH_6 \rightarrow 2Ga + B_2H_6 + 3H_2 \quad (2)$$

The vibrational spectra of the gallaborane imply the presence of a molecular unit common to the vapour and matrix-isolated states and only slightly modified in the solid state. Reference to the vibrational spectra of compounds containing terminal GaH_2 units[1,2] and di-hydrogen bridged tetrahydridoborate groups,[4a] *e.g.*, Me_2GaBH_4[4b] and $HGa(BH_4)_2$,[4c] adduces strong circumstantial evidence for the molecule $H_2Ga(\mu\text{-}H)_2BH_2$ possessing C_{2v} symmetry. This conclusion is endorsed by the more-or-less well resolved rotational structure displayed by several IR absorptions of the vapour, and by the number, relative intensities, energies, and response to deuteriation of the observed vibrational transitions.

At temperatures of 153—238 K, solutions of the hydride in $C_6D_5CD_3$ or methylcyclohexane display the ^1H and ^{11}B magnetic resonances characteristic of a 'rigid' terminal GaH_2[2,5,6] and a 'fluxional' BH_4[4,6] unit in a molecule having the

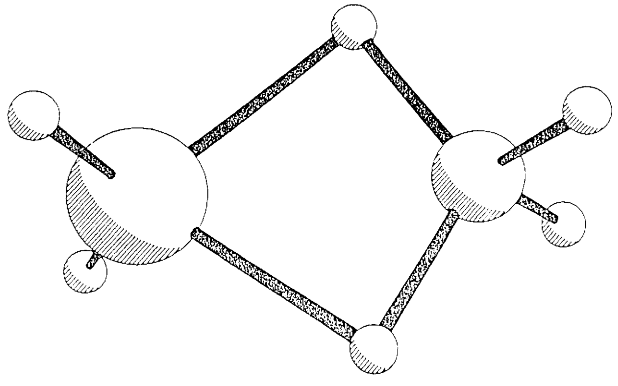
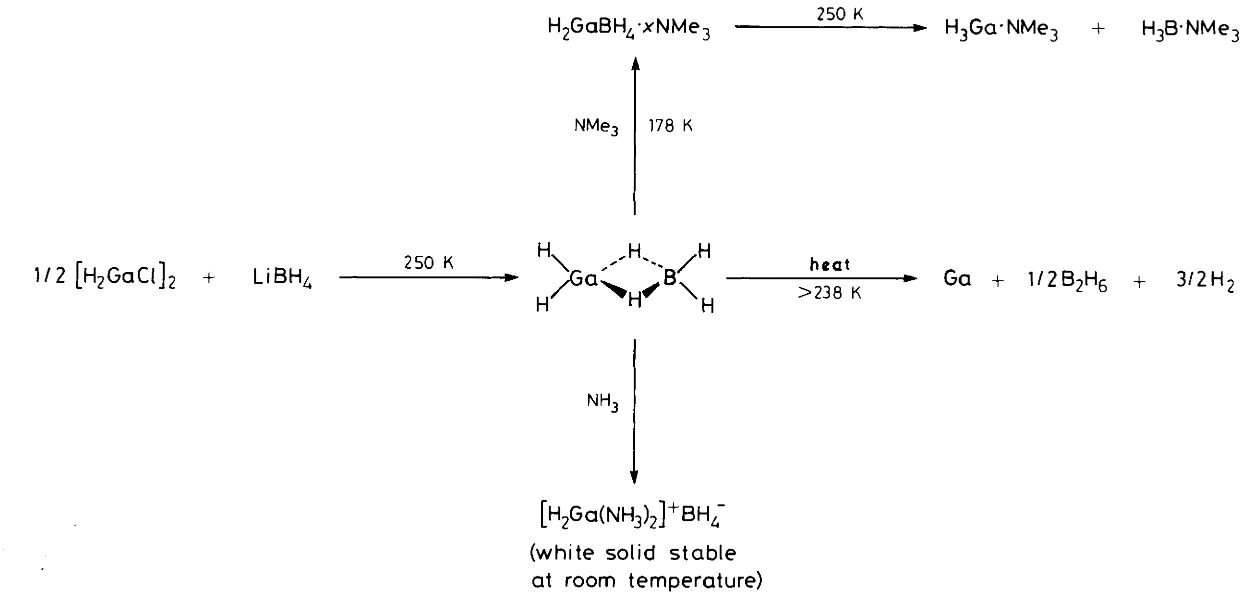


Figure 1. Perspective view of the molecule $H_2Ga(\mu\text{-}H)_2BH_2$ in the optimum refinement of the electron-diffraction analysis.

Table 1. Geometrical parameters (r_a)[a] for the gaseous molecules $H_2Ga(\mu\text{-}H)_2BH_2$, $Me_2Ga(\mu\text{-}H)_2BH_2$,[c] and $HGa\{(\mu\text{-}H)_2BH_2\}_2$.[d]

	Distance/pm or angle/°			
	$H_2Ga(\mu\text{-}H)_2BH_2$			
Parameter[e]	Experiment[b]	Theory[f]	$Me_2Ga(\mu\text{-}H)_2BH_2$	$HGa\{(\mu\text{-}H)_2BH_2\}_2$
$r(Ga\cdots B)$	217.9(0.2)	225.3	216.3(0.8)	217.2(0.5)
$r(Ga\text{–}X_t)$	158.6(0.8) (X = H)	159.5	194.4(0.4) (X = C)	156.5(2.4) (X = H)
$r(Ga\text{–}H_b)$	182.6(0.8)	179.8	179.1(3.0)	176.2—189.1
$r(B\text{–}H_b)$	133.4(0.8)	130.1	121.7(1.9)	125.0—145.6
$r(B\text{–}H_t)$	123.4(0.8)	119.9	119.2(1.9)	120.2(3.1)
$\angle H_b\text{–}Ga\text{–}H_b$	75.3(1.2)	70.5	68.4(4.6)	76.8(4.2)
$\angle H_b\text{–}B\text{–}H_b$	113.4(2.7)	105.8	111.8(3.8)	113.9(2.6)

[a] Estimated standard deviations given in parentheses. [b] This work. [c] Ref. 10. [d] Ref. 4c. [e] Subscript b = bridging, t = terminal. [f] Ref. 11a.



Scheme 1

formulation H_2GaBH_4. In addition, the spectra reveal the coexistence of a second component in dynamic equilibrium with the first, and whose properties point to a loosely bound aggregate, *e.g.*, $[H_2GaBH_4]_2$.[6] At temperatures above 243 K, decomposition becomes evident, with the appearance and growth of signals attributable to B_2H_6 and H_2 at the expense of those due to the two forms of the hydride.

The electron-scattering of gallaborane vapour was recorded photographically on the Edinburgh apparatus,[7] using a specially constructed all-glass inlet system[3] with the sample at *ca.* 238 K and nozzle at *ca.* 258 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.[7—9] The scattering can be satisfactorily interpreted, like the vibrational properties, on the basis of the structure $H_2Ga(\mu\text{-}H)_2BH_2$ illustrated in Figure 1. With the results derived from a single nozzle-to-plate distance (200 mm), the structure has so far been refined to give $R_G = 0.098$. The main parameters of interest are listed, together with those for the related molecules $Me_2Ga(\mu\text{-}H)_2BH_2$[10] and $HGa\{(\mu\text{-}H)_2BH_2\}_2$,[4c] in Table 1. The results provide not only cogent evidence for the expected diborane-like structure of the gallaborane molecule, but also the best definition yet of terminal and bridging Ga–H distances. In that they are also anticipated tolerably well by recent *ab initio* pseudopotential studies,[11a] they add reassuring substance to the increasingly lively theoretical speculation excited by this and related molecules.[11a,b]

The chemistry of gallaborane is now being explored, but the results of some preliminary experiments are incorporated in Scheme 1. As with gallane itself,[2] the compound claims particular attention through its reactions with bases containing Group 5 atoms as a possible new precursor to contaminant-free III-V semiconductors.[12]

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6 H_2GaBH_4 in $C_6D_5CD_3$ at 233 K has the following properties: (a) ^1H NMR (300 MHz) δ 1.05 (1 : 1 : 1 : 1 q, $J_{^{11}B\text{-}H}$ 89 Hz) and 5.0 [br. s (one-half the intensity of q at δ 1.05)]; (b) ^{11}B NMR (96.25 MHz) δ −24.0 p.p.m. (quintet). The ^1H and ^{11}B resonances of the second component **X** are close to those of monomeric H_2GaBH_4, but the $^1H\{^{11}B\}$ spectrum discloses that **X** is characterised, not by a singlet (*cf.* H_2GaBH_4), but by a *doublet* BH_4 resonance. This originates perhaps in an $[AB]_4$ system associated with two non-equivalent BH_4 groups, a feature consistent, in principle, with a dimer having for its skeleton a non-planar 8-membered ring composed of alternating GaH_2 and BH_2 groups linked *via* single hydrogen bridges (compare, for example, the structure of $[Me_2AlF]_4$: G. Gundersen, T. Haugen, and A. Haaland, *J. Organomet. Chem.*, 1973, **54**, 77).

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