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Preparation and Properties of Gallaborane, $GaBH_6$: Structure of the Gaseous Molecule $H_2Ga(\mu\text{-}H)_2BH_2$ As Determined by Vibrational, Electron Diffraction, and ab Initio Studies, and Structure of the Crystalline Solid at 110 K As Determined by X-ray Diffraction†

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Gallaborane ($GaBH_6$, **1**), synthesized by the metathesis of $LiBH_4$ with $[H_2GaCl]_n$ at ca. 250 K, has been characterized by chemical analysis and by its IR and ^1H and ^{11}B NMR spectra. The IR spectrum of the vapor at low pressure implies the presence of only one species, viz. $H_2Ga(\mu\text{-}H)_2BH_2$, with a diborane-like structure conforming to C_{2v} symmetry. The structure of this molecule has been determined by gas-phase electron diffraction (GED) measurements afforced by the results of ab initio molecular orbital calculations. Hence the principal distances (r_α in Å) and angles ($\angle_\alpha$ in deg) are as follows: r(Ga···B), 2.197(3); $r(Ga-H_t)$, 1.555(6); $r(Ga-H_b)$, 1.800(6); $r(B-H_t)$, 1.189(7); $r(B-H_b)$, 1.286(7); $\angle H_b-Ga-H_b$, 71.6(4); and $\angle H_b-B-H_b$, 110.0(5) (t = terminal, b = bridging). Aggregation of the molecules occurs in the condensed phases. X-ray crystallographic studies of a single crystal at 110 K reveal a polymeric network with helical chains made up of alternating pseudotetrahedral GaH_4 and BH_4 units linked through single hydrogen bridges; the average Ga···B distance is now 2.473(7) Å. The compound decomposes in the condensed phases at temperatures exceeding ca. 240 K with the formation of elemental Ga and H_2 and B_2H_6. The reactions with NH_3, Me_3N, and Me_3P are also described.

Introduction

The past decade has evinced a lively interest in gallium hydrides.[1−4] Synthetic advances have produced not only the binary hydride itself, $[GaH_3]_n$,[2,5] but also mono- or disubstituted derivatives, GaX_nH_{3-n}, where $n = 1$ or 2 and X = Cl,[6,7] NH_2,[8] NR_2,[4] N_3,[9] PR_2,[4] OR,[4] or R (R = an organic group).[4,10] Stabilization of the intrinsically labile GaH_n unit may be achieved (i) by making X very bulky (e.g. X = 2,4,6-Bu^t_3-C_6H_2)[4,10] and/or imparting additional coordinating capacity to it (e.g. X = NR_2[4] or 2,6-$(Me_2NCH_2)_2C_6H_3$[10]) or (ii) by *external* coordination to a suitable Lewis base (e.g. Me_3N, quinuclidine or Cy_3P).[4,11] Several of these compounds bid fair as precursors to epitaxial films or nanocrystals of gallium-containing semiconductor materials such as GaN;[4,8,9,11] others have found application in chemical synthesis.[4]

In terms of chemical vapor deposition (CVD), the most suitable sources are volatile compounds in which all extraneous bonds to the metal are easily and quantitatively cleaved. One compound clearly answering to this description is gallaborane ($GaBH_6$, **1**), the most volatile compound of gallium to be reported to date, although its instability at ambient temperatures is unlikely to command its widespread use for either CVD or synthetic operations. Here we report the synthesis and some of the physical and chemical properties of this compound. On the evidence of its IR spectrum and electron-diffraction pattern, the

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† This paper is dedicated by A.J.D. to Professor Hansgeorg Schnöckel of the Universität Karlsruhe to mark his 60th birthday.

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vapor of **1** at pressures up to about 50 Torr consists exclusively of the diborane-like molecules $H_2Ga(\mu\text{-}H)_2BH_2$, the structure of which has been determined by a combination of experimental and ab initio methods. Aggregation is the dominant feature of the condensed phases, as demonstrated unequivocally by the structure of a single crystal at 110 K; this has been shown by X-ray diffraction to comprise helical chains of alternating BH_4 and GaH_4 units each linked to its neighbors by two single hydrogen bridges. Chemical properties of **1** to be reported include its thermal decomposition (which provides a means of chemical analysis) and its reactions with the bases NH_3, NMe_3, and PMe_3. Preliminary accounts of some of these studies have appeared previously,[12,13] and the UV photoelectron spectrum of the gaseous molecule has also been reported.[14]

Results and Discussion

(a) Synthesis and Validation. As noted elsewhere,[2,4] monochlorogallane, $[H_2GaCl]_n$, conveniently synthesized by the reaction of gallium(III) chloride with an excess of Me_3SiH,[6,7] represents a potentially useful precursor to other monosubstituted derivatives of gallane, e.g. $H_2GaB_3H_8$[15] and H_2GaN_3.[9] We have found that monochlorogallane reacts with freshly recrystallized $LiBH_4$ in vacuo at ca. 250 K and in the absence of a solvent[2] to yield, in addition to small amounts of H_2 and B_2H_6, a highly volatile product shown to be gallaborane ($[H_2GaBH_4]_n$, **1**), formed in accordance with the metathesis reaction 1.

$$\frac{1}{n}[H_2GaCl]_n + LiBH_4 \xrightarrow[\text{ca. 250 K}]{\text{neat reagents}} \frac{1}{n}[H_2GaBH_4]_n + LiCl \qquad (1)$$

Compound **1** can be isolated by fractional condensation in vacuo of the volatile components of the reaction mixture, the vapor passing through a trap at 210 K but condensing in, and being retained by, a trap at 147 K. Fractionation gives a homogeneous product judged to be essentially pure gallaborane on the evidence of the spectroscopic properties to be described; the yields are typically about 80% on the basis of eq 1 and the quantity of monochlorogallane taken. The successful synthesis of **1**, like that of gallane, demands the use of scrupulously pure reagents and rigorous exclusion of moisture, oxygen, grease, or other contaminants;[2,5] accordingly, operations were carried out at pressures $<10^{-4}$ mmHg 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 at low temperatures as a white solid that melts at ca. 228 K. Crystals of the solid compound were formed adventitiously during attempts to grow single crystals by controlled freezing of what proved to be an impure sample of the bis(tetrahydroborate) ($[HGa(BH_4)_2]_n$, **2**), another thermally labile gallium hydride with a melting point near 200 K.[16] On synthesis from gallium(III) chloride, **2** is invariably accompanied by small amounts of **1**, from which it is not easily freed, and there is evidence too that the decomposition of **2** proceeds initially by the relatively facile reaction 2.

$$HGa(BH_4)_2 \rightarrow H_2GaBH_4 + \frac{1}{2}B_2H_6 \qquad (2)$$

X-ray crystallographic studies have led to the determination of the structure of a single crystal of **1** at 110 K, with the results to be described in section d. The rate of vaporization of pure **1** is consistent with a vapor pressure of ca. 1 Torr at 195 K. In the condensed phases, **1** decomposes rapidly at temperatures exceeding 238 K; the half-life of the vapor at room temperature is on the order of 2 min when the pressure is ca. 50 mmHg but can be extended significantly by operating at lower pressures.

As reported briefly elsewhere,[12] gallaborane has been authenticated chemically by quantitative assay of its decomposition products. Complete decomposition of a sample by warming to 343 K gives rise to elemental gallium and dihydrogen together with diborane, in accordance with reaction 3.

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

The identity and likely structure of **1** have been endorsed by its IR and ^1H and ^{11}B NMR spectra. The IR spectrum of the vapor at pressures up to 50 Torr argues strongly for the presence of the molecule $H_2Ga(\mu\text{-}H)_2BH_2$ with C_{2v} symmetry as the predominant species. This view is supported by an analysis of the electron diffraction pattern of the vapor at 240−260 K and by the results of ab initio calculations. The vibrational and NMR properties imply that aggregation of the $GaBH_6$ molecules occurs in solution and in the solid state, as borne out by the crystal structure.

(b) Properties of the Vapor. (i) IR Spectrum. IR spectra were recorded for isotopically normal and perdeuterated gallaborane vapor at pressures up to 50 Torr and near-ambient temperatures and for the vapor species isolated in solid dinitrogen matrixes at ca. 20 K. Representative spectra are illustrated in Figure 1, and the details are itemized in Table 1. Wavenumbers quoted in parentheses in the ensuing discussion refer to the perdeuterated compound.

The similarity of the IR spectra exhibited by the vapor and the solid N_2 matrixes indicates their origin in a common molecule. The pattern and frequencies of the absorptions, and particularly the clearly defined rotational structure characterizing many of the bands in the vapor spectrum, testify to a relatively simple molecule with a momental ellipsoid in which at least one of the principal moments of inertia is unusually small for a gallium derivative. Three features appear to give clear notice of the molecular identity.

(i) Many of the bands in the vapor spectrum display the rotational envelopes typical of a symmetric-top molecule. For example, the absorption at 2558 (1933.5) cm^{-1} clearly shows the P- and R-branches characteristic of a perpendicular-type transition of a symmetric top, and under high resolution, it is possible to discern the individual Q-branches corresponding to the transitions between different *K*-levels of the molecule. At ca. 3.5 cm^{-1}, the separation of these Q-branches points to a molecule with a very small moment of inertia about the principal axis, implying that only hydrogen atoms lie off this axis.

(ii) The strong doublet at 2558 (1933.5) and 2482 (1823) cm^{-1}, together with further prominent bands at ca. 2000 (1430), 1435 (1060), and 1130 (850) cm^{-1}, are the clear hallmarks of a bidentate BH_4 group,[17,18] analogous to that found in the molecule $Me_2Ga(\mu\text{-}H)_2BH_2$, for example.[19,20]

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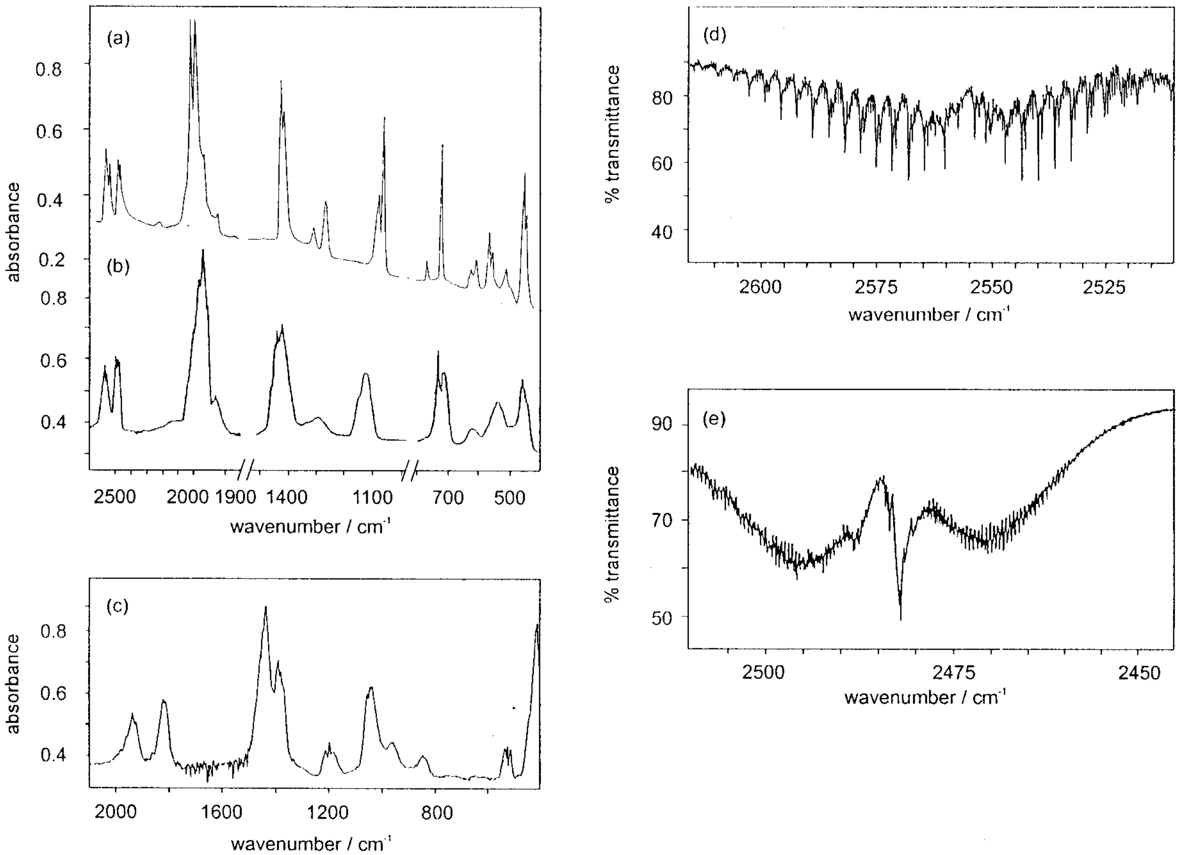

Figure 1. IR spectra of gallaborane and gallaborane-d_6 in the vapor or matrix-isolated states: (a) vapor of $GaBH_6$ isolated in a solid N_2 matrix at ca. 20 K; (b) vapor of $GaBH_6$; (c) vapor of $GaBD_6$; (d and e) ν_{14} and ν_1 bands of $GaBH_6$ vapor (pressure 0.15 Torr, path length 3.9 m, spectral resolution 0.06 cm^{-1}).

(iii) Absorptions near 2000 (1430) and at 729 (527) cm^{-1} suggest by their frequencies, contours, and H/D shifts that they originate in the stretching and scissoring vibrations, respectively, of a GaH_2 group [cf. $H_2Ga(\mu\text{-}X)_2GaH_2$, where X = H (ca. 1980 and 671 cm^{-1})[5] or X = Cl (ca. 2000 and 710 cm^{-1})[7]].

The IR spectrum is then most easily interpreted in terms of the diborane-like molecule $H_2Ga(\mu\text{-}H)_2BH_2$ with C_{2v} symmetry (Table 2). The 18 vibrational fundamentals are accommodated by the representation $7a_1 + 2a_2 + 4b_1 + 5b_2$, all but the $2a_2$ modes being IR-active. Earlier quantum chemical studies have predicted such a structure,[21] and the moments of inertia estimated from the optimum dimensions determined in this way imply that the molecule, although formally an asymmetric top, approximates to a prolate symmetric top, with $I_A = 8.394$ amu, $I_B = 65.449$ amu, and $I_C = 69.485$ amu Å^2 (1 amu = 1.6605×10^{-27} kg). With the choice of coordinate axes shown in Figure 2, a_1 modes are expected to give rise in the IR spectrum of the vapor to type-A bands, b_1 modes to type-C bands, and b_2 modes to type-B bands. Overall, the infrared bands are expected, and observed, to be those characteristic of a prolate asymmetric top; they are either type-A parallel bands, or type-B or -C perpendicular bands. Type-A bands should be recognizable by P-, Q-, and R-branches of comparable intensity and a P−R separation of about 20 cm^{-1}, type-B bands by a doublet structure also with a spacing of about 20 cm^{-1}, and type-C bands by a prominent Q-branch and relatively diffuse P- and R-branches.[22] With one very small moment of inertia (I_A) about the axis passing through the two heavy atoms, gallaborane may be expected in many respects to behave like B_2H_6 [23] so that, for example, Coriolis interactions due to rotation about the *A*-axis are likely to produce relatively large perturbations in the observed spectra.

Our interpretation leads to the vibrational assignments given in Tables 3 and 4. The analysis has been based on five main criteria: (a) the selection rules expected to govern the activity of modes in IR absorption; (b) the effect of deuteration on the energy of a given spectroscopic transition; (c) the envelope of the IR absorption displayed by the vapor (vide infra); (d) analogies with the vibrational properties of related molecules, notably Me_2GaBH_4,[19] $HGa(BH_4)_2$,[16] and $Al(BH_4)_3$;[24] and (e) comparisons with the frequencies and relative intensities of the absorptions forecast by ab initio calculations carried out previously[21] or by us. We attach particular weight to the evidence of the rovibrational features, the isotopic shifts, and the theoretical predictions, which has led to the unambiguous identification of most of the vibrational fundamentals.

There are some complications, however. First, the presence of two naturally occurring isotopes of boron, ^{10}B and ^{11}B,

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Table 1. IR Spectra of Gaseous and Matrix-Isolated Gallaborane and Gaseous Gallaborane-d_6 (Wavenumbers in cm^{-1})

vapor									
$GaBH_6$			$GaBD_6$				$GaBH_6$ in N_2 matrix		
$\tilde{\nu}$		intens[b]	$\tilde{\nu}$		intens[b]	$\tilde{\nu}_H/\tilde{\nu}_D$	$\tilde{\nu}$	intens[b]	assignment[b]
3670		vw							$\nu_5 + \nu_{14}$ (B_2)
2565	R	m, B	1940	R	m, B	1.3230:1	2558	m [c]	$\nu(B-H_t)$, ν_{14} (b_2)
2549	P		1927	P			2536	m	
2492	R	m, A	1828	R	m, A	1.3615:1	2482	m [c]	$\nu(B-H_t)$, ν_1 (a_1)
2482	Q		1823	Q			2465	m	
2472	P		1816	P					
2255		vw							$2\nu_5$ (A_1)
2217		vw, A					2220	vw	$\nu_{15} + \nu_{18}$ (A_1)
2156		vw, A							$\nu_4 + \nu_6$ (A_1)
2007		m, C	1450		m, C	1.3841:1	2018	s	$\nu(B-H_b)$, ν_{10} (b_1)
2005		m, B	1447		m, B	1.3856:1	1992	s, br	$\nu(Ga-H_t)$, ν_{15} (b_2)
1982		w, A	1428		w, A	1.3880:1	1965	m	$\nu(Ga-H_t)$, ν_2 (a_1)
1950	R	m, A	1383		m, A	1.4006:1	1925	m	$\nu(B-H_b)$, ν_3 (a_1)
1937	Q								
1925	P								
1870		mw, C					1870	w	$\nu_5 + \nu_{12}$ (B_1)
1575		vw, A							$2\nu_{12}$ (A_1)
1532		vw, A							$\nu_{16} + \nu_{17}$ (A_1)
1446	R	s, A	1066	R	s, A	1.3538:1	1432	s [c]	$\nu(Ga-H_b)$, ν_4 (a_1)
1435	Q		1060	Q			1422	s	
1426	P		1053	P					
1350		vw, B							$\nu_{16} + \nu_{17}$ (B_2)
1315		w, C	980		w, C	1.3418:1	1330	w [c]	$\nu(Ga-H_b)$, ν_{11} (b_1)
							1290	m	
1130		m, A?	850		w, A	1.3294:1	1125	m [c]	$\delta[B(H_t)_2]$, ν_5 (a_1)
							1120	m	
							1105	s	
930		vw, B	670		w, B?	1.3881:1			$\rho[B(H_t)_2]$, ν_{16} (b_2)
782		vw, C					770	w	$\rho[B(H_t)_2]$, ν_{12} (b_1)
741	R	m, A	537	R	m, A	1.3833:1	730	s	$\delta[Ga(H_t)_2]$, ν_6 (a_1)
729	Q		527	Q					
718	P		515	P					
620		w, B?	442		m, B?	1.4027:1	630	w [c]	$\rho[Ga(H_t)_2]$, ν_{17} (b_2)
							612	w	
544		m, C?	421		s, C?	1.2922:1	570	m [c]	$\rho[Ga(H_t)_2]$, ν_{13} (b_1)
							560	m	
468		m, A	412		s, A	1.1359:1	460	s [c]	$\nu(Ga\cdots B)$, ν_7 (a_1)
							452	m	

[a] Key: s, strong; m, medium; w, weak; v, very; br, broad. P, Q, and R refer to rotational branches, A, B, and C to band types (see the text). [b] Based on the structure $H_2Ga(\mu\text{-}H)_2BH_2$ with C_{2v} symmetry. [c] Matrix splitting.

Table 2. Fundamental Modes of the $GaBH_6$ Molecule in C_{2v} Symmetry

		$H_2Ga(\mu\text{-}H)_2BH_2$ with C_{2v} symmetry		
approx description of mode[a]	expected wavenumber range[b]/cm^{-1}	irred rep	no of IR-active modes	no of IR bands observed
$\nu(B-H_t)$	2400−2600	$a_1 + b_2$	2	2
$\nu(B-H_b)$ + ring def	1900−2100	$a_1 + b_1$	2	2
$\nu(Ga-H_t)$	1900−2050	$a_1 + b_2$	2	2
$\nu(Ga-H_b)$ + ring def	1200−1500	$a_1 + b_1$	2	2
$B(H_t)_2$ scissoring and twisting	1000−1200	$a_1 + a_2$	1	1
in-plane $\rho[B(H_t)_2]$	900−1000	b_2	1	1
out-of-plane $B(H_t)_2$ wagging	700−800	b_1	1	1
$Ga(H_t)_2$ scissoring	650−800	a_1	1	1
in-plane $\rho[Ga(H_t)_2]$	600−700	b_2	1	1
out-of-plane $Ga(H_t)_2$ wagging	500−600	b_1	1	1
$\nu(Ga\cdots B)$ ring def + $\nu(Ga-H_b)$	350−500	a_1	1	1
$Ga(\mu\text{-}H)_2BH_2$ bending	<500	b_2	1	
$Ga(\mu\text{-}H)_2B$ bridge twist	<500	a_2	0	

[a] Description of modes is based on those suggested for the analogous molecules Me_2GaBH_4,[19] $HGa(BH_4)_2$,[16] Ga_2H_6,[5] $Al(BH_4)_3$,[24] and $[H_2GaCl]_2$.[7] Key: t = terminal, b = bridging. [b] See, for example, refs 5, 7, 16−19, and 24.

produces overlapping absorptions; at high resolution the features due to the different isotopomers may be resolvable, but more often they blend. Contamination is another source of confusion with a compound as reactive and thermally labile as gallaborane. Small concentrations of $HGa(BH_4)_2$,[16] B_2H_6,[23] chlorogallanes,[7] and other impurities are difficult to exclude, and the sample of the deuterated compound was certainly contaminated with small amounts of incompletely deuterated isotopomers such as $GaBD_5H$. While sharpening the absorptions facilitated the identification of some near-degenerate transitions, matrix isolation tended also to introduce its own complications. Thus, several of the bands were split, presumably because the gallaborane molecules occupied different matrix sites, and although the spectrum underwent no marked changes when the

Table 3. Measured and Calculated Wavenumbers (in cm^{-1}), Assignments, and Product Rule Calculations for the Vibrational Fundamentals of the Molecules $GaBH_6$ and $GaBD_6$ in C_{2v} Symmetry[a]

irred rep	number of mode	description[b]	$GaBH_6$ $\tilde{\nu}_H$ obs	$GaBH_6$ $\tilde{\nu}_H$ calc	$GaBD_6$ $\tilde{\nu}_D$ obs	$GaBD_6$ $\tilde{\nu}_D$ calc	$\tilde{\nu}_H/\tilde{\nu}_D$ (obs)	$\Pi(\tilde{\nu}_H/\tilde{\nu}_D)_i$[c] calc	$\Pi(\tilde{\nu}_H/\tilde{\nu}_D)_i$[c] obs
a_1	1	sym $\nu(B-H_t)$	2482	2551.9	1823	1877.6	1.3615	7.7318	7.4849
	2	sym $\nu(Ga-H_t)$	1982	2030.3	1428	1472.4	1.3880		
	3	sym $\nu(B-H_b)$ + ring def	1937	1996.0	1383	1434.3	1.4006		
	4	sym $\nu(Ga-H_b)$ + ring def	1435	1473.3	1060	1081.4	1.3538		
	5	$B(H_t)_2$ scissor	1130	1143.6	850	870.3	1.3294		
	6	$Ga(H_t)_2$ scissor	729	712.4	527	531.9	1.3833		
	7	$\nu(Ga\cdots B)$ ring def + $\nu(Ga-H_b)$	468	461.9	412	439.4	1.1359		
a_2	8	$B(H_t)_2$ twist		1105.7		807.1		1.9922	
	9	$Ga(\mu-H)_2B$ bridge twist		464.3		319.0			
b_1	10	$\nu(B-H_b)$ + ring def	2007	1950.3	1450	1509.3	1.3841	3.4107	
	11	$\nu(Ga-H_b)$ + ring def	1315	1379.5	980	1013.3	1.3418		
	12	out-of-plane $B(H_t)_2$ wag	782	794.7		593.2			
	13	out-of-plane $Ga(H_t)_2$ wag	544	550.5	421	422.0	1.2922		
b_2	14	asym $\nu(B-H_t)$	2558	2639.9	1933.5	2012.2	1.3230	4.6892	
	15	asym $\nu(Ga-H_t)$	2005	2046.9	1447	1455.7	1.3856		
	16	in-plane $\rho[B(H_t)_2]$	930	957.8	670	740.9	1.3881		
	17	in-plane $\rho[Ga(H_t)_2]$	620	556.8	442	401.1	1.4027		
	18	$Ga(\mu-H)_2B$ bending	(212)[d]	214.5		140.7			

[a] The observed frequencies are taken from the IR spectra of the vapors and the calculated frequencies (unscaled) from MP2/6-311G* calculations. [b] Key: H_t, terminal H atom; H_b, bridging H atom. [c] The use of observed (anharmonic) vibration frequency data is expected to give an observed product several percent smaller than the calculated one (see ref 23, for example). [d] Value deduced from a possible combination mode.

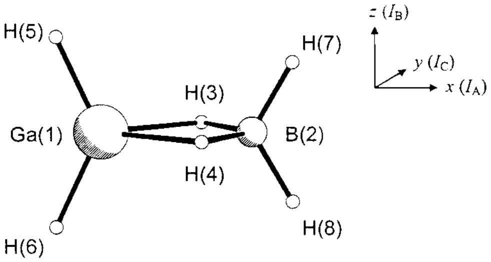

Figure 2. View of the $H_2Ga(\mu-H)_2BH_2$ molecule in the optimum refinement showing the coordinate axes and the axes of the momental ellipsoid.

Table 4. Geometrical Parameters Obtained in the New Analysis of the GED Data Collected for $GaBH_6$ (r_α/Å, $\angle_\alpha$/deg)

parameter[a]		GED[b]	ab initio[a]
	independent		
p_1	$r(Ga\cdots B)$	2.197(3)	2.192
p_2	$r(B/Ga-H)_{av}$	1.458(6)	1.452
p_3	$\Delta r(Ga-H_{b-t})$	0.245(6)	0.228
p_4	$\Delta r(B/Ga-H)_{av}$	0.440(5)	0.422
p_5	$\Delta r(B-H_{b-t})$	0.096(1)	0.0962(15)
p_6	$\angle H_t-B-H_t$	120.8(9)	121.1(10)
p_7	$\angle H_t-Ga-H_t$	130.1(9)	130.1(10)
	dependent		
	$r(Ga-H_b)$	1.800(6)	1.777
	$r(Ga-H_t)$	1.555(6)	1.549
	$r(B-H_b)$	1.286(7)	1.289
	$r(B-H_t)$	1.189(7)	1.193
	$\angle H_b-Ga-H_b$	71.6(4)	72.0
	$\angle H_b-B-H_b$	110.0(5)	108.3

[a] Values derived from B3PW91/6-311++G(2d,2p) calculation. Values quoted with uncertainties represent restraints applied in accordance with the SARACEN method; see the text for details. [b] Values in parentheses represent one standard deviation.

matrix was annealed at temperatures up to 33 K, there was also the risk that some of the weaker features arose not from the monomer but from aggregates, $[GaBH_6]_n$. There are limitations, too, imposed by the restricted wavenumber range of the current measurements (400−4000 cm^{-1}).

The clear doublet pattern of the absorptions near 2500 (1900) cm^{-1} must be associated with the $\nu(B-H_t)$ fundamentals (H_t = terminal H atom) of a bidentate BH_4 group.[16−19] The antisymmetric vibration, ν_{14} (b_2), is identifiable with the type-B band centered at 2558 (1933.5) cm^{-1}, and the symmetric vibration, ν_1 (a_1), with the type-A band at 2482 (1823) cm^{-1}, in compliance with the corresponding modes of the molecules $HGa(BH_4)_2$ [16] and Me_2GaBH_4.[19] This part of the spectrum is also strongly reminiscent of the corresponding region in the spectrum of B_2H_6 that features a type-B band at 2609 cm^{-1} and a type-A band at 2520 cm^{-1},[23] and the resemblance extends to the isotopic shifts. Thus, the H/D ratios and $^{10}B-^{11}B$ shifts are as follows: (a) for gallaborane, ν_{14} 1.3230:1 and 13.7 cm^{-1}; ν_1 1.3615:1 and 6.0 cm^{-1}; for diborane, ν_8 (b_{2u}) 1.3197:1 and 13.9 cm^{-1}; ν_{16} (b_{3u}) 1.3714:1 and 5.3 cm^{-1}.[23] On this evidence it is reasonable to conclude that the dimensions of the BH_2 unit in $GaBH_6$ are close to those in B_2H_6, where the best experimental estimates of $r_0(B-H_t)$ and $\angle_0 H_t-B-H_t$ are 1.201(2) Å and 121.0(4)°, respectively;[25] such a conclusion finds support too in the results of ab initio calculations (q.v.).

The two $\nu(Ga-H_t)$ [ν_2 (a_1) and ν_{15} (b_2)] and one of the $\nu(B-H_b)$ modes [ν_{10} (b_1)] (H_b = bridging H atom) must together be responsible for the broad, intense absorption centered near 2000 (1440) cm^{-1}. This accounts for the complicated nature of the spectrum hereabouts and the difficulty in deciding on the precise assignments. The spectrum of the vapor reveals an obvious pseudo-perpendicular band centered at 2005 (1447) cm^{-1}, which is likely therefore to arise from ν_{10} and/or ν_{15}. Closer inspection under high resolution (0.06 cm^{-1}) shows that the spacing of the Q-branches is irregular and more complicated than in the absorption at 2558 cm^{-1} (see Figure 1). We believe that the feature actually comprises *two* overlapping pseudo-perpendicular vibrational transitions with near-coincident band origins. The overlapping results in four sets of Q-branches, namely two sets of very closely spaced lines associated with the $^{69}Ga/^{71}Ga$ components of the antisymmetric $\nu(Ga-H_t)$ mode, ν_{15}, and two sets of rather more widely spaced lines associated with the $^{10}B/^{11}B$ components of the antisymmetric $\nu(B-H_b)$ mode, ν_{10}. Support for this assignment comes from the band at 1447 cm^{-1} in the spectrum of $GaBD_6$ vapor, where the low-energy flank ($\Delta K = -1$) comprises two sets of regularly spaced Q-branches, the spacing of which identifies their origin in a

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(25) Duncan, J. L.; Harper, J. *Mol. Phys.* **1984**, *51*, 371.

$\nu(B-D_b)$ mode; the high-energy flank is more complicated, presumably because of overlap with the antisymmetric $\nu(Ga-D_t)$ feature. There is an obvious pseudo-parallel or type-A band at 1937 (1383) cm^{-1}; a $^{10}B/^{11}B$ isotopic shift of 3 (4) cm^{-1} identifies it as the symmetric $\nu(B-H_b)$ mode [ν_3 (a_1)]. The remaining a_1 mode [the symmetric $\nu(Ga-H_t)$ mode, ν_2] must then be responsible for a partially obscured absorption at 1982 cm^{-1} in the spectrum of $GaBH_6$ and for a more easily discerned band at 1428 cm^{-1} in the spectrum of $GaBD_6$. The detailed assignments proposed in Tables 3 and 4 are fortified by the results of the quantum chemical calculations and by the frequencies of analogous modes in the molecules $HGa(BH_4)_2$,[16] Me_2GaBH_4,[19] Ga_2H_6,[5] and $[H_2GaCl]_2$.[7]

For each of the two $\nu(B-H_b)$ fundamentals there is an analogous mode approximating to $\nu(Ga-H_b)$ (while having significant $Ga(\mu\text{-}H)_2B$ ring deformation character), which is of the same symmetry. Analogies with related molecules, e.g. Ga_2H_6,[5] $HGa(BH_4)_2$,[16] Me_2GaBH_4,[19] and $Me_2Ga(\mu\text{-}H)_2GaMe_2$,[26] imply that these two modes are likely to occur in the region 1150−1450 (850−1100) cm^{-1}. The prominent type-A band at 1435 (1060) cm^{-1} is then the obvious choice for the a_1 mode, ν_4. The b_1 mode, ν_{11}, is harder to identify positively, being only weak in IR absorption, but it can reasonably be linked to the weak absorption at 1320 (980) cm^{-1}.

Next in order of decreasing frequency comes the $B(H_t)_2$ scissoring mode, ν_5 (a_1), for which the band at 1130 (850) cm^{-1} is the logical choice. Such an assignment is in keeping with the frequencies of the corresponding fundamentals in Me_2GaBH_4,[19] $HGa(BH_4)_2$,[16] and $Al(BH_4)_3$.[24] Although a type-A contour is clearly in evidence for the band of $GaBD_6$ at 850 cm^{-1}, it is far from obvious in the case of the 1130 cm^{-1} band of $GaBH_6$, which gives the appearance of considerable pseudo-perpendicular character. A possible explanation of this is that the type-A absorption at 1130 cm^{-1} is coincident with a combination transition with the B_1 or B_2 representation. Such a combination might be ν_9 (a_2) + ν_{17} (b_2) (setting the IR-silent fundamental ν_9 at ca. 510 cm^{-1}). Somewhat lower in frequency and predicted to give a weak type-B absorption is the $B(H_t)_2$ in-plane wagging vibration, ν_{16} (b_2), which we associate with a weak feature at 930 (670) cm^{-1}. Another weak band, this time at 782 cm^{-1} and appearing to have a type-C contour (but without any obvious counterpart in the spectrum of the deuterated compound), is most probably due to the corresponding rocking vibration, ν_{12} (b_1).

The frequency, well-developed type-A contour, and precedent all support the attribution of the band of medium intensity at 729 (527) cm^{-1} to the $Ga(H_t)_2$ scissoring mode, ν_6 (a_1). Wagging and rocking motions of the $Ga(H_t)_2$ unit [ν_{17} (b_2) and ν_{13} (b_1)], expected to occur at successively lower frequency, are then identified with the features at 620 (442) and 544 (421) cm^{-1}, respectively. The measured spectrum shows only one other band of appreciable intensity. With a type-A contour and medium-to-strong intensity, this occurs at 468 cm^{-1} and is characterized by a relatively modest shift on deuteration (to 412 cm^{-1}), credentials leading us to associate it with ν_7 (a_1), a complex motion incorporating deformation of the $Ga(\mu\text{-}H)_2B$ ring with $Ga\cdots B$ stretching as a primary feature.

All but one of the 16 IR-active fundamentals of the $H_2Ga(\mu\text{-}H)_2BH_2$ molecule have thus been located with some confidence. The one absentee is the skeletal puckering vibration, ν_{18} (b_2), which is anticipated to lie below 250 cm^{-1}, i.e. beyond the low-frequency threshold of the current measurements. Calculation offers the only access we have to the IR-silent a_2 fundamentals, ν_8 and ν_9, which involve twisting motions of the $B(H_t)_2$ and $Ga(H_t)_2$ fragments; frequencies near 1200 and 500 cm^{-1} are thus estimated. The remaining features in the observed spectrum of gallaborane, all of low intensity, can be interpreted satisfactorily as overtones or combinations of fundamentals. A very weak absorption near 2220 cm^{-1} may be associated with the combination $\nu_{15} + \nu_{18}$, implying that $\nu_{18} = 212$ cm^{-1}. The medium-weak type-C band at 1870 cm^{-1} can realistically be attributed only to the combination $\nu_5 + \nu_{12}$ (B_1), for which the frequency should be ca. 1910 cm^{-1}. Hence significant Fermi resonance must occur between this combination and the adjacent b_1 fundamental ν_{10}. For those symmetry classes offering a complete or virtually complete set of observed frequencies, the proposed assignments are consistent with the operation of the product rule, as indicated by the results included in Table 3.

At high resolution (0.06 cm^{-1}) the pseudo-perpendicular band of gaseous $GaBH_6$ ($GaBD_6$) at 2558 (1933.5) cm^{-1} clearly exhibits a series of well-defined Q-branches with a separation of ca. 3.5 (1.8) cm^{-1}. A preliminary analysis of the 2558 cm^{-1} band by combination differences then gives values of 1.7579(10) and 1.7675(10) for $A' - \bar{B}'$ and $A'' - \bar{B}''$, respectively (where the rotational constants A' and $\bar{B}'$ relate to the $v = 1$ state and A'' and $\bar{B}''$ to the $v = 0$ state, $\bar{B}$ being the average of the constants B and C). To evaluate $\bar{B}'$ and $\bar{B}''$ it would be necessary to carry out a similar analysis of the rotational structure associated with a pseudo-parallel band, e.g. that at 2482 (1823) cm^{-1}. Further studies requiring still higher resolution (<0.01 cm^{-1}) are still under way to resolve the closely spaced rotational lines forming the P- and R-branches of the 2482 cm^{-1} band,[27] although the separation of ca. 0.51 cm^{-1} clearly signifies that $\bar{B}$ is on the order of 0.25 cm^{-1}. The earlier ab initio studies[21] furnish estimates for $\bar{B}''$ and $A'' - \bar{B}''$ of 0.2501 and 1.7581 cm^{-1}, respectively, in excellent agreement with these experimental values. Accordingly, there can be little doubt about the essential structural features of the $GaBH_6$ molecule.

As expected, the frequencies deduced from HF/6-311G(d) calculations are mostly higher than the experimental ones, but the overall level of agreement is highly satisfactory. Discrepancies are well within the range set by the frequency differences between harmonic (theoretical) and anharmonic (experimental) vibrations, by the various approximations inherent in the theoretical method, and by the uncertainties associated with some of the experimental frequencies that may be subject, for example, to appreciable perturbation under the action of Fermi resonance (cf. B_2H_6 [23]). Hence we conclude that the assignments proposed here are unlikely to be far wide of the mark, with all the evidence vouching for a molecule with the structure $H_2Ga(\mu\text{-}H)_2BH_2$ conforming to C_{2v} symmetry. We have not in the circumstances attempted a detailed refinement of the vibrational force field, but have drawn on the theoretically based field, with appropriate scaling of the constants, to estimate vibrational amplitudes. This supplementary information then becomes input to our analysis of the electron diffraction pattern of the gaseous molecule (q.v.) and so serves an important function in fixing the most reliable structure that can be determined experimentally from the data currently available to us.

(ii) Structure of Gaseous Gallaborane: Electron Diffraction Measurements. Earlier studies have repeatedly emphasized the technical problems of carrying out gas electron diffraction (GED) measurements on such labile molecules as gallaborane[12] and other gallium hydrides.[5,6,15,16,26] As with digallane,[5] it has

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(26) Baxter, P. L.; Downs, A. J.; Goode, M. J.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1990**, 2873.

(27) Pulham, C. R.; Law, M. M.; Newnham, D. A. Unpublished results.

been necessary to use an all-glass inlet system which can be adequately preconditioned and then cooled to minimize thermal decomposition of the compound. The first measurements were made with the Edinburgh apparatus,[12] but despite repeated attempts, it proved impossible to secure satisfactory, reproducible results except at one, relatively short camera distance (ca. 200 mm); otherwise, the experiments failed through extreme problems associated either with fogging of the photographic plates or with extraneous scattering due to decomposition products of the gallaborane. The problem of fogging was partially alleviated by extending the cold trap of the Reading apparatus so as to envelop the nozzle of the inlet.[7] Hence, a measure of success was achieved at a long camera distance (ca. 500 mm) but not at a shorter distance, where a series of experiments with different sample and nozzle temperatures and developing conditions failed to elicit measurable scattering at the sort of vapor pressures it was necessary to use. It was therefore decided to combine the results from Edinburgh and Reading to produce a data set extending to a maximum value of 20.0 Å^{-1} in the variable s ($= 4\pi\lambda^{-1} \sin \theta$, where 2θ is the scattering angle).

Theoretical Calculations. Taken alone, the GED pattern of gallaborane gives only limited guidance to the structural and dynamic properties of the molecule. To arrive at the best estimate of the molecular structure it has therefore been vital to supplement the GED findings not only with all possible information about the vibrational properties (as noted above), but also with the results of ab initio calculations carried out with the GAUSSIAN 94 suite of programs.[28] In keeping with the findings of earlier studies,[21] these calculations confirm that the global minimum in the potential energy surface corresponds to the C_{2v} equilibrium structure $H_2Ga(\mu\text{-}H)_2BH_2$. Particular attention has been paid to the response of the calculated structure parameters to the level of theory and the basis set employed. Hartree–Fock (HF), Møller–Plesset (MP2, MP3, and MP4), and density functional theory (DFT) treatments were deployed with the 6-311G basis set, incorporating varying numbers of diffuse and polarization functions. The calculation which most closely reproduces the experimental geometry is given in Table 4; a summary of the geometric parameters obtained from all calculations performed is available in the Supporting Information.

From this graded series of calculations it was observed that distances relating to the gallium atom [$r(\text{Ga}\cdots\text{B})$, $r(\text{Ga}-\text{H}_b)$, and $r(\text{Ga}-\text{H}_t)$] were most sensitive to the quality of calculation. Supplementing the 6-311G basis set with further polarization and diffuse functions gave rise to only minor structural changes overall, with bond distances shortening on average by no more than 0.005 Å as the basis set improved with any given level of theory. The only major exceptions to this rule were the $\text{Ga}-\text{H}_b$ and $\text{Ga}-\text{H}_t$ distances, which could shorten by as much as 0.015 Å when polarization functions were added to the hydrogen atoms at levels above MP2(FC).

While the choice of basis set expressed minimal influence on the values of geometric parameters, larger structural changes were observed with changing the level of theory. The most obvious example is the Ga$\cdots$B distance, the parameter best defined by the experimental GED data (vide infra), which varied by as much as 0.04 Å. Introducing higher order excitations to Hartree–Fock theory (MP2, MP3, and MP4) consistently returned parameter values longer than the experimental value by 0.02 Å. Interestingly, incorporating all electrons into the correlation treatment at the MP2 and MP3 level shortened this bond, in line with experiment, but unfortunately at this level rather erratic values were returned for the parameters $r(\text{Ga}-\text{H}_b)$ and $r(\text{Ga}-\text{H}_t)$, as indicated above. On balance, the most reliable geometries were determined at the B3PW91 DFT level, where the majority of parameter values are within two esds of the experimental geometry.

Modeling the geometric and dynamic properties of the central $\text{Ga}(\mu\text{-H})_2\text{B}$ ring of gallaborane must account for significant shrinkage effects. There may not be any vibrational modes with frequencies less than ca. 250 cm^{-1}, but precedent[7,16,32] suggests that the $\text{Ga}(\mu\text{-H})_2\text{B}$ ring-puckering mode, ν_{18}, is likely to have a large amplitude. Such large amplitude motion is better approximated by curvilinear motion, rather than the conventional rectilinear system. Thus, estimates of vibrational amplitudes (u and k) required in the GED analysis were obtained from the construction of a harmonic force field [MP2/6-311G(d) force constants] using the program SHRINK,[29] which was scaled against the experimental vibrational frequencies (vide supra) to correct for the systematic overestimation of force constants by the ab initio calculation.

Structural Model Used in the Analysis of the GED Data. In the light of the IR spectrum and of the present and earlier[21] quantum chemical calculations, the gaseous gallaborane molecule was assumed to resemble B_2H_6 with an equilibrium structure $H_2Ga(\mu\text{-}H)_2BH_2$ possessing C_{2v} symmetry (see Figure 2). The model adopted for simulation of the molecular scattering intensities was then defined by seven independent structural parameters. To reduce correlation effects between similar bond lengths, it should be noted that a number of parameters must be defined as average and difference pairs; this is standard practice in gas-phase electron diffraction work. The structural parameters were thus defined as (i) $r(\text{Ga}\cdots\text{B})$, (ii) $r(\text{B/Ga}-\text{H})_{\text{av}} = [r(\text{B}-\text{H}_t) + r(\text{B}-\text{H}_b) + r(\text{Ga}-\text{H}_t) + r(\text{Ga}-\text{H}_b)]$, (iii) $\Delta r(\text{Ga}-\text{H}_{b-t})$, (iv) $\Delta r(\text{B/Ga}-\text{H})_{\text{av}} = [r(\text{Ga}-\text{H})_{\text{av}} - r(\text{B}-\text{H})_{\text{av}}]$, (v) $\Delta r(\text{B}-\text{H}_{b-t})$, (vi) $\angle\text{H}_t-\text{B}-\text{H}_t$, and (vii) $\angle\text{H}_t-\text{Ga}-\text{H}_t$. A theoretical $sI_m(s)$ curve was adjusted simultaneously to the two intensity curves (derived from the different camera distances) using a unit weight matrix (Figure 4). Least-squares analysis[30] of the molecular scattering intensities has then been performed to refine the structure of the gallaborane molecule.

Refinement of the Structural Model. The presence of a large number of similar interatomic distances and of some parameters involving hydrogen (a poor scatterer of electrons) prevented a complete structure solution using only experimental data. Information obtained from theory has therefore been included to allow a complete structural determination using the SARACEN method.[31] The essential feature of SARACEN is that information calculated ab initio is introduced into the refinement procedure as additional observations (or restraints),

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(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*, Revision D.4; Gaussian, Inc.: Pittsburgh, PA, 1995.

(29) (a) Sipachev, V. A. *J. Mol. Struct. (THEOCHEM)* **1985**, *121*, 143. (b) Sipachev, V. A. In *Advances in Molecular Structure Research*; Hargittai, I., Hargittai, M., Eds.; JAI Press: Greenwich, 1999; Vol. 5, p 263.

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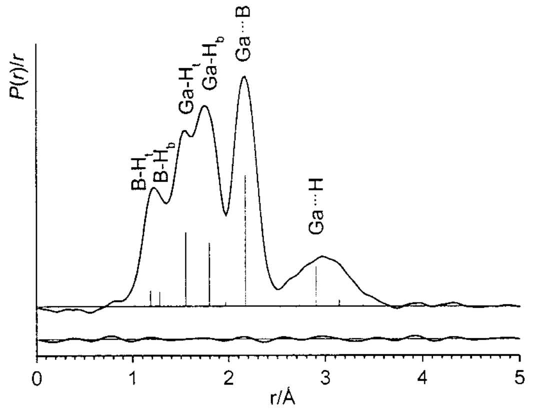

Figure 3. Observed and final difference radial distribution curves for $H_2Ga(\mu\text{-}H)_2BH_2$. Before Fourier inversion the data were multiplied by $s[\exp(-0.000\ 02s^2)/(Z_{Ga} - f_{Ga})(Z_B - f_B)]$.

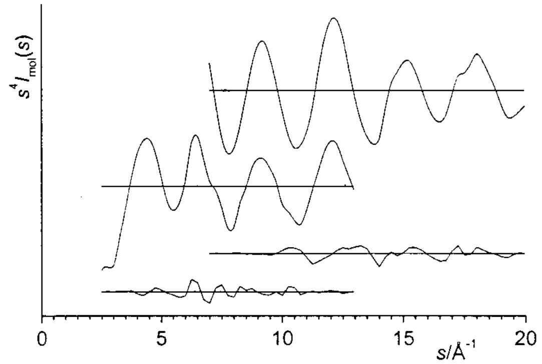

Figure 4. Observed and final difference combined molecular-scattering curves for $H_2Ga(\mu\text{-}H)_2BH_2$.

the weight of the observation being assigned according to the level of convergence achieved in a series of graded ab initio calculations. Using this approach it has been possible to refine the values of all structural parameters and all significant amplitudes of vibration *simultaneously* for the first time.

The radial distribution curve, $P(r)/r$ vs r, derived from the experiments after scaling, combination, and Fourier transformation, is depicted in Figure 3. In essence it comprises just four main peaks centered near $r = 1.25$, 1.70, 2.20, and 3.00 Å. The first two peaks correspond to scattering from the bonded atom pairs B−H and Ga−H, whereas peaks three and four are due primarily to scattering from the nonbonded atom pairs Ga···B and Ga···H, respectively. The best defined feature is r(Ga···B), which at 2.197 Å (cf. 2.192 Å from theory) is wholly consistent with a molecule containing a bis(hydrogen-bridged) $Ga(\mu\text{-}H)_2BH_2$ unit, as in $HGa(BH_4)_2$ [16] and Me_2GaBH_4,[20] rather than a mono- or tris(hydrogen-bridged) unit (cf. $H_2GaB_3H_8$[15] and $Me_2GaB_3H_8$[32]). There being observed no scattering corresponding to atom pairs with separations of more than 3.50 Å, we have every reason to suppose that gallaborane vapor, at pressures up to ca. 10 Torr and temperatures of 240−260 K, is essentially composed of monomeric molecules $GaBH_6$, with no significant contribution from any higher oligomer.

Defining all four B−H and Ga−H bond distances by parameter averages and differences (p_2 − p_5) greatly reduced the degree of correlation between these refining parameters, resulting in three of the four parameters refining to values exactly within the range predicted by theory (see Table 4). The parameter which failed to refine [p_5, $\Delta r(B-H_{b-t})$] corresponds to a feature which is too weakly defined on the radial distribution curve to be determined by GED data alone. It was therefore assigned a restraint, in accordance with the SARACEN method.[31] The two remaining parameters, p_6 ($\angle H_t-B-H_t$) and p_7 ($\angle H_t-Ga-H_t$), were also poorly expressed by the GED data, so they too were assigned restraints. For the three parameters so restrained, all values returned in the least-squares analysis were in very close agreement with the imposed values and the uncertainties slightly smaller. This demonstrates an important principle behind the SARACEN method: if a parameter refines to give a value and standard deviation in exact agreement with its restraint, then clearly no information regarding this parameter is contained within the GED data. If, however, the same value and a lower standard deviation are returned, then some experimental information must be present, since the same information is effectively delivered twice (i.e. once from the restraint and once from the experimental data).

Table 5. Bond Distances (r_a/Å) and Amplitudes of Vibration (Å) for Gallaborane Obtained in the GED Refinement

	atom pair	distance	amplitude
1	B(2)···Ga(1)	2.173(4)	0.108(5)
2	H(5)−Ga(1)	1.551(6)	0.086(13)
3	H(3)−Ga(1)	1.798(6)	0.047(17)
4	H(7)···Ga(1)	2.904(9)	0.308(22)
5	H(7)−B(2)	1.185(7)	0.082(11)
6	H(3)−B(2)	1.280(7)	0.094 (tied to 5)
7	H(5)···B(2)	3.147(11)	0.158[a]
8	H(7)···H(3)	1.969(11)	0.146[a]
9	H(5)···H(3)	2.732(11)	0.182[a]
10	H(7)···H(5)	3.393(8)	0.334[a]
11	H(8)···H(7)	2.054(15)	0.131[a]
12	H(4)···H(3)	2.077(14)	0.133[a]
13	H(7)···H(6)	4.160(13)	0.155[a]
14	H(6)···H(5)	2.804(15)	0.146[a]

[a] Fixed vibrational amplitudes originating in the Shrink force field derived from the MP2/6-311G(d) set of force constants.

Bond distances (r_α) and amplitudes of vibration deduced or fixed in the final refinement of the model are given in Table 5. Additional tables documenting the refinement (Cartesian coordinates and correlation matrix) are available in the Supporting Information. At 0.180 the final R factor (R_G) for the combined data sets was rather higher than usual but is a reflection of the far from ideal signal-to-noise ratio of the measured scattering.

The molecular parameters evaluated on the basis of the present analysis are similar in magnitude to those determined previously.[12] The Ga···B distance does not vary appreciably as between $H_2Ga(\mu\text{-}H)_2BH_2$ [2.197(3) Å], $HGa[(\mu\text{-}H)_2BH_2]_2$ [2.185(2) Å],[16] and $Me_2Ga(\mu\text{-}H)_2BH_2$ [2.163(8) Å].[20] Although the $Ga-H_t$ bond appears at 1.555(6) Å to be longer than in any other gaseous gallium(III) hydride molecule investigated so far,[5,7,15,16,33] the difference is not significant within the limits of experimental uncertainty. The average $\nu(Ga-H_t)$ stretching frequency of gallaborane is actually some 80 cm^{-1} *higher* than that of the gallane complex $Me_3N{\cdot}GaH_3$ [for which $r_\alpha(Ga-H_t)$ has been estimated to be 1.511(13) Å][34] and only about 20 cm^{-1} lower than that of $H_2Ga(\mu\text{-}Cl)_2GaH_2$ [$r_\alpha(Ga-H_t) = 1.523(20)$ Å].[7] The $Ga-H_b$ distance [1.800(6) Å] is in keeping with the corresponding parameters in other molecules featuring $Ga-H_b-B$ bridges, as attested by the following values (given as r_a in Å, for comparison): $H_2Ga(\mu\text{-}H)_2BH_2$, 1.798(6); $HGa[(\mu\text{-}H)_2BH_2]_2$, 1.788(7);[16] $Me_2Ga(\mu\text{-}H)_2BH_2$, 1.79(3);[20] $H_2Ga(\mu$-

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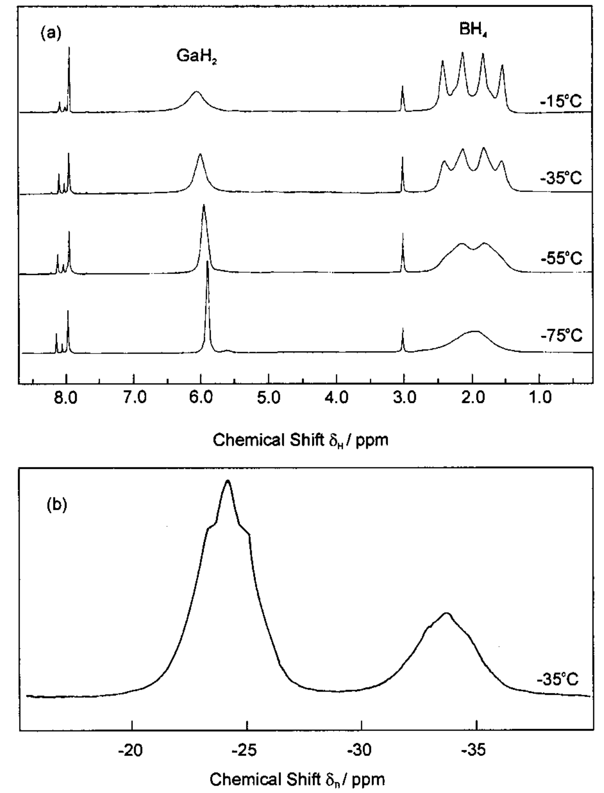
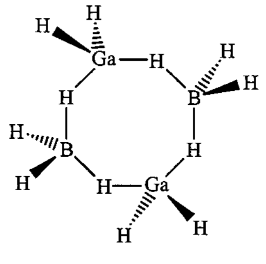


Figure 5. ^{1}H and ^{11}B NMR spectra of a toluene-d_8 solution of gallaborane at different temperatures.

H)$_2$B$_3$H$_6$, 1.81(4);[15] and Me$_2$Ga(μ-H)$_2$B$_3$H$_6$, 1.86(6).[31] Rather shorter distances (also r_a in Å) seem to be the rule in symmetrical Ga−H$_b$−Ga bridges, where the charge separation between the Ga and H$_b$ centers is likely to be smaller, e.g. H$_2$Ga(μ-H)$_2$GaH$_2$, 1.71(4);[5] Me$_2$Ga(μ-H)$_2$GaMe$_2$, 1.708(14).[26] Clearly the problem of placing Ga−H bond lengths on a reliable quantitative scale has yet to be resolved. The dimensions of the η^2-H$_2$BH$_2$ moiety do not differ significantly from those in analogous molecules, cf. r_a(B−H$_t$) (in Å), r_a(B−H$_b$) (in Å), and ∠H$_b$−B−H$_b$ (in deg) in the following molecules: H$_2$Ga(μ-H)$_2$BH$_2$, 1.185(7), 1.280(7), 110.0(5); HGa[(μ-H)$_2$BH$_2$]$_2$, 1.183(4), 1.269(4), 109.5(5);[16] Me$_2$Ga(μ-H)$_2$BH$_2$, 1.19(2), 1.22(2), 112(4);[20] and Al[(μ-H)$_2$BH$_2$]$_3$, 1.196(12), 1.283(12), 114.0(2).[35] A more precise structural specification of gallaborane may yet be gained from a microwave study, but the presence of Ga and B nuclei with $I = {}^3/_2$ will cause substantial splitting of lines and is likely therefore to hamper both detection and analysis. On balance, the best prospect for access to accurate estimates of the relevant rotational constants seems to be offered by the rovibrational spectrum of the molecule measured under high resolution (<0.01 cm^{-1}), and work is proceeding along these lines.[27]

(c) Properties of the Liquid Phase: ^{1}H and ^{11}B NMR Spectra. Liquid gallaborane has only a narrow range of stability, from its melting point near 228 K to its decomposition point near 238 K. Attempts to measure the Raman spectrum of the liquid at 233 K were frustrated by decomposition under the action of the exciting radiation. The ^{1}H NMR spectrum of a [^{2}H$_8$]toluene solution of gallaborane at 233 K comprised a broad 1:1:1:1 quartet [^1J(B−H) = 89 Hz] centered at δ_H 1.05 and a broad singlet at δ_H 5.0 with intensities roughly in the proportions 2:1 (see Figure 5a). Lowering the temperature brought about the reversible collapse of the quartet with a simultaneous sharpening of the higher frequency resonance. Warming the sample to temperatures above 243 K resulted not only in the decay of both resonances but also in the growth of a new 1:1:1:1 quartet [^1J(B−H) = 90 Hz] centered at δ_H 3.85 and a septet [^1J(B−H) = 48 Hz] centered at δ_H −0.85 attributable to diborane,[36] as well as a sharp singlet at δ_H 4.5 attributable to dihydrogen;[37] at room temperature the walls of the sample tube were observed to be coated with a metallic film, presumed to be elemental gallium. Of the resonances due to gallaborane, the broad singlet at δ_H 5.0 is characteristic of hydrogen atoms forming terminal bonds to gallium,[5,7,15,16,38] whereas the quartet at lower frequency is clearly identifiable with the magnetically equivalent hydrogen atoms of a tetrahydroborate group, by analogy with the behavior of other tetrahydroborate derivatives.[17] Changes in the line shape reflect varying degrees of thermal decoupling of the protons from the quadrupolar Ga and B nuclei[39] to which they are bound.

The ^{11}B NMR spectrum of the gallaborane solution at 238 K revealed not one but two partially resolved 1:4:6:4:1 quintets at δ_B −33.7 and −24.0, with ^1J(B−H) = 90 Hz in each case (Figure 5b). Increasing the temperature or reducing the concentration of the solution caused the high-frequency resonance to grow at the expense of the low-frequency one. Hence it appears that gallaborane exists in solution in different states of aggregation, with the high-frequency ^{11}B feature probably arising from the monomer H$_2$GaBH$_4$ and the low-frequency feature from a dimer, [H$_2$GaBH$_4$]$_2$. The latter may well adopt the cyclic structure **I** made up of alternating GaH$_4$ and BH$_4$ units linked to each other through single Ga−H−B bridges; it would thus resemble the hypothetical molecules B$_4$H$_{12}$ and Ga$_4$H$_{12}$, the structures of which have been calculated ab initio.[40]



I

Broad-band ^{11}B irradiation has no effect on the ^{1}H resonance at δ_H 5.0 but causes the quartet at δ_H 1.05 to collapse not to a singlet but to a sharp doublet at δ_H 1.02, with a separation of 8.5 Hz, and to a partially overlapping singlet at δ_H 1.09. Irradiation at the resonant frequency corresponding to the ^{11}B signal at δ_B −33.7, attributed to the dimer, showed that it correlates with the doublet ^{1}H resonance, whereas the ^{11}B signal at δ_B −24.0, believed to be due to the monomer, was shown similarly to correlate with the singlet ^{1}H resonance. The doublet pattern of the ^{1}H{^{11}B} resonance at δ_H 1.02 may correspond to an AB-pattern arising from the exo and endo H$_t$ atoms bound to boron in structure **I**, but we lack proof on this point.

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Table 6. Vibrational Spectra of a Solid Gallaborane Film at 77 K (Wavenumbers in cm^{-1})

Raman scattering		IR absorption					
$GaBH_6$		$GaBH_6$		$GaBD_6$			
$\tilde{\nu}$	intens[a]	$\tilde{\nu}$	intens[a]	$\tilde{\nu}$	intens[a]	$\tilde{\nu}_H/\tilde{\nu}_D$	assignment
				1930	mw		[b]
2532	w	2529	m	1910	m	1.3241	$\nu_{asym}(B-H_t)$
				1820	sh		[b]
2450	m	2450	m	1798	m	1.3626	$\nu_{sym}(B-H_t)$
		2431	sh	1767	sh	1.3758	
2381	m, br	2381	w, br				$\nu(B-H_b)$ + combinations or overtone bands
		2270	w, br	1659	w	1.3683	
2193	m	2187	w				
				1563	s		
2056	w	2089	s, br	1548	vs	1.3495	
				1540	s		
2032	s	2023	s	1464	s	1.3818	
2009	m	2008	s	1453	s	1.3820	$\nu_{asym}(Ga-H_t)$
1989	vs	1989	s	1426	m	1.3948	$\nu_{sym}(Ga-H_t)$
				1396	w		[b]
1472	vw						1146 + 338
1449	w	1450	vw				920 + 520
1387	sh	1400	m	1028	mw	1.3619	$\nu(Ga-H_b)$
1363	s						
		1311	vw				679 + 625
1236	vw	1239	m	957	m	1.2800	$\nu(Ga-H_b)$
		1211	m				
1146	m	1146	w	880	w	1.3023	$\delta[B(H_t)_2]$
1126	w	1111	m				
		1080	m	838	m	1.2888	
1059	w, br	1061	m				
920	vw, br			652	vw	1.4110	$\rho[B(H_t)_2]$
702	m	679	s	510	m	1.3314	$\delta[Ga(H_t)_2]$
690	sh						
625	m, br	610	w	445	m	1.3708	$\rho[Ga(H_t)_2]$
520	w	517	vw				
500	vw						274 + 230
		478	m, sh				
467	m	462	m	411	vs	1.1241	$\nu(Ga\cdots B)$
		452	m, sh				
401	w, br	[c]		[c]			skeletal deformation modes
338	vw						
274	w						
230	w						
181	s						

[a] s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder. [b] Band probably due to H-containing isotopomer. [c] Region not explored.

In its behavior in hydrocarbon solution, gallaborane thus resembles closely the bis(tetrahydroborate), $[HGa(BH_4)_2]_n$,[16] which appears also to exist as a mixture of the monomer and an oligomer of indeterminate nature.

(d) Properties of the Solid. (i) Vibrational Spectra. The IR and Raman spectra of annealed solid films of gallaborane-h_6 and -d_6 at 77 K give the frequencies listed in Table 6. Comparison with the IR spectrum of the vapor reveals significant changes of pattern and frequency, implying association of the discrete gallaborane molecules in the solid phase. Some indication of the form of association is provided by the following features.

(1) The doublet pattern of bands at 2529 (1910) and 2450 (1798) cm^{-1} implies the retention of terminal BH_2 moieties in the solid.

(2) Prominent absorptions near 2000 (1460) and 679 (510) cm^{-1} give grounds for believing that terminal GaH_2 moieties also survive the transition from the vapor to the solid state.

(3) The appearance of IR and Raman bands in the region 2130−2390 cm^{-1} attributable to $\nu(B-H_b)$ vibrations means that the frequency separation between the $\nu(B-H_t)$ and $\nu(B-H_b)$ fundamentals is significantly reduced in the solid. Such a situation is consistent with the presence of relatively ionic BH_4 units.[41−43]

The spectra differ in a number of respects from those of the solid tetrahydroborates $Be(BH_4)_2$,[41] $MeZnBH_4$,[42] and Me_2AlBH_4,[43] where the metal atoms are linked together through BH_4 groups each acting as bis(bidentate) bridges. Whether the BH_2 and GaH_2 units in solid gallaborane are bound through single hydrogen bridges to form an oligomer such as **I** or to give a polymeric array, however, it is impossible to judge on the evidence of the vibrational spectra alone.

(ii) Crystal Structure. The implications of the spectra are confirmed by the structure determined by X-ray diffraction of a single crystal at 110 K, illustrated in Figure 6. The compound crystallizes under these conditions in the monoclinic space group $I2/a$ with 12 $GaBH_6$ molecules per unit cell. Details of the data collection, structure solution, and refinement are presented in Table 7, and selected bond distances and angles are in Table 8. A preliminary account of the results has already been given.[13]

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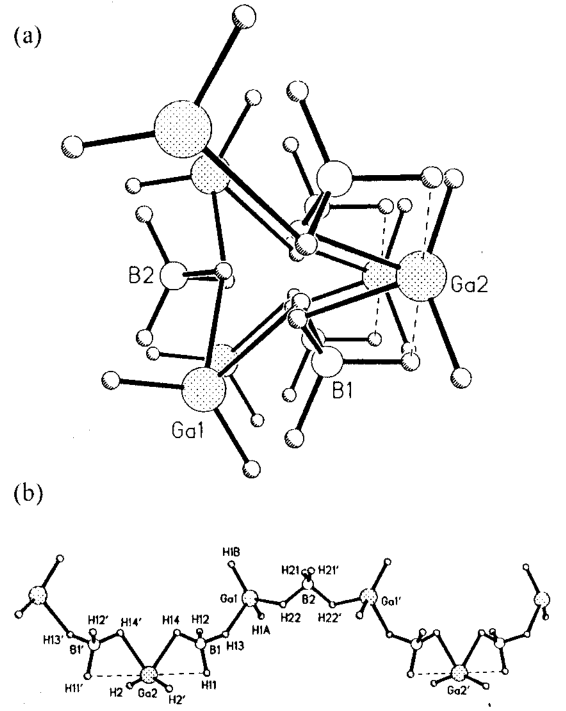

Figure 6. Structure of crystalline gallaborane at 110 K viewed (a) perpendicular to, and (b) along the helical axis. Primed atoms are symmetry-related to nonprimed atoms.

Table 7. Crystal Data and Structure Refinement for Gallaborane at 110(2) K

empirical formula	$GaBH_6$
formula weight	86.58
wavelength	0.710 73 Å
crystal system	monoclinic
space group	*I*2/*a*
unit cell dimensions	$a = 10.036(3)$ Å, $\alpha = 90°$ $b = 8.932(3)$ Å, $\beta = 100.57(2)°$ $c = 11.294(4)$ Å, $\gamma = 90°$
volume	995.2(6) $Å^3$
Z	12
density (calc)	1.733 g/cm^3
absorption coefficient	7.970 mm^{-1}
F(000)	504
crystal size	0.39 × 0.19 × 0.19 mm
θ range for data collection	2.93−24.99°
index ranges	$-14 \leq h \leq 0, 0 \leq k \leq 12, -15 \leq l \leq 15$
reflections collected	1015
independent reflections	864 [R(int) = 0.0216]
conventional R [$F > 4\,\sigma(F)$]	$R_1 = 0.0344$ [744 data]
R indices (all data)	$R_1 = 0.0472$, $wR_2 = 0.0990$
largest diff peak and hole	0.604 and −0.604 e A^{-3}

Hence we find that the crystal structure consists of helical chains made up of alternating pseudotetrahedral GaH_4 and BH_4 units; *between* the chains there are no contacts short enough to imply significant secondary interactions. **1** thus resembles the crystalline tetrahydroborates $Be(BH_4)_2$,[41] $MeZnBH_4$,[42] and Me_2AlBH_4[43] in forming helical chains of metal atoms linked by BH_4 bridges. However, it differs from these compounds in several respects. (a) The polymer chains repeat along a glide plane and not around a screw axis. (b) The BH_4 groups in **1** function primarily as bis(monodentate) bridges, $M(\mu\text{-}H)BH_2(\mu\text{-}H)M$ (M = metal atom), and not as bis(bidentate) bridges, $M(\mu\text{-}H)_2B(\mu\text{-}H)_2M$, as in the other tetrahydroborate helices, which feature no terminal B−H bonds.[41−43] (c) The structure of **1** is based around two molecules in an asymmetric unit with angular Ga···B···Ga linkages (∠Ga···B···Ga = ca. 159°), as well as angular B···Ga···B linkages (∠B···Ga···B = ca. 127°), contributing to the winding of the spirals; by contrast, the other tetrahydroborates, with almost linear M···B···M fragments, depend on the angularity of the B···M···B fragments to provide the winding of the spirals. (d) To a first approximation, the polymeric structure affords the Ga atoms in **1** the tetracoordinated environment they so often favor,[1] whereas hexa- or pentacoordinated metal atoms are otherwise the rule. There are in fact two distinct types of BH_4 unit in the structure of **1**. As shown in Figure 6, the unit based on B(1) forms primary interactions through H(13) to Ga(1) [2.04(7) Å] and through H(14) to Ga(2) [1.86(7) Å], and a weaker, secondary contact through H(11) to Ga(2) [2.41(6) Å], so that it could be said to function as a semi-tridentate bridge. On the other hand, the BH_4 unit based on B(2), which, like Ga(2), lies on a 2-fold axis, incontrovertibly links the two adjacent Ga centers through single hydrogen bridges [via H(22) and its symmetry equivalent, with Ga(1)−H(22) = 1.87(7) Å]. The only other metal tetrahydroborates known to display a similar mode of coordination are $[(\eta^5\text{-}C_5Me_5)Ir]_2H_3(BH_4)$[44a] and $[(\eta^5\text{-}C_5H_5)Mo]_2(\mu\text{-}SMe)_3(BH_4)$,[44b] in which a metal−metal bond is bridged on one side by the BH_4 group.

Table 8. Interatomic Distances (in Å) and Angles (in deg) in Crystalline Gallaborane at 110 K

Ga(1)−B(2)	2.463(3)	Ga(2)−H(14)	1.86(7)
Ga(1)−B(1)	2.499(7)	B(1)−H(11)	1.09(7)
Ga(1)−H(1A)	1.40(4)	B(1)−H(12)	1.06(7)
Ga(1)−H(1B)	1.41(4)	B(1)−H(13)	1.14(7)
Ga(1)−H(13)	2.04(7)	B(1)−H(14)	1.13(7)
Ga(1)−H(22)	1.87(7)	B(2)−Ga(1)#2	2.463(3)
Ga(2)−B(1)	2.457(7)	B(2)−H(21)	0.98(7)
Ga(2)−B(1)#1	2.457(7)	B(2)−H(22)	1.17(7)
Ga(2)−H(2)	1.41(4)		
B(2)−Ga(1)−B(1)	125.5(3)	H(2)−Ga(2)−H(14)	104(4)
B(2)−Ga(1)−H(1A)	105(3)	Ga(2)−B(1)−Ga(1)	160.3(3)
B(1)−Ga(1)−H(1A)	99(3)	Ga(2)−B(1)−H(11)	75(3)
B(2)−Ga(1)−H(1B)	99(3)	Ga(1)−B(1)−H(11)	119(4)
B(1)−Ga(1)−H(1B)	100(3)	Ga(2)−B(1)−H(12)	128(4)
H(1A)−Ga(1)−H(1B)	133(4)	Ga(1)−B(1)−H(12)	63(4)
B(2)−Ga(1)−H(13)	99(2)	H(11)−B(1)−H(12)	112(5)
B(1)−Ga(1)−H(13)	27(2)	Ga(2)−B(1)−H(13)	113(3)
H(1A)−Ga(1)−H(13)	113(4)	Ga(1)−B(1)−H(13)	54(3)
H(1B)−Ga(1)−H(13)	103(3)	H(11)−B(1)−H(13)	98(5)
B(2)−Ga(1)−H(22)	27(2)	H(12)−B(1)−H(13)	117(5)
B(1)−Ga(1)−H(22)	98(2)	Ga(2)−B(1)−H(14)	46(4)
H(1A)−Ga(1)−H(22)	114(3)	Ga(1)−B(1)−H(14)	117(4)
H(1B)−Ga(1)−H(22)	106(3)	H(11)−B(1)−H(14)	120(5)
H(13)−Ga(1)−H(22)	72(3)	H(12)−B(1)−H(14)	111(5)
B(1)−Ga(2)−H(2)	96(3)	H(13)−B(1)−H(14)	98(5)
B(1)−Ga(2)−B(1)#1	99(3)	Ga(1)−B(2)−H(21)	64(4)
B(1)−Ga(2)−H(14)	26(2)	Ga(1)−B(2)−H(22)	47(3)
B(1)#1−Ga(2)−H(14)	102(2)	H(21)−B(2)−H(22)	111(5)

Structural comparisons with the gaseous $H_2Ga(\mu\text{-}H)_2BH_2$ monomer are complicated by differences of temperature and technique, X-ray diffraction, unlike electron diffraction, measuring distances between centers of maximum electron density. There is little doubt, though, that crystallization and the attendant polymerization have the effects (i) of attenuating the Ga···B distance (from 2.18 to 2.47 Å) and (ii) of accentuating the greater length of the bridging compared with the terminal Ga−H distances [$\Delta r(Ga-H) = r(Ga-H_b) - r(Ga-H_t)$ increasing from 0.25 to 0.52 Å]. While the BH_4 groups of the solid, with H−B−H angles spanning the range 98−120°, do not deviate far from tetrahedral geometry, the GaH_4 groups are far from tetrahedral, with $\angle H_t-Ga-H_t = 133(3)°$ and $145(3)°$ and $\angle H_b-Ga-H_b = 72(3)°$ and $76(3)°$ at Ga(1) and Ga(2), respectively.

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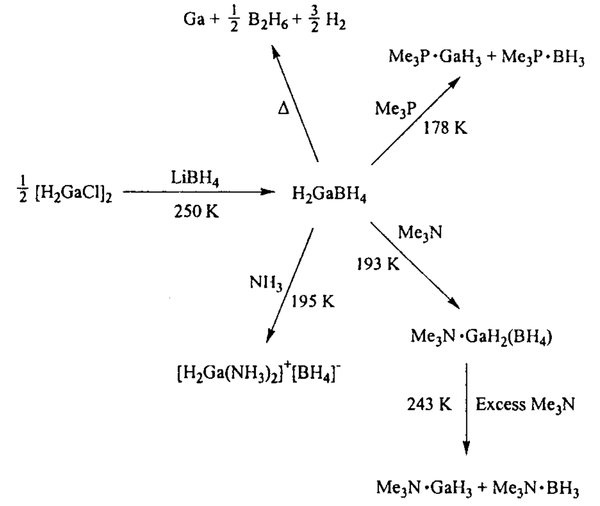
Scheme 1. Formation and Some Chemical Properties of Gallaborane



In keeping with the vibrational spectra of the solid (q.v.), these properties imply a significant degree of ionic character in the sense $[H_2Ga]^+[BH_4]^-$. The behavior follows the trend set by the crystal structures not only of various metal hydroborates, e.g. $MeZnBH_4$,[42] Me_2AlBH_4,[43] and $Me_2InB_3H_8$,[45] but also of other derivatives of the heavier main group elements, e.g. $TeCl_4$, which tends toward $TeCl_3{}^+Cl^-$.[46] It is curious then that the dimethyl derivative of gallaborane should adopt a more or less discrete molecular structure $Me_2Ga(\mu\text{-}H)_2BH_2$ in the solid state with $r(\text{Ga}\cdots\text{B}) = 2.269(5)$ Å and shortest *inter*molecular Ga···H contacts of 2.74(5) and 2.82(5) Å;[47] presumably this reflects both the partiality of gallium for 4-fold coordination (cf. Me_2AlBH_4 where 6-fold coordination of the Al center prevails) and the inadequacy of methyl groups as ligands able to bridge Ga centers.

Several factors must determine the way hydride molecules such as $GaBH_6$ aggregate and the structures they adopt in the condensed phases, namely the electronic properties and size of the metal atom, as well as the nature and number of any other substituents. It is possible that solid gallaborane provides a clue to the structure of solid gallane, $[GaH_3]_n$, which, unlike its aluminum analogue,[48] features both terminal and bridging Ga−H bonds but has so far eluded definitive characterization.[2,3,5] More crystallographic data are needed, ideally including the results of at least some neutron diffraction studies, to develop a fuller picture of the patterns and principles that are at work. Unfortunately, however, several of the compounds inviting structural investigation, e.g. $HGa(BH_4)_2$, H_2GaCl, Me_2AlH, and $MeM(BH_4)_2$ (M = Al or Ga), have withstood so far all attempts at crystallization.

(e) Chemical Properties of Gallaborane. We have investigated some of the chemical properties of gallaborane, with the results summarized in Scheme 1. Two aspects merit discussion: (i) the decomposition of the compound, and (ii) cleavage of the $Ga(\mu\text{-}H)B$ units by a nitrogen or phosphorus base either “symmetrically”, to give the molecular adducts $L\cdot GaH_3$ and $L\cdot BH_3$ (e.g. L = Me_3N or Me_3P), or “unsymmetrically”, to give a single salt-like product $[H_2GaL_2]^+[BH_4]^-$ (e.g. L = NH_3).

(i) Decomposition. As noted previously, the complete thermal decomposition of **1** in accordance with eq 3 has afforded a means of chemical analysis. The decomposition process was investigated more closely at temperatures ranging from 233 to 273 K to discover whether partial decomposition might yield gallaboranes of higher nuclearity or gallane itself. In this we were guided by the precedents set by diborane, pyrolysis of which yields initially tetraborane(10),[49] and also by the properties of 2-galla-*arachno*-tetraborane(10), $H_2GaB_3H_8$,[15] which is rather more robust than either gallane or gallaborane. The decomposition products of gallaborane, as the neat compound or in hydrocarbon solution, were variously fractionated and analyzed by mass balance and by their ^1H NMR and IR spectra, but no isolable products other than elemental gallium, dihydrogen, and diborane (and always in the proportions required by eq 3) were found, irrespective of the precise conditions.

(ii) Reactions with Nitrogen and Phosphorus Bases. With an excess of ammonia at 195 K gallaborane reacts to form a white solid with the composition $GaBH_6\cdot 2NH_3$, which is long-lived at ambient temperatures. The IR spectrum of this solid provides persuasive evidence that it is most aptly formulated as $[H_2Ga(NH_3)_2]^+[BH_4]^-$. Thus, the features characteristic of coordinated NH_3 molecules[50] are clearly present in the form of bands at 3250, 1620, ca. 1300, and 790 cm^{-1}, whereas bands at 1927, 750, and 640 cm^{-1} are identifiable with the stretching and bending modes of the GaH_2 unit in the $[H_2Ga(NH_3)_2]^+$ cation. There are, in addition, prominent bands at 2259 and 1099 cm^{-1} attributable to the IR-active t_2 fundamentals ν_3 and ν_4, respectively, of a more or less discrete $BH_4{}^-$ anion.[17,18] Indeed, the spectrum can be well simulated by a superposition of those due to $[H_2Ga(NH_3)_2]^+Cl^-$ [51] and $NaBH_4$.[17,18] There is a distinct resemblance also to the spectra reported previously for the compounds $[H_2Ga(NH_3)_2]^+[GaH_4]^-\cdot 2NH_3$[5] and $H_2Ge(CH_3)_2$[52] (isoelectronic with $[H_2Ga(NH_3)_2]^+$). Hence, the reaction evidently proceeds with asymmetric cleavage of the $Ga(\mu\text{-}H)B$ linkages of gallaborane, in accordance with eq 4.

$$GaBH_6 + 2NH_3 \rightarrow [H_2Ga(NH_3)_2]^+[BH_4]^- \tag{4}$$

Gallaborane also reacts with an excess of trimethylamine at 178 K. Warming the mixture to room temperature and recovery of the unchanged base left a white sublimable solid product that could be identified by its IR spectrum as an equimolar mixture of the two known molecular adducts $Me_3N\cdot GaH_3$ [33,53] and $Me_3N\cdot BH_3$.[54] When the reagents, condensed together on a CsI window initially at 77 K, were allowed to warm to 193 K and the excess of trimethylamine evaporated, the IR spectrum of the resulting solid film implied the formation of an adduct $GaBH_6\cdot n NMe_3$, in which the polymeric framework of the gallaborane was at least partially retained, but with red shifts averaging 55 and 73 cm^{-1} for the $\nu(B{-}H_t)$ and $\nu(Ga{-}H_t)$ vibrations, respectively. In this and other respects, the spectrum resembled quite closely those reported previously for the

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Table 9. GED Data Analysis Parameters

camera distance/mm	weighting functions/Å^{-1}					correlation parameter	scale factor, k^a	electron wavelength^b/pm
	Δs	$s_{\min}$	sw_1	sw_2	$s_{\max}$			
495.04	0.25	2.5	4.5	11.0	13.0	0.1348	1.36(5)	0.058 561
201.12	0.25	7.0	9.0	18.75	20.0	0.4462	1.18(10)	0.056 720

[a] Figures in parentheses are the estimated standard deviations. [b] Determined by reference to the scattering pattern of benzene vapor.

complexes $Me_3N{\cdot}AlH_2(BH_4)$[55] and $Me_3N{\cdot}GaH(BH_4)_2$.[16] Warming the window to 243 K resulted in decomposition of the gallaborane derivative with the formation of gallium metal and the release of H_2 as well as Me_3N.

There is a smooth reaction between gallaborane and an excess of trimethylphosphine at 195 K, also to give a sublimable white solid. This was shown by its IR spectrum (at 77 K) and by the ^1H, ^{11}B, and ^{31}P NMR spectra of a [$^2H_8$]toluene solution (at 243 K) to be an equimolar mixture of the molecular adducts $Me_3P{\cdot}GaH_3$[56] and $Me_3P{\cdot}BH_3$.[57] It follows, therefore, that the reactions with both Me_3N and Me_3P parallel those of diborane with the same reagents, resulting ultimately in symmetrical cleavage of the Ga(μ-H)B linkages of gallaborane, as in eq 5.

$$GaBH_6 + 2L \rightarrow L{\cdot}GaH_3 + H_3B{\cdot}L \quad (L = Me_3N \text{ or } Me_3P) \tag{5}$$

Experimental Section

(a) Synthesis of Gallaborane. Gallaborane was prepared by the reaction between $LiBH_4$ (Aldrich, 95% pure, freshly recrystallized from dry Et_2O) and monochlorogallane, $[H_2GaCl]_n$, itself made by the reduction of $GaCl_3$ with an excess of Me_3SiH.[6] This took place at 250 K (eq 1) under rigorously solvent- and grease-free conditions in all-glass apparatus; all the exposed sections to which the gallaborane had access were cooled by a stream of cold nitrogen gas.[2,5] In a typical experiment, finely powdered $LiBH_4$ (100 mg, 4.59 mmol) reacted with monochlorogallane (ca. 200 mg, 1.9 mmol H_2GaCl) in the space of 1 h. The volatile products were separated by fractional condensation in vacuo through a train of traps held at 210, 147, and 77 K. Gallaborane (ca. 130 mg, 1.5 mmol $GaBH_6$) collected in the 147 K trap as a white solid. Minor products included dihydrogen and diborane. Perdeuterated gallaborane was synthesized similarly from $LiBD_4$ and $[D_2GaCl]_n$.

(b) Chemical Analysis and Authentication. A sample of gallaborane was allowed to decompose at room temperature with the deposition of gallium metal on the walls of the ampule; to ensure complete decomposition, the temperature was held latterly at 343 K for 12 h. The volatile products, consisting of diborane and dihydrogen, were withdrawn quantitatively by means of a Toepler pump and separated by condensation of the diborane in a spiral trap cooled to 77 K. Assay of the metallic residue by atomic absorption and of the gaseous products by tensimetric means gave the following results:

	$GaBH_6$ taken	Ga residue	H_2 evolved	B_2H_6 evolved
expt 1 found/mmol	2.34	2.28	3.44	1.32
proportions	1.00	0.97	1.47	0.56
expt 2 found/mmol	1.10	1.10	1.74	0.60_7
proportions	1.00	1.00	1.58	0.55

Within the limits of experimental uncertainty, these results confirm the empirical formula $GaBH_6$.

The authenticity of a sample of the compound was checked by reference to its vaporization properties, the IR spectrum of the annealed solid condensate at 77 K, and/or the ^1H and ^{11}B NMR spectra of a [$^2H_8$]toluene solution at subambient temperature. Such a sample was stored at 77 K in a sealed, evacuated, all-glass ampule equipped with a break-seal, until required.

(c) Spectroscopic Measurements. IR spectra were recorded using one of two spectrometers, viz. a Mattson Galaxy (4000−400 cm^{-1}) or a Nicolet 7199 FT-IR instrument (4000−700 cm^{-1}), the former having a DTGS detector and the latter an MCT-A detector. Gaseous samples were contained either in a Pyrex-bodied cell fitted with CsI windows and having a path length of 10 cm (pressure ca. 50 Torr, near-ambient temperatures, spectral resolution 2 cm^{-1}) or in a multipass gas cell equipped with aluminum mirrors giving a path length of 3.9 m (pressure 0.15 Torr, ambient temperatures, spectral resolution 0.06 cm^{-1}). Solid nitrogen matrixes, typically at dilutions estimated to be ca. 1:200, were prepared by continuous codeposition of the gallaborane vapor (conducted via an appropriately cooled, preconditioned glass inlet) with an excess of the matrix gas on a CsI window cooled to ca. 20 K by means of a Displex closed-cycle refrigerator (APD CS 202).[57] Raman spectra were excited at $\lambda = 514.5$ nm with the output of a Spectra-Physics Model 165 Ar$^+$ laser and measured with a Spex Ramalog 5 spectrophotometer operated with a computerized data-handling center; the resolution was 2 cm^{-1}. Solid films of the gallaborane and other volatile materials were presented for spectroscopic analysis by allowing the vapor to condense on a CsI window (for IR measurements) or a copper block (for Raman measurements) contained in an evacuated glass shroud and maintained at 77 K.

^1H, ^{11}B, and ^{31}P NMR spectra of [$^2H_8$]toluene solutions of gallaborane, its decomposition products, and other derivatives were measured at temperatures between 190 and 300 K using a Bruker AM300 instrument, the operating frequency being 300, 96.25, and 121.5 MHz for ^1H, ^{11}B, and ^{31}P, respectively.

(d) Electron Diffraction Measurements. Electron diffraction measurements were made with an all-glass inlet system which could be cooled to minimize decomposition of the vapor en route to the diffraction chamber. The assembly used with the Edinburgh apparatus has been described previously.[5,12,58] A somewhat different design was adopted for the inlet system to the Reading apparatus,[60] and to alleviate the problem of fogging of the photographic plates, the cold trap of this apparatus was extended so as to envelope the nozzle.[7] The gallaborane sample was held at a temperature between 231 and 243 K, while the nozzle temperature was held between 244 and 258 K. Before any measurements were made on the gallaborane vapor, the inlet system was preconditioned by exposing it to a slow stream of the vapor for ca. 2 min. Various measures were adopted in an attempt to produce plates with a uniform background, e.g. leaving the exposed plates under continuous pumping for 24 h before developing them and/or leaving the washed plates exposed to air for 24 h. Several sets of measurements were made at both Edinburgh and Reading with varying degrees of success. Careful analysis to determine which of the results offered the best signal-to-noise ratio led to the selection of one set of measurements at a camera distance of ca. 50 cm (made at Reading) and one set of measurements at a camera distance of ca. 20 cm (made at Edinburgh), the relevant conditions being specified in Table 9. The precise nozzle-to-plate distances and electron wavelengths were determined from the scattering patterns measured for benzene vapor[61] immediately prior to

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each experiment. Tracing of the plates was carried out with the aid either of a computer-controlled Joyce-Loebl MDM6 microdensitometer at Daresbury[62] or of an AGFA Arcus II scanner at Reading.[63] The results spanning the ranges $2.5 \leq s \leq 13.0$ and $7.0 \leq s \leq 20.0$ Å^{-1} were processed by the methods described elsewhere[64] using the scattering factors taken from ref 65.

(e) Theoretical Calculations. Ab initio calculations were carried out with the program suite GAUSSIAN 94.[28] How the method, level of theory, and basis set (number of diffuse and polarization functions, etc.) influenced the computed structural parameters was assessed by scrutinizing the results of various calculations. Hartree−Fock (HF), Møller−Plesset (MP2, MP3, and MP4), and DFT (B3PW91) calculations were performed with a 6-311G basis set, to which differing numbers of diffuse and polarization functions were added. In addition, a set of calculations was undertaken to assess the effects of the Gaussian frozen-core (FC) approximation, which divides electrons into two categories, core and valence, with only the valence electrons considered in the electron-correlation treatment. The approximation is known to be critical for the group 13 elements Ga, In, and Tl, as the corresponding 3d, 4d, or 5d orbitals are often incorrectly placed in the core region, when a close examination of the orbital energies shows these orbitals to lie closer in energy to the outer valence orbitals than to the inner core orbitals. Consequently, sets of MP2(FULL) and MP3(FULL) calculations were implemented with all electrons (core and valence) included in the electron correlation treatment.

The vibrational force field associated with the optimized structure of $GaBH_6$ at the MP2/6-311G(d) level served as the starting point for computing the vibrational parameters of the molecule. Sets of u and k vibrational corrections based on curvilinear motion were derived using the program SHRINK,[29] with scaling against the experimental frequencies being carried out to eliminate systematic errors in the ab initio frequency calculations.

(f) X-ray Crystallography. Hydridogallium bis(tetrahydroborate) $[HGa(BH_4)_2$, **2**] was prepared from $GaCl_3$ and $LiBH_4$ and purified by the procedures described elsewhere.[16] A single crystal of what proved to be gallaborane, present as a contaminant, was grown by careful cooling of the sample that was contained in a preconditioned Pyrex glass capillary mounted on the diffractometer. A stable solid/liquid phase boundary was established at about 213 K, and crystal growth effected from this boundary by slow cooling to 190 K at a rate of approximately 90 K h^{-1}. Crystal data, data collection details, metrical parameters, and solution refinement procedures are collected in Tables 7 and 8. The data were collected on a Stoe Stadi 4 four-circle diffractometer, an Oxford Cryosystems low-temperature device[66] maintaining a crystal temperature of 110 K. Following corrections for Lp effects and absorption (ψ scan, $T_{\min} = 0.457$, $T_{\max} = 0.740$), the structure was solved by Patterson methods for the Ga positions, and the B and H atoms were located in subsequent F maps (SHELXTL[67]). The structure was refined by full-matrix least squares against F^2. The positions of H atoms bound to B centers were refined freely, and those of H atoms bound to Ga centers made subject to H−Ga similarity restraints. At convergence, R_1 stood at 0.0344 and wR_2 at 0.0990 (for all data) for 60 parameters. The final ΔF-synthesis maximum and minimum were $+0.604$ and -0.604 e Å^{-3}, respectively.

Even with the relatively low precision of the H-atom parameters, the H atoms showed up very clearly in the electron density maps. Since the presence of boron (at least ^{11}B) impairs the potential of neutron diffraction measurements, our results probably represent the best structural data available for a simple mixed hydride of this type. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany on quoting the depository number CSD-406271.

(g) Chemical Properties. (i) Reaction with NH_3. Gallaborane (57 mg, 66 mmol $GaBH_6$) reacted with an excess of NH_3 (BOC, purified by condensing on Na and fractionating in vacuo) at 195 K; after 30 min the mixture was allowed to warm to 238 K over a period of 1 h to ensure completion of the reaction. The material volatile at 195 K (unchanged NH_3) was evaporated to leave a white solid stable at room temperature as the sole product. Hence, it was found that 23 mg (1.35 mmol) of NH_3 had been consumed, corresponding to a stoichiometry of NH_3:$GaBH_6$ = 2.05:1. The IR spectrum of the solid showed the following bands in the region 4000−400 cm^{-1} (wavenumbers in cm^{-1}; s strong, m medium, w weak, v very, br broad, sh shoulder): 3250 vs, br [ν(N−H)]; 2259 vs, br [ν_3 (t_2) BH_4^-]; 1968 sh, 1927 m [ν(Ga−H_t)]; 1620 w [δ_{as}(NH_3)]; 1401 m (impurity); 1331/1280 m [δ_s(NH_3)]; 1186 w, 1099 m [ν_4 (t_2) BH_4^-]; 790 m [ρ(NH_3)]; 750 sh [δ(GaH_2)]; 640 w [ρ(GaH_2)]; 520 w, br, 480 w [ν(Ga−N)].

(ii) Reaction with NMe_3. Gallaborane reacted with an excess of NMe_3 (prepared from $[Me_3NH]C1$ and NaOH and purified by fractionation in vacuo) for 1 h at 178 K. The mixture was then warmed to 243 K before evaporation of the unchanged base to leave a white solid. This was identified as a mixture of the known molecular complexes $Me_3N{\cdot}GaH_3$ and $Me_3N{\cdot}BH_3$ after sublimation and condensation of a portion of the vapor on a CsI window held at 77 K; the IR spectrum of the resulting deposit was entirely consistent with a superposition of the spectra previously reported for each of these two adducts.[53,54] No other product was detected.

In a separate experiment, small amounts of gallaborane and NMe_3 were condensed together on a CsI window cooled to 77 K. The window was allowed to warm to 193 K before evaporation of any material volatile at this temperature. The IR spectrum of the solid film remaining on the window showed the following bands in the region 4000−400 cm^{-1} (wavenumbers in cm^{-1}; s strong, m medium, w weak, br broad, sh shoulder): 2979 m, 2945 w, br [ν(C−H)]; 2448/2410 s [ν(B−H_t)]; 2353 m, 2313 m, 2228 m, 2198 w, 2040 m, br [ν(B−H_b)]; 1939/1912 s [ν(Ga−H_t)]; 1468 s [δ_{as}(CH_3)]; 1403 w [δ_s(CH_3)]; 1253 m [ρ(CH_3) + ν_{as}(C−N)]; 1169 sh, 1165 m [ρ(CH_3)]; 1114 s, 1100 m [δ(BH_2)]; 1001 s [ρ(BH_2)]; 956 w, 858 w [ν(C−N)]; 824 w, 713 s [δ(GaH_2)]; 513 m [ρ(GaH_2)]; 497 m [ν(Ga−N)]. The solid decomposed at 243 K, turning gray with the simultaneous release of NMe_3 and H_2.

(iii) Reaction with PMe_3. Gallaborane reacted with an excess of PMe_3 (purified by fractionation in vacuo) at 195 K. Evaporation of the unchanged phosphine left a white sublimable solid. Vacuum sublimation on to a CsI window at 77 K gave a deposit whose IR spectrum displayed all the absorptions characteristic of the two known adducts $Me_3P{\cdot}GaH_3$[56] and $Me_3P{\cdot}BH_3$.[57] Confirmation was provided by the ^1H, ^{11}B, and ^{31}P NMR spectra of a toluene-d_8 solution of the solid product. Thus, the presence of equimolar quantities of $Me_3P{\cdot}GaH_3$ and $Me_3P{\cdot}BH_3$ was verified by the following features. (a) For $Me_3P{\cdot}GaH_3$: ^1H δ_H 0.725 doublet (PMe_3), 4.13 broad singlet (GaH_3); ^{31}P δ_P −39.2 singlet.[56] (b) For $Me_3P{\cdot}BH_3$: ^1H δ_H 0.695 doublet, ^2J(P−H) 58 Hz (PMe_3), 1.09 1:1:1:1 quartet, ^1J(B−H) 95 Hz (BH_3); ^{11}B δ_B −36.9 doublet of 1:3:3:1 quartets (BH_3); ^{31}P δ_P −4.4 1:1:1:1 quartet (PMe_3).[57]

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Supporting Information Available: Tables of the least-squares correlation matrix, Cartesian coordinates, and computed parameters for gallaborane. This material is available free of charge via the Internet at http://pubs.acs.org.

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