Group 3 Tetrahydroborates. Part 4.[1] The Molecular Structure of Hydridogallium Bis(tetrahydroborate) in the Gas Phase as determined by Electron Diffraction

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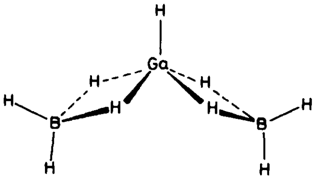
Gaseous $Ga(BH_4)_2H$, as studied by electron diffraction, appears to consist of monomeric $HGa[(\mu-H)_2BH_2]_2$ molecules with five-fold co-ordination of the gallium atom, a single terminal (t) Ga–H bond, and two doubly bridged (b) tetrahydroborate groups. The primary features of the structure involve the dimensions: r(Ga–B) 217.2(0.5), r(Ga–H) (average) 177.4(1.7), and r(B–H) (average) 127.7(1.4) pm; B–Ga–B 112.2(1.5)° (distances correspond to r_a; figures in parentheses are the estimated standard deviations of the last digits). Results are given for refinements based on a structural model with C_{2v} symmetry imposed, but a significantly better fit to the experimental data is achieved if this constraint is relaxed so that the $Ga(\mu-H)_2B$ moieties assume an unsymmetrical form with $r(Ga-H_b)$ 176.2(1.5) and 189.1(2.5) pm and $r(B-H_b)$ 125.0(8.1) and 145.6(3.3) pm. The five hydrogen atoms directly bound to the gallium atom form a slightly distorted rectangularly based pyramid. The features of the structure are collated with those of other hydridogallium and tetrahydroborate derivatives.

In our investigations of molecular species in which the tetrahydroborate group competes with ligands like H, CH_3, or NH_3 for co-ordination of an aluminium or gallium centre [2,3] we have determined the structures of the tetrahydroborates $M(BH_4)Me_2$ (M = Al or Ga) [4] and $Al(BH_4)_2Me$ [1] by analysing the electron-scattering patterns of the gaseous molecules. We now report the results of applying a similar analysis to the novel species hydridogallium bis(tetrahydroborate) whose synthesis and characterization have been the focus of recent studies.[2,5]

To judge by its vapour density, hydridogallium bis(tetrahydroborate) vaporizes as monomeric molecules. The two most plausible structures involve either (*i*) a five-co-ordinate gallium atom with a single terminal Ga–H bond and two doubly bridged tetrahydroborate groups (1) or (*ii*) a cyclic skeleton with a four-co-ordinate gallium atom derived from the topologically favoured form [6] of the hypothetical borane B_3H_9 (2). The presence in the i.r. spectrum of features characteristic of a single Ga–H and dihydrogen-bridged $Ga(\mu-H)_2BH_2$ units,[2,5,7] taken with the absence of the sort of spectral pattern normally associated with the $-BH_2-H-BH_2-$ unit,[2,8] argues strongly in favour of structure (1). There is then a range of possible models for the framework of the molecule depending upon the configuration of the five hydrogen atoms directly co-ordinated to the gallium atom. At one extreme, the unique terminal hydrogen atom occupies the apex and the bridging hydrogen atoms make up the rectangular base of a pyramid (corresponding to C_{2v} symmetry); at the other, the arrangement approximates to a trigonal bipyramid with the terminal hydrogen atom in an equatorial site (corresponding to C_2 symmetry). The partially resolved rotational structure of the i.r. band associated with an H_t–GaB_2 deformation mode points to, but does not establish, principal moments of inertia which are consistent with C_2 more than C_{2v} symmetry for the gaseous molecule.[2] The results of the electron-diffraction studies reported here are analysed to resolve these uncertainties and to determine the dimensions and amplitudes of vibration of the molecule.



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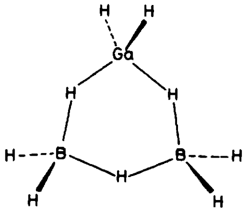

(2)

EXPERIMENTAL

Gallium(III) chloride was produced by the direct reaction of the elements and purified by repeated vacuum sublimation; lithium tetrahydroborate supplied by B.D.H. was recrystallized from diethyl ether immediately before use. Hydridogallium bis(tetrahydroborate) was prepared, as reported previously,[2,5] by the interaction of the powdered solids at *ca.* 228 K in the absence of a solvent, the product being removed from the solid mixture under continuous pumping. Fractionation *in vacuo* gave samples of $Ga(BH_4)_2H$ which were judged to be pure on the evidence of the melting point (*ca.* 203 K), the vapour pressure at 228 K (*ca.* 10 mmHg †), and the i.r. spectrum of the vapour.[2,5] Our experience is that decomposition of the liquid tends to set in at temperatures much above 228 K whereas the vapour at a pressure of *ca.* 10 mmHg has a half-life typically in the order of 10 min at room temperature with the formation of gallium metal, hydrogen, and diborane in accordance with equation (1).[5] In common with related compounds,

$$Ga(BH_4)_2H \longrightarrow Ga + \tfrac{3}{2}H_2 + B_2H_6 \qquad (1)$$

$Ga(BH_4)_2H$ is also sensitive to attack by traces of oxygen or moisture and apparatus intended to contain it was

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† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

conditioned accordingly.[1,4] Purified samples of the compound were stored at 77 K.

The first attempts to measure electron-scattering patterns involved a Balzers KD.G2 gas-diffraction apparatus but yielded photographic plates of relatively poor quality. Subsequent measurements were made using Kodak Electron Image plates and the Edinburgh/Cornell gas-diffraction apparatus.[9,10] Before each series of exposures, the glass ampoule containing the sample was re-evacuated while the contents were held first at 77 and then at 178 K to remove any hydrogen or diborane resulting from decomposition. With the sample held at 228 K and the nozzle close to 298 K, the scattering pattern of the vapour was then measured at nozzle-to-plate distances of 128.5 and 284.9 mm. The electron wavelength was 5.126 pm, as determined by reference to the scattering pattern of benzene vapour, and the nozzle-to-plate distances corresponded in these circumstances to a range of 10—360 nm^{-1} in the scattering variable s. The intensities of the patterns recorded on each of the six plates judged to be satisfactory were measured using a modified Jarrell-Ash microdensitometer.[11]

Some problems were experienced as a result of a reaction between the photographic emulsion and the vapour of $Ga(BH_4)_2H$. This reaction caused a significant deterioration of the signal-to-noise ratio, particularly at low scattering intensities on the plates exposed at the shorter nozzle-to-plate distance. It was found that the effects could be minimized by leaving the plates in air for 24 h before developing.

Calculations were performed on an ICL 2970 computer at the Edinburgh Regional Computing Centre using the programs for data reduction [10] and least-squares refinement [12] described previously and with the complex scattering factors listed by Schäfer *et al.*[13] The weighting functions used to set up the off-diagonal weight matrix are given in Table 1 together with the correlation parameters and final scale factors.

TABLE 1

Nozzle-to-plate distances, weighting functions, correlation parameters, and scale factors

Nozzle-to-plate distance/mm	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation, p/h	Scale factor, k *
			nm^{-1}				
128.5	4	84	100	216	248	−0.0763	0.996(63)
284.9	2	32	56	120	160	0.2872	0.912(42)

* Values refer to refinement A (see Table 2). Figures in parentheses are the estimated standard deviations of the last digits.

STRUCTURE ANALYSIS

The vibrational spectra of $Ga(BH_4)_2H$ in the gaseous and solid phases [2,5] favour the adoption of structure (1), with two bidentate tetrahydroborate groups. The radial-distribution curve, $P(r)/r$ *vs.* r, derived from the experimental data sets after scaling, combination, and Fourier transformation, is depicted in Figure 1. Of the prominent peaks, that at *ca.* 120 pm is identified with scattering from all the directly bonded B–H atom pairs. The broad feature at 150—190 pm is similarly due to all the directly bonded Ga–H atom pairs. Most conspicuous is the peak near 215 pm which must be associated with the Ga–B pairs and the location of which leaves little doubt that the molecule contains dihydrogen-bridged $Ga(\mu\text{-}H)_2BH_2$ units, as in structure (1), rather than the monohydrogen-bridged $Ga(\mu\text{-}H)BH_2$ units implied by structure (2). This conclusion receives strong support from the Ga–B distance of *ca.* 234 pm determined by electron diffraction of the molecule $Me_2GaB_3H_8$ wherein the gallium atom is linked *via* a *single* hydrogen bridge to each of two boron atoms of the B_3H_8 fragment.[14] The weaker, relatively broad features of the radial-distribution curve near 300 and 360 pm are associated mainly with scattering from the non-bonded atom pairs Ga ··· H_t and B ··· B respectively. Other weak features can be ascribed to distal B ··· H and H ··· H non-bonded atom pairs.

The electron-scattering pattern of the vapour was analysed first in terms of a structural model possessing C_{2v} symmetry with the five hydrogen atoms directly linked to the gallium located at the vertices of a rectangular-based

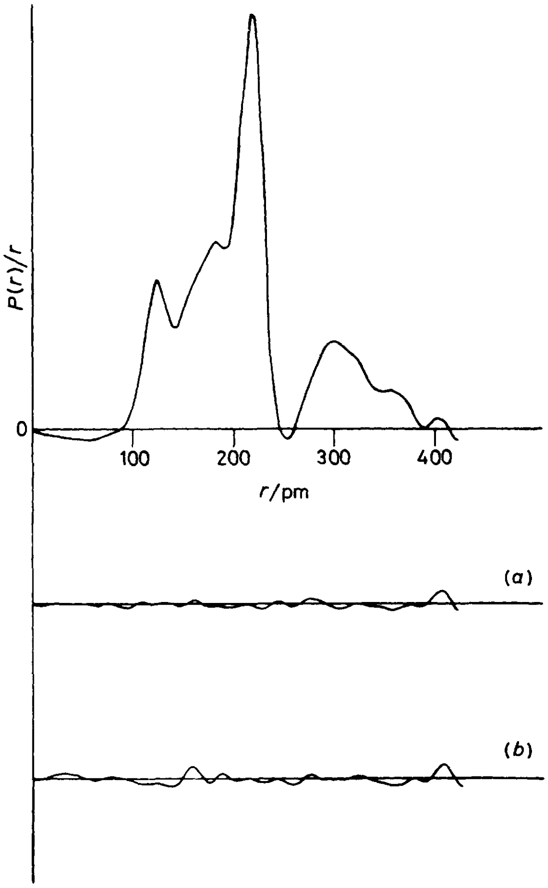

FIGURE 1 Observed radial-distribution curve, $P(r)/r$ against r, for $Ga(BH_4)_2H$. Before Fourier inversion the data were multiplied by $s\cdot\exp[(-0.000\,020\,s^2)/(z_{Ga}-f_{Ga})(z_B-f_B)]$. Final difference curves are shown (*a*) for refinement A involving a model with C_2 symmetry and unsymmetrical $Ga(\mu\text{-}H)_2B$ bridges and (*b*) for refinement B involving a model with C_{2v} symmetry and symmetrical $Ga(\mu\text{-}H)_2B$ bridges

pyramid. The calculations failed, however, to give a reasonable account of the measured scattering. The principal flaw could be traced to the peak in the experimental radial-distribution curve arising from the directly bound Ga–H atom pairs. The shape of this feature could not be reproduced by the scattering intensity derived from a unique Ga–H_t and four equivalent Ga–H_b bonds and any reasonable values for the corresponding amplitudes of vibration. Hence we were led to modify the model to admit the possibility of non-equivalent Ga–H_b distances within each of the Ga(μ-H)$_2$BH$_2$ moieties. To enable the bond order of each of the Ga–H_b–B bridges to be conserved, non-equivalence of the two B–H_b distances was also allowed. Another modification included the facility to permit the simultaneous rotation of the Ga(μ-H)$_2$BH$_2$ units about the Ga–B axes. This twisting was defined by an angle θ such that the condition θ = 0 corresponds to a molecular conformation in which the planes of the two Ga(μ-H)$_2$B groupings are normal to the HGaB$_2$ skeleton whereas θ = 45° produces an $H_tGa(H_b)_4$ polyhedron approximating to a trigonal bipyramid with the terminal hydrogen atom occupying an equatorial site. Such a model conforms overall to C_2 symmetry. We have assumed moreover that the B–H_t bond lengths in each tetrahydroborate group are equal and that the plane containing the B(H_t)$_2$ fragment not only bisects the H_bBH_b angle but is normal to the Ga(H_b)$_2$B plane.

TABLE 2

Molecular parameters [a] for Ga(BH$_4$)$_2$H

(a) Independent geometrical parameters

	Parameter	Distance/pm or angle/°	
		Refinement A, C_2 model	Refinement B, C_{2v} model
P_1	r(Ga–B)	217.2(0.5)	217.4(0.4)
P_2	r(Ga–H) (average)	177.4(1.7)	174.4(1.9)
P_3	r(B–H) (average)	127.7(1.4)	122.2(1.1)
P_4	Δ_1, r(Ga–H_b) (average) – r(Ga–H_t)	26.1(1.7)	27.7(2.5)
P_5	Δ_2, r(Ga–H_b') – r(Ga–H_b)	12.9(2.6)	0 [b]
P_6	Δ_3, r(B–H_b) (average) – r(B–H_t)	15.1(7.4)	4.2(5.5)
P_7	Δ_4, r(B–H_b') – r(B–H_b)	–20.5(7.9)	0 [b]
P_8	Angle H_t–B–H_t	125.0(5.0) [c]	125.0(5.0) [a]
P_9	Angle B–Ga–B	112.2(1.5)	111.4(1.4)
P_{10}	θ, Ga(μ-H)$_2$B twist	4.1(6.0)	0 [b]

(b) Molecular distances, interbond angles, and amplitudes of vibration

Parameter	Refinement A, C_2 model		Refinement B, C_{2v} model	
	Distance/pm or angle/°	Amplitude/pm	Distance/pm or angle/°	Amplitude/pm
r(Ga–H_t)	156.5(2.4)	6.0 [b]	152.3(3.5)	9.5(1.2)
r(Ga–H_b)	176.2(1.5)	9.5 [b]	180.0(1.6)	13.6 [d]
r(Ga–H_b')	189.1(2.5)	9.5 [b]		
r(B–H_t)	120.2(3.1)	6.5 [e]	120.1(2.3)	8.3 [f]
r(B–H_b')	125.0(8.1)	7.1 [e]	124.3(3.6)	9.9(1.4)
r(B–H_b)	145.6(3.3)	7.9(3.1) (u_{12})		
r(Ga–B)	217.2(0.5)	7.3(0.7) (u_1)	217.4(0.4)	6.9(0.7)
r(Ga · · · H_t)	292.7(2.2)	18.4(3.0) (u_{11})	292.9(2.0)	16.6(2.0)
r(B · · · B)	360.6(2.5)	9.4(3.6) (u_{13})	359.1(2.8)	9.2(3.9)
Angle H_b–Ga–H_b'	76.8(4.2)	—	69.7(3.3)	—
R_G	0.159		0.190	

[a] Figures in parentheses are the estimated standard deviations of the last digits; the unsymmetrically bridging hydrogens are designated H_b and H_b'. [b] Fixed. [c] See text. [d] Tied to the Ga–H_t amplitude. [e] Tied to the B–H_b amplitude u_{12} in the ratios 1 : 1.1 and 1 : 1.2. [f] Tied to the B–H_b amplitude.

The final model used to describe the hydridogallium bis(tetrahydroborate) molecule employed the ten independent parameters specified in Table 2(a). The optimum solution found for the structure constrained to preserve C_{2v} symmetry (for which R_G exceeded 0.2) was used to initiate refinement calculations designed to investigate the effects first of conceding non-equivalence of the Ga–H_b and B–H_b distances and then of twisting the BH$_4$ groups about the Ga–B axes. A markedly better account of the experimental scattering pattern was thus achieved although the effects of correlation made it impossible to refine independently the amplitudes of vibration associated with the Ga–H distances. A wide range of values was tried for these amplitudes; the values listed as refinement A in Table 2 correspond to the best solution judged in terms of the R factor, R_G, but do not lend themselves to refinement.

The amplitudes thus determined are admittedly rather smaller than might be expected by comparison with the metal–hydrogen distances of some related compounds [*e.g.* Al(BH$_4$)$_2$Me 10 pm,[1] Al(BH$_4$)$_3$ 12.5 pm,[15] and Ga(BH$_4$)Me$_2$ 10 pm [4]] but are well within the range of values found for the Ge–H bonds of typical hydridogermanium compounds (5—13 pm).[16] A more exact evaluation of the amplitudes of vibration of the Ga(BH$_4$)$_2$H molecule could be realised only *via* a detailed normal co-ordinate analysis, whereas it has been possible to date to offer no more than a partial assignment of the vibrational spectra in terms of the appropriate group vibrations.[2] The lack of information about the vibrational properties of the molecule had the additional consequence of precluding any assessment of shrinkage effects. A possible explanation of the C_2 structure apparently favoured by the molecule might, it is true, be founded on a model intrinsically retaining C_{2v} symmetry while subject to a large amplitude of rocking of the BH$_4$ groups about their rest positions. Such a vibration would,

TABLE 3

Least-squares correlation matrix ($\times 100$) * corresponding to refinement A for the molecule $Ga(BH_4)_2H$

Distances							Angles		Vibrational amplitudes				Scale factors		
P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_9	P_{10}	u_1	u_{11}	u_{12}	u_{13}	k_1	k_2	
100	**72**	13	−23	**63**	53	56	−24	58	−57	−37	35	2	−22	−26	P_1
	100	40	−28	52	54	41	−15	**65**	−50	−45	34	0	−25	−37	P_2
		100	−36	−27	**65**	22	0	18	−40	4	29	0	10	25	P_3
			100	−3	**−61**	**−63**	3	−12	58	7	−26	−1	5	−18	P_4
				100	13	35	−18	**60**	−29	−27	25	2	−20	−40	P_5
					100	**85**	−16	57	**−88**	−2	**61**	3	7	27	P_6
						100	−20	59	**−87**	−2	58	4	8	22	P_7
							100	−26	21	11	−25	−16	11	10	P_9
								100	−58	−12	**70**	4	−6	−7	P_{10}
									100	18	−53	−3	10	−9	u_1
										100	19	3	**85**	**76**	u_{11}
											100	−1	18	36	u_{12}
												100	2	0	u_{13}
													100	**65**	k_1
														100	k_2

* Numbers in bold type indicate marked correlation.

however, imply a change in Ga–H bond length of at least 20 pm in the course of its motion. Our experience of other molecules containing dihydrogen-bridged tetrahydroborate groups, *e.g.* $M(BH_4)Me_2$ (M = Al or Ga) [4] and $Al(BH_4)_2Me$,[1] gives no grounds for invoking a motion of this kind or indeed for anticipating that the results of our calculations would be radically altered by due allowance for shrinkage effects. The estimated standard deviations (e.s.d.s) which we associate with the molecular parameters calculated here are likely to be at least comparable in magnitude with the effects of shrinkage; such deviations take into account not only the effects of correlation but also any systematic errors in the electron wavelength, nozzle-to-plate distance, *etc.*

With the aid of a molecular model possessing C_2 symmetry we have been able in our least-squares analysis of the molecular-scattering intensities to compass the simultaneous refinement of the 13 independent parameters listed under refinement A in Table 2 as well as the scale factors for the two data sets. The convergence of the structural refinement proceeded satisfactorily on the whole. As revealed by the final least-squares correlation matrix reproduced in Table 3, pronounced correlation occurs between Δ_1, Δ_2, Δ_3, and Δ_4 and between the Ga–B and average Ga–H distances; there are as a result relatively large e.s.d.s associated with the final values taken by some of the structural parameters.

The angle H_t–B–H_t does not yield to refinement. After refining the rest of the parameters to optimum values, therefore, we have carried out calculations to explore the dependence of R_G on this angle. It appears that R_G is at a minimum for an angle of 125°, but our attempts at refinement on the basis of this value have been frustrated by very strong correlation between the H_t–B–H_t angle and the other parameters implicating the terminal hydrogen atoms of the tetrahydroborate groups. In the circumstances we we have had little option but to assign to this angle a value of 125° with a probable e.s.d. on the evidence of our calculations in the order of 5°.

The success of the calculations may be judged by the difference (*i*) between the experimental radial-distribution curve and that simulated for the best model (Figure 1), and (*ii*) between the experimental and calculated intensities of molecular scattering (Figure 2). A perspective view of the $Ga(BH_4)_2H$ molecule in the ultimate form consistent with this model is shown in Figure 3.

After optimizing the refinement on the basis of a molecular model with C_2 symmetry, we have carried out further calculations in which the structural parameters deduced

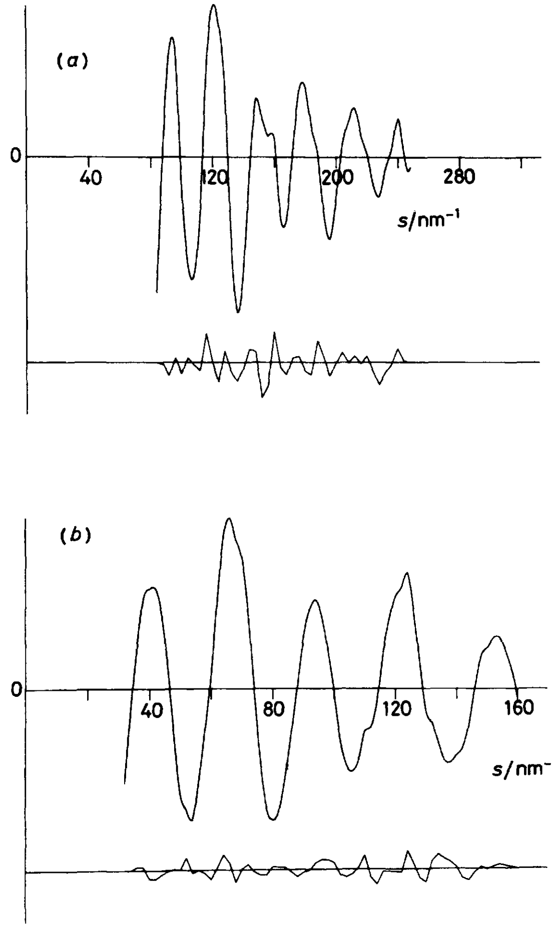

FIGURE 2 Experimental and final difference molecular-scattering intensities based on refinement A for $Ga(BH_4)_2H$; nozzle-to-plate distances (*a*) 128.5 and (*b*) 284.9 mm

for the skeleton of the $Ga(BH_4)_2H$ molecule have again been constrained to preserve C_{2v} symmetry. Hence we have sought to check whether the unsymmetrical form apparently assumed by the $Ga(\mu\text{-}H)_2B$ moieties gives the best account of the experimental data. The calculations reveal two significant features. First, the R factor, R_G, increases from 0.159 for the C_2 model to 0.190 for the optimum solution afforded by the C_{2v} model (see also Figure 1). Secondly, there is an increase in the amplitudes of vibration of the directly bound Ga–H atom pairs now amenable to refinement as a single parameter. There is otherwise little change in the values deduced for the remaining molecular parameters (see refinement B in Table 2). The C_2 structure with its unsymmetrical $Ga(\mu\text{-}H)_2B$ units seems therefore to represent the more likely equilibrium geometry for the $Ga(BH_4)_2H$ molecule.

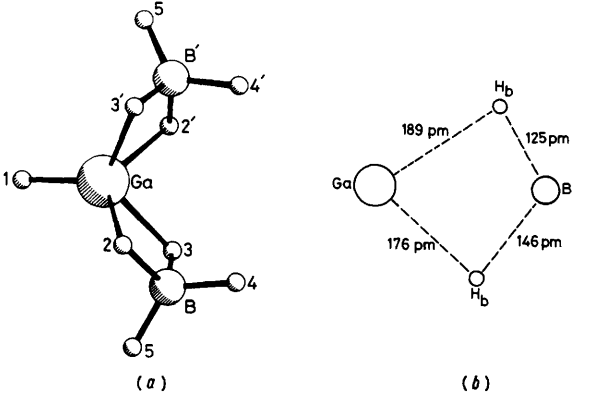

FIGURE 3 (a) Perspective view of the molecule $Ga(BH_4)_2H$ and (b) geometry of the bridging $Ga(\mu\text{-}H)_2B$ groupings corresponding to refinement A

DISCUSSION

The most unusual feature about the structure of hydridogallium bis(tetrahydroborate) which complies best with the measured electron-scattering pattern is the unsymmetrical nature of the dihydrogen bridges linking the BH_4 groups to the metal centre. None of the molecular structures involving bidentate or tridentate tetrahydroborate groups investigated hitherto shows any clear sign of non-equivalent hydrogen bridges and certainly nothing transcending either the effects of crystal packing or the limited accuracy with which such hydrogen atoms can be located by X-ray diffraction. To judge by its electron-diffraction pattern, however, the $Ga(BH_4)_2H$ molecule adopts in the optimum refinement a conformation in which each of the four-membered $Ga(H_b)_2B$ rings possesses $Ga\text{–}H_b$ distances of 176 and 189 pm and $B\text{–}H_b$ distances of 125 and 146 pm (see Figure 3). This dissymmetry tends towards the formulation $Ga(H_t)\text{–}B(H_t)$ with a direct gallium–boron bond and the adoption of a semi-terminal role by the bridging hydrogen atoms. Some supporting evidence for the non-equivalence of the bridging hydrogen atoms is to be found in the vibrational spectra of $Ga(BH_4)_2H$ which contain not one but two features attributable to $Ga\text{–}H_b$ stretching modes, at *ca.* 1 300 and at *ca.* 1 400 cm^{-1},[2] whereas the corresponding modes of dimethylgallium tetrahydroborate have been assigned frequencies close to 1 400 cm^{-1}.[17]

In the absence of independent information about the vibrational properties of the molecule, there is no cause to attach undue weight to the relatively small spans ascribed by the optimum solution to the vibrational amplitudes of directly bonded $Ga\text{–}H_b$ and $B\text{–}H_b$ distances. It is true that the values are significantly smaller than those associated with the molecular model retaining C_{2v} symmetry, albeit at the overall expense of an inferior account of the experimental results. Other sources of independent information must also be tapped before it is possible realistically to investigate any subtle effects on the terminal $B(H_t)_2$ fragments evoked by the apparent dissymmetry of the $Ga(H_b)_2B$ units.

At 217 pm, the Ga–B distance in $Ga(BH_4)_2H$ differs but little from that in $Ga(BH_4)Me_2$ (216 pm) [4] approximating to the sum of the tetrahedral covalent radii of the gallium and boron atoms (214 pm). This lends support to the assignment of a major role to direct metal–boron bonding, a feature also inferred from the Raman [2,17,18] and u.v. photoelectron [2,19] spectra exhibited by these and other tetrahydroborate molecules.

Structural characterization has been extended previously to only a handful of compounds containing terminal Ga–H bonds. Nevertheless, at 156.5 pm, the $Ga\text{–}H_t$ bond length in $Ga(BH_4)_2H$ is consistent with the relatively wide range of 138—173 pm spanned by corresponding bond lengths in crystalline cyclic or cage-like complexes containing four- or five-co-ordinate gallium atoms linked to oxygen, nitrogen, and at least one terminal hydrogen atom.[20] It is also consistent with the appreciably narrower range of 150—156 pm spanned by the Ge–H bonds of typical hydridogermanium compounds.[16]

The magnitude of the B–Ga–B angle (112°) might be taken to imply that $Ga\text{–}H_t$ is a sterically demanding group, perhaps with its relatively localized bonding electrons occupying more space in the valence shell of the gallium atom than the delocalized electrons associated with the 'electron deficient' $Ga(\mu\text{-}H)_2B$ units. With reference to the numbering scheme of Figure 3, however, closer inspection reveals that the angles subtended by the different Ga–H bonds are as follows: H(1)GaH(2) 117, H(1)GaH(3) 119, H(2)GaH(2′) 126, and H(3)GaH(3′) 121°. Hence it appears that the five hydrogen atoms are distributed more or less uniformly about the gallium atom to which they are directly linked. The apparent peculiarities of the structure then seem to stem less from the influence of the $Ga\text{–}H_t$ group than from the co-ordination number of the metal atom and the mode of ligation of the BH_4 groups. Co-ordination numbers in excess of four are still far from common in gallium compounds [21] and it is relevant perhaps to note how the reaction of lithium tetrahydroborate with gallium(III) chloride affords not the six-fold co-ordination of the tris(tetrahydroborato)-derivative $Ga(BH_4)_3$ [to be expected by analogy with the corresponding reaction between $LiBH_4$ and aluminium(III) chloride] [15,22] but the uneasy five-fold co-ordination of the bis(tetrahydroborato)-derivative $Ga(BH_4)_2H$. The constraints of co-ordination number and ligating properties may likewise account for the formation of the four-co-ordinate compound $Ga(BH_4)(Me)H$ in place of the expected five-co-ordinate species $Ga(BH_4)_2Me$ when $LiBH_4$ reacts with methylgallium dichloride.[3]

Investigations of the effect of varying the $Ga(\mu\text{-}H)_2B$ twist angle θ have shown that the *R* factor passes through a minimum when $\theta = 4°$ although this value is subject to an e.s.d. of about 6°. Such a twisting is barely significant, particularly as we note that it is described exactly by the in-phase torsional mode of the two BH_4 groups. Nevertheless the distortion is in such a direction as to place the longer $Ga\text{-}H_b$ bonds along the axis of a trigonal bipyramid while also increasing rather than decreasing the interaction between the terminal hydrogen atoms H(4) and H(4′) otherwise held apart by the unsymmetrical geometry of the $Ga(\mu\text{-}H)_2B$ groups. Within the limits of our calculations, the $Ga(BH_4)_2H$ molecule resembles $Al(BH_4)_2Me$[1] in that the five atoms directly co-ordinated to the metal centre complete what approximates to a rectangular pyramid rather than a trigonal bipyramid. In the circumstances, the demands of the tetrahydroborate group as a bidentate ligand with an unusually small ' bite ' may well regulate the geometry of the co-ordination polyhedron centred on the metal atom; certainly the conjunction of two such ligands with a monodentate ligand is expected to give a rectangular pyramid on the basis of calculations designed to minimize the total repulsion energy in the co-ordination sphere of the central atom.[23]

The i.r. spectrum of gaseous hydridogallium bis(tetrahydroborate) includes near 730 cm^{-1} an absorption characterized by partially resolved *P*, *Q*, and *R* branches of roughly equal intensity.[2] This is believed to arise from the in-plane deformation mode of the $H_t\text{-}GaB_2$ skeleton. The atomic co-ordinates in the optimum refinement of the electron-scattering pattern have been used to calculate the principal moments of inertia of the $Ga(BH_4)_2H$ molecule which emerges as an asymmetric rotor possessing C_2 symmetry. Hence it is possible to identify the contour of the band near 730 cm^{-1} with that of an ' AC hybrid '.[24] At 19.9 cm^{-1}, the *P*–*R* separation thus calculated is in reasonable agreement with the measured separation of 23 ± 1 cm^{-1}, particularly in view of the approximations which the calculations must entail.

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