Group 3 Tetrahydroborates. Part 2.[1] The Molecular Structures of Dimethylaluminium Tetrahydroborate and Dimethylgallium Tetrahydroborate in the Gas Phase as determined by Electron Diffraction

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The molecular geometries of $Al(BH_4)Me_2$ and $Ga(BH_4)Me_2$ in the gas phase have been studied by electron diffraction. Both species appear to be monomeric molecules with skeletons having C_{2v} symmetry and containing bidentate tetrahydroborate groups. Salient parameters † for $Al(BH_4)Me_2$ are: r_a(Al–C) 192.9(0.4), r_a(Al–B) 212.8(0.8), r_a(Al–H_b) 177.0(3.2), r_a(B–H_b) 123.0(1.7), r_a(B–H_t) 120.7(1.7) pm; C–Al–C 118.4(0.7), H_b–Al–H_b 70.6(4.8)° (t = terminal, b = bridging). The corresponding parameters † for $Ga(BH_4)Me_2$ are: r_a(Ga–C) 194.4(0.4), r_a(Ga–B) 216.3(0.8), r_a(Ga–H_b) 179.1(3.0), r_a(B–H_b) 121.7(1.9), r_a(B–H_t) 119.2(1.9) pm; C–Ga–C 118.8(1.2), H_b–Ga–H_b 68.4(4.6)°. Exchange of methyl for tetrahydroborate groups in molecules of the type $M(BH_4)_{3-n}(CH_3)_n$ (M = Al or Ga, n = 2 or 3; M = Al, n = 0) evokes but small changes in the dimensions of the $(CH_3)_2M$ and $M(BH_4)$ groups although there are signs suggestive of modest variations of the bonding within these two groups.

THE tetrahydroborate group has attracted considerable attention by the versatility of its ligation with respect to metal atoms.[2,3] In addition to compounds which contain more-or-less discrete $[BH_4]^-$ anions, there are known to exist well defined derivatives in which the metal is linked to the boron atom *via* triple,[2,3] double,[2,3] or even single [4] hydrogen bridges. On the other hand, definitive information is far from extensive, and deductions concerning the mode of co-ordination of the tetrahydroborate group in a given compound commonly hinge on the circumstantial evidence of its vibrational spectrum.[5] Even where more direct methods of structural analysis have been applied, the overall picture lacks definition in three main respects: (*i*) only for the species B_2H_6,[6] $Al(BH_4)_3$,[7] $Be(BH_4)_2$,[8] $Be(BH_4)(C_5H_5)$,[9] $Zr(BH_4)_4$,[10] and $Ti(BH_4)(C_5H_5)_2$ [11] has electron diffraction been exploited with the aim of determining the structures of gaseous tetrahydroborate molecules; (*ii*) only for the species B_2H_6,[6,12] $Be(BH_4)_2$,[8,13] $Zr(BH_4)_4$,[10,14] and $Ti(BH_4)(C_5H_5)_2$ [11,15] have structure determinations sought to span both the crystalline and the gaseous phases; and (*iii*) the dimensions of the tetrahydroborate group itself have usually defied precise characterization. Although there are signs that certain tetrahydroborates have access to two or more structural modifications differing but little in energy,[3,8,13,16] it is difficult at this stage to evaluate the various factors likely to exercise a structure-determining influence.

In the course of our investigations of ' mixed ' hydrides formed by the Group 3 elements, we have been concerned with the synthesis and properties of molecular species in which the tetrahydroborate group competes with the ligands H and CH_3 for co-ordination of an aluminium or gallium centre; such species include methylaluminium tetrahydroborates, $Al(BH_4)_{3-n}Me_n$ (n = 1 or 2),[16,17] and the gallium tetrahydroborates $Ga(BH_4)Me_2$,[1] $Ga(BH_4)Me(H)$,[18] and $Ga(BH_4)_2H$.[16,19] The vapour densities imply that the dimethylaluminium [16,17] and dimethylgallium [1] compounds vaporize in the form of monomeric $M(BH_4)Me_2$ molecules (M = Al or Ga), and the vibrational spectra of the vapours [1,16] are consistent with a molecular model $Me_2M(\mu\text{-}H)_2BH_2$ having C_{2v} symmetry and containing a four-co-ordinate M atom linked to a bidentate tetrahydroborate group. Here we report the results of a structural analysis of these two molecules in the gas phase as determined by the sector-microphotometer method of electron diffraction. Such studies were urged among other things by the need to establish reliable points of reference for related molecules such as $Ga(BH_4)_2H$ [20] the structural analysis of which is open to more than one interpretation.

EXPERIMENTAL

The synthesis and manipulation of dimethylaluminium and dimethylgallium tetrahydroborate were accomplished using a conventional high-vacuum line having stopcocks and ground-glass joints lubricated with Apiezon L grease. Aluminium(III) and gallium(III) chloride were prepared by the direct interaction of the metal with chlorine and purified by repeated sublimation *in vacuo*. Lithium tetrahydroborate, supplied by B.D.H., was recrystallized immediately prior to use from diethyl ether. Aluminium tris(tetrahydroborate) was generated by heating $Li[BH_4]$ with aluminium(III) chloride at *ca.* 100 °C; [21] for the preparation of trimethylaluminium and trimethylgallium, an excess of the appropriate metal was heated with dimethylmercury.[22] Trimethylaluminium and aluminium tris(tetrahydroborate) in the proportions $AlMe_3 : Al(BH_4)_3 = 2 : 1$ were allowed to react at room temperature for *ca.* 2 h to effect virtually quantitative redistribution in accordance with equation (1).[16,17] The synthesis of dimethylgallium tetrahydroborate was achieved by the metathetical reaction between dimethylgallium chloride and $Li[BH_4]$ in the absence of a solvent at −15 °C [equation (2)].[1]

$$Al_2Me_6 + Al(BH_4)_3 \longrightarrow 3Al(BH_4)Me_2 \qquad (1)$$

Trap-to-trap distillation of the products of reactions (1) and (2) gave samples of dimethylaluminium tetrahydroborate (m.p. 14—15 °C) and dimethylgallium tetrahydro-

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† Figures in parentheses are the estimated standard deviations.

TABLE 1

Weighting functions, correlation parameters, and scale factors

Compound	Camera distance/mm	Δs/nm^{-1}	$s_{\text{min.}}$/nm^{-1}	sw_1/nm^{-1}	sw_2/nm^{-1}	$s_{\text{max.}}$/nm^{-1}	p/h	Scale factor, k
$Al(BH_4)Me_2$	250	4	72	85	250	304	0.413	0.443(22)
	500	2	32	45	125	156	0.480	0.576(25)
	1 000	1	13	22	65	75	0.499	0.389(25)
$Ga(BH_4)Me_2$	250	4	64	120	260	300	0.433	0.924(50)
	500	2	30	45	133	154	0.492	0.785(33)
	1 000	1	17	20	67	75	0.499	0.688(36)

borate (m.p. 1—2 °C) each judged to be pure by the criteria (*i*) of its vapour pressure and (*ii*) of the i.r. spectrum of its vapour.[1,16,17] Our experiments have shown that gaseous

$$\tfrac{2}{3}GaMe_3 + \tfrac{1}{3}GaCl_3 \xrightarrow{15\text{—}45\,°C} GaMe_2Cl \xrightarrow[-15\,°C]{Li[BH_4]} Ga(BH_4)Me_2 \qquad (2)$$

$Al(BH_4)Me_2$ at a pressure of 10—20 mmHg * undergoes minimal decomposition in 24 h at room temperature;[16] by contrast, gaseous $Ga(BH_4)Me_2$ under similar conditions decomposes with a half-life in the order of 3 h with the formation of gallium metal, hydrogen, and methylboranes.[1] Both compounds are extremely sensitive to attack by traces of oxygen or moisture, and it was a prerequisite to securing reproducible behaviour that the surfaces of any apparatus intended to contain either tetrahydroborate should first be conditioned, *e.g.* by heating under high vacuum or by preliminary exposure to a sample of the vapour followed by pumping to waste of any volatile material.

Electron scattering patterns were recorded photographically on Agfa–Gevaert Replica 23 or Ilford N60 plates using a Balzers KD.G2 gas-diffraction apparatus.[23] The sample was contained in an ampoule closed by a greaseless stopcock, access to the nozzle of the diffraction apparatus being gained *via* a greased metal–glass taper joint. Before each series of exposures, the ampoule was evacuated while the contents were held first at 77 and then at 178 K to remove any hydrogen or diborane resulting from decomposition of the sample. With the sample of $Al(BH_4)Me_2$ or $Ga(BH_4)Me_2$ held at 273 K (corresponding to an equilibrium vapour pressure of *ca.* 10 mmHg) and the nozzle at room temperature (*ca.* 298 K), exposures were taken at nozzle-to-plate distances of 250, 500, and 1 000 mm, thereby affording a range of 10—300 nm^{-1} in the scattering variable s. The measurements were accumulated in digital form using a Joyce–Loebl automatic microdensitometer giving for its output 760 data points measured at equal intervals along each of eight diameters of a given plate. The electron wavelength used, 5.660 pm for the aluminium compound and 5.674 pm for the gallium compound, was determined from the diffraction pattern of benzene vapour.

All calculations were performed on an ICL 4–75 computer at the Edinburgh Regional Computing Centre using the programs for data reduction[24] and least-squares refinement[25] previously described. The weighting functions used to set up the off-diagonal weight matrices, correlation parameters, and scale factors are given in Table 1. The complex scattering factors listed by Schafer *et al.*[26] were used throughout the calculations: distances quoted correspond to r_a.

STRUCTURE ANALYSIS

The i.r. spectra of gaseous and matrix-isolated dimethylaluminium and dimethylgallium tetrahydroborates, taken in conjunction with the vapour densities, imply but do not prove that the predominant vapour species are of the form $Me_2M(\mu\text{-}H)_2BH_2$ (M = Al or Ga) belonging to the C_{2v} symmetry group.[1,16] Not only are the spectral features characteristic of a non-linear MMe_2 group readily apparent, but the pattern of absorptions normally associated with a doubly bridged tetrahydroborate group is strongly in evidence.[2,3,5,27] Such a model, illustrated in Figure 1, is characterized by a planar $C_2MB(H_t)_2$ skeleton with the $M(H_b)_2B$ moiety defining a plane normal to that of the skeleton (t = terminal, b = bridging). For the purposes of our analysis we have assumed that each CH_3M unit conforms locally to C_{3v} symmetry and that each CH_3 group is staggered with respect to the other bonds radiating from the M atom, thereby preserving the C_{2v} symmetry of the $C_2M(\mu\text{-}H)_2BH_2$ skeleton; such a conformation corresponds to that favoured by the CH_3 groups in tetramethyldiborane[28] and in molecules of the type $Me_2Al(\mu\text{-}X)_2AlMe_2$ (X = Me,[29] H,[30] Cl,[31] or SMe[32]). With these assumptions the geometry of the $M(BH_4)Me_2$ molecule may be described in terms of nine independent parameters: these are the four internuclear distances M–C, M–B, C–H_m (where m denotes the hydrogen of a methyl group), and M–H_b; a mean B–H distance and Δ(B–H), the difference between the B–H_b and B–H_t distances; and the three angles M–C–H_m, C–M–C, and H_t–B–H_t.

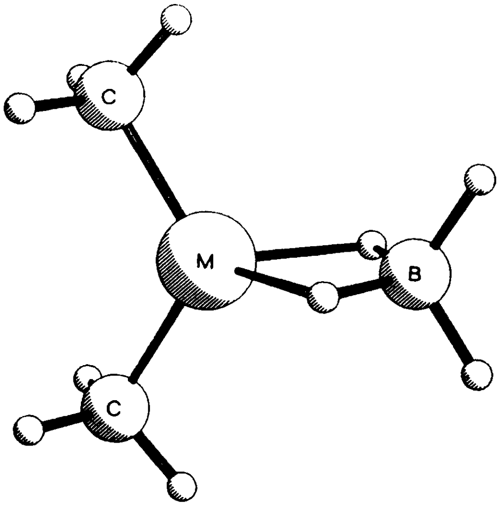

FIGURE 1 Perspective view of the molecule $M(BH_4)Me_2$ (M = Al or Ga)

Theoretical molecular-scattering intensities have been calculated by established procedures,[33] and the structure of each molecule has been refined on this basis by full-matrix least-squares analysis; in the process each camera setting was assigned an appropriate scale factor which has itself been separately refined. We have not applied shrinkage corrections in any of our refinements; although rela-

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 eV ≈ 1.60 × 10^{-19} J.

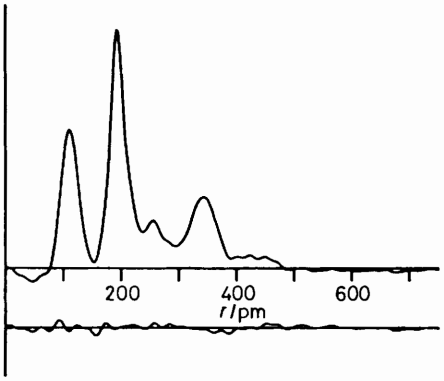

FIGURE 2 Observed and difference radial-distribution curves, $P(r)/r$, for $Al(BH_4)Me_2$. Before Fourier inversion the data were multiplied by $s\ .\ \exp[(-0.000\ 035\ s^2)/(z_{Al}-f_{Al})(z_C-f_C)]$

tively large-amplitude vibrations of the $C_2M(\mu\text{-}H)_2BH_2$ skeleton may affect estimates of some of the less well defined parameters, there is no reason to suppose that shrinkage effects will make any significant difference to the results, within the limits of error stipulated by the estimated standard deviations. Such deviations of the molecular parameters derived from the least-squares analysis take into account the effects of correlation, whether involving the data points or the molecular parameters themselves, and have been increased to allow for systematic errors in the electron wavelength, camera height, *etc.*

(*i*) *Dimethylaluminium Tetrahydroborate.*—Combination of the experimental molecular-scattering intensities measured with different nozzle-to-plate distances for the $Al(BH_4)Me_2$ molecule affords *via* Fourier inversion the radial-distribution curve $P(r)/r$ depicted in Figure 2. Most prominent is a composite feature near 200 pm originating mainly in the Al–C scattering distance but including also components derived from the Al–B and Al–H_b distances. Near 110 pm is located another composite peak corresponding to the C–H_m, B–H_b, and B–H_t distances, whereas a broad feature centred at *ca.* 330 pm corresponds to the B · · · C and C · · · C non-bonded distances. The weak, relatively poorly defined peaks still unaccounted for, evident for example at 250, 430, and 450 pm, arise from other non-bonded distances, *e.g.* Al · · · H_m, B · · · H_m, and C · · · H. The absence of any appreciable peaks in the region above 400 pm contrasts with the radial-distribution curve for the Al_2Me_6 molecule [29] and so bears out the implications of the vapour density and the i.r. spectrum that the vapour contains few, if any, aggregates of the type $[Me_2Al(BH_4)]_n$ (where $n \geqslant 2$).

Least-squares calculations of the electron scattering pattern have enabled the simultaneous refinement of seven out of the nine independent geometric parameters described above [the five distances Al–C, Al–B, Al–H_b, B–H(average), and C–H_m, and the two angles Al–C–H_m and C–Al–C], as well as five vibrational parameters (the amplitudes of vibration of the distances Al–C, Al–B, C · · · C, B · · · C, and Al · · · H_m). The refinement of the structure has met with satisfactory convergence on the whole; the final least-squares correlation matrix, given in Table 2, confirms that most of the parameters are reasonably well defined, although certain of them [the distances Al–H, B–H(average) and B–H(average), C–H, and the amplitudes of vibration of the distances C · · · C, B · · · C] are strongly correlated. The circumstances of this correlation are inevitably created by the overlapping of peaks in the radial-distribution curve, with the result that the relevant scattering distances and amplitudes of vibration are simply not well defined. The parameter Δ(B–H), the difference between the bridging and terminal B–H distances, did not yield to refinement; accordingly, after refinement of the other parameters, a series of calculations has been performed to study the dependence of the R factor on Δ(B–H) spanning the range Δ(B–H) = 0—7 pm. Hence we have found that R_G varies smoothly from 0.173 0 at the minimum [Δ(B–H) = 2.3 pm] to 0.175 5 at Δ(B–H) = 7 pm. As in B_2H_6 [6] and $Al(BH_4)_3$,[7] the angle H_t–B–H_t is not well defined; in the event it has been set equal to the value found in $Al(BH_4)_3$ (116.2°). In view of the relative paucity of detail offered by the radial-distribution curve for a molecule of this complexity, it has been possible to refine independently only a comparatively small number of vibrational amplitudes. The remaining amplitudes we have fixed at values

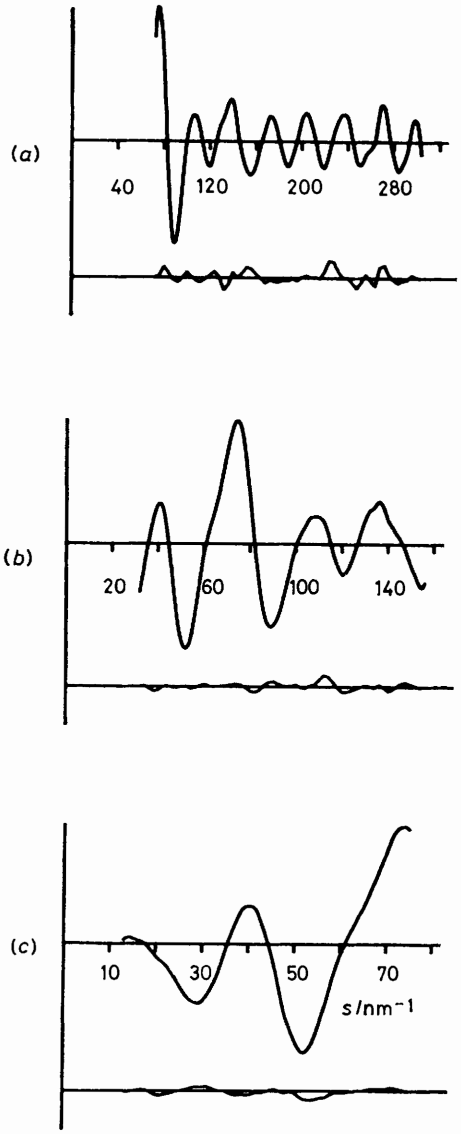

FIGURE 3 Experimental and final difference molecular-scattering intensities for $Al(BH_4)Me_2$; nozzle-to-plate distances (*a*) 250, (*b*) 500, and (*c*) 1 000 mm

TABLE 2

Least-squares correlation matrix multiplied by 100 for the molecule $Al(BH_4)Me_2$

r_1	r_2	r_3	r_4	r_6	Angle 1	Angle 2	u_1	u_2	u_7	u_8	u_9	k_1	k_2	k_3	
100	39	43	−30	7	−31	9	−8	−17	−6	0	−15	−18	−29	−17	r_1
	100	−8	20	1	−36	37	33	5	6	21	−26	34	33	9	r_2
		100	−68	1	−8	−3	−39	−35	−17	−20	3	−67	−83	−39	r_3
			100	−7	1	−2	48	32	18	20	−8	65	76	29	r_4
				100	−18	1	−18	−2	−4	−7	−8	−24	−9	2	r_6
					100	−72	0	11	−29	−27	12	0	2	9	Angle 1
						100	6	0	33	45	−16	5	5	2	Angle 2
							100	45	20	26	1	75	57	20	u_1
								100	7	9	12	29	35	18	u_2
									100	64	−1	25	23	10	u_7
										100	−5	30	30	13	u_8
											100	5	−8	−13	u_9
												100	75	28	k_1
													100	34	k_2
														100	k_3

TABLE 3

Least-squares correlation matrix multiplied by 100 for the molecule $Ga(BH_4)Me_2$

r_1	r_2	r_3	r_4	r_6	Angle 1	Angle 2	u_1	u_2	u_7	u_8	u_9	k_1	k_2	k_3	
100	55	15	−8	12	−14	3	15	4	−11	−2	−14	5	2	−5	r_1
	100	−11	18	13	−16	13	28	−5	−17	4	−18	34	36	13	r_2
		100	−61	1	7	−7	−27	−13	−10	−26	−12	−71	−79	−43	r_3
			100	6	−1	−3	35	15	11	20	6	59	63	29	r_4
				100	−17	3	−11	1	5	−1	−11	−13	−2	7	r_6
					100	−91	−1	12	−28	−37	3	−9	−6	5	Angle 1
						100	0	−7	16	33	−3	6	3	−1	Angle 2
							100	44	4	20	15	68	48	18	u_1
								100	−3	−1	30	11	13	13	u_2
									100	59	5	9	11	1	u_7
										100	3	32	29	10	u_8
											100	18	6	−6	u_9
												100	75	32	k_1
													100	37	k_2
														100	k_3

in line with those determined for related molecules, notably B_2H_6 [6] and $Al(BH_4)_3$.[7]

The success of the refinement may be judged by reference to the difference between the experimental radial-distribution curve and that calculated for the best model (Figure 2); Figure 3 affords a similar comparison between the experimental and calculated molecular scattering. The structural details and vibrational amplitudes of the optimum refinement, corresponding to $R_G = 0.17$ ($R_D = 0.09$), are listed in Table 4, together with the estimated standard deviations.

(*ii*) *Dimethylgallium Tetrahydroborate*.—The electron scattering patterns due to dimethylgallium tetrahydroborate lend themselves to an analysis which follows closely the example set by the dimethylaluminium compound. That the structures of the two molecules are closely matched

TABLE 4

Molecular parameters for dimethyaluminium and dimethylgallium tetrahydroborate

	$Al(BH_4)Me_2$ [a]		$Ga(BH_4)Me_2$ [a]	
Parameter	Distance	Amplitude	Distance	Amplitude
(*a*) Independent distances and amplitudes/pm				
r_1(M–C)	192.9 (0.4)	4.0 (0.6)	194.4 (0.4)	5.5 (0.5)
r_2(M · · · B)	212.8 (0.8)	6.8 (0.9)	216.3 (0.8)	8.1 (0.9)
r_3(M–H)	177.0 (3.2)	10.0 [b]	179.1 (3.0)	10.0 [b]
r_4(B–H) (mean)	121.8 (1.6)		120.5 (1.9)	
r_5 Δ(B–H)	2.3 [c]		2.5 [c]	
r_6(C–H)	107.8 (0.5)	6.5 [b]	107.4 (0.7)	6.5 [b]
(*b*) Dependent distances and amplitudes/pm				
d_7(C · · · C)	331.4 (1.4)	7.7 (1.8)	334.7 (2.4)	13.5 (3.5)
d_8(C · · · B)	353.0 (0.9)	10.1 (1.5)	356.8 (1.1)	8.8 (1.5)
d_9[M · · · H (methyl)]	252.3 (1.3)	17.8 (1.3)	251.5 (0.9)	15.9 (1.0)
d_{10}(M · · · H_t)	295.0 (1.8)	24.1 [b]	297.1 (1.8)	25.0 [b]
d_{11}(B–H_b)	123.0 (1.7)	8.9 [b]	121.7 (1.9)	8.5 [b]
d_{12}(B–H_t)	120.7 (1.7)	7.5 [b]	119.2 (1.9)	7.5 [b]
(*c*) Independent angles/°				
1(M–C–H)	110.8 (0.8)		109.5 (1.0)	
2(C–M–C)	118.4 (0.7)		118.8 (1.2)	
3 (H_t–B–H_t)	116.2 [b]		116.2 [b]	

[a] Figures in parentheses are the estimated standard deviations. [b] Fixed. [c] See text.

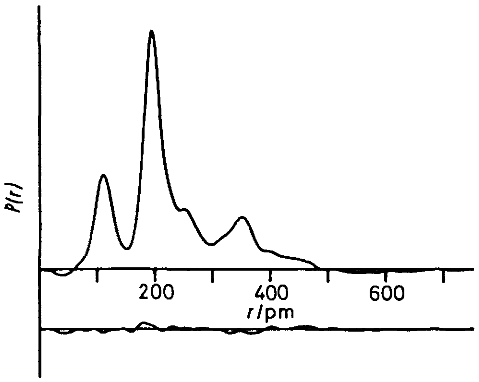

FIGURE 4 Observed and difference radial-distribution curves, $P(r)/r$, for $Ga(BH_4)Me_2$. Before Fourier inversion the data were multiplied by $s \, . \, \exp[(-0.000\,035\,s^2)/(z_{Ga} - f_{Ga})(z_C - f_C)]$

is at once made clear by the remarkable correspondence of the two radial-distribution curves (Figures 2 and 4). With $Ga(BH_4)Me_2$, as with $Al(BH_4)Me_2$, there can be little doubt that the strongest peak in the radial-distribution curve, located near 200 pm, depends on the lengths and amplitudes of vibration of the bonds radiating from the metal atom, the Ga–C bonds being most conspicuous by their contribution. The other principal features associated with $Ga(BH_4)Me_2$, notably at *ca.* 110, 260, and 330 pm, plainly have their counterparts in the radial-distribution curve of $Al(BH_4)Me_2$ and may be assigned accordingly. In our least-squares calculations on the $Ga(BH_4)Me_2$ molecule we have again refined a total of 12 structural variables comprising seven geometric parameters [the distances Ga–C, Ga–B, Ga–H_b, B–H(average), and C–H_m, and the angles Ga–C–H_m and C–Ga–C] and five vibrational parameters (the amplitudes of vibration of the distances Ga–C, Ga–B, C $\cdots$ C, B $\cdots$ C, and Ga $\cdots$ H_m). Problems of correlation and poor definition parallel those presented by the aluminium compound. Again Δ(B–H) did not yield to refinement, and, unlike $Al(BH_4)Me_2$, $Ga(BH_4)Me_2$ shows very little change in the R factor as Δ(B–H) varies in the range 0—6 pm; we have therefore fixed this parameter at 2.5 pm close to the best value for the aluminium compound. No complications have otherwise attended convergence of the refinements with the realization of a final R_G of 0.17 ($R_D = 0.10$). Details of the correlation matrix and of the molecular parameters calculated in the final refinement are presented in Tables 3 and 4 respectively, while the correspondence of the observed to the simulated molecular-scattering intensities may be gauged by reference to Figure 5.

DISCUSSION

There is a remarkable similarity between the dimensions we have deduced for the two molecules $Al(BH_4)Me_2$ and $Ga(BH_4)Me_2$. Thus, the replacement of aluminium by gallium witnesses an elongation by no more than 1—4 pm of the bonds linking the metal to the carbon, boron, and bridging hydrogen atoms. The metal–ligand distances are therefore consistent with the identical values assigned by Pauling [34] to the tetrahedral covalent radii of the two metal atoms, with their implication of comparatively inefficient screening of the increased nuclear charge by the $3d^{10}$ shell in gallium.

The dimensions of $Al(BH_4)Me_2$ and $Ga(BH_4)Me_2$ conform quite closely with those of related molecules (see Tables 5 and 6), as typified by the Al–B distances in $Al(BH_4)Me_2$ (212.8 pm) and $Al(BH_4)_3$ (214.3 pm).[7] On the other hand, the Al–B distance is significantly shorter than that in the alumina-*nido*-carborane $Me_2AlB_9C_2H_{12}$ (230—234 pm),[35] where the aluminium atom is believed to be linked *via* a *single* hydrogen bridge to each of two adjacent boron atoms in the open pentagonal B_3C_2 face of an icosahedral $B_9C_2H_{12}$ fragment. The Al–B distance in $Al(BH_4)Me_2$ is 5—10 pm shorter than the mean of the B–B and Al–Al distances found in diborane [6] and the diborane-like molecules $(Me_2MH)_2$ (M = B [28] or Al [30]). No such comparison is possible with the Ga–B distance (216.3 pm) in $Ga(BH_4)Me_2$ since species containing the unit $Ga(\mu\text{-}H)_2Ga$ have so far eluded structural characterization, but it is noteworthy that the metal–boron

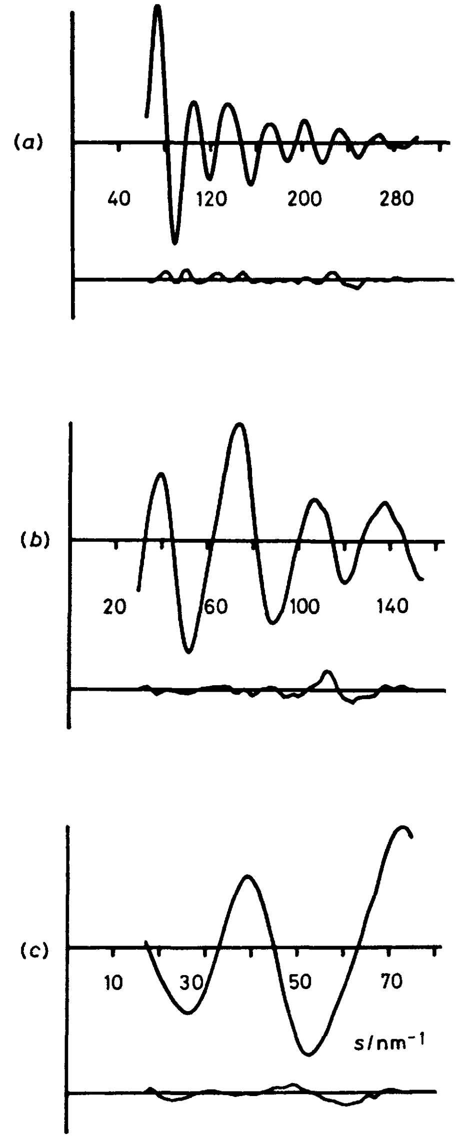

FIGURE 5 Experimental and final difference molecular-scattering intensities for $Ga(BH_4)Me_2$; nozzle-to-plate distances (*a*) 250, (*b*) 500, and (*c*) 1 000 mm

TABLE 5

Dimensions of the M(BH_4) group in molecular tetrahydroborates of the metal M

Compound	Mode of ligation [a]	Phase/ method [b]	Distance/pm				Angle/°			Ref.
			M–B	M–H_b	B–H_b	B–H	H_b–M–H_b	H_b–B–H_b	H_t–B–H_t	
B_2H_6	B	Vapour/ED	177.5 (0.4)		133.9 (0.6)	119.6 (0.8)		97.0 (0.3)	119.9 (0.9)	6
B_2H_6	B	Solid/X	176 (1)		125 (2)	109 (2), 106 (2)		90 (2)	121.6 (1.0)	12
$Al(BH_4)_3$	B	Vapour/ED	214.3 (0.3)	180.1 (0.6)	128.3 (1.2)	119.6 (1.2)	73.4 (0.8)	114.0 (0.2)	116.2 (2.2)	7
$Al(BH_4)_3{\cdot}NMe_3$	B	Solid/X	224 (1)	185 (4)	130 (3)	122 (4)	70.2 (3.2)	105.6 (4.6)	117.0 (6.6)	*c*
$Al(BH_4)Me_2$	B	Vapour/ED	212.8 (0.8)	177.0 (3.2)	123.0 (1.7)	120.7 (1.7)	70.6 (4.8)	112.5 (3.7)	116.2 [d]	This work
$Ga(BH_4)Me_2$	B	Vapour/ED	216.3 (0.8)	179.1 (3.0)	121.7 (1.9)	119.2 (1.9)	68.4 (4.6)	111.8 (3.8)	116.2 [d]	This work
$Ti(BH_4)(C_5H_5)_2$	B	Vapour/ED	231 (4)	189 (5)						11
	B	Solid/X	237 (1)	175 (8)	123 (8)	140 (10)	60 (5)	91 (7)	129 (9)	15
$[Co(BH_4)H\{P(C_6H_{11})_3\}_2]$	B	Solid/X	213 (1)	184 (9)	135 (9)	129 (9)				*e*
$[Cu(BH_4)(PPh_3)_2]$	B	Solid/X	218.5 (0.6)	182 (3)	107 (3)	109 (5)	59 (2)	112 (3)	113 (4)	*f*
$[Cu(BH_4)(PMePh_2)_3]$	U	Solid/X	265.0 (0.5)	147 [g]	119 [g]					4
$Zr(BH_4)_4$	T	Vapour/ED	230.8 (0.3)	221.1 (1.4)	127.2 (1.8)	117.6 (4.2)	55.6 (1.0)	108.4 (1.1)		10
$[N(PPh_3)_2][Mo(BH_4)(CO)_4]$	B	Solid/X	241 (2)	202 (8)	120 (10)	111 (11)	59 (4)	112 (6)	113 (7)	3

Figures in parentheses are the estimated standard deviations.

[a] B = Bidentate, U = unidentate, T = tridentate. [b] ED = Electron diffraction, X = *X*-ray diffraction. [c] N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *Inorg. Chem.*, 1968, **7**, 1575. [d] Value assumed. [e] M. Nakajima, H. Moriyama, A. Kobayashi, T. Saito, and Y. Sasaki, *J.C.S. Chem. Comm.*, 1975, 80. [f] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 1967, **6**, 2223; J. T Gill and S. J. Lippard, *ibid.*, 1975, **14**, 751. [g] No error limits quoted.

TABLE 6

Dimensions of the MMe_2 group (M = Al or Ga)

Compound	Phase/method [a]	M–C/pm	C–M–C/°	Ref.
$AlMe_3$	Vapour/ED	195.7 (0.3)	120 [b]	29
$AlMe_2(C_5H_5)$	Vapour/ED	195.2 (0.3)	124 (3)	*c*
$Al(BH_4)Me_2$	Vapour/ED	192.9 (0.4)	118.4 (0.7)	This work
$Me_2AlB_9C_2H_{12}$	Solid/X	195.6 (1.0)	131.9 (0.6)	35
$AlMe_3{\cdot}NMe_3$	Vapour/ED	198.7 (0.5)	114.8 (0.2)	*d*
$Rb[AlMe_4]$	Solid/X	200.6 (0.8)	106.0 (0.2) 115.6 (0.3)	51
Al_2Me_6	Vapour/ED	195.7 (0.3)	117.3 (1.5)	29
$(Me_2AlH)_2$	Vapour/ED	194.7 (0.3)	118.5 (0.9)	30
$(Me_2AlCl)_2$	Vapour/ED	193.5 (0.4)	126.9 (0.8)	31
$[Me_2Al(SMe)]_2$	Vapour/ED	194.5 (0.4)	128.6 (2.5)	32
$[Me_2Al(N{=}CMe_2)]_2$	Solid/X	197.4 (0.3)	120.1 (0.2)	*e*
$[Me_2Al(NMe_2)]_2$	Solid/X	195.0 (0.8)	115.7 (0.5)	*f*
$[Me_2Al(NHMe)]_3$	Solid/X	197.3 (0.5)	116.9 (0.4)	*f*
$[Me_2Al(OCPhNPh)]_2$	Solid/X	194.0 (0.8)	117.6 (0.5)	*g*
$[Me_2Al(OBu^t)]_2$	Vapour/ED	196.2 (1.5)	121.7 (1.7)	*h*
$[Me_2Al(OMe)]_3$	Vapour/ED	195.7 (0.3)	117.3 (0.8)	47
$(Me_2AlF)_4$	Vapour/ED	194.7 (0.4)	131.2 (1.9)	46
$GaMe_3$	Vapour/ED	196.7 (0.2)	118.6 (0.4)	44
$GaMe_2(C_5H_5)$	Solid/X	196.5 (0.2)	127.0 (0.2)	*i*
$Ga(BH_4)Me_2$	Vapour/ED	194.4 (0.4)	118.8 (1.2)	This work
$[(GaMe_2)_2C_2O_4]$	Solid/X	194.1 (1.6)	136.3 [j]	*j*
$[AsMe_4][GaMe_2Cl_2]$	Solid/X	198.0 (0.9)	125.3 (0.6)	*k*
$[Me_2Ga(OCH_2CH_2NMe_2)]_2$	Solid/X	195.6 (0.5)	126.7 (0.4)	*l*
$[Me_2Ga(N_2C_3H_3)]_2$	Solid/X	194.7 (0.7)	121.6 (0.6)	*m*
$[Me_2Ga(O_2C_7H_5)]_2$	Solid/X	194.5 (0.4)	136.6 (0.3)	*n*

Figures in parentheses are the estimated standard deviations.

[a] ED = Electron diffraction, X = *X*-ray diffraction. [b] Value assumed. [c] D. A. Drew and A. Haaland, *Acta Chem. Scand.*, 1973, **27**, 3735. [d] G. A. Anderson, F. R. Forgaard, and A. Haaland, *Acta Chem. Scand.*, 1972, **26**, 1947. [e] S. K. Seale and J. L. Atwood, *J. Organometallic Chem.*, 1974, **73**, 27. [f] G. M. McLaughlin, G. A. Sim, and J. D. Smith, *J.C.S. Dalton*, 1972, 2197. [g] Y. Kai, N. Yasuoka, N. Kasai, and M. Kakudo, *J. Organometallic Chem.*, 1971, **32**, 165. [h] A. Haaland and O. Stokkeland, *J. Organometallic Chem.*, 1975, **94**, 345. [i] K. Mertz, F. Zettler, H. D. Hausen, and J. Weidlein, *J. Organometallic Chem.*, 1976, **122**, 159. [j] No error limits quoted; H. D. Hausen, K. Mertz, and J. Weidlein, *J. Organometallic Chem.*, 1974, **67**, 7. [k] H. D. Hausen, H. J. Guder, and W. Schwarz, *J. Organometallic Chem.*, 1977, **132**, 37. [l] S. J. Rettig, A. Storr, and J. Trotter, *Canad. J. Chem.*, 1975, **53**, 58. [m] D. F. Rendle, A. Storr, and J. Trotter, *Canad. J. Chem.*, 1975, **53**, 2930. [n] S. J. Rettig, A. Storr, and J. Trotter, *Canad. J. Chem.*, 1976, **54**, 1278.

distances in both $Al(BH_4)Me_2$ and $Ga(BH_4)Me_2$ are comparable with the sums of the tetrahedral covalent radii of the relevant atoms (*ca.* 214 pm in both cases).[34] As in molecules such as $(Me_2AlH)_2$,[30] $Al(BH_4)_3$,[7] and $Zr(BH_4)_4$,[10] this feature is difficult to reconcile with any model which does not admit a significant degree of direct bonding between the heavy atoms linked by hydrogen bridges.[36] Certainly the Raman[1,16,37] and photoelectron[38] spectra of tetrahydroborates like $M(BH_4)Me_2$ (M = Al or Ga) and $M'(BH_4)_4$ (M′ = Zr, Hf, or U) give grounds for assigning a significant role to direct metal–boron bonding.

The Al–H_b distance in $Al(BH_4)Me_2$ (177 pm) is not significantly different from that in $Al(BH_4)_3$ (180 pm),[7] albeit somewhat longer than those in $(Me_2AlH)_2$ (168 pm)[30] and $AlH_3{\cdot}NMe_3$ (156 pm)[39] and in crystalline aluminium hydride (171.5 pm)[40] and lithium tetrahydroaluminate (155 pm).[41] Structural characterization has not previously been extended to any species containing gallium linked to bridging hydrogen atoms, but we note that the Ga–H_b distance in $Ga(BH_4)Me_2$ (179 pm) is substantially longer than the Ga–H_t distances reported for some crystalline cyclic derivatives of gallane (141—173 pm).[42] Some of these comparisons are clouded by the different operational definitions of a bond distance given by electron and neutron diffraction on the one hand [used to characterize $(Me_2AlH)_2$, $AlH_3{\cdot}NMe_3$, and aluminium hydride] and *X*-ray diffraction on the other (used to characterize $Li[AlH_4]$ and the cyclic gallane derivatives). In fact, a metal–hydrogen distance measured by electron or neutron diffraction is likely to emerge as somewhat longer than the corresponding distance measured by *X*-ray diffraction; if C–H bonds are any guide,[43] however, the difference is unlikely to be much in excess of 10 pm.

The metal–carbon distances in $M(BH_4)Me_2$ are amongst the shortest to be reported for molecules incorporating the Me_2M unit (M = Al or Ga). Thus, comparisons between gaseous molecules, which avoid the vagaries of crystal-packing effects and different degrees of aggregation of MMe_2X species, show that the M–C distances are 2—3 pm shorter in $M(BH_4)Me_2$ than in the corresponding MMe_3 molecule;[29,44] by contrast, the B–C distance is actually 1.2 pm *longer* in tetramethyldiborane, $Me_2B(\mu\text{-}H)_2BMe_2$,[28] than in trimethylborane.[45] Although this feature might be taken as a sign of polarization of the tetrahydroborate molecule in the sense $Me_2M^{\delta+}BH_4^{\delta-}$, such a view is not easily reconciled with the observations (*i*) that the M–C distance is shorter than in molecules like $(Me_2AlF)_4$[46] and $[Me_2Al(OMe)]_3$,[47] and (*ii*) that the C–M–C bond angles appear, if anything, to be less and not greater than 120°.

Our structural analysis of the molecules $Al(BH_4)Me_2$ and $Ga(BH_4)Me_2$ also reveals average B–H distances 4—5 pm shorter than those in alkali-metal tetrahydroborates,[2,3] as well as differences of only 2—3 pm between the bridging and terminal B–H distances. Admittedly the difference between the two distances, Δ(B–H), is relatively poorly defined, the value for $Al(BH_4)Me_2$ being subject to an uncertainty in the order of ± 4 pm; it is none-the-less several times smaller than the corresponding parameter in the molecules B_2H_6 (14 pm),[6] $Al(BH_4)_3$ (9 pm),[7] and $Zr(BH_4)_4$ (9 pm).[10] In none of these cases are the dimensions of the co-ordinated tetrahydroborate group precisely defined by electron diffraction; the uncertainty arises mainly from the insensitivity of the scattering pattern to departures of the BH_4 group from regular tetrahedral symmetry, but may well be exacerbated by large-amplitude vibrations of a skeleton such as $C_2M(\mu\text{-}H)_2BH_2$.[7,29]

A qualitative molecular-orbital analysis of the $M(BH_4)Me_2$ molecule using as basis functions the *ns* and *np* atomic orbitals (a.o.s) of the M atom, σ-type symmetry orbitals for the two terminal methyl groups, and the 2*p* a.o.s of boron leads to a tentative energy scheme of the form depicted in Figure 6; in keeping with the evidence of photoelectron spectra,[38] we expect the 2*s* a.o. of boron to be localized principally on the boron atom. Whereas symmetrical molecules like B_2H_6 or $Me_2B(\mu\text{-}H)_2BMe_2$ belonging to the point group D_{2h} allow relatively clearcut distinctions to be drawn between the functions of the different molecular orbitals (m.o.s), many of these distinctions are lost under the C_{2v} symmetry of $M(BH_4)Me_2$. Of the six m.o.s mainly responsible for the bonding of the skeleton, only the b_1 orbital is clearly identifiable with the bridging $M(\mu\text{-}H)_2B$ unit; the b_2 orbitals span both the M–C and B–H_t bonds, and most complicated of all are the three a_1 orbitals with bonding contributions encompassing the M–C, B–H_t, and $M(\mu\text{-}H)_2B$ units. Since the component atoms do not differ widely in electronegativity, it is difficult to identify even primary components in the composition of a particular m.o., but the experience of photoelectron spectroscopy[16,38,48,49] prompts us to believe that the occupied orbitals highest in energy include a major contribution from M–C σ bonding. It is of interest, therefore, that the first band in the photoelectron spectrum of $Al(BH_4)Me_2$ occurs at an ionization energy *ca.* 0.5 eV greater than that of the corresponding feature in the spectrum of $AlMe_3$.[16,48] Hence there is evidence from more than one source that substitution of a tetrahydroborate for a methyl group in the MMe_3 molecule has the effect of stabilizing the M–C bonds in the Me_2M residue. This change presumably reflects the mixing of the localized M–C, B–H_t, and $M(\mu\text{-}H)_2B$ orbitals admitted by the topology of the less symmetrical $M(BH_4)Me_2$ molecule; introduction of the tetrahydroborate ligand thus imparts a greater degree of delocalization to the bonding of the Me_2M fragment. Polarization of the M–B skeleton, combined with the mixing of the $a_1[B\text{-}H_t]$ and $a_1[M(\mu\text{-}H)_2B]$ symmetry orbitals, is also compatible with a move towards equalization of the terminal and bridging B–H distances of the tetrahydro-

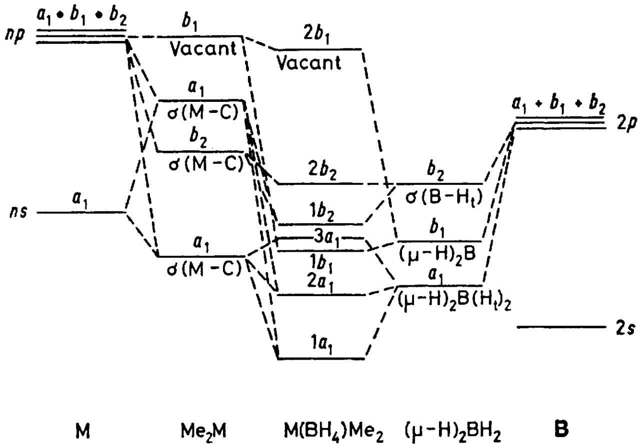

FIGURE 6 Tentative molecular-orbital energy scheme for the skeleton of the molecule $M(BH_4)Me_2$ (M = Al or Ga)

borate group. In the stretching force constants k_t and k_b relating, respectively, to the terminal and bridging B–H bonds of the co-ordinated tetrahydroborate group, we find a parallel trend borne out, for example, by the following values (in N m^{-1}): B_2H_6, k_t 354, k_b 168;[50] $M(BH_4)Me_2$, k_t *ca.* 340, k_b *ca.* 210.[16] That both the M–C and average B–H distances are shorter than their counterparts in the appropriate saturated species, *e.g.* $[AlMe_4]^-$ [51] and $[BH_4]^-$,[2,3] testifies to the 'electron-deficient' or acidic character of the $M(BH_4)Me_2$ molecules implied not only by the molecular-orbital scheme but also by the reactions of the molecules with Lewis bases.[1,16,17]

The refined amplitudes of vibration of the $M(BH_4)Me_2$ molecules listed in Table 4 are in sensible agreement with the corresponding parameters previously determined for the species MMe_3 [29,44] and $Al(BH_4)_3$.[7]

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