Molecular Structures of Dimethylaluminium Octahydrotriborate and Dimethylgallium Octahydrotriborate in the Gas Phase as determined by Electron Diffraction

By **C. John Dain** and **Anthony J. Downs,*** Department of Inorganic Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QR
David W. H. Rankin,* Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The structures of the gaseous molecules $Me_2AlB_3H_8$ and $Me_2GaB_3H_8$ have been studied by electron diffraction. Each species appears to have a skeleton analogous to that of B_4H_{10}, the metal atom being linked to each of two boron atoms of the octahydrotriborate group *via* a single hydrogen bridge (H_b). The following structural parameters (distances correspond to r_a) have been deduced: (*i*) for $Me_2AlB_3H_8$ r(Al–C) 193.2(0.8), r(Al–B) 230.7(0.8), r(Al–H_b) 190.6(4.1) pm, C–Al–C 126.8(1.5), and the dihedral angle α defining the folding of the AlB_3 skeleton 117.6(0.7)°; (*ii*) for $Me_2GaB_3H_8$ r(Ga–C) 193.0(0.7), r(Ga–B) 234.4(0.9), r(Ga–H_b) 198.9(4.8) pm, C–Ga–C 130.3(1.9), and α 117.1(0.9)°.

THE octahydrotriborate group resembles the tetrahydroborate group in its capacity to vary the mode of its ligation to metal centres. Thus the crystal structures of the compounds $[Be(B_3H_8)_2]$,[1] $[Cu(B_3H_8)(PPh_3)_2]$,[2] and $[NMe_4][Cr(B_3H_8)(CO)_4]$ [3] reveal that the octahydrotriborate group acts as a bidentate ligand whereas in $[Mn(B_3H_8)(CO)_3]$ [4] it acts as a tridentate ligand with respect to a mononuclear metal centre. To these two options there has lately been added a third with the disclosure that the octahydrotriborate group in the μ-bromo-hexacarbonyldimanganese derivative $[Mn_2(B_3H_8)(\mu\text{-}Br)(CO)_6]$ acts as a bis(bidentate) ligand bridging the two manganese atoms through pairs of Mn–H–B bonds.[5] The different modes of co-ordination are illustrated schematically in Figure 1. The volatile molecular compounds $Me_2MB_3H_8$ (M = Al or Ga) were first reported in 1972,[6] and they have subsequently found some use in the synthesis of other octahydrotriborate derivatives.[7] The i.r. spectra of the vapours indicate that the molecules $Me_2AlB_3H_8$ and $Me_2GaB_3H_8$ have similar structures and the n.m.r. spectra of solutions at low temperatures imply that these structures are akin to those of the species $[Cu(B_3H_8)(PPh_3)_2]$ [2] and $[NMe_4][Cr(B_3H_8)(CO)_4]$ [3] with a B–B unit of the B_3H_8 ligand linked *via* two single hydrogen bridges to the metal atom [as in Figure 1(*a*)]. Hence it appears that the molecules have much in common with tetraborane(10), an apical BH_2 group of which gives place to the MMe_2 moiety.

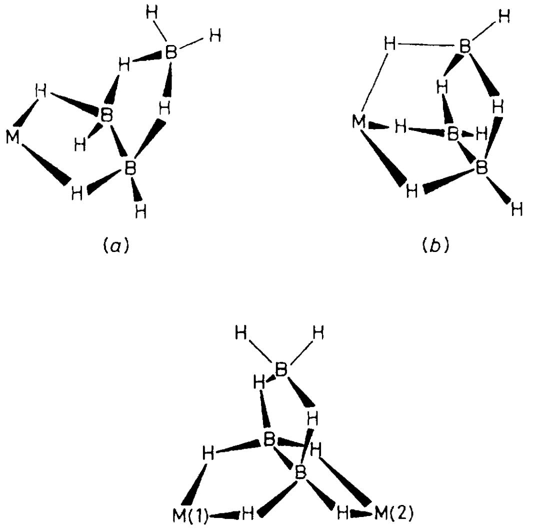

FIGURE 1 Different modes of co-ordination open to the octahydrotriborate anion

Following our investigations of the structures of the gaseous tetrahydroborate molecules $M(BH_4)Me_2$ (M = Al or Ga) [8] and of tetraborane(10) itself,[9] we have sought to determine the structures of the gaseous octahydrotriborate molecules $Me_2MB_3H_8$ by analysis of their electron-diffraction patterns. This represents the first attempt to determine the structure of an octahydrotriborate molecule in the gas phase.

EXPERIMENTAL

The synthesis and manipulation of dimethylaluminium and dimethylgallium octahydrotriborate were performed using a conventional high-vacuum line having stopcocks and ground-glass joints lubricated with Apiezon L grease. Following the procedure of Borlin and Gaines,[6] the compounds were each prepared by the metathetical reaction between the appropriate dimethylmetal chloride and tetramethylammonium octahydrotriborate (Strem Chemicals Inc.) in the absence of a solvent at room temperature. Fractional distillation *in vacuo* gave samples of dimethylaluminium and dimethylgallium octahydrotriborate judged to be pure on the evidence of the vapour pressures of the liquids and the i.r. spectra of the vapours.[6] Although the thermal stability of the compounds is described as ' marginal ' by Borlin and Gaines,[6] our experiments show that the vapours at a pressure of 10—20 mmHg * undergo minimal decomposition in 20 min at room temperature. Like the analogous tetrahydroborates,[8,10] however, both compounds are extremely sensitive to attack by traces of oxygen or moisture and apparatus intended to contain either compound was conditioned accordingly.

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

Electron-scattering patterns were recorded photographically on Kodak Electron Image plates using the Edinburgh/Cornell gas diffraction apparatus.[11-13] With the samples held at a temperature designed to give a vapour pressure of the order of 13 mmHg (273 K for the dimethylaluminium compound and 297 K for the dimethylgallium compound), the scattering patterns of the vapours were recorded at nozzle-to-plate distances of *ca.* 128 and 285 mm. The electron wavelengths, as determined by reference to the scattering pattern of benzene vapour, varied from 5.097 to 5.872 pm.

The compounds gave much trouble through the propensity of the vapours to react with the emulsion of the photographic plates. The effects could be minimised, it was found, by leaving the plates in air for 24—48 h before developing them. Even so the best plates obtained with the dimethylgallium compound at a nozzle-to-plate distance of *ca.* 285 mm had flaws which led to a discontinuity in the scattering curve near $s = 82$ nm^{-1} which was not reproduced in the curve derived from the exposures taken at a nozzle-to-plate distance of *ca.* 128 mm. Rather than discard these results, minimal weighting was assigned to the scattering intensities in the vicinity of the discontinuity.

TABLE 1

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

Molecule	Nozzle-to-plate distance/mm	Δs/nm^{-1}	$s_{\text{min.}}$/nm^{-1}	sw_1/nm^{-1}	sw_2/nm^{-1}	$s_{\text{max.}}$/nm^{-1}	Correlation, p/h	Scale factor, k *	Electron wavelength/pm
$Me_2AlB_3H_8$	128.16	4	72	92	280	328	0.3372	0.625(23)	5.8720
	285.06	2	24	42	130	160	0.4563	0.830(16)	5.1189
$Me_2GaB_3H_8$	128.45	4	68	100	230	288	0.0676	1.009(37)	5.1336
	285.06	2	24	44	130	166	0.4915	0.914(32)	5.0969

* Figures in parentheses are the estimated standard deviations of the last digits.

Calculations, performed on an ICL 2970 computer at the Edinburgh Regional Computing Centre, used the programs for data reduction[12] and least-squares refinement[14] described elsewhere with the complex scattering factors listed by Schäfer *et al.*[15] The weighting functions and correlation parameters used to set up the off-diagonal weight matrices are listed in Table 1 together with the electron wavelengths and scale factors.

STRUCTURE ANALYSIS

In the light of the evidence in favour of a di-hydrogen-bridged octahydrotriborate group afforded by the i.r. spectra of the vapours and the n.m.r. spectra of solutions at low temperatures,[6] we have adopted a structural model for each of the molecules $Me_2MB_3H_8$ (M = Al or Ga) which is akin to the B_4H_{10} molecule while conforming to C_s symmetry. The model makes use of the 17 independent geometrical parameters defined in Table 2. The local symmetry of the apical $(H_t)_2B(H_b')_2$ and the Me–M–Me units was assumed to be C_{2v} and that of each MCH_3 group to be C_{3v}, as illustrated in Figure 2.

Combination of the scaled experimental data sets yields the radial-distribution curves depicted in Figures 3 and 4. These emphasise the structural similarity of the molecules $Me_2AlB_3H_8$ and $Me_2GaB_3H_8$ but there is a remarkable dearth of detail. Each curve exhibits no more than four well developed peaks. The feature at *ca.* 120 pm comprises the scattering from all the C–H and B–H atom pairs. Second and most conspicuous is the peak near 180 pm associated with the M–C, M–H_b, B(1)–B(2), and B(1)–B(3) atom pairs. Next at *ca.* 230 pm is a peak corresponding to the M–B and various non-bonded distances including M $\cdots$ H_m, C $\cdots$ H, B $\cdots$ H, and H $\cdots$ H. Finally there is a relatively broad and plainly composite feature near 340 pm originating in scattering from the non-bonded atom pairs M $\cdots$ B(2), C $\cdots$ C, and B(1) $\cdots$ C supplemented by various C $\cdots$ H, B $\cdots$ H, and H $\cdots$ H distances. Tridentate binding of the octahydrotriborate ligand such as characterises the molecule $[Mn(B_3H_8)(CO)_3]$[4] would have given rather different results with significantly more scattering arising from pairs of atoms separated by *ca.* 180 pm (corresponding to M–H_b bonds) and 230—250 pm (corresponding to M–B contacts) and less from pairs separated by *ca.* 330 pm.

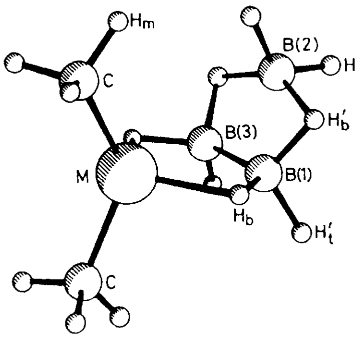

FIGURE 2 Perspective view of the dimethylaluminium and dimethylgallium octahydrotriborate molecule

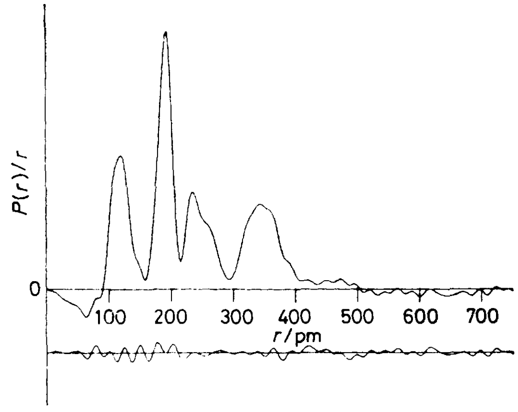

FIGURE 3 Observed and difference radial-distribution curves, $P(r)/r$ against r, for dimethylaluminium octahydrotriborate. Before Fourier inversion the data were multiplied by $s \cdot \exp[(-0.000\,015\,s^2)/(z_{Al} - f_{Al})(z_B - f_B)]$

Little is known about the vibrational properties of octahydrotriborate derivatives. Hence there was no help from this source to indicate the magnitude of possible shrinkage effects or to augment the sparse information about amplitudes of vibration afforded by the electron-diffraction data.

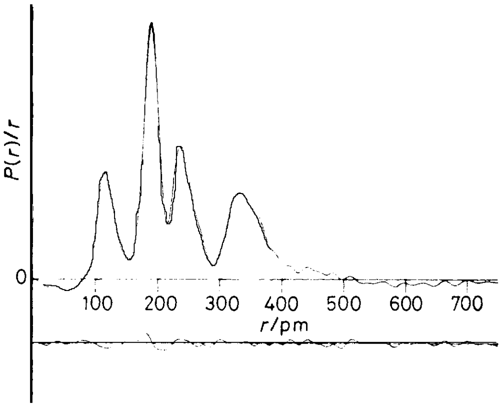

FIGURE 4 Observed and difference radial-distribution curves, $P(r)/r$ against r, for dimethylgallium octahydrotriborate. Before Fourier inversion the data were multiplied by $s \cdot \exp[(-0.000\,015\,s^2)/(z_{Ga} - f_{Ga})(z_B - f_B)]$

As expected, therefore, the structure analysis was severely hampered by marked correlation between structural parameters arising from the composite nature of each peak in the radial-distribution curve; for example, the B(1)–B(3), B(1)–B(2), M–C, and M–H_b distances were all subject to strong correlation, as were the B–H and C–H distances. These problems were exacerbated by the degree to which the molecular scattering was dominated by the heavier atoms making it particularly difficult to locate precisely the positions of hydrogen atoms. We were obliged therefore to assign fixed values to most parameters of the B_3H_8 group based on corresponding parameters of the B_4H_{10} molecule.[9] It has been established not only that the B–H–B bridges in B_4H_{10} are unsymmetrical but also that the bridging hydrogen atoms do not lie on the planes defined by the folded diamond of boron atoms which make up the skeleton of the molecule. The electron-diffraction data gave no scope for exploring the finer structural details of the molecules $Me_2MB_3H_8$ (M = Al or Ga), and we have assumed (*i*) that the bridging hydrogen atoms are coplanar with the heavy-atom planes MB(1)B(3) and B(1)B(2)B(3), (*ii*) that the distances B(1)–H_b and B(1)–H_b' are equal (*i.e.* $\Delta_3 = 0$), and (*iii*) that the differences between the apical and the middle B–H_t distances (Δ_2) and between the B(1)–H_b' and B(2)–H_b' distances (Δ_4) are the same as in the B_4H_{10} molecule. Likewise the parameters relating to the B–H_t units and the distances B(1)–B(3) and B(1)–B(2) were equated with the corresponding parameters in B_4H_{10}.

With the help of these assumptions, we have been able to refine simultaneously nine or ten of the 17 geometrical parameters used to specify the $Me_2MB_3H_8$ molecules (see Table

TABLE 2

Molecular parameters for dimethylaluminium and dimethylgallium octahydrotriborate[a]

Parameter	$Me_2AlB_3H_8$	$Me_2GaB_3H_8$
(*a*) Independent geometrical parameters[b]		
P_1 r[B(1)–B(3)]/pm	170.5[c]	170.5[c]
P_2 r[B(1)–B(2)]/pm	185.6[c]	185.6[c]
P_3 r[M–B(1)]/pm	230.7 (0.8)	234.4 (0.9)
P_4 r(M–C)/pm	193.2 (0.8)	193.0 (0.7)
P_5 r(C–H_m)/pm	109.1 (0.7)	112.0[c]
P_6 r(M–H_b)/pm	190.6 (4.1)	198.9 (4.8)
P_7 r(B–H) (average)/pm	129.1 (1.0)	127.8 (1.1)
P_8 Δ_1/pm, r(B–H_b) (average) − r(B–H_t) (average)	8.8 (4.2)	14.0 (2.2)
P_9 Δ_2/pm, r[B(2)–H_t] − r[B(1)–H_t']	−2.8[c]	−2.8[c]
P_{10} Δ_3/pm, r[B(1)–H_b] − r[B(1)–H_b']	0.0[c]	0.0[c]
P_{11} Δ_4/pm, r[B(1)–H_b'] − r[B(2)–H_b']	17.0[c]	17.0[c]
P_{12} Angle B(3)–B(1)–H_t'/°	111.0[c]	111.0[c]
P_{13} Angle M–C–H_m/°	114.0 (1.5)	112.7 (1.3)
P_{14} Angle C–M–C/°	126.8 (1.5)	130.3 (1.9)
P_{15} Angle H_t–B(2)–H_t/°	122.0[c]	122.0[c]
P_{16} Dihedral angle, α/°[d]	117.6 (0.7)	117.1 (0.9)
P_{17} Angle of ' tip ' of MC_2 unit, β/°[e]	4.9 (0.6)	2.6 (0.9)

	$Me_2AlB_3H_8$		$Me_2GaB_3H_8$	
Parameter	Distance/pm	Amplitude/pm	Distance/pm	Amplitude/pm
(*b*) Interatomic distances and vibrational amplitudes[b]				
d_1(C–H_m)	109.1 (0.7)	6.5[c]	112.0[c]	6.5[c]
d_2(M–C)	193.2 (0.8)	6.7 (0.5)	193.0 (0.7)	7.4 (0.5)
d_3(M–H_b)	190.6 (4.1)	8.5[c]	198.9 (4.8)	8.5[c]
d_4[B(1)–H_b]	127.0 (2.4)	6.5[c]	127.7 (1.7)	6.5[c]
d_5[B(1)–B(3)]	170.5[c]	7.5[c]	170.5[c]	7.5[c]
d_6[B(1)–H_t']	125.2 (2.1)	7.5[c]	120.8 (1.2)	7.5[c]
d_7[B(1)–H_b']	127.0 (2.4)	7.5[c]	127.7 (1.7)	7.5[c]
d_8[B(2)–H_b']	144.0 (2.4)	7.5[c]	144.7 (1.7)	7.5[c]
d_9[B(2)–H_t]	122.4 (2.1)	7.5[c]	118.0 (1.2)	7.5[c]
d_{10}[M–B(1)]	230.7 (0.8)	9.5 (0.5)	234.4 (0.9)	9.8 (0.6)
d_{11}[M · · · B(2)]	325.3 (1.1)	8.9 (1.2)	328.1 (1.3)	10.4 (1.4)
d_{12}[B(1)–B(2)]	185.6[c]	10.0[c]	185.6[c]	10.0[c]
d_{13}(M · · · H_m)	257.6 (1.4)	13.0[c]	257.8 (1.6)	14.3 (1.4)

[a] Figures in parentheses are the estimated standard deviations of the last digits. [b] Atoms are numbered as in Figure 2. [c] Fixed. [d] Dihedral angle between the planes MB(1)B(3) and B(1)B(2)B(3). [e] Tilt of CMC unit with respect to the MB(1)B(3) plane about an axis through M parallel to the B(1)–B(3) bond.

TABLE 3

Least-squares correlation matrix (× 100) for the molecule dimethylaluminium octahydrotriborate

Distances						Angles				Vibrational amplitudes			Scale factors		
P_3	P_4	P_5	P_6	P_7	P_8	P_{13}	P_{14}	P_{16}	P_{17}	$u_{\mathrm{Al-C}}$	$u_{\mathrm{Al-B(1)}}$	$u_{\mathrm{Al\cdots B(2)}}$	k_1	k_2	
100	−48	3	59	−11	−1	54	19	−54	−21	33	−32	22	−22	−15	P_3
	100	12	−89	29	15	−69	22	40	53	−23	11	−38	29	35	P_4
		100	−13	52	61	−45	0	−3	16	−4	−9	−1	−9	6	P_5
			100	−31	−17	70	−14	−45	−46	38	−27	43	−20	−30	P_6
				100	67	−52	3	−4	30	14	−2	−2	31	43	P_7
					100	−40	2	−3	21	7	−6	−1	15	24	P_8
						100	−4	−38	−47	21	−18	27	−16	−19	P_{13}
							100	−23	27	0	−6	−27	0	5	P_{14}
								100	0	−26	22	−29	9	−6	P_{16}
									100	−5	0	7	17	35	P_{17}
										100	−14	24	48	22	$u_{\mathrm{Al-C}}$
											100	−14	10	−4	$u_{\mathrm{Al-B(1)}}$
												100	1	3	$u_{\mathrm{Al\cdots B(2)}}$
													100	34	k_1
														100	k_2

2). The calculations admitted the refinement of only three amplitudes of vibration for the dimethylaluminium compound and four for the dimethylgallium compound. The remaining amplitudes were fixed at values in line with those determined for the related molecules B_4H_{10}[9] and $M(BH_4)Me_2$ (M = Al or Ga).[8]

For both molecules the analysis has led to a satisfactory convergence of the structural refinement. The final least-

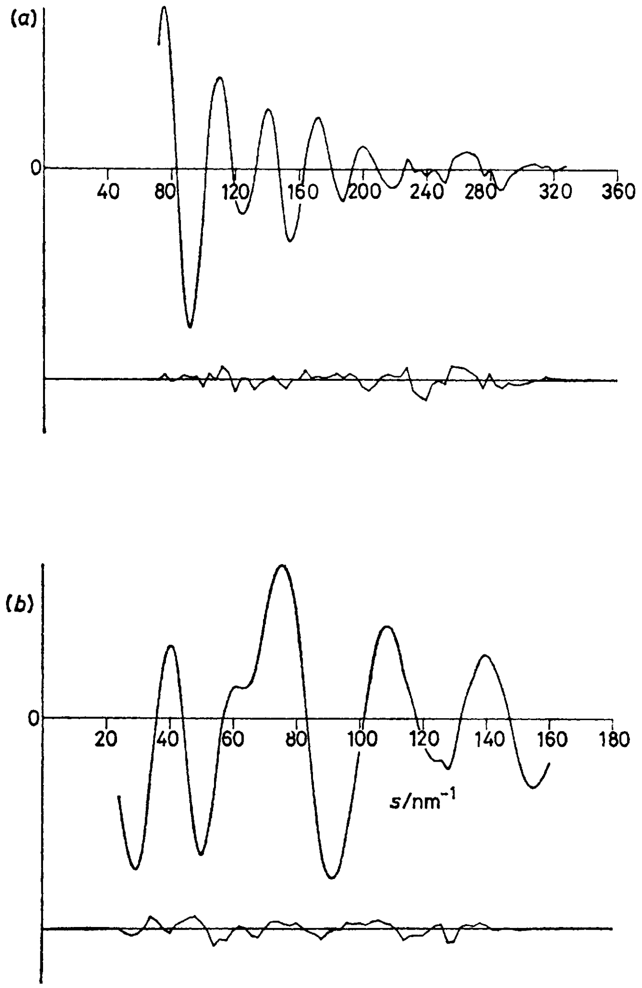

FIGURE 5 Experimental and final difference molecular-scattering intensities for dimethylaluminium octahydrotriborate; nozzle-to-plate distances (*a*) 128.16 and (*b*) 285.06 mm

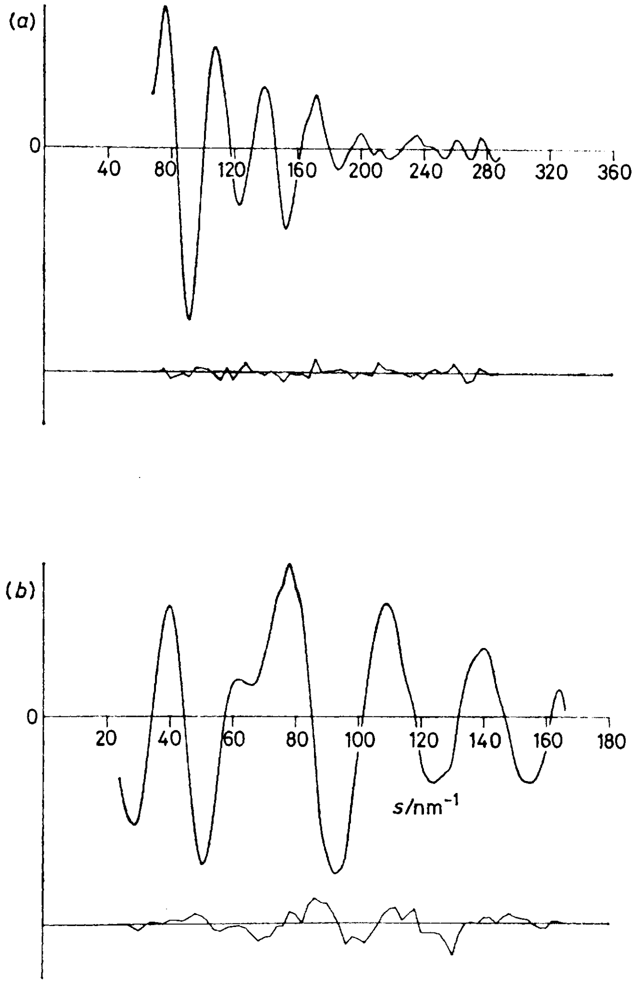

FIGURE 6 Experimental and final difference molecular-scattering intensities for dimethylgallium octahydrotriborate; nozzle-to-plate distances (*a*) 128.45 and (*b*) 285.06 mm

TABLE 4

Least-squares correlation matrix (× 100) for the molecule dimethylgallium octahydrotriborate

Distances					Angles				Vibrational amplitudes				Scale factors		
P_3	P_4	P_6	P_7	P_8	P_{13}	P_{14}	P_{16}	P_{17}	u_{Ga-C}	$u_{Ga-B(1)}$	$u_{Ga\cdots B(2)}$	$u_{Ga\cdots H_m}$	k_1	k_2	
100	−61	−60	−8	−6	66	16	−63	8	−47	−12	25	32	−8	7	P_3
	100	−91	0	1	−60	16	45	−13	71	15	−46	−9	−9	−5	P_4
		100	0	−1	59	16	47	18	67	−23	53	9	24	10	P_6
			100	51	−8	−9	−14	14	37	7	20	9	54	32	P_7
				100	−3	−5	−6	11	30	9	9	4	42	27	P_8
					100	3	−55	11	−41	−37	35	1	4	27	P_{13}
						100	−40	−18	6	−7	−43	−3	−20	−7	P_{14}
							100	−25	25	12	−24	−23	−11	−26	P_{16}
								100	0	0	57	10	22	29	P_{17}
									100	19	−20	2	39	25	u_{Ga-C}
										100	−7	67	21	2	$u_{Ga-B(1)}$
											100	11	37	31	$u_{Ga\cdots B(2)}$
												100	29	17	$u_{Ga\cdots H_m}$
													100	43	k_1
														100	k_2

squares correlation matrices, reproduced in Tables 3 and 4, show no major correlations implicating refining parameters although there are of course strong correlations between fixed and refining parameters. The success of the calculations may be judged by the differences (*i*) between the experimental and calculated radial-distribution curves (Figures 3 and 4) and (*ii*) between the experimental and calculated intensities of molecular scattering (Figures 5 and 6). Table 2 lists the values of the geometric and vibrational parameters associated with the optimum refinements which corresponded to values of $R_G = 0.159$ ($R_D = 0.099$) for the dimethylaluminium compound and $R_G = 0.139$ ($R_D = 0.138$) for its dimethylgallium counterpart. A perspective view of the $Me_2MB_3H_8$ molecule (M = Al or Ga) in its ultimate form is shown in Figure 2.

DISCUSSION

The electron-diffraction patterns of the molecules $Me_2AlB_3H_8$ and $Me_2GaB_3H_8$ leave little doubt about the similarity not only of their structures but also of their dimensions, even allowing for the need to fix the values of numerous parameters in the refinement calculations. A comparison with the dimensions of tetraborane(10)[9] and some other octahydrotriborate derivatives whose structures have been determined by crystallographic methods is presented in Table 5. The results of the present studies are significant on several counts.

In the first place, the electron-scattering pattern of each of the $Me_2MB_3H_8$ molecules bears out the conclusions drawn from the i.r. and n.m.r. spectra[6] that the octahydrotriborate ligand is bound to the metal atom *via* two of its boron atoms and two single hydrogen bridges.

Secondly, at 230.7 and 234.4 pm, the shortest aluminium–boron and gallium–boron distances are comparable with the corresponding distances in related molecules containing a bidentate octahydrotriborate group bound to a medium-sized metal atom {as in the species $[Cu(B_3H_8)(PPh_3)_2]$,[2] $[NMe_4][Cr(B_3H_8)(CO)_4]$,[3] and $[Mn_2(B_3H_8)(\mu\text{-Br})(CO)_6]$[5] listed in Table 5}. Such metal–boron distances, like those (227—232 pm)[4] in the tricarbonylmanganese derivative of a tridentate octahydrotriborate group, $[Mn(B_3H_8)(CO)_3]$, and in the alumina-*nido*-carborane $Me_2AlB_9C_2H_{12}$ (230—234 pm),[16] seem to be more-or-less characteristic of the linking of the metal with two adjacent boron atoms of a polyboron fragment *via* single hydrogen bridges. The metal–boron distances in the $Me_2MB_3H_8$ molecules are appreciably longer than those in the corresponding tetrahydro-

TABLE 5

A comparison of the molecular parameters of dimethylaluminium and dimethylgallium octahydrotriborate with those of tetraborane(10) and other octahydrotriborate derivatives[a]

		d/pm									
Compound	Phase/ method[b]	B(1)–B(2)	B(1)–B(3)	B(1)–H_b'	B(2)–H_b'	B–H_t	M–H_b	B(1)–H_b	M–B	Dihedral angle, α/°	Ref.
$Me_2AlB_3H_8$	Vapour/ED	185.6[c]	170.5[c]	127.0 (2.4)	144.0 (2.4)	122—125 (2)	190.6 (4.1)	127.0 (2.4)	230.7 (0.8)	117.6 (0.7)	This work
$Me_2GaB_3H_8$	Vapour/ED	185.6[c]	170.5[c]	127.7 (1.7)	144.7 (1.7)	118—121 (1)	198.9 (4.8)	127.7 (1.7)	234.4 (0.9)	117.1 (0.9)	This work
B_4H_{10}	Vapour/ED	185.6 (0.4)	170.5 (1.2)	131.5 (0.9)	148.4 (0.9)	119.4 (0.7) 122.1 (1.4)	148.4 (0.9)	131.5 (0.9)	185.6 (0.4)	117.1 (0.7)	9
$Be(B_3H_8)_2$	Solid/*X*	183.4 (0.4)	176.6 (0.3)	105—121 (2)	130—138 (2)	105—114 (2)	150 (2)	117 (2)	197.4 (0.7)	115.0 (2.0)	1
$[Cu(B_3H_8)(PPh_3)_2]$	Solid/*X*	182 (2)	176 (1)	115 (9)	152 (9)	100—130	185 (5)	121 (6)	230 (1)	118 (2)	2
$[NMe_4][Cr(B_3H_8)(CO)_4]$	Solid/*X*	182 (1)	178 (1)	115 (7)	143 (7)	107—122	178 (6)	129 (6)	243 (2)	119 (2)	3
$[Mn_2(B_3H_8)(\mu\text{-Br})(CO)_6]$	Solid/*X*	185 (2)	171 (2)	112—117	141—150	126—150	150—176	89—115	230—236 (2)	127 (3)	5

[a] Estimated standard deviations are given in parentheses where values are available. [b] ED = Electron diffraction, *X* = *X*-ray diffraction. [c] Fixed.

borates $M(BH_4)Me_2$ (212.8 and 216.3 pm for M = Al and Ga respectively) [8] or in related molecules containing an aluminium or gallium atom bound to boron *via* a double hydrogen bridge [*e.g.* $Al(BH_4)_3$ 214.3 pm,[17] $Al(BH_4)_2Me$ 215.2 pm,[18] and $Ga(BH_4)_2H$ 217.2 pm [19]]. They are also appreciably longer than those in the metallocarboranes $Me_2GaB_4C_2H_6$ (211 and 222 pm) [20] and $EtAlB_9C_2H_{11}$ (214 pm) [21] wherein direct binding of the metal and boron atoms is clearly implicated and the metal–boron distances are close to the sum of the tetrahedral covalent radii (*ca.* 214 pm).

Thirdly, although it has not been possible in the circumstances of the analysis to locate the bridging hydrogen atoms with the precision and certainty we had hoped for, the $M-H_b$ bonds at 191 pm in $Me_2AlB_3H_8$ and 199 pm in $Me_2GaB_3H_8$ are unusually long. By contrast, the corresponding bond lengths in the tetrahydroborate molecules $M(BH_4)Me_2$ are 177 and 179 pm for M = Al and Ga respectively. These circumstances are matched, however, by the discrepancy between the lengths of the bridge bonds in B_2H_6 (133.9 pm) [22] and those to the apical BH_2 groups in B_4H_{10} (148.4 pm).[9] Conventional wisdom associates this discrepancy, at least in part, with the charge distribution in the B_4H_{10} molecule, a more positive charge being attributed to the apical than to the middle sites of the heavy-atom framework.

Fourthly, there is the notable difference between the C–M–C bond angles in the octahydrotriborate molecules $Me_2MB_3H_8$ and those in the equivalent tetrahydroborate species [8] [*cf.* $Me_2AlB_3H_8$ 126.8°, $Al(BH_4)Me_2$ 118.4°, $Me_2GaB_3H_8$ 130.3°, $Ga(BH_4)Me_2$ 118.8°]. A similar widening of the C–M–C bond angle is found, for example, in certain molecules like $(Me_2AlF)_4$ (131.2°) [23] and $[(GaMe_2)_2C_2O_4]$ (136.3°) [24] in which the metal atom is linked to a relatively electronegative ligand.

Finally, it has been feasible to determine the angle β describing the tipping of the MC_2 unit about an axis through the metal atom and perpendicular to the mirror plane of the molecule. For both $Me_2AlB_3H_8$ and $Me_2GaB_3H_8$, β is found to be small (4.9 and 2.6° respectively) but significant. We believe that these values are more likely to reflect puckering of the five-membered ring $M(H_b)B(1)B(3)(H_b)$ and the displacement of the bridging hydrogen atoms to locations above the MB(1)B(3) plane than to signify a departure of the $Me_2M(H_b)_2$ unit from local C_{2v} symmetry. Such puckering of the $M(H_b)B(1)B(3)(H_b)$ ring can be interpreted as relieving the potential non-bonded $CH_3 \cdots H_t$ contact between the opposing MMe_2 and apical BH_2 fragments. Certainly it is a feature of the B_4H_{10} molecule (*i.e.* M = B) [9] and of other compounds known to contain a bidentate B_3H_8 group.[2,3] The precise location of the bridging hydrogen atoms in the molecules $Me_2AlB_3H_8$ and $Me_2GaB_3H_8$ depends upon the scattering due to the non-bonded atom pairs $C \cdots H_b$ and $B(2) \cdots H_b$; it is unfortunate that this scattering is largely masked by that due to other pairs of atoms of comparable separation.

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