

## Group 3 Tetrahydroborates. Part 1. The Synthesis and Properties of Dimethylgallium Tetrahydroborate

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The synthesis, characterization, and properties of  $\text{Ga}(\text{BH}_4)\text{Me}_2$  are reported. Although first prepared *via* the interaction of  $\text{GaMe}_3$  and diborane, the compound is more satisfactorily prepared by the reaction of  $\text{GaMe}_2\text{Cl}$  with  $\text{Li}[\text{BH}_4]$  in the absence of a solvent at  $-15^\circ\text{C}$ . Subsequent characterization has been based on the vapour-phase molecular weight, on the mass, vibrational, and  $^1\text{H}$  n.m.r. spectra of the material, and on elemental analysis of the ammonia adduct  $\text{Ga}(\text{BH}_4)\text{Me}_2 \cdot 2\text{NH}_3$ . The i.r. spectrum of the gaseous tetrahydroborate is consistent with a molecular model  $\text{Me}_2\text{Ga}(\mu\text{-H})_2\text{BH}_2$  having  $C_{2v}$  symmetry and containing four-co-ordinate gallium linked to a bi-dentate tetrahydroborate group; such a structure appears to persist in the condensed phases, although the vibrational spectra suggest increased polarization in the sense  $[\text{GaMe}_2]^+[\text{BH}_4]^-$ . Chemical studies have disclosed, *inter alia*, ready hydrogen-methyl exchange between the boron and gallium centres, as well as instances of symmetrical and unsymmetrical cleavage of the  $\text{Ga}(\mu\text{-H})_2\text{B}$  skeleton.

MUCH of the interest in tetrahydroborates stems from the versatility of ligation of the tetrahydroborate group. In addition to compounds which contain more-or-less discrete  $[\text{BH}_4]^-$  anions, there exist numerous well defined derivatives in which the tetrahydroborate ligand is linked to a metal atom *via* either double or triple hydrogen bridges;<sup>1</sup> reasons have also been advanced for thinking that the copper complex  $[\text{Cu}(\text{BH}_4)(\text{PMePh}_2)_3]$  contains a single Cu-H-B bridge.<sup>2</sup> The situation is further complicated, moreover, by the tendency of the tetrahydroborate group in a given compound to vary its ligation from one phase to another; such is the case, for example, with the compounds  $\text{Be}(\text{BH}_4)_2^3$  and  $\text{Al}(\text{BH}_4)\text{Me}_2$ .<sup>4</sup> No less remarkable are the n.m.r. properties of molecular tetrahydroborates which imply a unique fluxional capacity of the  $\text{BH}_4$  group;<sup>5</sup> with but one or two exceptions,<sup>6</sup> the bridging and terminal hydrogen atoms of the group appear to be magnetically equivalent.

Of the tetrahydroborates formed by the Group 3 elements only the aluminium compound  $\text{Al}(\text{BH}_4)_3$  is well characterized,<sup>1</sup> and little attention has been paid until recently either to derivatives of  $\text{Al}(\text{BH}_4)_3$  or to analogues involving heavier Group 3 atoms. The balance has now been redressed to some extent, however, in studies of the methylaluminium tetrahydroborates  $\text{Al}(\text{BH}_4)_{3-n}\text{Me}_n$  ( $n = 1$  or  $2$ )<sup>7</sup> and of the novel hydridogallium compound  $\text{Ga}(\text{BH}_4)_2\text{H}$  whose preparation and characterization we recently notified.<sup>8</sup> The only other tetrahydroborate of gallium for which there is reasonable evidence is dimethylgallium tetrahydroborate; this was alluded to by Schlesinger *et al.*<sup>9</sup> in 1943, although their brief report sheds little light on the physical and chemical properties of the compound.

As part of our investigations of 'mixed' hydrides formed by the Group 3 elements, we have confirmed that  $\text{Ga}(\text{BH}_4)\text{Me}_2$  is formed *via* the interaction of trimethylgallium and diborane, discovered a more satisfactory route to the compound, and investigated some of its physical and chemical properties, with the results to be discussed.

### EXPERIMENTAL

(i) *General Procedures: Purification of Reagents.*—Synthesis and manipulation of dimethylgallium tetrahydroborate were accomplished using a conventional high-vacuum line having stopcocks and ground-glass joints lubricated with Apiezon 'L' grease. Lithium tetrahydroborate, supplied by B.D.H. or Koch-Light Ltd., was recrystallized prior to use from dry diethyl ether; the perdeuteriated compound (Koch-Light Ltd., 98 atom %  $^2\text{H}$ ) was used without purification. Trimethylgallium was prepared by the method described by Coates<sup>10</sup> and purified by trap-to-trap distillation *in vacuo*. Gallium(III) chloride was prepared by the direct interaction of gallium metal with chlorine and purified by repeated sublimation *in vacuo*. Ammonia as supplied by I.C.I. Ltd. was dried by treatment with sodium; trimethylamine was prepared by the action of alkali on recrystallized trimethylammonium chloride (Koch-Light Ltd.) and dried over 'Drierite'; diborane was synthesized by the method of Weiss and Shapiro.<sup>11</sup> Fractional distillation of each of these reagents gave a sample judged to be pure by the criteria of tensimetric and i.r. measurements. [ $^2\text{H}_8$ ]Toluene originating from E. Merck Ltd. was purified by distillation through a column of molecular sieves. Elemental analyses were by the Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, West Germany.

(ii) *Physical Measurements.*—Infrared spectra were

<sup>1</sup> B. D. James and M. G. H. Wallbridge, *Progr. Inorg. Chem.*, 1970, **11**, 99; T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263.

<sup>2</sup> J. C. Bommer and K. W. Morse, *J.C.S. Chem. Comm.*, 1977, 137.

<sup>3</sup> J. W. Nibler, D. F. Shriver, and T. H. Cook, *J. Chem. Phys.*, 1971, **54**, 5257; D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1971, **93**, 2322.

<sup>4</sup> A. J. Downs and P. D. P. Thomas, unpublished work.

<sup>5</sup> H. Beall and C. H. Bushweller, *Chem. Rev.*, 1973, **73**, 465 and refs. therein.

<sup>6</sup> T. J. Marks and J. R. Kolb, *J.C.S. Chem. Comm.*, 1972, 1019; H. D. Empsall, E. Mentzer, and B. L. Shaw, *ibid.*, 1975, 861.

<sup>7</sup> P. R. Oddy and M. G. H. Wallbridge, *J.C.S. Dalton*, 1976, 869.

<sup>8</sup> A. J. Downs and P. D. P. Thomas, *J.C.S. Chem. Comm.*, 1976, 825.

<sup>9</sup> H. I. Schlesinger, H. C. Brown, and G. W. Schaeffer, *J. Amer. Chem. Soc.*, 1943, **65**, 1786.

<sup>10</sup> G. E. Coates, *J. Chem. Soc.*, 1951, 2003.

<sup>11</sup> H. G. Weiss and I. Shapiro, *J. Amer. Chem. Soc.*, 1959, **81**, 6167.

recorded using a Perkin-Elmer model 225 or 457 spectrophotometer. Gaseous samples were contained in a cell having a path length of 10 cm and fitted with CsI windows; solid samples were investigated either as a polycrystalline film deposited *in vacuo* on a cooled CsI window, or in the form of a Nujol mull smeared between KBr plates. The spectra were calibrated by reference to sharp lines in the absorption spectra of carbon dioxide, water, ammonia, or polystyrene. The Raman spectra were excited at 514.5 nm by the output from a Spectra-Physics model 165 argon-ion laser and measured with a Spex Ramalog 5 spectrophotometer equipped with a third monochromator; the power levels at the sample were of the order of 100–200 mW. Liquid samples for Raman measurements were contained in Pyrex capillaries (1–2 mm internal diameter), whereas solids were studied as polycrystalline films deposited *in vacuo* on the surface of a polished high-purity copper block.<sup>12</sup> Calibration of the spectra was accomplished by reference to the atomic-emission lines of a He–Ne lamp. Studies of the vibrational spectra of Ga(BH<sub>4</sub>)Me<sub>2</sub> either in the solid or matrix-isolated condition involved the use of a Displex miniature refrigerator (Air Products, model CS 202); some experiments also exploited a low-temperature i.r. cell in which the central CsI window was cooled by a reservoir of liquid nitrogen or acetone–CO<sub>2</sub>. Hydrogen-1 n.m.r. spectra were recorded for *ca.* 1 mol dm<sup>-3</sup> solutions of Ga(BH<sub>4</sub>)Me<sub>2</sub> in C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> contained in soda-glass sample tubes (5 mm internal diameter), using a Perkin-Elmer model R/32 spectrometer operating at 90 MHz. Mass spectra were obtained by means of either a Perkin-Elmer model RSM 4 or an A.E.I. model MS 902 instrument.

(iii) *Synthesis of Dimethylgallium Tetrahydroborate.*—(a) *From trimethylgallium and diborane.* Trimethylgallium (typically *ca.* 1 mmol) and a five-fold excess of diborane were allowed to react at –15 °C for 3 h. Trap-to-trap distillation *in vacuo* of the volatile material gave *dimethylgallium tetrahydroborate* as transparent crystals involatile at –45 °C, in 20–40% yields based on equation (1). The



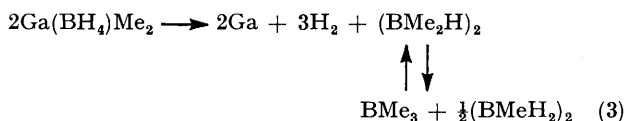
product melted at *ca.* 1 °C and had a vapour pressure at 0 °C of 13–14 mmHg; \* vapour-density measurements gave a molecular weight in the range 114–118 [monomeric Ga(BH<sub>4</sub>)Me<sub>2</sub> requires 114.6]. The i.r. spectrum of the material volatile at –45 °C confirmed the presence of methylboranes<sup>13</sup> as well as unchanged diborane.

(b) *From dimethylgallium chloride and lithium tetrahydroborate.* Dimethylgallium chloride was prepared *in situ* by the interaction in the appropriate stoichiometric proportions of GaMe<sub>3</sub> and gallium(III) chloride, the reaction being taken to completion by increasing the temperature of the mixture to *ca.* 45 °C. To GaMe<sub>2</sub>Cl (1.4 g, 1 mmol) was added an excess (1.0 g) of powdered lithium tetrahydroborate (4.6 mmol) or [<sup>2</sup>H<sub>4</sub>]tetrahydroborate (3.9 mmol), and the solid mixture was allowed to stand at –15 °C for 4 h, while the volatile products were removed and trapped at –196 °C under continuous pumping. Fractionation of the volatile material gave dimethylgallium tetrahydroborate or [<sup>2</sup>H<sub>4</sub>]-

tetrahydroborate in yields of *ca.* 80% based on equation (2).



(iv) *Chemical Properties of Dimethylgallium Tetrahydroborate.*—(a) *Thermal decomposition.* A known amount of Ga(BH<sub>4</sub>)Me<sub>2</sub> held in an ampoule at room temperature for *ca.* 48 h underwent complete decomposition. Analysis of the products by tensimetric and i.r. measurements revealed that in a typical experiment 0.42 mmol of Ga(BH<sub>4</sub>)Me<sub>2</sub> gave 0.63 mmol of H<sub>2</sub>, 0.37 mmol of BMe<sub>3</sub> and other methylated boranes,<sup>13</sup> and 24.7 mg of a grey involatile residue adjudged, on the evidence of its low melting point, to be gallium metal (0.35 mmol). Significantly, no traces of methane were detected, and the results thus imply that decomposition at room temperature proceeds as in (3).



(b) *Reaction with ammonia.* Dimethylgallium tetrahydroborate (81.1 mg, 0.707 mmol) was treated with a greater than six-fold excess of ammonia. After 2 h at –80 °C excess of ammonia was removed by pumping on the mixture held at –20 °C. The weight of the white solid remaining corresponded to the uptake of 23.4 mg (1.370 mmol) of ammonia, and the composition Ga(BH<sub>4</sub>)Me<sub>2</sub>·2NH<sub>3</sub> thus implied was substantiated by elemental analysis (Found: C, 16.4; H, 10.95; B, 7.10; Ga, 46.4; N, 18.65. Ga(BH<sub>4</sub>)Me<sub>2</sub>·2NH<sub>3</sub> requires C, 16.15; H, 10.85; B, 7.25; Ga, 46.9; N, 18.85%).

(c) *Reaction with trimethylamine.* With trimethylamine, Ga(BH<sub>4</sub>)Me<sub>2</sub> formed a white crystalline solid at –80 °C; tensimetric measurements implied the formation of an adduct Ga(BH<sub>4</sub>)Me<sub>2</sub>·NMe<sub>3</sub>, but this decomposed at temperatures much above –45 °C to give *inter alia* hydrogen, trimethylamine–borane (identified by its i.r. spectrum<sup>14</sup>), and gallium metal. By allowing the reagents to interact at –80 °C on the CsI window of a low-temperature i.r. cell and recording the spectrum of the product held at –196 °C, the following absorptions (cm<sup>-1</sup>) were observed to develop in the range 250–4 000 cm<sup>-1</sup> (s = strong, m = medium, w = weak, v = very, sh = shoulder, and br = broad): Ga(BH<sub>4</sub>)Me<sub>2</sub>·NMe<sub>3</sub>: 3 005w, 2 960s, 2 920m, 2 900m, 2 435s, 2 400s, 2 290w, 2 250m, 2 080s, 1 470s, 1 390s, 1 250m, 1 240m (sh), 1 210m, 1 170m, 1 108s, 1 098s, 1 000s, 970m, 822s, 770s, 748vs, 725m, 705m, 597s, 550s, 490s, 400m,br, and 325s; Ga(BD<sub>4</sub>)Me<sub>2</sub>·NMe<sub>3</sub>: 3 000w, 2 960m, 2 900w, 2 415w, 1 855m (sh), 1 835s, 1 770s, 1 755m (sh), 1 680mw, 1 645w, 1 545s, 1 475s, 1 445w, 1 415w, 1 408w, 1 255m, 1 250m, 1 240w, 1 212s, 1 115w, 1 098w, 1 010m, 1 000s, 880mw, 840m, 830s, 770s, 750s, 720mw, 705m, 602s, 550s, 495s, 425w (sh), 412s, and 290s.

(d) *Reaction with hydrogen chloride.* Dimethylgallium tetrahydroborate reacted with an equimolar quantity of hydrogen chloride at –45 °C (2 h). The volatile products were hydrogen and diborane; the identities of the diborane and of the third product, GaMe<sub>2</sub>Cl,<sup>15</sup> were confirmed by their i.r. spectra. Tensimetric measurements showed in a typical experiment that 0.21 mmol of the tetrahydroborate gave

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

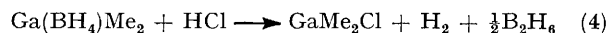
<sup>12</sup> A. J. Downs and G. P. Gaskill, unpublished work.

<sup>13</sup> L. A. Woodward, J. R. Hall, R. N. Dixon, and N. Sheppard, *Spectrochim. Acta*, 1959, **15**, 249; W. J. Lehmann, C. O. Wilson, jun., and I. Shapiro, *J. Chem. Phys.*, 1960, **32**, 1088; **33**, 590; 1961, **34**, 476, 783.

<sup>14</sup> W. Sawodny and J. Goubeau, *Z. phys. Chem. (Frankfurt)*, 1965, **44**, 227.

<sup>15</sup> B. Armer and H. Schmidbaur, *Chem. Ber.*, 1967, **100**, 1521.

0.20 mmol of  $H_2$  and 0.10 mmol of  $B_2H_6$ , in accordance with reaction (4).



#### RESULTS AND DISCUSSION

(i) *Synthetic Methods*.—Although we have been able to confirm that the reaction of trimethylgallium with diborane gives rise to dimethylgallium tetrahydroborate, this is far from an ideal method of synthesis. Even with modifications of the conditions originally outlined by Schlesinger *et al.*,<sup>9</sup> the yields of the tetrahydroborate, never more than modest, are wayward. Not only is the preparation awkward to perform on a scale sufficient to give significant amounts ( $\geq 500$  mg) of the tetrahydroborate, but it is easily thwarted by the presence of any unchanged  $GaMe_3$  which defies effective separation from the tetrahydroborate by trap-to-trap distillation. In our search for a more productive and dependable method of synthesis, we have emulated the strategy successfully used for making such compounds as aluminium tris(tetrahydroborate),<sup>16</sup> zirconium tetrakis(tetrahydroborate),<sup>17</sup> and hydridogallium bis(tetrahydroborate)<sup>8</sup> by turning to the metathesis (2). The reaction has been found to proceed smoothly at *ca.*  $-15^\circ C$  in the absence of a solvent, thereby affording a relatively clean and efficient route to  $Ga(BH_4)Me_2$  or its deuteriated derivatives.

(ii) *Physical Properties of Dimethylgallium Tetrahydroborate*.—In agreement with the findings of Schlesinger *et al.*,<sup>9</sup>  $Ga(BH_4)Me_2$  emerges as a thermally fragile material melting at *ca.*  $1^\circ C$  and having a vapour pressure at  $0^\circ C$  of 13–14 mmHg. Vapour-density measurements imply that the compound vaporizes in the form of monomeric  $Ga(BH_4)Me_2$  molecules, although the near-identity of the molecular weights of  $GaMe_3$  and  $Ga(BH_4)Me_2$  limits the usefulness of such measurements as a means of specific characterization. The mass spectrum of  $Ga(BH_4)Me_2$  failed to reveal a feature attributable to the molecular ion; clearly in evidence, however, are peaks attributable to such species as  $[^{71}GaMe_2]^+$ ,  $[^{69}GaMe_2]^+$ ,  $[^{71}Ga(^{11}BH_4)Me]^+$ ,  $[^{69}Ga(^{11}BH_4)Me]^+$ ,  $[^{71}GaMe]^+$ ,  $[^{69}GaMe]^+$ ,  $^{71}Ga^+$ , and  $^{69}Ga^+$ . These assignments have been confirmed by comparing the mass spectra of the species  $Ga(BH_4)Me_2$  and  $Ga(BD_4)Me_2$  and by reference to the intensity patterns associated with the different naturally abundant isotopes of gallium and boron.

In many respects therefore  $Ga(BH_4)Me_2$  resembles the isoelectronic  $GaMe_3$ ,<sup>18</sup> although the higher melting point

and lower vapour pressure of the tetrahydroborate are signs of more highly developed aggregation, possibly with a move towards the ionic formulation  $[GaMe_2]^+ [BH_4]^-$ , at least in the solid state. By contrast, solid trimethylgallium is isomorphous<sup>19</sup> with trimethylindium and presumably consists of rather loosely constructed tetrameric units  $(GaMe_3)_4$  analogous to those found in both trimethylindium<sup>20</sup> and trimethylthallium.<sup>21</sup>

*Hydrogen-1 n.m.r. spectrum*. The  $^1H$  n.m.r. spectrum of a solution of  $Ga(BH_4)Me_2$  in  $[^2H_6]$ toluene at room temperature comprises (i) a moderately sharp singlet centred on  $\tau$  9.9 and (ii) a relatively broad quartet centred on  $\tau$  8.4. The ratio of the intensity of the singlet to that of the quartet (*ca.* 3 : 2) confirms the origins of the singlet in the methyl protons and of the quartet in the  $^{11}BH_4$  group ( $^{11}B$ ,  $I = \frac{3}{2}$ ). Some components of a weaker septet due to the  $^{10}BH_4$  group ( $^{10}B$ ,  $I = 3$ ) are also discernible. Both the chemical shifts of the resonances and the coupling constant  $^4J(^{11}B-H)$  89 Hz correspond closely with the values found for related compounds, *e.g.*  $GaMe_3$ <sup>22</sup> and  $Al(BH_4)_3$ .<sup>5,7,23,24</sup> No coupling between either set of protons and gallium ( $^{71}Ga$ ,  $I = \frac{3}{2}$ ;  $^{69}Ga$ ,  $I = \frac{3}{2}$ ) is apparent. Decreasing the temperature of the solution causes little change in the methyl resonance but leads to progressive collapse of the quartet due to the tetrahydroborate group until at  $< -60^\circ C$  it is supplanted by a single resonance centred on *ca.*  $\tau$  8.2. In this respect the protons of the tetrahydroborate group conform to the pattern characteristic of molecular tetrahydroborates.<sup>5</sup> At room temperature all the protons of the  $BH_4$  group are magnetically equivalent, implying rapid exchange between the terminal and bridging hydrogen atoms. The collapse of the  $^1H-^{11}B$  multiplet can be understood in terms of a decoupling mechanism based on the diminution in spin-lattice relaxation time dictated by the correlation time  $\tau_c$  characterizing the molecular tumbling responsible for quadrupole relaxation and by the relation  $\tau_c \propto \eta/T$ , where  $\eta$  is the macroscopic viscosity of the solution and  $T$  the temperature.<sup>5,24</sup> With the dimethylgallium compound, as with other tetrahydroborates, there is no sign of so much as an incipient development of distinct  $^1H$  resonances due to terminal and bridging hydrogen atoms, even at temperatures approaching  $-100^\circ C$ .

*Vibrational spectra*. Details of the vibrational spectra of dimethylgallium tetrahydroborate and  $[^2H_4]$ tetrahydroborate, whether in the solid, liquid, gaseous, or matrix-isolated condition, are contained in Table 1, and representative spectra are illustrated in Figure 1. Following the example of Nibler and his co-workers,<sup>3,25,26</sup>

<sup>16</sup> H. I. Schlesinger, H. C. Brown, and E. K. Hyde, *J. Amer. Chem. Soc.*, 1953, **75**, 209.

<sup>17</sup> W. E. Reid, jun., J. M. Bish, and A. Brenner, *J. Electrochem. Soc.*, 1957, **104**, 21.

<sup>18</sup> G. E. Coates and K. Wade, 'Organometallic Compounds,' Methuen, London, 1967, vol. 1, p. 343.

<sup>19</sup> E. M. Johnson, D.Phil. Thesis, University of Oxford, 1971.

<sup>20</sup> E. L. Amma and R. E. Rundle, *J. Amer. Chem. Soc.*, 1958, **80**, 4141.

<sup>21</sup> G. M. Sheldrick and W. S. Sheldrick, *J. Chem. Soc. (A)*, 1970, 28.

<sup>22</sup> J. B. DeRoos and J. P. Oliver, *Inorg. Chem.*, 1965, **4**, 1741; A. Leib, M. T. Emerson, and J. P. Oliver, *ibid.*, p. 1825.

<sup>23</sup> P. C. Maybury and J. E. Ahnell, *Inorg. Chem.*, 1967, **6**, 1286; N. Davies, B. D. James, and M. G. H. Wallbridge, *J. Chem. Soc. (A)*, 1969, 2601; N. Davies, C. A. Smith, and M. G. H. Wallbridge, *ibid.*, 1970, 342; T. H. Cook and G. L. Morgan, *J. Amer. Chem. Soc.*, 1970, **92**, 6487.

<sup>24</sup> T. J. Marks and L. A. Shimp, *J. Amer. Chem. Soc.*, 1972, **94**, 1542.

<sup>25</sup> D. A. Coe and J. W. Nibler, *Spectrochim. Acta*, 1973, **A29**, 1789.

<sup>26</sup> D. A. Coe, J. W. Nibler, T. H. Cook, D. Drew, and G. L. Morgan, *J. Chem. Phys.*, 1975, **63**, 4842; L. J. Allamandola and J. W. Nibler, *J. Amer. Chem. Soc.*, 1976, **98**, 2096.

we have analysed the spectra in terms of the group vibrations appropriate to the molecule  $\text{Ga}(\text{BH}_4)\text{Me}_2$  to arrive at the assignments listed in Table 2. The co-ordinates common to a particular symmetry class is certainly acknowledged by an approximate n.c.a. of the molecules  $\text{Ga}(\text{BH}_4)\text{Me}_2$  and  $\text{Ga}(\text{BD}_4)\text{Me}_2$  in which the

TABLE 1

Vibrational spectra ( $\text{cm}^{-1}$ )<sup>a</sup> of dimethylgallium tetrahydroborate and  $[\text{}^2\text{H}_4]$ tetrahydroborate

Vapour, 290 K, I. r.		$\text{N}_2$ matrix, 10 K, I. r.	Liquid, 290 K, Raman		Solid, 20 K, Raman		Solid, 77 K, I. r.		Assignment
$\text{Ga}(\text{BH}_4)\text{Me}_2$	$\text{Ga}(\text{BD}_4)\text{Me}_2$	$\text{Ga}(\text{BH}_4)\text{Me}_2$	$\text{Ga}(\text{BH}_4)\text{Me}_2$	$\text{Ga}(\text{BD}_4)\text{Me}_2$	$\text{Ga}(\text{BH}_4)\text{Me}_2$	$\text{Ga}(\text{BD}_4)\text{Me}_2$	$\text{Ga}(\text{BH}_4)\text{Me}_2$	$\text{Ga}(\text{BD}_4)\text{Me}_2$	
						87w 107s			$\nu_{38}(b_2)$ TL
			161s,p?	156s,p?	125m 154s 172m 189m	126 (sh) 152s 162 (sh)			$\nu_{26}(b_1)$ $\nu_{12}(a_1)$
					313w,dp 369mw,dp	231m 280s	317mw 370mw	278mw	$\nu_{12}(a_2), \nu_{25}(b_1)$ $\nu_{17}(a_2)$ $\nu_{38}(b_2)$
355w 445s, $\perp$	270w 422s, $\perp$	440s $\delta$ 452m $\delta$	424s,p	386s,p	367s 395m 410m (sh)	355s	393s	363s	$\nu_{11}(a_1)$
482w				463w,p?		464w		459w	$2\nu_{17}(A_1)$ $\nu_{17} + \nu_{18}(A_1)$ OR $\nu_{17} + \nu_{25}(B_2)$
553m, $\perp$	555m, $\perp$	555s	557vs,p	553vs,p	543w $\delta$ 552vs $\delta$ 590vw	543w (sh) $\delta$ 553vs $\delta$	548m	551s	$\nu_{16}(a_1)$
616s, $\perp$	615s, $\perp$	616s $\delta$ 619s $\delta$	623m,dp	619m,dp	610w 622m	619m	626s	626s	$\nu_{11} + \nu_{12}(A_1)$ $\nu_{34}(b_2)$
666w	668w	666vw							$\nu_{10} + \nu_{26}(B_1)$ $\nu_9(a_1)$
736m	738m	720w	700vw,p?	691vw,dp	704w 728vw	699w	700vw 726mw	700w,br 722m 729w (sh)	$\nu_{16}(a_2), \nu_{23}(b_1),$ $\nu_{24}(b_1), \nu_{25}(b_2)$
791s 965w	790s	767m 786m	760vw,dp?	745w,dp	770vw	761vw	755s 777m	776m	$\nu_{32}(b_2)$
1 129s, $\perp$	852mw	1 122vs $\delta$ 1 130m $\delta$	1 123mw,p? 1 140mw,dp?	844vw 812w,dp	970m $\delta$ 977w $\delta$	740m $\delta$ 748w $\delta$	967m $\delta$ 975w $\delta$	830mw 834w (sh)	$\nu_8(a_1)$ $\nu_{15}(a_2)$ $\nu_{24} + \nu_{25}(A_1)$ $\nu_{10} + \nu_{11}(A_1)$ $\nu_{17} + \nu_{24}(B_2)$ $\nu_9 + \nu_{11}(A_1)$ $2\nu_{10}(A_1)$ $\nu_{10} + \nu_{24}(B_2)$
				952w,vbr		957w 1 060w,br 1 099w 1 164w		903w 926mw	$\nu_7(a_1)$
1 222m, $\perp$	1 221m, $\perp$	1 218m	1 212s,p	1 210s,p	1 200s 1 205w 1 216w	1 198s	1 200w	1 182w	$\nu_{31}(b_2)$
			1 240 (sh)		1 245w	1 237w	1 223s 1 216m 1 244m	1 214m	$2\nu_{34}(A_1)$
1 320m	1 295w 1 340m	1 302mw 1 314w		1 320vw		1 280?vw,br	1 292vw	1 272w 1 283w	$\nu_{10} + \nu_{24}(B_1)$ $\nu_{10} + \nu_{25}(B_2)$ $\nu_9 + \nu_{34}(B_2)$ $\nu_7 + \nu_{26}(B_1), \nu_{16} + \nu_{24}(B_1)$ , OR $\nu_{23} + \nu_{24}(A_1)$ $\nu_7 + \nu_{12}(A_1)$ OR $\nu_{12} + \nu_{21}(B_2)$
1 405s 1 455s	997s 1 068s	1 400m 1 454m	1 420mw,p	1 031mw,p	1 400mw	1 014m	1 407s	1 016s 1 391mw 2 $\nu_9(A_1)$ 1 459mw 1 467w (sh)	$\nu_9(a_1)$ $\nu_{22}(b_1)$ $\nu_5(a_1), \nu_{14}(a_2),$ $\nu_{21}(b_1), \nu_{25}(b_2)$
1 775w		1 466m	1 435m,p	1 468?vw		1 393w,br	1 460w,br		$\nu_{10} + \nu_{21}(B_2)$ $\nu_7 + \nu_9(A_1)$
1 922s	1 414s	1 958w $\epsilon$ 1 967w $\epsilon$ 1 982w $\epsilon$	1 909w,p 2 030m,p	1 501m,p	2 060w	1 459mw	2 035mw	1 479w 1 491w	$\nu_4(a_1)$
1 980vs	1 472m	2 012s	1 982w,p		2 091mw 2 130m (sh)	1 524s	2 108s	1 530s 1 542m (sh) $\delta$ 1 560mw $\delta$ 1 580mw 1 649w 1 629w	$\nu_6 + \nu_{10}(A_1)$ $\nu_{20}(b_1)$
2 089m 2 248w	1 585w,br 1 680w,br		2 428s,p	1 780s,p	2 200vw	1 578w,br 1 653w	2 198w 2 290w	1 580mw 2 $\nu_8(A_1)$ 1 629w	$\nu_8 + \nu_{22}(B_2)$ $2\nu_8(A_1)$ $2\nu_{15}(A_1)$
2 470vs, $\perp$	1 807vs, $\perp$	2 447s $\delta$ 2 453 (sh) $\delta$	2 496m,dp	1 882m,dp	2 386s	1 755s 1 801w	2 400vs	1 758vs 1 795mw	$\nu_3(a_1)$
2 540vs, $\perp$	1 913vs, $\perp$	2 515s $\delta$ 2 527mw $\delta$			2 450m 2 462 (sh)	1 843s	2 459vs	1 839vs	$\nu_{29}(b_2)$
2 657w	1 856w 1 950 (sh),br					1 861m		1 859m 1 925w	$\nu_6 + \nu_8(A_1)$ $\nu_7 + \nu_{24}(B_1)$ $\nu_5 + \nu_{21}(B_2), \nu_{14} + \nu_{21}(B_1)$ , OR $\nu_{20} + \nu_{21}(A_1)$ $\nu_5 + \nu_{25}(B_2)$
2 850w 2 924mw 2 977mw	2 860vw 2 922mw 2 978mw	2 855w 2 915mw	2 921s,p 2 985m,dp	2 917s,p 2 980m,dp	2 921s 2 989m	2 920s 2 992m	2 920w 2 985mw	2 848vw 2 920w 2 992m	$2\nu_5, 2\nu_{14}, 2\nu_{21}$ , OR $2\nu_{20}(A_1)$ $\nu_8(a_1), \nu_{28}(b_2)$ $\nu_1(a_1), \nu_{13}(a_2)$ $\nu_{13}(b_1), \nu_{22}(b_2)$ $\nu_3 + \nu_{10}(A_1)$
3 027w (sh)									

<sup>a</sup> Assignments refer to a  $\text{Ga}(\text{BH}_4)\text{Me}_2$  or  $\text{Ga}(\text{BD}_4)\text{Me}_2$  molecule with  $C_{2v}$  symmetry. s = Strong, m = medium, w = weak, v = very, sh = shoulder, br = broad, p = polarized, dp = depolarized, TL = translational or librational mode, and  $\perp$  = perpendicular-type contour.  $\delta$  Distinct isotopic feature.  $\epsilon$  Matrix-splitting effects.  $\delta$  May be due to traces of  $\text{Ga}(\text{BD}_2\text{H})\text{Me}_2$ .

descriptions of the normal modes thus employed appear at least to be self-consistent, although how closely they represent the true picture it is impossible to say in the absence of a detailed normal-co-ordinate analysis (n.c.a.). That there is significant mixing of some of the internal

methyl groups are treated as point masses.<sup>4</sup> On the evidence of this analysis, however, all but one or two of the descriptions we have applied to the modes do appear to be apt to the extent that they specify the *principal* component of each motion. The only modes which

beggar any simple description are the three involving rocking of the terminal  $\text{BH}_2$  fragment, bending of the  $\text{Ga}(\mu\text{-H})_2\text{B}$  bridge and antisymmetric in-plane bending of the  $\text{GaC}_2\text{B}$  skeleton (all belonging to the  $b_2$  symmetry class, see Table 2), the internal co-ordinates of which are comprehensively intermixed.

as recourse to the product rule as applied to the fundamentals of  $\text{Ga}(\text{BH}_4)\text{Me}_2$  and  $\text{Ga}(\text{BD}_4)\text{Me}_2$  belonging to a given symmetry class; (e) the appearance of distinct features arising from the different naturally occurring isotopes  $^{10}\text{B}/^{11}\text{B}$ ,  $^{12}\text{C}/^{13}\text{C}$ , and  $^{69}\text{Ga}/^{71}\text{Ga}$ ; (f) the relative intensities of the Raman and i.r. bands attributable to a

TABLE 2  
Proposed assignment of the fundamentals of dimethylgallium tetrahydroborate and  $[\text{}^2\text{H}_4]$ tetrahydroborate

Symmetry class and activity	Number	Approximate description	Band $\sigma$ ( $\text{cm}^{-1}$ )				$\nu_{\text{H}}/\nu_{\text{D}}$	
			Solid		Vapour		Solid	Vapour
			$\text{Ga}(\text{BH}_4)\text{Me}_2$	$\text{Ga}(\text{BD}_4)\text{Me}_2$	$\text{Ga}(\text{BH}_4)\text{Me}_2$	$\text{Ga}(\text{BD}_4)\text{Me}_2$		
$a_1$ Raman, i.r.	$\nu_1$	antisym CH str.	2 989	2 992	2 977	2 978	0.999	1.000
	$\nu_2$	sym CH str.	2 921	2 920	2 924	2 922	1.000	1.001
	$\nu_3$	sym $\text{BH}_t$ str.	2 386	1 755	2 470	1 807	1.360	1.367
	$\nu_4$	sym $\text{BH}_b$ str.	2 035 *	1 485 *	1 922	1 414	1.370	1.359
	$\nu_5$	antisym $\text{CH}_3$ def.	1 460 *	1 459 *			1.001	
	$\nu_6$	sym $\text{GaH}_b$ str.	1 400	1 014	1 405	997	1.381	1.409
	$\nu_7$	sym $\text{CH}_3$ def.	1 200	1 198			1.002	
	$\nu_8$	$\text{BH}_t$ def.	1 095	828	1 129	852	1.322	1.325
	$\nu_9$	$\text{CH}_3$ rock	704	699	ca. 700	ca. 700	1.007	
	$\nu_{10}$	sym GaC str.	552	553	553	555	0.998	0.996
	$\nu_{11}$	GaB str.	395	355	445	422	1.113	1.055
	$\nu_{12}$	sym $\text{GaC}_2$ def.	154	152			1.013	
$a_2$ Raman	$\nu_{13}$	antisym CH str.	2 989	2 992			0.999	
	$\nu_{14}$	antisym $\text{CH}_3$ def.	1 400—1 470	1 400—1 470				
	$\nu_{15}$	$\text{BH}_t$ twist	1 146	815			1.406	
	$\nu_{16}$	$\text{CH}_3$ rock	700—800	700—800				
	$\nu_{17}$	bridge twist	315	231			1.364	
	$\nu_{18}$	$\text{CH}_3$ torsion	ca. 170	ca. 170				
$b_1$ Raman, i.r.	$\nu_{19}$	antisym CH str.	2 989	2 992	2 977	2 978	0.999	1.000
	$\nu_{20}$	antisym $\text{BH}_b$ str.	2 091	1 524	1 980	1 472	1.372	1.345
	$\nu_{21}$	antisym $\text{CH}_3$ def.	1 460 *	1 459 *			1.001	
	$\nu_{22}$	antisym $\text{GaH}_b$ str.	1 407 *	1 016 *	1 455	1 068	1.385	1.362
	$\nu_{23}$	$\text{BH}_t$ wag	ca. 730 <sup>b</sup>	ca. 550 <sup>b</sup>			1.327	
	$\nu_{24}$	$\text{CH}_3$ rock	700—800	700—800	700—800	700—800		
	$\nu_{25}$	$\text{CH}_3$ torsion	ca. 170	ca. 170				
	$\nu_{26}$	out-of-plane $\text{GaC}_2\text{B}$ def.	125	126			0.992	
$b_2$ Raman, i.r.	$\nu_{27}$	antisym CH str.	2 989	2 992	2 977	2 978	0.999	1.000
	$\nu_{28}$	sym CH str.	2 921	2 920	2 924	2 922	1.000	1.001
	$\nu_{29}$	antisym $\text{BH}_t$ str.	2 450	1 843	2 540	1 913	1.329	1.328
	$\nu_{30}$	antisym $\text{CH}_3$ def.	1 460 *	1 459 *			1.001	
	$\nu_{31}$	sym $\text{CH}_3$ def.	1 216	1 213	1 222	1 221	1.002	1.001
	$\nu_{32}$	$\text{BH}_t$ rock <sup>c</sup>	970	740	965	<sup>b</sup>	1.311	
	$\nu_{33}$	$\text{CH}_3$ rock	700—800	700—800	700—800	700—800		
	$\nu_{34}$	antisym GaC str.	622	619	616	615	1.005	1.002
	$\nu_{35}$	bridge bend <sup>c</sup>	367	280	355	270	1.311	1.315
	$\nu_{36}$	antisym in-plane $\text{GaC}_2\text{B}$ def. <sup>c</sup>	(ca. 98)	87			1.126	

<sup>a</sup> The bands of the solid compounds are taken from the Raman spectra except for those marked \* which are taken from the i.r. spectra. The bands of the vapours are those defined by the i.r. spectra. Numbers in parentheses were derived from n.c.a. calculations. <sup>b</sup> Probably obscured by more intense features. <sup>c</sup> There is pronounced coupling between the  $b_2$  internal co-ordinates defining the following motions:  $\text{BH}_t$  rocking, bridge-bending, and antisymmetric in-plane  $\text{GaC}_2\text{B}$  deformation.

Each of the assignments proposed is based on one or more of the following criteria: (a) analogy with the vibrational assignments favoured for other molecules containing either a  $\text{GaMe}_2$ <sup>27</sup> or a co-ordinated  $\text{BH}_4$  group,<sup>3,4,25,26,28,29</sup> (b) the selection rules expected to govern the activity in i.r. absorption or Raman scattering of the vibrational modes associated with the  $\text{Ga}(\text{BH}_4)\text{Me}_2$  molecule; (c) the polarization properties of the Raman scattering exhibited by the liquid tetrahydroborate; (d) the effect of deuteration at the  $\text{BH}_4$  group on the frequency of a given spectroscopic feature, as well

particular mode; (g) the nature of the envelope associated with a given i.r. absorption of the vapour, with its implications for the direction in which the dipole moment oscillates with respect to the molecular framework; and (h) compliance with a reasonable set of potential constants as mediated by the approximate n.c.a. cited earlier.

The i.r. spectrum of gaseous  $\text{Ga}(\text{BH}_4)\text{Me}_2$  is most plausibly interpreted in terms of a molecular model of  $C_{2v}$  symmetry involving four-fold co-ordination of the gallium atom and a di-hydrogen-bridged  $\text{Ga}(\mu\text{-H})_2\text{BH}_2$

<sup>27</sup> R. S. Tobias, M. J. Sprague, and G. E. Glass, *Inorg. Chem.* 1968, **7**, 1714.

<sup>28</sup> T. J. Marks, W. J. Knelly, J. R. Kolb, and L. A. Shimp, *Inorg. Chem.*, 1972, **11**, 2540.

<sup>29</sup> W. L. Smith and I. M. Mills, *J. Chem. Phys.*, 1964, **41**, 1479.

moiety. Not only are the spectral features characteristic of a non-linear  $\text{GaMe}_2$  group readily apparent,<sup>27</sup> but the pattern of absorptions normally associated with a

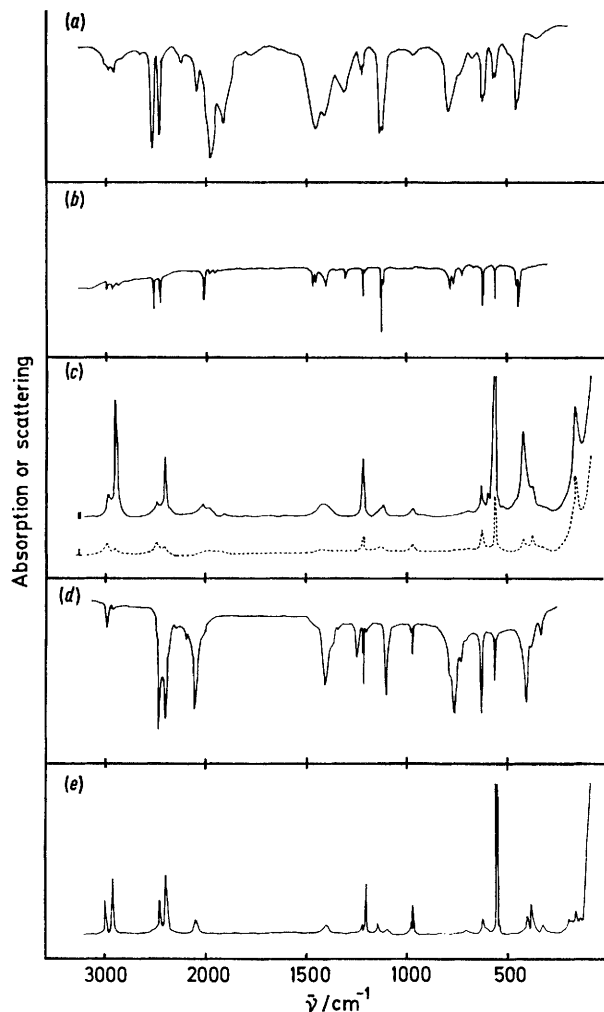


FIGURE 1 The vibrational spectra of dimethylgallium tetrahydroborate: (a) i.r. spectrum of the vapour at 290 K (pressure *ca.* 10 Torr, pathlength 10 cm); (b) i.r. spectrum of an  $\text{N}_2$  matrix at 10 K [ $\text{N}_2 : \text{Ga}(\text{BH}_4)\text{Me}_2 = \text{ca. } 500 : 1$ ]; (c) Raman spectrum of the liquid at 290 K; (d) i.r. spectrum of an annealed solid film at 77 K; and (e) Raman spectrum of an annealed solid film at 20 K

doubly bridged tetrahydroborate group is strongly in evidence.<sup>1,25,26,28,29</sup> The molecular model is illustrated in Figure 2 which also suggests approximate dimensions based on the preliminary results of electron diffraction of the vapour<sup>30</sup> and on the structures of the related molecules  $\text{GaMe}_3$ ,<sup>31</sup>  $\text{Al}(\text{BH}_4)\text{Me}_2$ ,<sup>30</sup> and  $\text{Ga}(\text{BH}_4)_2\text{H}$ ,<sup>30</sup> also determined by electron diffraction. Hence the principal moments of inertia of the molecules  $\text{Ga}(\text{BH}_4)\text{Me}_2$  and  $\text{Ga}(\text{BD}_4)\text{Me}_2$  have been estimated, with the results collected in Table 3. Formally, both molecules are asymmetric tops but they approximate to oblate symmetric tops with the  $\text{C}_2\text{GaB}$  plane containing the

<sup>30</sup> M. T. Barlow, A. J. Downs, D. W. H. Rankin, and P. D. P. Thomas, unpublished work.

axes of  $I_A$  and  $I_B$ , and perpendicular to the axis of  $I_C$ , where  $I_A \approx I_B < I_C$ . The 36 vibrational modes are

TABLE 3

Moments of inertia, envelopes of vapour-phase i.r. absorptions, and product-rule calculations for the molecules  $\text{Ga}(\text{BH}_4)\text{Me}_2$  and  $\text{Ga}(\text{BD}_4)\text{Me}_2$

Molecular property	$\text{Ga}(\text{BH}_4)\text{Me}_2$	$\text{Ga}(\text{BD}_4)\text{Me}_2$
Molecular mass/a.m.u. *	114.631	118.656
$I_A$ /a.m.u. $\text{Å}^2$ *	90.30	94.66
$I_B$ /a.m.u. $\text{Å}^2$ *	101.99	123.19
$I_C$ /a.m.u. $\text{Å}^2$ *	187.73	208.74

Envelopes of vapour-phase i.r. absorptions

Symmetry class	Property of envelope	calc.	obs.	calc.	obs.
$a_1$	{Band type <sup>a</sup>	$\perp$	$\perp$	$\perp$	$\perp$
	{ $\Delta\nu_{PR}/\text{cm}^{-1}$	16.7	16	15.7	15
$b_1$	{Band type <sup>a</sup>	$\parallel$	$\parallel$	$\parallel$	$\parallel$
	{ $\Delta\nu_{PR}/\text{cm}^{-1}$	25.1		23.6	
$b_2$	{Band type <sup>a</sup>	$\perp$	$\perp$	$\perp$	$\perp$
	{ $\Delta\nu_{PR}/\text{cm}^{-1}$	16.8	16	15.8	15

Product-rule calculations

Symmetry class	Product-rule factor, <sup>b</sup> $\frac{\nu_i, \text{H} \nu_j, \text{H} \dots}{\nu_i, \text{D} \nu_j, \text{D} \dots}$	
	calc.	obs.
$a_1$	3.9249	3.862
$a_2$	1.9518	1.916
$b_1$	2.5263	2.501
$b_2$	2.6331	2.590

\* 1 a.m.u. =  $1.6605 \times 10^{-27}$  kg.

<sup>a</sup> Designated on the assumption that each molecule approximates to an oblate symmetric top. <sup>b</sup> The observed product-rule factors relate to the vibrational spectra of the solid compounds.

accommodated by the representation  $12a_1 + 6a_2 + 8b_1 + 10b_2$ , all of them being Raman-active and all but the

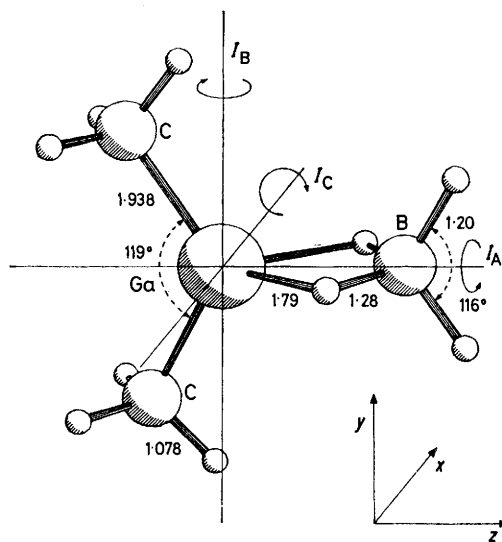


FIGURE 2 Structure of  $\text{Ga}(\text{BH}_4)\text{Me}_2$  showing the axes of the principal moments of inertia. The bond lengths are in  $\text{Å}$  (ref. 30). The  $\text{Ga} \cdots \text{B}$  separation is 2.152  $\text{Å}$

$6a_2$  modes being allowed in i.r. absorption. With the choice of co-ordinate axes shown in Figure 2, the form of

<sup>31</sup> B. Beagley, D. G. Schmidling, and I. A. Steer, *J. Mol. Structure*, 1974, **21**, 437.

the momental ellipsoid is likely to be such that  $a_1$  modes of the gaseous molecule give rise in i.r. absorption to type A bands,  $b_1$  modes to type C bands, and  $b_2$  modes to type B bands. On the other hand, whereas a type C band is expected to be relatively distinctive with a prominent  $Q$  branch, there is little to distinguish a type A from a type B band, both tending to assume the characteristics of perpendicular-type bands with the approach of the molecule to an oblate symmetric top. Thus, estimates<sup>32</sup> of the separation between the  $P$  and  $R$  branches are virtually identical for type A and B bands. It is true that the central branch of a type A band should be a singlet and that of a type B band a doublet, but with components separated by no more than *ca.* 4  $\text{cm}^{-1}$ ; accordingly, under conditions of modest resolution both type A and B bands may be expected to look alike with somewhat poorly defined  $P$ ,  $Q$ , and  $R$  branches of roughly equal intensity. It follows that the envelopes of i.r. absorptions due to gaseous dimethylgallium tetrahydroborate and  $[\text{}^2\text{H}_4]$ tetrahydroborate are unlikely under such conditions to provide a means of classification beyond differentiating between  $b_1$  modes, with their pseudo-parallel-type contours, and  $a_1$  or  $b_2$  modes, with their pseudo-perpendicular-type contours. In practice, torsional motions of the methyl groups and other low-frequency modes may well combine with the overlap of near-degenerate modes to limit still further the utility of band shape as a criterion of vibrational symmetry, although some bands [*e.g.* those at 445, 553, 616, 1 129, 1 222, 2 470, and 2 540  $\text{cm}^{-1}$ , all with perpendicular-type contours, in the spectrum of  $\text{Ga}(\text{BH}_4)\text{Me}_2$ ] do show clear signs of partially resolved rotational structure.

Comparison of the vibrational spectra of solid, liquid, gaseous, and matrix-isolated dimethylgallium tetrahydroborate and  $[\text{}^2\text{H}_4]$ tetrahydroborate reveals relatively minor changes with the transition from the gaseous to the condensed phases. Hence it seems reasonable to assume that the molecular unit present in the vapour is in fact common to the solid, liquid, and vapour phases. The spectra of the solid compounds do imply, however, that there is a significant weakening of the interaction between the  $\text{GaMe}_2$  and  $\text{BH}_4$  units in a move towards the ionic formulation  $[\text{GaMe}_2]^+[\text{BH}_4]^-$ . Thus, relative to the spectrum of the vapour, the frequency separation of those bands attributable to  $\text{B-H}_t$  and  $\text{B-H}_b$  stretching motions ( $t$  = terminal,  $b$  = bridging) is reduced from *ca.* 550 to little more than 300  $\text{cm}^{-1}$ , and there is a concomitant decrease in the frequencies of both the  $\text{Ga-H}_b$  and  $\text{Ga-B}$  stretching modes. The enhanced intensity of the absorption associated with the antisymmetric  $\text{Ga-C}$  stretching mode relative to that associated with the corresponding symmetric mode [ $I_{\text{antisym}}/I_{\text{sym}}$  1.35 for the vapour and 2.85 for solid  $\text{Ga}(\text{BH}_4)\text{Me}_2$  at 77 K] also implies an opening out of the  $\text{H}_3\text{C-Ga-CH}_3$  angle. On the other hand, it appears that the degree of ionic character is not nearly so pronounced as in solid beryllium

bis(tetrahydroborate),<sup>3</sup> methylzinc tetrahydroborate,<sup>33</sup> or dimethylaluminium tetrahydroborate.<sup>4</sup> It is a mark of this disparity, for example, that the metal-boron stretching mode gives rise to Raman scattering which is demonstrably more intense for solid and liquid  $\text{Ga}(\text{BH}_4)\text{Me}_2$  than for solid  $\text{Zn}(\text{BH}_4)\text{Me}$ . The intensity of the  $\text{Ga-B}$  stretching mode in Raman scattering, allied with a depolarization ratio of the order of 0.1 for the liquid, and with the absence of pronounced coupling with other types of motion, implies for  $\text{Ga}(\text{BH}_4)\text{Me}_2$ , as for  $\text{Hf}(\text{BH}_4)_4$ ,<sup>34</sup> a sizeable mean polarizability derivative  $\alpha'(M-B)$  suggestive of appreciable  $M-B$  bonding ( $M = \text{Ga}$  or  $\text{Hf}$ ).

Most of the i.r. and Raman bands are satisfactorily accounted for on the basis of the molecular model depicted in Figure 2. Some uncertainty inevitably surrounds the assignment of certain specific fundamentals, notably some of those involving motion of the bridging hydrogen atoms where analogies tend to be sparse and sometimes confusing. Thus, although the various criteria (*a*)–(*h*) give little cause to doubt the assignments proposed for the  $a_1$  fundamentals  $\nu_1$ – $\nu_{12}$ , assignment of some of the  $a_2$  fundamentals is less obvious. For the  $\text{BH}_t$  twisting mode  $\nu_{15}$  we favour a frequency at 1 146  $\text{cm}^{-1}$  for the  $\text{Ga}(\text{BH}_4)\text{Me}_2$  molecule in the solid phase, corresponding to a Raman line apparently without a counterpart in the i.r. spectrum, and which decreases in frequency by a factor of nearly 2<sup>†</sup> on deuteration of the tetrahydroborate group; the frequency associated with this type of motion in related tetrahydroborates<sup>3,4,25,26,28,29</sup> lends support to such an assignment. On the other hand, the bridge-twisting mode  $\nu_{17}$  is more difficult to identify. There is no obvious candidate for this fundamental in the region suggested by Coe and Nibler<sup>25</sup> for the corresponding vibration in  $\text{Al}(\text{BH}_4)_3$  [ $\text{Al}(\text{BD}_4)_3$ ] [*i.e.* 1 146 (813  $\text{cm}^{-1}$ )]. Some reservations must be held, however, about an assignment which imputes to  $\text{Al}(\text{BH}_4)_3$  [ $\text{Al}(\text{BD}_4)_3$ ] a frequency markedly *higher* than that calculated for the corresponding mode of  $\text{B}_2\text{H}_6$  ( $\text{B}_2\text{D}_6$ ) [833 (592  $\text{cm}^{-1}$ )].<sup>29</sup> We prefer to attribute the Raman scattering at 315 (231  $\text{cm}^{-1}$ ) due to solid  $\text{Ga}(\text{BH}_4)\text{Me}_2$  [ $\text{Ga}(\text{BD}_4)\text{Me}_2$ ] to  $\nu_{17}$ ; a medium-to-weak band at 317  $\text{cm}^{-1}$  in the i.r. spectrum of solid  $\text{Ga}(\text{BH}_4)\text{Me}_2$  may then be due to the overtone  $2\nu_{12}(A_1)$  or it may represent  $\nu_{17}$  made active in i.r. absorption by the effects of either relatively unsymmetrical siting of individual  $\text{Ga}(\text{BH}_4)\text{Me}_2$  molecules or of intermolecular correlation within the unit cell of the solid compound. The assignments of both  $\nu_{15}$  and  $\nu_{17}$  are in accord not only with product-rule calculations (see Table 3), but also with the attribution to the relevant principal force constants of values compatible with those of related molecules.<sup>33,35</sup> There is still less to aid our search for the two  $\text{CH}_3$  torsional modes  $\nu_{18}(a_2)$  and  $\nu_{25}(b_1)$ , but the assignments of Tables 1 and 2 are not radically different

<sup>32</sup> W. A. Seth Paul and G. Dijkstra, *Spectrochim. Acta*, 1967, **A23**, 2861; W. A. Seth Paul, *J. Mol. Structure*, 1969, **3**, 403.

<sup>33</sup> J. W. Nibler and T. H. Cook, *J. Chem. Phys.*, 1973, **58**, 1596.

<sup>34</sup> T. A. Keiderling, W. T. Wozniak, R. S. Gay, D. Jurkowitz, E. R. Bernstein, S. J. Lippard, and T. G. Spiro, *Inorg. Chem.*, 1975, **14**, 576.

<sup>35</sup> D. M. Adams and R. G. Churchill, *J. Chem. Soc. (A)*, 1970, 697.

from those of related molecules, *e.g.*  $\text{SeMe}_2$ <sup>36</sup> and  $\text{AsX}_{3-n}\text{Me}_n$  ( $\text{X} = \text{halogen}$ ),<sup>37</sup> and are in keeping with the finding that the frequencies vary but little with deuteration of the tetrahydroborate group. We believe that the  $b_1$  B-H<sub>t</sub> wagging mode  $\nu_{23}$  is obscured by more intense features, *viz.* those due to  $\text{CH}_3$  rocking fundamentals in  $\text{Ga}(\text{BH}_4)\text{Me}_2$  and to the Ga-C stretching fundamentals in  $\text{Ga}(\text{BD}_4)\text{Me}_2$ ; the approximate frequencies we have assigned in the Tables are upheld by the observation that the intensity quotient  $I_{\text{antisym}}/I_{\text{sym}}$  of the i.r. bands attributed to the antisymmetric and symmetric Ga-C stretching vibrations appears to decrease when  $\text{BH}_4$  gives place to  $\text{BD}_4$ , suggesting that the band due to the symmetric Ga-C stretching vibration of  $\text{Ga}(\text{BD}_4)\text{Me}_2$  masks the development of an additional feature. With the  $b_2$  vibrations  $\nu_{32}$  and  $\nu_{35}$  we associate respectively the bands near 970 (740) and 370 (280  $\text{cm}^{-1}$ ) in the i.r. and Raman spectra of  $\text{Ga}(\text{BH}_4)\text{Me}_2$  [ $\text{Ga}(\text{BD}_4)\text{Me}_2$ ]. Rocking of the terminal  $\text{BH}_2$  unit is an important component of  $\nu_{32}$ , and the frequencies we favour are in the vicinity of those reported for this kind of motion in  $\text{B}_2\text{H}_6$  ( $\text{B}_2\text{D}_6$ ) [915 (725  $\text{cm}^{-1}$ )]<sup>29</sup> and  $\text{Al}(\text{BH}_4)_3$  [ $\text{Al}(\text{BD}_4)_3$ ] [967 (735  $\text{cm}^{-1}$ )].<sup>25</sup> Bending of the  $\text{Ga}(\mu\text{-H})_2\text{B}$  bridge plays an important part in  $\nu_{35}$  and again it is reassuring to discover that the frequencies proposed are similar to those reported for the bridge-bending fundamentals of  $\text{B}_2\text{H}_6$  ( $\text{B}_2\text{D}_6$ ) [368 (262  $\text{cm}^{-1}$ )]<sup>29</sup> and  $\text{Al}(\text{BH}_4)_3$  [ $\text{Al}(\text{BD}_4)_3$ ] [255 (194  $\text{cm}^{-1}$ )].<sup>25</sup> In both cases, however, the degree of mixing between the internal co-ordinates associated with the  $b_2$  modes  $\nu_{32}$ ,  $\nu_{35}$ , and  $\nu_{36}$  in the dimethylgallium compound is incompatible with any close analogies. We are at a loss to discover a sound basis of assigning the modes associated principally with the out-of-plane and antisymmetric in-plane deformation of the  $\text{GaC}_2\text{B}$  skeleton, *i.e.*  $\nu_{26}(b_1)$  and  $\nu_{36}(b_2)$ , respectively. In the circumstances, the frequencies attributed to these two fundamentals must be more than usually speculative, although our approximate n.c.a. encourages the belief that they are unlikely to be too wide of the mark.

Table 3 includes the results of product-rule calculations. Where the theoretical and observed product-rule factors,  $P$ , can be compared for a given symmetry species the agreement is reasonable, allowing for the fact that anharmonicity usually yields an observed factor which is lower than the theoretical result. Indeed the qualification  $P_{\text{calc.}} \geq P_{\text{obs.}}$  has been employed in trying to identify certain of the more contentious assignments within a particular symmetry class.

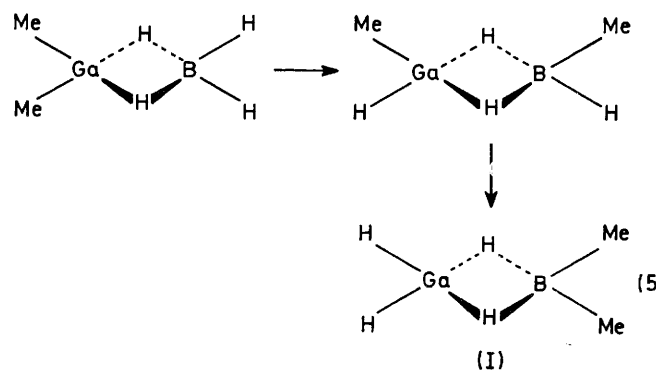
At least some of the low-frequency Raman lines of the solid must be ascribed to translational and librational motions in the unit cell. Certain spectral bands are also attributable to the presence of small amounts of impurity, *e.g.*  $\text{Ga}(\text{BD}_3\text{H})\text{Me}_2$  contaminating the sample of  $\text{Ga}(\text{BD}_4)\text{Me}_2$ ; otherwise all the features still unaccounted for, which are almost all of low intensity, can be satisfactorily interpreted as overtones or combinations of the

<sup>36</sup> J. R. Durig, C. M. Player, jun., J. Bragin, and Y. S. Li, *J. Chem. Phys.*, 1971, **55**, 2895.

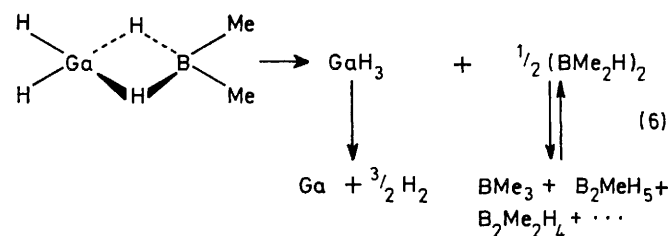
<sup>37</sup> H. F. Shurvell, M. R. Gold, and A. R. Norris, *Canad. J. Chem.*, 1972, **50**, 2691.

fundamentals associated with the molecules  $\text{Ga}(\text{BH}_4)\text{Me}_2$  or  $\text{Ga}(\text{BD}_4)\text{Me}_2$  (see Table 1).

(iii) *Chemical Properties of Dimethylgallium Tetrahydroborate.*—(a) *Thermal decomposition.* Our experiments showed that gaseous  $\text{Ga}(\text{BH}_4)\text{Me}_2$  at a pressure of *ca.* 10 mmHg decomposes with a half-life of the order of 3 h at room temperature. The products of thermal decomposition consist of gallium metal, hydrogen, and a mixture of trimethylborane and methylated boranes. In relation to equation (3) the mass of gallium formed is on the low side, whereas the pressure of condensable volatile material is on the high side. These small discrepancies may well be accounted for by the formation of small quantities of  $\text{GaMe}_3$ . The identity of the products and the failure to detect any methane among these products lead us to conclude that decomposition proceeds *via* an initial intra- or inter-molecular exchange process (5). Since there is reason to believe that the thermally



unstable hydridogallium compound  $\text{Ga}(\text{BH}_4)_2\text{H}$  decomposes by a dissociative route<sup>4,8</sup> and that unco-ordinated gallium hydride decomposes rapidly into gallium and hydrogen at ambient temperatures,<sup>38</sup> it is not unreasonable to suppose that an intermediate such as (I) decomposes in a similar manner:



It may be remarked that  $\text{Ga}(\text{BH}_4)\text{Me}_2$  is thermally much less stable than its aluminium analogue  $\text{Al}(\text{BH}_4)\text{Me}_2$ .<sup>4,7</sup> If the mechanism we have suggested is correct, this finding may be rationalized in terms of the superior thermal stability of the unit  $\text{H}_2\text{Al}(\mu\text{-H})_2$  compared with  $\text{H}_2\text{Ga}(\mu\text{-H})_2$ . The mechanism also invites speculation about the stability of related tetrahydroborate derivatives of gallium, and it is perhaps significant that the ease of

<sup>38</sup> N. N. Greenwood and M. G. H. Wallbridge, *J. Chem. Soc.*, 1963, 3912; D. F. Shriver, R. W. Parry, N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *Inorg. Chem.*, 1963, **2**, 867.



decomposition appears to increase in the sequence  $\text{Ga}(\text{BH}_4)\text{Me}_2 < \text{Ga}(\text{BH}_4)(\text{Me})\text{H}^{39} < \text{Ga}(\text{BH}_4)_2\text{H}^4$ .

(b) *Ammonolysis: the displacement of the  $[\text{BH}_4]^-$  anion.* In common with other molecular tetrahydroborates such as  $\text{Al}(\text{BH}_4)_3$ ,<sup>40,41</sup>  $\text{Ga}(\text{BH}_4)_2\text{H}$ ,<sup>4,8</sup> and  $\text{B}_2\text{H}_6$  itself,<sup>42</sup>  $\text{Ga}(\text{BH}_4)\text{Me}_2$  reacts with an excess of ammonia to form a white solid adduct  $\text{Ga}(\text{BH}_4)\text{Me}_2 \cdot 2\text{NH}_3$  in which the tetrahydroborate group has effectively been displaced from the co-ordination sphere of the gallium as the anion  $[\text{BH}_4]^-$ . That the adduct may be formulated as  $[\text{GaMe}_2(\text{NH}_3)_2]^+[\text{BH}_4]^-$  is strongly supported by the presence in the i.r. spectrum of prominent bands associated with the  $[\text{BH}_4]^-$  anion (at 2 255 and 1 097  $\text{cm}^{-1}$ ),<sup>1</sup> with the  $[\text{GaMe}_2]^+$  moiety,<sup>27</sup> and with co-ordinated ammonia.<sup>43</sup> Unlike the parent compound, the adduct appears to be stable indefinitely at room temperature. A second noteworthy property of the adduct is its ready sublimation *in vacuo* at room temperature. An experiment in which the vapour species were trapped in a solid argon matrix held at 12 K indicated that sublimation occurs *via* dissociation (7).



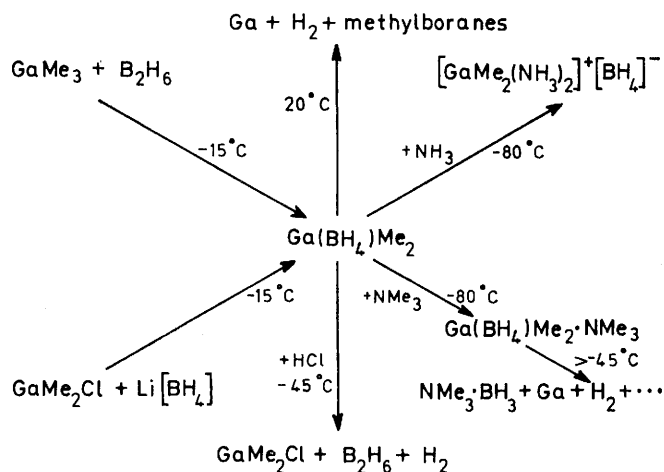
(c) *Reaction with trimethylamine.* Attempts to isolate an adduct of  $\text{Ga}(\text{BH}_4)\text{Me}_2$  with trimethylamine stable at room temperature were unsuccessful; at *ca.*  $-80^\circ\text{C}$  the reagents appear to afford a white crystalline solid which decomposes at temperatures much above  $-45^\circ\text{C}$  to give *inter alia* trimethylamine-borane, gallium metal, and hydrogen. When interaction of the reagents occurs on a CsI window held at  $-80^\circ\text{C}$  the i.r. spectrum of the mixture (cooled to  $-196^\circ\text{C}$ ) suggests the formation of a simple molecular adduct [presumably  $\text{Ga}(\text{BH}_4)\text{Me}_2 \cdot \text{NMe}_3$ ]. The spectrum appears to imply, moreover, that the  $\text{Ga}(\text{BH}_4)\text{Me}_2$  retains its molecular structure in the adduct; there is, for example, no evidence suggesting a change in the mode of co-ordination of the tetrahydroborate group with adduct formation.

The thermal instability of the gallium compound  $\text{Ga}(\text{BH}_4)\text{Me}_2 \cdot \text{NMe}_3$  is in notable contrast to that of its aluminium analogue  $\text{Al}(\text{BH}_4)\text{Me}_2 \cdot \text{NMe}_3$  which is said to be stable at room temperature.<sup>7</sup> Whether the difference arises from kinetic or thermodynamic factors, *e.g.* the more pronounced class 'a' character<sup>44</sup> or larger Drago-Wayland parameters (both  $\chi_A$  and  $E_A$ )<sup>45</sup> associated with aluminium as an acceptor centre, there is insufficient evidence to judge.

(d) *Reaction with hydrogen chloride.* The products of the reaction between equimolar quantities of  $\text{Ga}(\text{BH}_4)\text{Me}_2$  and hydrogen chloride at  $-45^\circ\text{C}$  are  $\text{GaMe}_2\text{Cl}$ , hydrogen, and diborane [equation (4)]. The failure to detect the

formation of any methane leaves no doubt that the  $\text{BH}_4$  is attacked in preference to the  $\text{GaMe}_2$  moiety, illustrating yet again the unusual inertness of the latter with respect to protonic reagents.

*Conclusions.*—Our experiments have verified one route and established a new and more efficient alternative route to the hitherto rather poorly characterized compound  $\text{Ga}(\text{BH}_4)\text{Me}_2$ . The vibrational spectra and other physical properties of the compound point to the persistence of the molecule  $\text{Me}_2\text{Ga}(\mu\text{-H})_2\text{BH}_2$ , belonging to the  $C_{2v}$  symmetry group, throughout the solid, liquid, and vapour phases, although there is a significant move towards a more ionic type of structure,  $[\text{GaMe}_2]^+[\text{BH}_4]^-$ , in the condensed phases. The compound is of limited thermal stability, being apparently susceptible to ready methyl-hydrogen exchange between the gallium and boron centres. With ammonia it emulates diborane in undergoing unsymmetrical cleavage of the  $\text{Ga}(\mu\text{-H})_2\text{BH}_2$  skeleton; by contrast, symmetrical cleavage of this skeleton is presumably involved when the molecular



SCHEME The formation, and some reactions, of  $\text{Ga}(\text{BH}_4)\text{Me}_2$

adduct  $\text{Ga}(\text{BH}_4)\text{Me}_2 \cdot \text{NMe}_3$  decomposes at temperatures above *ca.*  $-45^\circ\text{C}$  to give trimethylamine-borane as well as gallium metal and hydrogen. The  $\text{Ga}(\mu\text{-H})_2\text{B}$  fragment is significantly more susceptible to attack by protonic reagents like hydrogen chloride and water than is the  $\text{GaMe}_2$  part of the molecule.

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<sup>39</sup> M. T. Barlow, unpublished work.

<sup>40</sup> P. H. Bird and M. G. H. Wallbridge, *J. Chem. Soc. (A)*, 1967, 664.

<sup>41</sup> K. N. Semenenko, S. P. Shilkin, O. V. Kravchenko, and V. B. Polyakova, *Bull. Acad. Sci., U.S.S.R.*, 1974, **23**, 1379.

<sup>42</sup> See, for example, K. Wade, 'Electron Deficient Compounds,' Nelson, London, 1971, p. 74.

<sup>43</sup> K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' 2nd edn., Wiley-Interscience, New York, 1970, p. 150.

<sup>44</sup> S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

<sup>45</sup> R. S. Drago, *J. Chem. Educ.*, 1974, **51**, 300.