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

By Anthony J. Downs * and Patrick D. P. Thomas, Department of Inorganic Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QR

The synthesis, characterization, and properties of Ga(BH₄)Me₂ are reported. Although first prepared via the interaction of GaMe₃ and diborane, the compound is more satisfactorily prepared by the reaction of GaMe₃Cl with $Li[BH_4]$ in the absence of a solvent at -15 °C. Subsequent characterization has been based on the vapour-phase molecular weight, on the mass, vibrational, and ¹H n.m.r. spectra of the material, and on elemental analysis of the ammonia adduct Ga(BH₄)Me₂·2NH₃. The i.r. spectrum of the gaseous tetrahydroborate is consistent with a molecular model Me₂Ga(μ -H)₂BH₂ having C_{2v} symmetry and containing four-co-ordinate gallium linked to a bidentate tetrahydroborate group; such a structure appears to persist in the condensed phases, although the vibrational spectra suggest increased polarization in the sense $[GaMe_{a}]^{+}[BH_{a}]^{-}$. 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 Ga(µ-H)₂B 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 $[BH_4]^-$ 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;¹ reasons have also been advanced for thinking that the copper complex $[Cu(BH_4)(PMePh_2)_3]$ contains a single Cu-H-B bridge.² 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 $Be(BH_4)_2^3$ and $Al(BH_4)$ -Me₂.⁴ No less remarkable are the n.m.r. properties of molecular tetrahydroborates which imply a unique fluxional capacity of the BH₄ group;⁵ with but one or two exceptions,⁶ the bridging and terminal hydrogen atoms of the group appear to be magnetically equivalent.

Of the tetrahydroborates formed by the Group 3elements only the aluminium compound $Al(BH_4)_3$ is well characterized,¹ and little attention has been paid until recently either to derivatives of $Al(BH_4)_3$ or to analogues involving heavier Group 3 atoms. The balance has now been redressed to some extent, however, in studies of the methylaluminium tetrahydroborates $Al(BH_4)_{3-n}Me_n$ $(n = 1 \text{ or } 2)^7$ and of the novel hydridogallium compound Ga(BH₄)₂H whose preparation and characterization we recently notified.⁸ The only other tetrahydroborate of gallium for which there is reasonable evidence is dimethylgallium tetrahydroborate; this was alluded to by Schlesinger et al.⁹ in 1943, although their brief report sheds little light on the physical and chemical properties of the compound.

¹ 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. 2

J. C. Bommer and K. W. Morse, J.C.S. Chem. Comm., 1977, 137. 3

³ 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.

A. J. Downs and P. D. P. Thomas, unpublished work

⁵ H. Beall and C. H. Bushweller, Chem. Rev., 1973, 73, 465 and refs. therein.

As part of our investigations of 'mixed' hydrides formed by the Group 3 elements, we have confirmed that $Ga(BH_4)Me_2$ 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 highvacuum 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 % 2H) was used without purification. Trimethylgallium was prepared by the method described by Coates 10 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.¹¹ Fractional distillation of each of these reagents gave a sample judged to be pure by the criteria of tensimetric and i.r. measurements. [2H8]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

⁶ 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. ⁷ P. R. Oddy and M. G. H. Wallbridge, *J.C.S. Dalton*, 1976,

869.

A. J. Downs and P. D. P. Thomas, J.C.S. Chem. Comm., 1976,

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

¹⁰ G. E. Coates, J. Chem. Soc., 1951, 2003.

¹¹ 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.¹² 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(BH₄)Me₂ 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-CO₂. Hydrogen-1 n.m.r. spectra were recorded for ca. 1 mol dm⁻³ solutions of Ga(BH₄)Me₂ in $C_6D_5CD_3$ 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

$$GaMe_3 + B_2H_6 \longrightarrow Ga(BH_4)Me_2 + \frac{1}{2}(BMeH_2)_2$$
 (1)

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(BH₄)Me₂ requires 114.6]. The i.r. spectrum of the material volatile at -45 °C confirmed the presence of methylboranes ¹³ as well as unchanged diborane.

(b) From dimethylgallium chloride and lithium tetrahydroborate. Dimethylgallium chloride was prepared in situ by the interaction in the appropriate stoicheiometric proportions of GaMe₃ and gallium(III) chloride, the reaction being taken to completion by increasing the temperature of the mixture to ca. 45 °C. To GaMe₂Cl (1.4 g, 1 mmol) was added an excess (1.0 g) of powdered lithium tetrahydroborate (4.6 mmol) or [${}^{2}H_{4}$]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 [${}^{2}H_{4}$]-

J.C.S. Dalton

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

$$GaMe_{2}Cl + Li[BH_{4}] \longrightarrow Ga(BH_{4})Me_{2} + LiCl \qquad (2)$$

(iv) Chemical Properties of Dimethylgallium Tetrahydroborate.—(a) Thermal decomposition. A known amount of $Ga(BH_4)Me_2$ 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 $Ga(BH_4)Me_2$ gave 0.63 mmol of H_2 , 0.37 mmol of BMe₃ and other methylated boranes,¹³ 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(BH₄)Me₂·2NH₃ thus implied was substantiated by elemental analysis (Found: C, 16.4; H, 10.95; B, 7.10; Ga, 46.4; N, 18.65. Ga(BH₄)Me₂·2NH₃ requires C, 16.15; H, 10.85; B, 7.25; Ga, 46.9; N, 18.85%). (c) Reaction with trimethylamine. With trimethylamine,

 $Ga(BH_4)Me_2$ formed a white crystalline solid at -80 °C; tensimetric measurements implied the formation of an adduct Ga(BH₄)Me₂·NMe₃, but this decomposed at temperatures much above -45 °C to give inter alia hydrogen, trimethylamine-borane (identified by its i.r. spectrum 14), 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⁻¹) were observed to develop in the range 250-4000 cm⁻¹ (s = strong, m = medium, w = weak, v = very, sh = shoulder, and br = broad): Ga(BH₄)Me₂·NMe₃: 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(BD₄)Me₂·NMe₃: 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, GaMe₂Cl,¹⁵ 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 \approx 13.6 \times 9.8 Pa.

¹² A. J. Downs and G. P. Gaskill, unpublished work.

¹³ 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.

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

¹⁵ 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).

 $Ga(BH_4)Me_2 + HCl \longrightarrow GaMe_2Cl + H_2 + \frac{1}{2}B_2H_6$ (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.*,⁹ 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 (≥ 500 mg) of the tetrahydroborate, but it is easily thwarted by the presence of any unchanged GaMe₃ 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),¹⁶ zirconium tetrakis(tetrahydroborate),¹⁷ and hydridogallium bis(tetrahydroborate)⁸ by turning to the metathesis (2). The reaction has been found to proceed smoothly at *ca*. -15 °C in the absence of a solvent, thereby affording a relatively clean and efficient route to Ga(BH₄)Me₂ or its deuteriated derivatives.

(ii) Physical Properties of Dimethylgallium Tetrahydroborate.---In agreement with the findings of Schlesinger et al., $Ga(BH_4)Me_2$ emerges as a thermally fragile material melting at ca. 1 °C and having a vapour pressure at 0 °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(BH₄)Me₂ 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]⁺, [⁶⁹Ga(¹¹BH₄)Me]⁺, [⁷¹GaMe]⁺, [⁶⁹GaMe]⁺, ⁷¹Ga⁺, and ⁶⁹Ga⁺. 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 GaMe₃,¹⁸ although the higher melting point

17 W. E. Reid, jun., J. M. Bish, and A. Brenner J. Electrochem. Soc., 1957, 104, 21. ¹⁸ G. E. Coates and K. Wade, 'Organometallic Compounds,'

Methuen, London, 1967, vol. 1, p. 343. ¹⁹ E. M. Johnson, D.Phil. Thesis, University of Oxford, 1971.

²⁰ E. L. Åmma and R. E. Rundle, J. Amer. Chem. Soc., 1958,

80, 4141. ²¹ G. M. Sheldrick and W. S. Sheldrick, J. Chem. Soc. (A), 1970,

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

and lower vapour pressure of the tetrahydroborate are signs of more highly developed aggregation, possibly with a move towards the ionic formulation [GaMe₂]⁺- $[BH_4]^-$, at least in the solid state. By contrast, solid trimethylgallium is isomorphous 19 with trimethylindium and presumably consists of rather loosely constructed tetrameric units (GaMe₃)₄ analogous to those found in both trimethylindium ²⁰ and trimethylthallium.²¹

Hydrogen-1 n.m.r. spectrum. The ¹H n.m.r. spectrum of a solution of $Ga(BH_4)Me_2$ in $[{}^{2}H_8]$ toluene at room temperature comprises (i) a moderately sharp singlet centred on τ 9.9 and (*ii*) a relatively broad quartet centred on τ 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 ¹¹BH₄ group (¹¹B, $I = \frac{3}{2}$). 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 ${}^{4}/({}^{11}B-H)$ 89 Hz correspond closely with the values found for related compounds, e.g. GaMe₃²² and Al(BH₄)₃.^{5,7,23,24} No coupling between either set of protons and gallium (⁷¹Ga, $I = \frac{3}{2}$; ⁶⁹Ga, $I = \frac{3}{2}$ 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 °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.⁵ At room temperature all the protons of the BH₄ group are magnetically equivalent, implying rapid exchange between the terminal and bridging hydrogen atoms. The collapse of the ¹H-¹¹B multiplet can be understood in terms of a decoupling mechanism based on the diminution in spin-lattice relaxation time dictated by the correlation time τ_e characterizing the molecular tumbling responsible for quadrupole relaxation and by the relation $\tau_{\rm e} \propto \eta/T$, where η is the macroscopic viscosity of the solution and T the temperature.^{5,24} 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 °C.

Vibrational spectra. Details of the vibrational spectra of dimethylgallium tetrahydroborate and $[^{2}H_{4}]$ 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,^{3, 25, 26}

²⁵ D. A. Coe and J. W. Nibler, Spectrochim. Acta, 1973, A29,

1789.
²⁶ 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.

¹⁶ H. I. Schlesinger, H. C. Brown, and E. K. Hyde, J. Amer. Chem. Soc., 1953, 75, 209.

²³ 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. ²⁴ T. J. Marks and L. A. Shimp, J. Amer. Chem. Soc., 1972, 94,

^{1542.}

we have analysed the spectra in terms of the group vibrations appropriate to the molecule $Ga(BH_4)Me_2$ 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 $Ga(BH_4)Me_2$ and $Ga(BD_4)Me_2$ in which the

	Vibrat	ional spect	ra (cm ⁻¹) ^a o	f dimethylg	gallium tetr	ahydrobora	ate and $[^{2}H_{4}]$]tetrahydro	borate
Vapour, 2	290 K, I.r.	N ₂ matrix,	Liquid, 290	K, Raman	Solid, 20	K, Raman	Solid, 7	7 K, I.r.	
$Ga(BH_4)Me_2$	$Ga(BD_4)Me_2$	10 K, 1.r. Ga(BH ₄)Me ₂	Ga(BH ₄)Me ₂	$Ga(BD_4)Me_2$	$Ga(BH_4)Me_2$	Ga(BD ₄)Me ₂ 87w 107s	Ga(BH ₄)Me ₂	Ga(BD ₄)Me ₂	Assignment v38 (b2) TL
			161s,p?	156s,p?	125m 154s 172m 189m	126 (sh) 152s 162 (sh)			$ \begin{cases} \nu_{26} & (b_1) \\ \nu_{12} & (a_1) \\ \\ \nu_{18} & (a_2), \ \nu_{25} & (b_1) \end{cases} $
355w	270w	140e b	313w,dp 369mw,dp	230vw,dp 280m,dp	315m 367s	231m 280s	317mw 370mw	278mw	$\nu_{17} (a_2) \\ \nu_{35} (b_2)$
482w	1223, _	452m b	} 424s,p	386s,p 463w,p?	$410 \mathrm{m} (\mathrm{sh})$	355s 464w	393s	363s 459w	$v_{11}(a_1)$ $2v_{17}(A_1)$ $v_{17} + v_{10}(A_1)$ or $v_{17} + v_{17}$
553m,⊥	555m,⊥	555s	557vs,p	553vs,p	543w b 552vs b	<pre>543w (sh) b 553vs b</pre>	} 548m	551s	$ \begin{array}{c} \nu_{17} & \nu_{18} & \nu_{17} & \nu_{17} & \nu_{28} \\ \nu_{20} & \nu_{10} & (a_1) \end{array} $
616s,⊥	615s,⊥	616s b] 619s b	594w,p } 623m,dp	592w,p 619m,dp	590vw 610w 622m	} 619m	626s	626s	$\nu_{11} + \nu_{12} (A_1) \\ \nu_{34} (b_2)$
666w	668w	666vw	700vw p?	691vw dp	704w	699w	70000	700w br	$\nu_{10} + \nu_{20} (B_1)$
736m	738m	720w	760mm dp2	001 0 W ,up	728vw	761	726mw	722m 729w (sh)	$\left\{ \begin{array}{c} \nu_{9} (a_{1}) \\ \nu_{16} (a_{2}), \nu_{23} (b_{1}), \\ \mu_{16} (b_{2}), \nu_{23} (b_{1}), \end{array} \right.$
791s 965w	790s	786m	975mw,dp	745w,dp	970m b	} 740m b	777m 967m b	756s 776m	$\int \frac{\nu_{24}(b_1)}{(b_2)}, \nu_{33}(b_2)}{(b_2)}$
1 129s,⊥	852mw	1 122vs b 1 130m b	}1 123mw,p?	844vw	1 095w) 748w 0 828w) 975w 8 1 100s	830mw 834w (sh)	$\left\{ \nu_{8}\left(a_{1}\right) \right\}$
			1 140mw,dp?	812w,dp	1 146w	815m		903w 926mw	$\nu_{15} (a_2) \\ \nu_{34} + \nu_{35} (A_1) \\ \nu_{10} + \nu_{11} (A_1)$
				952w,vbr		957w 1 060w,br 1 099w 1 164w		1 050w	$ \begin{aligned} \nu_{17} + \nu_{24}(B_2) \\ \nu_9 + \nu_{11}(A_1) \\ 2\nu_{10}(A_1) \\ \nu_{24} + \nu_{24}(B_2) \end{aligned} $
1 222m,⊥	1 221m,⊥	1 218m	1 212s,p	1 210s,p	1 200s 1 205w 1 216w	}1 198s 1 213m	1 200w 1 213s	1 182w	$\nu_{10} + \nu_{34} (\omega_2)$ $\nu_{7} (a_1)$
			1 240 (sh)		1 245w	1 237w	1 216m 1 244m 1 265?vw	1 272w	$\frac{2\nu_{31}}{\nu_{10}} + \frac{2\nu_{24}}{\nu_{24}} (B_1)$
1 320m	1 295w 1 340m	1 302mw 1 314w		1 320vw	1 340vw	1 280?vw,br	1 292vw 1 341w 1 368mw	1 283w	$\nu_{10} + \nu_{33} (B_2) \\ \nu_9 + \nu_{34} (B_2) \\ \nu_7 + \nu_{28} (B_1), \nu_{16} + \nu_{34} \\ (B_1), \text{ or } \nu_{33} + \nu_{34} (A_1) \\ \nu_7 + \nu_{12} (A_1) \text{ or }$
1 405s 1 455s	997s 1 068s	1 400m 1 454m	1 420mw,p	1 031mw,p	1 400mw	1 014m	1 4 07s	1 016s	$\nu_{12} + \nu_{31} (B_2) \\ \nu_{6} (a_1) \\ \nu_{22} (b_1)$
		1 466m		1 435m,p	1 468?vw	1 393w,br	1 460w,br	1 391mw 1 459mw 1 467w (sh)	$\begin{cases} 2\nu_{9} (A_{1}) \\ \nu_{5} (a_{1}), \nu_{14} (a_{2}), \\ \nu_{21} (b_{1}), \nu_{30} (b_{2}) \end{cases}$
1775w			1 909w,p						$ \begin{array}{l} \nu_{10} + \nu_{21} \left(B_2 \right) \\ \nu_7 + \nu_8 \left(A_1 \right) \end{array} $
1 922s	1 414s	1 958w c 1 967w c 1 982w c	} 2 030m,p	1 501m,p	2 060w	1 459mw	2 035mw	1 479w 1 491w	$\Big\} v_4 (a_1)$
1 980vs	1 472m	2 012s	1 982w,p		2 091mw 2 130m (sh)	}1 524s	2 108s	1 530s 1 542m (sh) d	$ \begin{cases} \nu_6 + \nu_{10} (A_1) \\ \nu_{20} (b_1) \end{cases} $
2 089m 2 248w	1 585w,br 1 680w,br				2 200vw	1 578w,br 1 653w	2 198w	1 560mw d 1 580mw 1 649w	
2 470vs,⊥	1 807vs,⊥	2 447s b	la 4980 m	1 7805 5	9 2860	1 755s	2 290w	1 629w 1 758vs	$\begin{cases} 2\nu_{15} (A_1) \\ \dots (A_n) \end{cases}$
2 540vs,⊥	1 913vs,⊥	2 453 (sh b) 2 515s b	{" ##05,p	1 000 J-	2 450m	1 801w	∫ ² 400∨S	1 795mw	$\int_{a}^{b} \frac{1}{2} $
0.657	1 856w 1 950 (sh),br	2 527mw b	}2 490m,up	r 995m'ab	2 462 (sh)	}1 861m	2 45375	1 859m 1 825w	$\nu_{29} (O_2) \\ \nu_6 + \nu_8 (A_1) \\ \nu_7 + \nu_{24} (B_1) \\ (B_1) \\ (B_2) \\ (B_2) $
2 001W							0.545		$(B_1), \text{ or } \nu_{30} + \nu_{31} (A_1)$
2 850w 2 924mw 2 977mw	2 860vw 2 922mw 2 978mw	2 855w 2 915mw 2 980mw	2 921s,p 2 985m,dp	2 917s,p 2 980m,dp	2 921s 2 989m	2 920s 2 992m	2 765vw 2 920w 2 985mw	2 848vw 2 920w 2 992m	$\begin{array}{c} \nu_{3} + \nu_{35} \left(B_{2} \right) \\ 2\nu_{5}, 2\nu_{14}, 2\nu_{21}, \text{ or } 2\nu_{30} \left(A_{1} \right) \\ \nu_{2} \left(a_{1} \right), \nu_{28} \left(b_{2} \right) \\ \nu_{1} \left(a_{1} \right), \nu_{13} \left(a_{2} \right), \end{array}$
3 027w (sh)									$\nu_{19} (o_1), \nu_{27} (o_2) \\ \nu_3 + \nu_{10} (A_1)$

TABLE 1

a Assignments refer to a Ga(BH₄)Me₂ or Ga(BD₄)Me₂ molecule with C_{20} 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. b Distinct isotopic feature. c Matrix-splitting effects. c May be due to traces of Ga(BD₃H)Me₂.

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.⁴ 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

813

1978

beggar any simple description are the three involving rocking of the terminal BH₂ fragment, bending of the $Ga(\mu-H)_2B$ bridge and antisymmetric in-plane bending of the GaC_2B 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 $Ga(BH_4)Me_2$ and $Ga(BD_4)Me_2$ belonging to a given symmetry class; (e) the appearance of distinct features arising from the different naturally occurring isotopes ${}^{10}B/{}^{11}B$, ${}^{12}C/{}^{13}C$, and ${}^{69}Ga/{}^{71}Ga$; (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 $[{}^{2}H_{4}]$ tetrahydroborate

			Band a (cm ⁻¹)					
Symmetry			Solid		Vapour		$\nu_{\rm H}/\nu_{\rm D}$	
activity	Number	Approximate description	Ga(BH ₄)Me,	$Ga(BD_4)Me_2$	Ga(BH ₄)Me,	$Ga(BD_4)Me_2$	Solid	Vapour
7. Raman	ν.	antisym CH str	2 989	2 992	2 977	2 978	0.999	1.000
i r	×1 V-	sym CH str	$\frac{1}{2}$ 921	2 920	2 924	$\frac{1}{2}$ 922	1.000	1.001
1.1.	₽ <u>2</u> Ve	sym BH, str	2 386	1 755	2 470	1 807	1.360	1.367
	×3 V.	sym BH_{h} str	2 035 *	1 485 *	1 922	1 414	1.370	1.359
	× 4 V-	antisym CH ₂ def	1 460 *	1 459 *	2 0		1.001	2.000
	Ve	sym GaH _b str.	1 400	1 014	$1 \ 405$	997	1.381	1.409
	ν- ν-	sym CH ₂ def.	1 200	1 1 9 8			1.002	
	v	BH _t def.	1 095	828	$1\ 129$	852	1.322	1.325
	vo	CH ₂ rock	704	699	ca. 700	ca. 700	1.007	
	V 10	svm GaC str.	552	553	553	555	0.998	0.996
	V 10	GaB str.	395	355	445	422	1.113	1.055
	ν_{12}	sym GaC ₂ def.	154	152			1.013	
i_2 Raman	ν_{13}	antisym CH str.	2 989	2 992			0.999	
	ν_{14}	DU twict	1 4001 470	1 400-1 470 915			1 406	
	ν_{15}	CH rook	700 800	700 800			1.400	
	ν_{16}	bridge twist	215	200 <u></u>			1 364	
	ν_{17}	CH torsion	515 ca 170	a^{231}			1.504	
	ν_{18}		<i>cu</i> . 170	<i>cu</i> . 170				
b. Raman	V10	antisym CH str.	2989	2992	$2 \ 977$	2978	0.999	1.000
i.r.	V 20	antisym BH _b str.	2 091	1524	1 980	$1 \ 472$	1.372	1.345
	20 Va1	antisym CH, def.	1 460 *	1 459 *			1.001	
	21 V 99	antisym GaH _b str.	1 407 *	1 016 *	$1 \ 455$	1.068	1.385	1.362
	22 V93	BH_t wag	ca. 730 ^b	ca. 550 ^b			1.327	
	V2.1	CH ₃ rock	700 - 800	700 - 800	700 - 800	700 - 800		
	V25	CH ₃ torsion	ca. 170	ca. 170				
	ν_{26}	out-of-plane GaC ₂ B def.	125	126			0.992	
b ₂ Raman,	ν_{27}	antisym CH str.	2989	2 992	2 977	2 978	0.999	1.000
i.r.	ν_{28}	sym CH str.	2 921	2920	2924	2922	1.000	1.001
	ν_{29}	antisym BH_t str.	$2 \ 450$	1843	2540	1 913	1.329	1.328
	ν_{30}	antisym CH ₃ def.	1 460 *	1 459 *			1.001	
	ν_{31}	sym CH ₃ def.	$1\ 216$	$1\ 213$	1 222	1 221	1.002	1.001
	ν_{32}	BH _t rock ^e	970	740	965	<i>b</i>	1.311	
	ν_{33}	CH ₃ rock	700 - 800	700-800	700-800	700-800		
	ν_{34}	antisym GaC str.	622	619	616	615	1.005	1.002
	ν_{35}	bridge bend ^e	367	280	355	270	1.311	1.315
	ν_{36}	antisym in-plane GaC ₂ B def. ^c	(ca. 98)	87			1.126	

^a 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. ^b Probably obscured by more intense features. ^c There is pronounced coupling between the b_2 internal co-ordinates defining the following motions: BH_t rocking, bridge-bending, and antisymmetric in-plane GaC₂B 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 GaMe2 27 or a co-ordinated BH4 group; 3, 4, 25, 26, 28, 29 (b) the selection rules expected to govern the activity in i.r. absorption or Raman scattering of the vibrational modes associated with the Ga- $(BH_{4})Me_{2}$ molecule; (c) the polarization properties of the Raman scattering exhibited by the liquid tetrahydroborate; (d) the effect of deuteriation at the 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 Ga(BH₄)Me₂ 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 Ga(µ-H)2BH2

²⁷ R. S. Tobias, M. J. Sprague, and G. E. Glass, Inorg. Chem. 1968, 7, 1714.

²⁸ T. J. Marks, W. J. Kennelly, J. R. Kolb, and L. A. Shimp, Inorg. Chem., 1972, 11, 2540. ²⁹ W. L. Smith and I. M. Mills, J. Chem. Phys., 1964, 41, 1479.

J.C.S. Dalton

moiety. Not only are the spectral features characteristic of a non-linear $GaMe_2$ group readily apparent,²⁷ 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 N_2 matrix at 10 K $[N_2:Ga(BH_4)Me_2 = ca. 500:1]$; (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.^{1,25,26,28,29} The molecular model is illustrated in Figure 2 which also suggests approximate dimensions based on the preliminary results of electron diffraction of the vapour ³⁰ and on the structures of the related molecules $GaMe_3$,³¹ Al(BH₄)Me₂,³⁰ and $Ga(BH_4)_2H$,³⁰ also determined by electron diffraction. Hence the principal moments of inertia of the molecules $Ga(BH_4)Me_2$ and $Ga(BD_4)Me_2$ 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 C₂GaB plane containing the axes of $I_{\rm A}$ and $I_{\rm B}$, and perpendicular to the axis of $I_{\rm C}$, where $I_{\rm A} \lesssim I_{\rm B} < I_{\rm C}$. The 36 vibrational modes are

TABLE 3

Moments of inertia, envelopes of vapour-phase i.r. absorptions, and product-rule calculations for the molecules Ga(BH₄)Me₂ and Ga(BD₄)Me₂

Molecular property	$Ga(BH_4)Me_2$	$Ga(BD_4)Me_2$
Molecular mass/a.m.u. *	114.631	118.656
I _A /a.m.u. Å ² *	90.30	94.66
$I_{\rm B}/{\rm a.m.u.}$ Å ² *	101.99	123.19
$I_{\rm C}/{\rm a.m.u.}$ Å ² *	187.73	208.74

Envelopes of vapour-phase i.r. absorptions

Symmetry	Property	of
Oymmoor y	rachered	<u> </u>

class	envelope	calc.	obs.	calc.	obs.
a_1	${ Band type a \ \Delta \nu_{PR}/cm^{-1} }$	16.7	$\frac{1}{16}$	15.7	$\stackrel{\perp}{15}$
b_1	$\begin{cases} \text{Band type }^a \\ \Delta \nu_{PR}/\text{cm}^{-1} \end{cases}$	$\parallel 25.1$		23.6	
b_2	${ Band type a \ \Delta \nu_{PR}/cm^{-1} }$	16.8	$\frac{\perp}{16}$	15.8	$\stackrel{\perp}{15}$

Product-rule calculations

	Product-rule factor, $b \frac{\nu_{i,\mathbf{H}} \cdot \nu_{j,\mathbf{H}}}{\nu_{i,\mathbf{D}} \cdot \nu_{j,\mathbf{D}}}$		
Symmetry class	calc.	obs.	
a_1	3.9249	3.862	
a,	1.9518	1.916	
b_1	2.5263	2.501	
b_2	2.6331	2.590	

* 1 a.m.u. = 1.6605×10^{-27} kg.

^a Designated on the assumption that each molecule approximates to an oblate symmetric top. ^b 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 $Ga(BH_4)Me_2$ showing the axes of the principal moments of inertia. The bond lengths are in Å (ref. 30). The $Ga \cdots B$ separation is 2.152 Å

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

³¹ B. Beagley, D. G. Schmidling, and I. A. Steer, J. Mol. Structure, 1974, 21, 437.

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

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 Qbranch, 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 ³² 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 [²H₄]tetrahydroborate are unlikely under such conditions to provide a means of classification beyond differentiating between b_1 modes, with their pseudoparallel-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 lowfrequency 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 cm⁻¹, all with perpendicular-type contours, in the spectrum of $Ga(BH_4)Me_2$ do show clear signs of partially resolved rotational structure.

Comparison of the vibrational spectra of solid, liquid, gaseous, and matrix-isolated dimethylgallium tetrahydroborate and $[{}^{2}H_{4}]$ 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 GaMe₂ and BH₄ units in a move towards the ionic formulation $[GaMe_2]^+[BH_4]^-$. Thus, relative to the spectrum of the vapour, the frequency separation of those bands attributable to $B-H_t$ and $B-H_b$ stretching motions (t = terminal, b = bridging) is reduced from ca. 550 to little more than 300 cm^{-1} , and there is a concomitant decrease in the frequencies of both the Ga-H_b and Ga-B stretching modes. The enhanced intensity of the absorption associated with the antisymmetric Ga-C stretching mode relative to that associated with the corresponding symmetric mode $[I_{antisym}/I_{sym} 1.35$ for the vapour and 2.85 for solid $Ga(BH_4)Me_2$ at 77 K] also implies an opening out of the H₃C-Ga-CH₃ angle. On the other hand, it appears that the degree of ionic character is not nearly so pronounced as in solid beryllium

bis(tetrahydroborate),³ methylzinc tetrahydroborate,³³ or dimethylaluminium tetrahydroborate.⁴ 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 $Ga(BH_4)$ -Me₂ than for solid Zn(BH₄)Me. The intensity of the 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 $Ga(BH_4)Me_2$, as for $Hf(BH_4)_4$,³⁴ a sizeable mean polarizability derivative $\bar{\alpha}'(M-B)$ suggestive of appreciable M-B bonding (M = Ga or 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 $v_1 - v_{12}$, assignment of some of the a_2 fundamentals is less obvious. For the BH_t twisting mode v_{15} we favour a frequency at $1 \, 146 \, \mathrm{cm}^{-1}$ for the $\mathrm{Ga}(\mathrm{BH}_4)\mathrm{Me}_2$ 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[‡] on deuteriation of the tetrahydroborate group; the frequency associated with this type of motion in related tetrahydroborates 3,4,25,26,28,29 lends support to such an assignment. On the other hand, the bridge-twisting mode v_{17} is more difficult to identify. There is no obvious candidate for this fundamental in the region suggested by Coe and Nibler²⁵ for the corresponding vibration in $Al(BH_4)_3 [Al(BD_4)_3] [i.e. 1 146 (813 cm^{-1})].$ Some reservations must be held, however, about an assignment which imputes to $\mathrm{Al}(\mathrm{BH}_4)_3$ $[\mathrm{Al}(\mathrm{BD}_4)_3]$ a frequency markedly higher than that calculated for the corresponding mode of B₂H₆ (B₂D₆) [833 (592 cm⁻¹)].²⁹ We prefer to attribute the Raman scattering at 315 (231 cm⁻¹) due to solid $Ga(BH_4)Me_2$ [Ga(BD₄)Me₂] to v_{17} ; a medium-toweak band at 317 cm⁻¹ in the i.r. spectrum of solid $Ga(BH_4)Me_2$ may then be due to the overtone $2\nu_{12}(A_1)$ or it may represent v_{17} made active in i.r. absorption by the effects of either relatively unsymmetrical siting of individual Ga(BH₄)Me₂ molecules or of intermolecular correlation within the unit cell of the solid compound. The assignments of both v_{15} and v_{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.^{33,35} There is still less to aid our search for the two CH₃ torsional modes $v_{18}(a_2)$ and $v_{25}(b_1)$, but the assignments of Tables 1 and 2 are not radically different

 ³² W. A. Seth Paul and G. Dijkstra, Spectrochim. Acta, 1967,
 A23, 2861; W. A. Seth Paul, J. Mol. Structure, 1969, 3, 403.
 ³³ J. W. Nibler and T. H. Cook, J. Chem. Phys., 1973, 58, 1596.

³⁴ 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.

³⁵ D. M. Adams and R. G. Churchill, J. Chem. Soc. (A), 1970, 697.

from those of related molecules, e.g. SeMe₂³⁶ and AsX_{3-n}- Me_n (X = halogen),³⁷ and are in keeping with the finding that the frequencies vary but little with deuteriation of the tetrahydroborate group. We believe that the b_1 B-H_t wagging mode v_{23} is obscured by more intense features, viz. those due to CH_3 rocking fundamentals in $Ga(BH_4)Me_2$ and to the Ga-C stretching fundamentals in $Ga(BD_4)Me_2$; the approximate frequencies we have assigned in the Tables are upheld by the observation that the intensity quotient $I_{antisym}/I_{sym}$ of the i.r. bands attributed to the antisymmetric and symmetric Ga-C stretching vibrations appears to decrease when BH₄ gives place to BD_4 , suggesting that the band due to the symmetric Ga-C stretching vibration of Ga(BD₄)Me₂ masks the development of an additional feature. With the b_2 vibrations v_{32} and v_{35} we associate respectively the bands near 970 (740) and 370 (280 cm⁻¹) in the i.r. and Raman spectra of $Ga(BH_4)Me_2$ [$Ga(BD_4)Me_2$]. Rocking of the terminal BH₂ unit is an important component of v_{32} , and the frequencies we favour are in the vicinity of those reported for this kind of motion in B_2H_6 (B_2D_6) $[915 (725 \text{ cm}^{-1})]^{29}$ and $Al(BH_4)_3 [Al(BD_4)_3] [967 (735)]^{-1}$ cm⁻¹)].²⁵ Bending of the $Ga(\mu-H)_2B$ bridge plays an important part in ν_{35} and again it is reassuring to discover that the frequencies proposed are similar to those reported for the bridge-bending fundamentals of B_2H_6 (B_2D_6) [368 (262 cm⁻¹)]²⁹ and Al(BH₄)₃ [Al(BD₄)₃] $[255 (194 \text{ cm}^{-1})]^{.25}$ In both cases, however, the degree of mixing between the internal co-ordinates associated with the b_2 modes v_{32} , v_{35} , and v_{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 GaC₂B skeleton, *i.e.* $v_{26}(b_1)$ and $v_{36}(b_2)$, 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 $P_{\text{calc.}} \ge P_{\text{obs.}}$ 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.* $Ga(BD_3H)Me_2$ contaminating the sample of $Ga(BD_4)Me_2$; otherwise all the features still unaccounted for, which are almost all of low intensity, can be satisfactorily interpreted as overtones or combinations of the

J. R. Durig, C. M. Player, jun., J. Bragin, and Y. S. Li, J. Chem. Phys., 1971, 55, 2895.
 ³⁷ H. F. Shurvell, M. R. Gold, and A. R. Norris, Canad. J.

J.C.S. Dalton

fundamentals associated with the molecules $Ga(BH_4)Me_2$ or $Ga(BD_4)Me_2$ (see Table 1).

(iii) Chemical Properties of Dimethylgallium Tetrahydroborate.—(a) Thermal decomposition. Our experiments showed that gaseous $Ga(BH_4)Me_2$ 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 GaMe₃. 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 $Ga(BH_4)_2H$ decomposes by a dissociative route ^{4,8} and that unco-ordinated gallium hydride decomposes rapidly into gallium and hydrogen at ambient temperatures,³⁸ it is not unreasonable to suppose that an intermediate such as (I) decomposes in a similar manner:



It may be remarked that $Ga(BH_4)Me_2$ is thermally much less stable than its aluminium analogue $Al(BH_4)$ - Me_2 .^{4,7} If the mechanism we have suggested is correct, this finding may be rationalized in terms of the superior thermal stability of the unit $H_2Al(\mu-H)_2$ compared with $H_2Ga(\mu-H)_2$. The mechanism also invites speculation about the stability of related tetrahydroborate derivatives of gallium, and it is perhaps significant that the ease of

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

³⁸ 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 $Ga(BH_4)Me_2 < Ga(BH_4)(Me)H^{39} < Ga(BH_4)_2H^4$

(b) Ammonolysis: the displacement of the $[BH_4]^$ anion. In common with other molecular tetrahydroborates such as $Al(BH_4)_3$,^{40,41} $Ga(BH_4)_2H$,^{4,8} and B_2H_6 itself,⁴² Ga(BH₄)Me₂ reacts with an excess of ammonia to form a white solid adduct Ga(BH₄)Me₂·2NH₃ in which the tetrahydroborate group has effectively been displaced from the co-ordination sphere of the gallium as the anion $[BH_4]^-$. That the adduct may be formulated as $[GaMe_2(NH_3)_2]^+[BH_4]^-$ is strongly supported by the presence in the i.r. spectrum of prominent bands associated with the $[BH_4]^-$ anion (at 2 255 and 1 097 cm⁻¹),¹ with the $[GaMe_2]^+$ moiety,²⁷ and with co-ordinated ammonia.43 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).

$$[GaMe_2(NH_3)_2]^+[BH_4]^- \rightleftharpoons Ga(BH_4)Me_2 + 2NH_3 \quad (7)$$

(c) Reaction with trimethylamine. Attempts to isolate an adduct of $Ga(BH_4)Me_2$ with trimethylamine stable at room temperature were unsuccessful; at ca. -80 °C the reagents appear to afford a white crystalline solid which decomposes at temperatures much above -45 °C to give inter alia trimethylamine-borane, gallium metal, and hydrogen. When interaction of the reagents occurs on a CsI window held at -80 °C the i.r. spectrum of the mixture (cooled to -196 °C) suggests the formation of a simple molecular adduct [presumably Ga(BH₄)Me₂. NMe_a]. The spectrum appears to imply, moreover, that the $Ga(BH_4)Me_2$ 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 $Ga(BH_4)Me_2 \cdot NMe_3$ is in notable contrast to that of its aluminium analogue Al(BH₄)Me₂·NMe₃ which is said to be stable at room temperature.⁷ Whether the difference arises from kinetic or thermodynamic factors, e.g. the more pronounced class ' a ' character 44 or larger Drago-Wayland parameters (both C_{Λ} and E_{Λ})⁴⁵ 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 $Ga(BH_4)Me_2$ and hydrogen chloride at -45 °C are GaMe₂Cl, hydrogen, and diborane [equation (4)]. The failure to detect the

 M. T. Barlow, unpublished work.
 P. H. Bird and M. G. H. Wallbridge, J. Chem. Soc. (A), 1967, 664.

formation of any methane leaves no doubt that the BH_4 is attacked in preference to the GaMe₂ 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 $Ga(BH_4)Me_2$. The vibrational spectra and other physical properties of the compound point to the persistence of the molecule $Me_2Ga(\mu-H)_2BH_2$, 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, [GaMe₂]⁺[BH₄]⁻, in the condensed phases. The compound is of limited thermal stability, being apparently susceptible to ready methylhydrogen exchange between the gallium and boron centres. With ammonia it emulates diborane in undergoing unsymmetrical cleavage of the $Ga(\mu-H)_2BH_2$ skeleton; by contrast, symmetrical cleavage of this skeleton is presumably involved when the molecular



SCHEME The formation, and some reactions, of Ga(BH₄)Me₂

adduct Ga(BH₄)Me₂·NMe₃ decomposes at temperatures above ca. -45 °C to give trimethylamine-borane as well as gallium metal and hydrogen. The Ga(µ-H)₂B fragment is significantly more susceptible to attack by protonic reagents like hydrogen chloride and water than is the GaMe, part of the molecule.

We thank the S.R.C. for a research grant enabling the purchase of the Raman spectrometer and for the award of a studentship (to P. D. P. T.), Jesus College, Oxford, for the award of a Graduate Scholarship (also to P. D. P. T.), and Drs. D. W. H. Rankin and K. R. Seddon for their help in measuring the mass spectra.

[7/1891 Received, 28th October, 1977]

⁴³ K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' 2nd edn., Wiley-Interscience, New York,

1970, p. 150. ⁴⁴ S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

⁴⁵ R. S. Drago, J. Chem. Educ., 1974, 51, 300.

K. N. Scmenenko, S. P. Shilkin, O. V. Kravchenko, and V. B. Polyakova, *Bull. Acad. Sci.*, U.S.S.R., 1974, 23, 1379.
 ⁴² See, for example, K. Wade, ' Electron Deficient Compounds,' Nuclear Review 1971.

Nelson, London, 1971, p. 74.