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Structural characterisation of dimethylgallium tetrahydroborate and its adducts with diethyl ether and tetrahydrofuran

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The structures of dimethylgallium tetrahydroborate and its 1 : 1 adducts with diethyl ether and tetrahydrofuran have been investigated by single crystal X-ray diffraction at low temperatures. The structure of dimethylgallium tetrahydroborate has been shown to consist of discrete $GaMe_2(BH_4)$ units in which each BH_4 group exhibits bidentate ligation to a single Me_2Ga unit, but in which there are long-range interactions between the Ga and the terminal hydrogen atom of a BH_4 group in each of two neighbouring molecules. The structures of the adducts show that they are composed of molecules in which the Ga is 5-coordinate and asymmetrically bound to a bidentate BH_4 unit. The adducts display enhanced thermal stability compared to that of uncoordinated $GaMe_2(BH_4)$, but reversibly dissociate in the gas phase at ambient temperature. The infrared spectra of the compounds are discussed on the basis of their structures.

Introduction

Metal tetrahydroborates have attracted significant interest over the years for several reasons. They have been used as reagents and precursors in the preparation of metals,[1] metal hydrides,[2] borides,[3] or alkyls.[4] Covalent derivatives often have significant volatility and so have been used in chemical vapour deposition processes to produce metal-containing thin films.[5] Structural studies of metal tetrahydroborates have shown that the BH_4 groups can coordinate to a metal centre through one, two, or three bridging hydrogen atoms and that the energy differences between these modes of ligation are often small.[6] The tetrahydroborate group may also coordinate to more than one metal centre as in the case of $GaH_2(BH_4)$,[7] $Be(BH_4)_2$,[8] and $ZnMeBH_4$.[9] Furthermore, recent crystallographic studies of some tetrahydroborate derivatives of aluminium compounds [*viz.* $AlMe_2(BH_4)$] have shown that striking changes in structure can occur on moving from the gas phase to the solid.[10] Thus in the gas phase dimethylaluminium tetrahydroborate is a molecular species in which the tetrahydroborate group adopts bidentate coordination to one metal,[11] but in the solid phase the structure is one of helical polymeric chains in which Me_2Al and BH_4 units alternate such that the BH_4 groups adopt bidentate coordination to each of the adjacent metal atoms.[10] By contrast, for aluminium tris(tetrahydroborate) the differences between structures in the gas and solid phases are not so great: both feature discrete $Al(BH_4)_3$ units in which the BH_4 units are bidentate and the aluminium adopts trigonal prismatic coordination.[10] The reason why $AlMe_2(BH_4)$ adopts a polymeric structure whilst $Al(BH_4)_3$ does not is presumably because the bidentate coordination of the BH_4 group allows the Al of $Al(BH_4)_3$ to maintain its 6-coordination. This tendency for aluminium to adopt 6-coordination is much more pronounced than for gallium, *cf.* solid state structures of $AlCl_3$ and $GaCl_3$,[12] and so this prompted us to discover what structure is adopted by dimethylgallium tetrahydroborate in the solid phase. Infrared spectroscopy and gas electron diffraction have shown that this compound exists in the gas phase as discrete $GaMe_2(BH_4)$ molecules in which the BH_4 group is bidentate, but infrared spectra of the solid at −196 °C suggested significant structural changes involving the BH_4 group.[13] Given the apparent ease with which the structures adopted by these compounds can be changed, we wished to investigate the effects on structure of cocrystallisation with a weak donor molecule. Earlier studies of the chemistry of dimethylgallium tetrahydroborate had focused on relatively strong donors such as Me_3N and NH_3. With Me_3N, infrared spectra at low temperatures suggested that an adduct was formed in which the $GaMe_2(BH_4)$ retained its molecular structure, but which decomposed on warming above −45 °C. With NH_3, displacement of the BH_4^- anion occurred to give a compound formulated as $[GaMe_2(NH_3)_2]^+[BH_4]^-$.[13]

Experimental

(i) Synthesis

Preparation of dimethylgallium tetrahydroborate and its adducts was achieved using a conventional high-vacuum line incorporating grease-less valves equipped with Teflon keys and ground-glass joints lubricated with Voltalef 90 grease. Diethyl ether and THF were purified by distillation from CaH_2 followed by storage over 4 Å molecular sieves that had previously been baked under vacuum at 200 °C. Lithium tetrahydroborate (Aldrich) was recrystallised from dry diethyl ether under dry nitrogen. Dimethylgallium chloride was prepared from the reaction between trimethylgallium (Fluorochem) and gallium(III) chloride (Aldrich).[14] Dimethylgallium tetrahydroborate, **1**, was prepared from the reaction between $[GaMe_2Cl]_2$ and $LiBH_4$ using the method of Downs and Thomas.[13] After fractionation through traps fitted with grease-less valves, a sample was obtained which was judged to be pure by reference to infrared spectra of both the solid and gas phases, and ^1H NMR spectra of solutions in [$^2H_8$]toluene (dried over activated 4 Å molecular sieves).[13] The diethyl ether adduct of dimethylgallium tetrahydroborate, **2**, was prepared by condensing $GaMe_2(BH_4)$ (0.25 g, 2.18 mmol) in an ampoule containing a 10-fold excess of Et_2O and allowing the mixture to warm to 20 °C over a period of 30 min. On fractionation through traps fitted with grease-less valves, the diethyl ether adduct collected as a colourless liquid in a a trap held at −30 °C. The THF adduct was prepared in a similar fashion, and on fractionation collected as a colourless liquid in a trap held at −20 °C. Based

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on the amount of dimethylgallium tetrahydroborate taken, both adducts were formed in quantitative yields with negligible signs of decomposition on fractionation. Infrared spectra of the compounds were recorded using a Perkin-Elmer Paragon FTIR spectrometer, as vapours contained in a 10 cm path length gas cell and as polycrystalline films deposited on a CsI window held at −196 °C. ^1H and ^{11}B NMR spectra were recorded for samples dissolved in [$^2H_8$]toluene at 24 °C using a Bruker AC200 spectrometer, mass spectra using a Hiden HAL/3F residual gas analyser equipped with an all-glass inlet system. NMR data: **1**, δ_H −0.24 (6H, s, 2 CH_3) and 1.28 [4H, quartet, $J(^{11}BH)$ 85 Hz; BH_4]; δ_B −15.2 [quintet, $J(^{11}BH)$ 85 Hz, BH_4]; **2**, δ_H −0.13 (6H, s, 2 CH_3), 1.20 [4H, quartet, $J(^{11}BH)$ 85, BH_4], 0.81 (6H, t, *J* 7, 2 CH_3), and 3.12 (4H, q, *J* 7, 2 CH_2); δ_B −22.7 [quintet, $J(^{11}BH)$ 85 Hz, BH_4]; **3**, δ_H −0.12 (6H, s, 2 CH_3), 1.02 [4H, quartet, $J(^{11}BH)$ 85, BH_4], 1.06 (4H, m, 2 CH_2), and 3.14 (4H, m, 2 CH_2); δ_B −27.8 [quintet, $J(^{11}BH)$ 85 Hz, BH_4].

(ii) Crystal growth

Since each of the compounds is a liquid at ambient temperatures, single crystals were grown by slow cooling of the samples in sealed capillaries mounted on the diffractometer.[15] Capillaries were secured with Araldite glue to a thermally insulating Tufnol pip which was then attached to a goniometer head and mounted in the cold stream of an Oxford Cryosystems low-temperature device attached to a Stoë Stadie-4 circle diffractometer.[16] A stable solid/liquid phase boundary was established within the sample and crystal growth effected by slow cooling at rates of approximately 5, 30, and 80 K h^{-1} for **1**, **2**, and **3**, respectively. Crystals of **1**, **2**, and **3** were grown at temperatures of 273, 227, and 248 K respectively.

(iii) Crystal data

All structures were solved by Patterson methods and refined against F^2 (SHELXTL).[17]

Dimethylgallium tetrahydroborate 1. $C_2H_{10}BGa$, $M = 114.63$, orthorhombic, space group $P2_12_12_1$, $a = 6.4050(8)$, $b = 7.4178(11)$, $c = 11.8428(13)$ Å, $U = 562.66(13)$ Å^3, $Z = 4$, $T = 220(2)$ K, μ(Mo-Kα) = 5.273 mm^{-1}, 2931 reflections measured, 529 unique ($R_{int} = 0.0601$), final $wR(F^2)$ was 0.0533, $R1 = 0.234$.

Dimethylgallium tetrahydroborate–diethyl ether 2. $C_6H_{20}BGaO$, $M = 188.75$, triclinic, space group $P\bar{1}$, $a = 7.4628(12)$, $b = 7.8998(13)$, $c = 10.539(2)$ Å, $\alpha = 87.926(9)$, $\beta = 77.525(10)$, $\gamma = 64.083(8)$°, $U = 544.4(2)$ Å^3, $Z = 2$, $T = 190(2)$ K, μ(Mo-Kα) = 2.469 mm^{-1}, 2026 reflections measured, 1924 unique ($R_{int} = 0.0344$), $wR(F^2)$ 0.0801, $R1 = 0.365$.

Dimethylgallium tetrahydroborate–tetrahydrofuran 3. $C_6H_{18}BGaO$, **3** $M = 186.73$, monoclinic, space group $P2_1/c$, $a = 11.5311(15)$, $b = 7.6473(13)$, $c = 12.552(2)$ Å, $\beta = 115.422(9)$°, $U = 999.73$ Å^3, $Z = 4$, $T = 190(2)$ K, μ(Mo-Kα) = 2.469 mm^{-1}, 3958 reflections measured, 1704 unique ($R_{int} = 0.0226$). $wR(F^2) = 0.06$; $R1 = 0.0238$.

CCDC reference number 186/2292.

See http://www.rsc.org/suppdata/dt/b0/b007026m/ for crystallographic files in .cif format.

Results and discussion

The crystal structure of dimethylgallium tetrahydroborate

The structure of $GaMe_2(BH_4)$ in the crystal is illustrated in Fig. 1. Bond distances and angles are listed in Table 1. By contrast to the structures of $GaH_2(BH_4)$ and $AlMe_2(BH_4)$, for which polymeric structures are adopted,[7,10] the results show that the solid is composed of discrete $GaMe_2(BH_4)$ molecules in which the BH_4 group is bidentate.

Table 1 Selected bond lengths (Å) and angles (°) for $GaMe_2(BH_4)$, $GaMe_2(BH_4)\cdot OEt_2$ and $GaMe_2(BH_4)\cdot THF$ at 220 K

	$GaMe_2(BH_4)$	$GaMe_2(BH_4)\cdot OEt_2$	$GaMe_2(BH_4)\cdot THF$
Ga(1)–C(1)	1.927(5)	1.950(4)	1.944(2)
Ga(1)–C(2)	1.923(5)	1.949(4)	1.946(2)
Ga(1) · · · B(1)	2.269(5)	2.346(5)	2.326(3)
Ga(1)–H(1)	1.91(5)	1.95(4)	1.82(3)
Ga(1)–H(2)	1.88(5)	1.67(3)	2.02(3)
B(1)–H(1)	1.12(5)	1.17(3)	1.15(3)
B(1)–H(2)	1.04(5)	1.17(3)	1.10(3)
B(1)–H(3)	1.10(5)	1.07(3)	1.10(3)
B(1)–H(4)	1.12(5)	1.07(3)	1.08(3)
Ga(1) · · · H(4)#1	2.74(5)	—	—
Ga(1) · · · H(3)#2	2.82(5)	—	—
Ga(1)–O	—	2.119(2)	2.109(2)
C(2)–Ga(1)–C(1)	137.4(2)	130.4(2)	130.12(12)
C(2)–Ga(1)–B(1)	111.1(2)	109.2(2)	105.21(12)
C(1)–Ga(1)–B(1)	111.6(2)	106.3(2)	112.00(12)
C(2)–Ga(1)–O	—	99.99(14)	98.90(9)
C(1)–Ga(1)–O	—	99.40(14)	98.34(9)
O–Ga(1)–B(1)	—	109.6(2)	109.99(10)
H(1)–Ga(1)–H(2)	56(2)	58(2)	57.2(12)
H(1)–B(1)–H(2)	112(3)	98(3)	110(2)

Symmetry operators: #1 $x -\frac{1}{2}, -y + \frac{3}{2}, -z$; #2 $-x + 2, y -\frac{1}{2}, -z + \frac{1}{2}$.

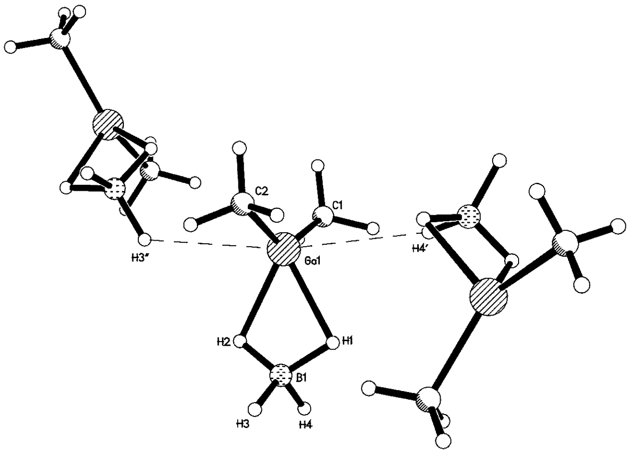

Fig. 1 Structure of solid dimethylgallium tetrahydroborate at 220 K as determined by X-ray diffraction.

It is also apparent, however, that the terminal hydrogen atom of a BH_4 group in each of two neighbouring molecules is interacting with the Ga. At 2.74(5) and 2.82(5) Å these distances are much longer than the primary bridging Ga–H bonds found in this molecule and in $GaH_2(BH_4)$, but are similar, however, to the secondary Ga · · · H contacts [at 2.41(6) Å] involving B–H bonds found in $GaH_2(BH_4)$.[7] Furthermore, the effect of these interactions on the primary bond lengths and angles of the $GaMe_2(BH_4)$ units is striking. Table 2 compares these parameters with those of the gas-phase structure and with those of $AlMe_2(BH_4)$ and $GaH_2(BH_4)$ in the solid and gas phases.

On going from the gas to the solid, the Ga · · · B distance in $GaMe_2(BH_4)$ increases from 2.163(8) to 2.269(5) Å. Similar increases are observed in $AlMe_2(BH_4)$ for which the Al · · · B distance increases from 2.128(8) to 2.392(6) and 2.419(6) Å,[10] and in $GaH_2(BH_4)$ for which the Ga · · · B distance increases from 2.179 (2)Å to an average value of 2.473(7) Å[7,18] on moving from the gas to the solid. That this increase is smaller for $GaMe_2(BH_4)$ reflects (i) the much weaker interactions involved compared with those in $AlMe_2(BH_4)$ where the Al atom becomes 6-coordinate in the solid phase, and (ii) the fact that for $GaH_2(BH_4)$ the BH_4 group is bridging two metal centres *via* single hydrogen bridges. Related to the increase in the Ga · · · B distance on condensation is the increase in the Ga–H distance

Table 2 Comparison of selected bond lengths (Å) and angles (°) for $GaMe_2(BH_4)$, $AlMe_2(BH_4)$, and $GaH_2(BH_4)$

	$GaMe_2(BH_4)$		$AlMe_2(BH_4)$		$GaH_2(BH_4)$	
Parameter	solid[a]	vapour[b]	solid[c]	vapour[b]	solid[d]	vapour[e]
M–X (X = C or H)	1.923(5) 1.927(5)	1.944(4)	1.912(5) 1.926(5)	1.929(4)	1.41(5)	1.586(8)
M···B	2.269(5)	2.163(8)	2.419(6) 2.392(6)	2.128(8)	2.457(7) 2.463(3) 2.499(7)	2.179(2)
M–H_b	1.88(5) 1.91(5)	1.791(30)	1.82(4) 2.22(5)	1.77(3)	1.87(7) 2.04(7)	1.826(8)
X–M–X (X = C or H)	137.4(2)	118.8(12)	130.5(2)	118.4(7)	133(3)	Not determined

[a] This work. [b] Ref. 11. [c] Ref. 10. [d] Ref. 7. [e] Ref. 18.

from 1.79(3) to 1.88(5)–1.91(5) Å. These changes are also mirrored in the infrared spectra of gaseous and solid $GaMe_2(BH_4)$ for which there is a significant decrease in energy of the Ga–H and Ga–B stretching modes on condensation.[13]

In line with the infrared spectra of $GaMe_2(BH_4)$, the M–C bond length decreases in the condensed phase and the C–M–C angle increases from 118.8(12) to 137.4(2)°. Surprisingly, this opening out of the C–M–C angle is greater than that observed for $AlMe_2(BH_4)$ [118.4(7)° for the vapour and 130.5(2)° for the solid]. In reference 10 we explained this opening out in terms of a change from a discrete molecular structure to a polymer incorporating alternate $[Me_2Al]^+$ and $[BH_4]^-$ ions, but such an explanation seems inappropriate in the case of $GaMe_2(BH_4)$ for which there is much less evidence of an ionic formulation. This is supported by the infrared spectrum of $GaMe_2(BH_4)$ which show the presence of distinct B–H_t and B–H_b bonds, unlike the spectra of Me_2AlBH_4 which shows only a single band at 2194 cm^{-1} indicative of a semi-ionic BH_4 group bridging two aluminium centres. One possible explanation is that the opening of this angle is caused by the two secondary Ga···H contacts, but it seems unlikely that the relative weakness of these interactions would be sufficient to cause such a large perturbation. The origin of this unexpectedly large C–Ga–C angle in solid $GaMe_2(BH_4)$ is therefore not obvious, and raises some interesting questions about the nature of the bonding in this compound. That such apparently similar compounds adopt such very different structures in the solid state is remarkable and illustrates how intermolecular interactions can dramatically be modified by subtle changes in electronic properties. We can, however, go some way to explaining qualitatively the trends observed in the solid state structures of this class of molecule. The difference in solid-state structures between $GaMe_2(BH_4)$ and $AlMe_2(BH_4)$ is yet another example of the tendency of Al to adopt higher coordination numbers than gallium, *e.g.* $GaCl_3$ *cf.* $AlCl_3$,[12] and reflects the lower electronegativity of Al that leads to more ionic character in its bonding and hence a higher coordination number. The replacement of methyl groups by hydrogen atoms on Ga serves to reduce the electron density on the Ga, thereby increasing the polarity of Ga–H_b and Ga–H_t bonds with the result that these become involved in intermolecular interactions and hence polymeric chains are formed. Furthermore, methyl groups show a lower propensity for bridging than do hydrogen atoms. A more quantitative approach would clearly be desirable and so we are currently probing the solid-state structures of these molecules using plane wave DFT calculations.

$GaMe_2(BH_4)$·OEt_2 (2) and $GaMe_2(BH_4)$·THF (3)

The structures of compounds **2** and **3** in the crystal are illustrated in Figs. 2 and 3. Bond distances and angles are listed in Table 1. For both compounds the Ga–C and Ga···B bond lengths increase compared with those of $GaMe_2(BH_4)$ in line with the increased coordination number of the Ga atom in **2** and **3**. On the basis of the lengths of the Ga–O bonds in **2** and **3** [2.119(2) and 2.109(2) Å, respectively], one would surmise that THF is the better donor, but curiously this is not mirrored in the relative increases in the Ga···C and Ga···B bond lengths; in fact it is **2** which has the longer bond lengths.

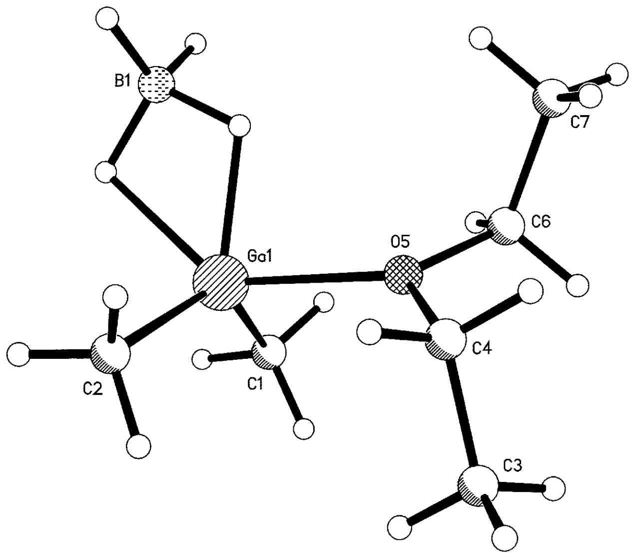

Fig. 2 Structure of solid $GaMe_2(BH_4)$·OEt_2 at 190 K as determined by X-ray diffraction.

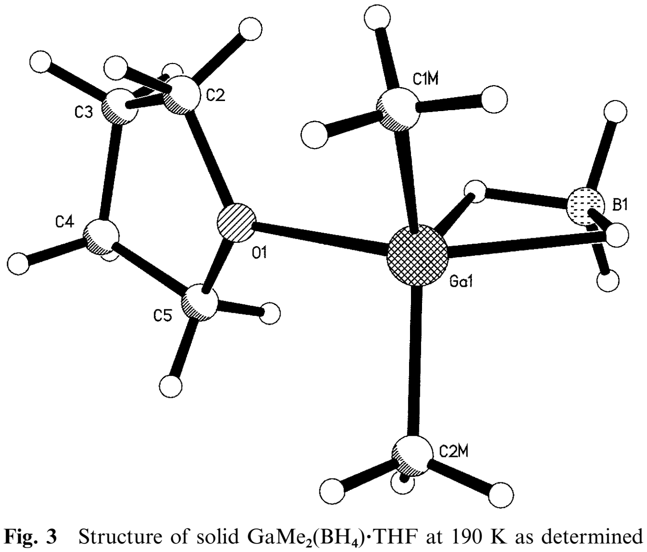

Fig. 3 Structure of solid $GaMe_2(BH_4)$·THF at 190 K as determined by X-ray diffraction.

Table 3 Vibrational bands (cm^{-1}) in the region 1900–2600 cm^{-1} for $GaMe_2(BH_4)$ and its adducts

$GaMe_2(BH_4)$[a]		$GaMe_2(BH_4)\cdot OEt_2$[b]	$GaMe_2(BH_4)\cdot NMe_3$[b]	$GaMe_2(BH_4)\cdot THF$[a]	$[GaMe_2(NH_3)_2]^+[BH_4]^-$[a]
vapour	solid	solid	solid	solid	solid
2540vs					
2470vs	2459vs				
		2437vs	2446vs	2435s	
	2400vs	2400vs	2400s	2400s	
	2290w	2316w	2315w	2290w	
2248w		2217s	2215s	2250m	2255s
	2198w		2192s		
2089m	2108s				
	2082s	2077s	2069s	2080s	
1980vs	2035mw				
1922s					

[a] Ref. 13. [b] This work.

On coordination of the donor molecules the C–Ga–C angles become slightly narrower and the C_2BGa units deviate from co-planarity. Although a degree of caution should be exercised when comparing Ga–H bond lengths based on X-ray data, it is noticeable that there is a marked asymmetry in the lengths in **2** and **3** [1.67(3) and 1.95(4) Å and 1.82(3) and 2.02(3) Å respectively], which perhaps points to the BH_4 unit adopting asymmetric coordination to the Ga atom of the adducts, *i.e.* a tendency towards the adoption of monodentate coordination. Unfortunately, the precision with which the B–H bond lengths themselves can be determined in the X-ray experiment prevents independent confirmation of this, although supporting evidence does come from the infrared studies of these compounds (see below).

Infrared spectra of compounds 2 and 3

The infrared spectra of solid deposits of compounds **2** and **3** at −196 °C in the region associated with B–H stretching modes (listed in Table 3) show certain similarities, but also some substantial differences, to those of solid $GaMe_2(BH_4)$. There are also very close similarities to the reported spectra of $GaMe_2(BH_4)\cdot NMe_3$.[13] The pattern of bands in the region 2000–2500 cm^{-1} is generally diagnostic of the type of coordination adopted by the BH_4 unit in such compounds. For all three adducts there are two prominent bands near 2440 and 2400 cm^{-1} that are characteristic of the asymmetric and symmetric B–H_t stretching modes of a bidentate BH_4 unit, and this pattern is mirrored in the spectrum of solid $GaMe_2(BH_4)$.[13] Descending in energy, the next two prominent bands occur near 2215 and 2070 cm^{-1} for **2** and **3**, and at 2250 and 2080 cm^{-1} for the amine adduct. For solid $GaMe_2(BH_4)$ these bands occur at 2108 and 2035 cm^{-1}. These are normally assigned to the asymmetric and symmetric B–H_b stretching modes of a bidentate BH_4 unit. However, the energy of the band near 2215 cm^{-1} for **2** and **3** (or 2250 cm^{-1} for the amine adduct) is substantially higher than the corresponding mode in solid $GaMe_2(BH_4)$. Such a shift is usually ascribed to increasing ionic character (formation of a tetrahedral BH_4 unit) whereby the energies of the bridging and terminal B–H stretching modes converge, *e.g.* $[GaMe_2(NH_3)_2]^+[BH_4]^-$ which displays a single band at 2255 cm^{-1}, or solid $AlMe_2(BH_4)$ which displays a single band at 2194 cm^{-1}. However, this cannot be the explanation for the shift of the band observed for the adducts, since none of the other B–H stretching modes is substantially shifted when compared with that of solid $GaMe_2(BH_4)$. This observation therefore points to an unsymmetrically bound bidentate BH_4 group in these adducts in which one of the B–H_b bonds is substantially shorter than the other. Although this feature is not resolved directly by consideration of the B–H bond lengths in the crystal structures of these adducts, it is apparent from the asymmetry in the Ga–H bond lengths.

The infrared spectra of adducts **2** and **3** as vapours contained in a gas cell at ambient temperature are in marked contrast to those of the solid adducts, and show bands corresponding to free $GaMe_2(BH_4)$ and Et_2O or THF, *i.e.* the adducts are completely dissociated and no sign of interaction is observed between the components. Further support for this complete dissociation at ambient temperature comes from the mass spectra of the adducts, which show that even at the lowest possible ionisation threshold the only signals that are observed correspond to free $GaMe_2(BH_4)$ and Et_2O or THF. Such a result is not without precedent for other adducts of $GaMe_2(BH_4)$; $[GaMe_2(NH_3)_2]^+[BH_4]^-$ has been reported to sublime *via* dissociation to the parent compound and ammonia.[13]

NMR spectra

The ^1H NMR spectrum of compound **1** dissolved in $[^2H_8]$-toluene at 24 °C displays a singlet at δ_H −0.24, corresponding to the CH_3 protons, and a characteristic quartet centred at δ_H 1.28 corresponding to the H atoms attached to ^{11}B. The ^{11}B spectrum shows a quintet at δ_B −15.2 with $J_{B\text{–}H} = 85$ Hz. As with many tetrahydroborates, interchange between bridging and terminal H atoms is fast on the NMR timescale.

The spectra of compounds **2** and **3** show that the ratio of Et_2O or THF to $GaMe_2(BH_4)$ is indeed 1 : 1, although on occasions a slight excess of Et_2O or THF was indicated. This is most likely caused by slight decomposition of the adducts on transfer to the NMR tubes and subsequent sealing under vacuum. The 1 : 1 ratio does not, of course, confirm that the adducts survive intact in solution, but the small shifts in the ^1H spectra (to δ_H −0.13 and −0.12 for **2** and **3**, respectively) and the substantially larger shifts in the ^{11}B spectra (to δ_B −22.7 and −27.8, respectively) strongly suggest that these are discrete complexes. The shift of the methyl protons in **2** and **3** to slightly higher frequency would not be expected on the basis of the increased electron density on the Ga atom caused by coordination of a donor atom. Instead it suggests that for the compounds in solution the geometry of the Me_2Ga group may be different from that of **1**, as indicated in the crystal structures. Further support for this comes from the substantial shifts to lower frequency of the ^{11}B signals for **2** and **3** compared to that of **1**. This is typical of a move towards a less tightly bound BH_4 unit found for compounds such as $[Bu_4N]^+[BH_4]^-$ that gives rise to ^{11}B signals at δ_B −35 in benzene.[19]

Thermal stability

One of the most notable aspects of these compounds is their enhanced thermal stability when compared to that of $GaMe_2(BH_4)$ and $GaMe_2(BH_4)\cdot NMe_3$, which decompose rapidly at ambient temperature and at −45 °C, respectively.[13] The only other adduct of $GaMe_2(BH_4)$ that has substantial thermal stability is $[GaMe_2(NH_3)_2]^+[BH_4]^-$. It has been observed for several other uncoordinated hydrides of gallium that decomposition is much more facile in the condensed phases than in the gas phase, and this points to an intermolecular pathway. Given that for $GaMe_2(BH_4)$ there are significant intermolecular interactions present in the solid (and presumably also in the liquid), this explains its low thermal stability. Coordination of a weak donor ligand *e.g.* Et_2O or THF increases the coordination number of the Ga thereby reducing the tendency for intermolecular association and hence blocks potential decomposition pathways. However, with stronger donors such as Me_3N cleavage of the $M(\mu\text{-}H)_2M$ or $M(\mu\text{-}H)_2B$ is common, *e.g.* the formation of $Me_3N{\cdot}GaH_3$ from Ga_2H_6. Thus in the reaction between $GaMe_2(BH_4)$ and Me_3N spectroscopic evidence shows that the adduct $GaMe_2(BH_4){\cdot}NMe_3$ is formed first. Further warming presumably results in cleavage with subsequent (possibly base catalysed) decomposition of $[GaMe_2H]_x$ or $GaMe_2H{\cdot}NMe_3$. Thus the thermal stability of **2** and **3** can be attributed to the relatively weak donor power of Et_2O and THF, which are sufficiently strong donors to break up intermolecular interactions in $GaMe_2(BH_4)$, but insufficiently strong to cleave the $M(\mu\text{-}H)_2B$ unit.

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