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HYDRIDOGALLIUM BIS(TETRAHYDROBORATE), $HGa(BH_4)_2$: SYNTHESIS AND PROPERTIES

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Abstract—The 'mixed' gallium–boron hydride $HGa(BH_4)_2$ has been synthesized by the reaction between lithium tetrahydroborate and gallium(III) chloride or dichlorogallane, $[HGaCl_2]_2$, in the absence of a solvent at 238–263 K. The compound, which decomposes to elemental gallium, dihydrogen and B_2H_6 at ambient temperatures, has been characterized by chemical analysis, by vapour-density measurements, and by its vibrational, mass, and ^1H and ^{11}B NMR spectra. The physical and spectroscopic properties of the compound imply that the monomeric molecule $HGa(BH_4)_2$ (with a single terminal Ga—H bond and two bidentate BH_4 groups) is subject to loose aggregation in the condensed phases. Thus, the NMR spectra of toluene-d_8 solutions at temperatures in the range 190–270 K suggest that the monomer and an oligomer $[HGa(BH_4)_2]_n$ (where $n = 2$ in all probability) co-exist in equilibrium. Chemical properties of the gallane to be investigated include (i) the reactions with bases as varied as CO, NMe_3 and NH_3, which bring about homolytic or heterolytic cleavage of the $Ga(\mu\text{-}H)_2BH_2$ fragments; and (ii) the exchange or protolysis reactions induced by Me_3Ga or HCl and MeOH, respectively. No evidence was found for the formation of gallium tris(tetrahydroborate), $Ga(BH_4)_3$, even at low temperatures.

Several tetrahydroborate derivatives of aluminium have been characterized quite fully.[1,2] Best known is the tris(tetrahydroborate), $Al(BH_4)_3$, prepared typically by metathesis between aluminium(III) chloride and an alkali-metal tetrahydroborate; this is notable for its volatility, structure (with a trigonal prismatic arrangement of the bridging hydrogen atoms about the central aluminium atom) and fluxionality. Other such derivatives include Me_2AlBH_4,[4–6] $MeAl(BH_4)_2$[4,5,7] and the involatile hydride, $[HAl(BH_4)_2]_n$.[8]

Analogous compounds of gallium remained relatively sparsely characterized until 1976–1978, when the compounds Me_2GaBH_4[6,9] and $HGa(BH_4)_2$[10] were first described in some detail. The hydridogallium derivative was then noteworthy for being a rare example of a base-free gallium hydride. The principal component of the vapour at low pressures is the monomeric molecule $HGa(BH_4)_2$, the structure of which has been determined both experimentally (on the basis of its vibrational spectra and electron diffraction pattern)[11,12] and through *ab initio* calculations.[12] The consensus is that the molecule has the structure **1** conforming to C_{2v} symmetry and with five-fold coordination of the gallium, a single terminal Ga—H bond and two

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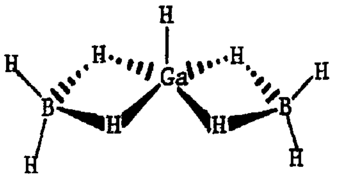
bidentate BH_4 groups. Gallium tetrahydroborates are thermally less robust than their aluminium counterparts and typically decompose to gallium metal at ambient temperatures. Hence they offer a means of vapour transport of gallium, as well as a potential source of thin films of pure gallium or its compounds.[13]



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In this paper we describe the synthesis and some of the physical and chemical properties of hydridogallium bis(tetrahydroborate), $HGa(BH_4)_2$. The results afford evidence (i) of loose aggregation of the $HGa(BH_4)_2$ molecules in the condensed phases, (ii) of homolytic or heterolytic cleavage of the $Ga(\mu\text{-}H)_2BH_2$ fragments at the hands of different bases, (iii) of Me—BH_4 exchange with Me_3Ga, and (iv) of protolysis induced by HCl or MeOH.

RESULTS AND DISCUSSION

Synthesis and physical properties of hydridogallium bis(tetrahydroborate)

Hydridogallium bis(tetrahydroborate) has been prepared by the interaction of powdered gallium(III) chloride with an excess (typically *ca* fourfold) of freshly recrystallized lithium tetrahydroborate under solvent-free conditions. According to the precise state and purity of the reagents and the efficiency of mixing, the reaction sets in at, or above, 238 K and, with slow warming of the mixture to a temperature not exceeding 263 K, is typically complete in 4–5 h. The volatile products are trapped *in vacuo* at 77 K; subsequent fractional condensation reveals just two principal components, diborane and hydridogallium bis(tetrahydroborate), formed in amounts usually corresponding to 40–70% of those expected on the basis of the quantity of gallium(III) chloride taken and consumed in accordance with eq. (1).

$$\tfrac{1}{2}Ga_2Cl_6 + 3LiBH_4 \xrightarrow{238\text{–}263\ K} HGa(BH_4)_2 + \tfrac{1}{2}B_2H_6 + 3LiCl \qquad (1)$$

There is no sign of the tris(tetrahydroborate) derivative $Ga(BH_4)_3$, the product to be expected by analogy with the corresponding reaction which takes place at higher temperatures between aluminium(III) chloride and lithium tetrahydroborate.[3]

An alternative route to hydridogallium bis(tetrahydroborate) starts from dichlorogallane, $[HGaCl_2]_2$, itself prepared by metathesis between gallium(III) chloride and trimethylsilane.[14] Solid dichlorogallane reacts with an excess of lithium tetrahydroborate, under conditions similar to those employed with gallium(III) chloride, to generate hydridogallium bis(tetrahydroborate) in yields of 40–60% according to eq. (2).

$$\tfrac{1}{2}[HGaCl_2]_2 + 2LiBH_4 \xrightarrow{238\text{–}263\ K} HGa(BH_4)_2 + 2LiCl \qquad (2)$$

In this case, however, gallaborane, i.e. the monotetrahydroborate H_2GaBH_4,[15–17] is apt to be formed as a by-product and to contaminate the bis(tetrahydroborate) unless appropriate steps are taken with fractionation to eliminate this more volatile component.

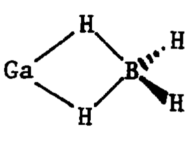
A sample of the gallane judged to be essentially pure on the evidence of its spectroscopic properties[11,12] is stripped of any less volatile material by passage through a trap cooled to 228 K and condenses as a white homogeneous solid in a trap cooled to 190 K. Although the compound is appreciably more robust than gallane[16,18] and gallaborane,[15,16] it decomposes at ambient temperatures and its successful synthesis and manipulation call for scrupulous attention to practical technique.[18,19]

Hydridogallium bis(tetrahydroborate) melts at about 200 K to give a colourless, relatively mobile liquid which has a vapour pressure of *ca* 10 mmHg at 228 K. Estimates of the vapour density give an RMM for the vapour species in the range 97–105, whereas the monomer $HGa(BH_4)_2$ requires 100.4. The mass spectrum of the vapour includes peaks attributable to the molecular ion [$m/z = 100$ and 102 for $H^{69}Ga(^{11}BH_4)_2^+$ and $H^{71}Ga(^{11}BH_4)_2^+$, respectively], to the fragments $GaB_2H_n^+$ ($n = 6$–8), $GaBH_n^+$ ($n = 3$–6), GaH_n^+ ($n = 0$–3), $B_2H_n^+$ ($n = 3$–6) and BH_n^+ ($n = 0$–3), and also to hydroxy- and chloro-gallium impurities introduced in the sampling. There is no suggestion of any molecular ion containing two or more gallium atoms ($m/z \geq 138$) and no reason therefore to believe that the vapour contains any oligomers $[HGa(BH_4)_2]_n$ ($n = 2, 3 \ldots$); the same inference has been drawn from analyses of the IR spectrum and electron diffraction pattern of the vapour.

Decomposition of the neat liquid sets in at temperatures much above 228 K, and, in common with related compounds,[19] the gallane is also extremely susceptible to attack by traces of oxygen or moisture. The decomposition leads to the formation of gallium metal, dihydrogen and diborane in accordance with eq. (3), which affords a means of quantitative analysis.[12]

$$HGa(BH_4)_2 \longrightarrow Ga + \tfrac{3}{2}H_2 + B_2H_6. \quad (3)$$

The vibrational spectra of hydridogallium bis(tetrahydroborate) have already been described in some detail.[12] As noted previously, they provide persuasive evidence that the main—possibly exclusive—component of the vapour at low pressures is the monomeric molecule $HGa[(\mu\text{-}H)_2BH_2]_2$ (**1**) with C_{2v} symmetry. On condensation at 77 K, a solid film of the gallane gives IR and Raman spectra quite similar to those observed or expected for discrete $HGa(BH_4)_2$ molecules. With progressive annealing of the deposit, however, the spectra underwent changes suggestive of significant intermolecular interactions. The pattern remains that characteristic of a di-hydrogen-bridged BH_4 group,[9,20–22] and a prominent IR absorption centred near 2000 cm^{-1} may well be due to what is essentially the stretching vibration of a terminal Ga—H unit.[12,16,18] The corresponding alane, $[HAl(BH_4)_2]_n$, which is an involatile, viscous liquid at normal temperatures,[8] is believed, but not known, to form relatively strongly bound aggregates through Al—H—Al bridging. Although it is not possible to rule out Ga—H—Ga bridging in the solid gallane, the IR spectrum gives no signs diagnostic of such a unit,[18,19,23] and it is more likely that bridging of the metal centres occurs via the BH_4 groups, which may change their mode of coordination from simple η^2 (**2**) to μ_2,η^2 (**3**). The change in the IR spectrum wrought by the switch from the vapour to the annealed solid is less dramatic with $HGa(BH_4)_2$ than with $MeZnBH_4$,[24] the solid form of which displays vibrational properties consistent with something approaching the formulation $MeZn^+BH_4^-$.



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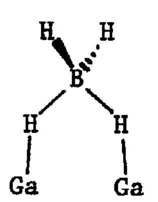

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NMR spectra

The ^1H NMR spectrum of a toluene-d_8 solution of hydridogallium bis(tetrahydroborate) at 253 K consists of a broad singlet at δ 5.0, with a shoulder on the low-frequency flank, and a 1:1:1:1 quartet [$J(^{11}B—H) = 95$ Hz] centred at δ 1.0 with about eight times the intensity of the singlet resonance (see Fig. 1). The singlet is plainly due to the terminal GaH proton[15,16,18,25–27] and the quartet to the protons of the BH_4 groups.[20,28] Cooling the sample to 213 K causes the GaH resonance to sharpen and split into two distinct components, whereas the BH_4 resonance broadens to a 'double-humped' signal as a result of partial decoupling of the boron nuclei.[20,28] Decreasing the concentration of the solution by a factor of 10 gives very similar spectra for the solute except that the low-frequency GaH resonance is significantly weaker relative to the high-frequency one. Hence the solution appears to contain two species in dynamic equilibrium.

This conclusion is endorsed by the ^{11}B NMR spectra of the solutions (Fig. 1). The normal spectrum reveals not one but two signals centred at δ_B *ca* -24 and -34; with the sample at 213 K these are relatively broad, but sharpen on proton decoupling. Dilution of the solution causes the resonance at δ_B -24 to decrease in intensity relative to that at δ_B -34. On the other hand, decreasing the temperature of a given sample causes the resonance at δ_B -24 to grow at the expense of that at δ_B -34. All these signs are consistent with a monomer–oligomer equilibrium, as in eq. (4), with n probably equal to 2. Changes in the relative intensities as a function of temperature imply an enthalpy change for this reaction of the order of -1 kJ mol^{-1}.

$$nHGa(BH_4)_2 \rightleftharpoons [HGa(BH_4)_2]_n \quad (4)$$

With the sample at 213 K and broad-band ^{11}B decoupling, the ^1H spectrum retains the GaH resonance near δ 5.0 but develops a doublet centred on δ 0.99 with a splitting of 9 Hz for the BH_4 resonance. This doublet coalesces to a singlet as the temperature is raised to 243 K. Selective decoupling at the frequency associated with the boron atoms in the oligomer (δ_B -24) gives in place of the doublet a broad singlet with a shoulder on the low-frequency side. By contrast, decoupling at the frequency associated with the boron atoms in the monomer ($\delta_B - 34$) gives a doublet centred at δ 0.985 with a separation of 9 Hz and exhibiting some broadening on the high-frequency side (Fig. 1c). A triple-resonance experiment with broad-band ^{11}B decoupling and simultaneous selective proton decoupling at the resonance frequency of the GaH proton causes the doublet due to the BH_4 protons to show significant flattening on the low-frequency side (Fig. 1d). Hence it appears that the BH_4 protons in the monomer are responsible for the doublet which originates in coupling to the GaH proton; this overlaps the singlet at slightly higher frequency which originates

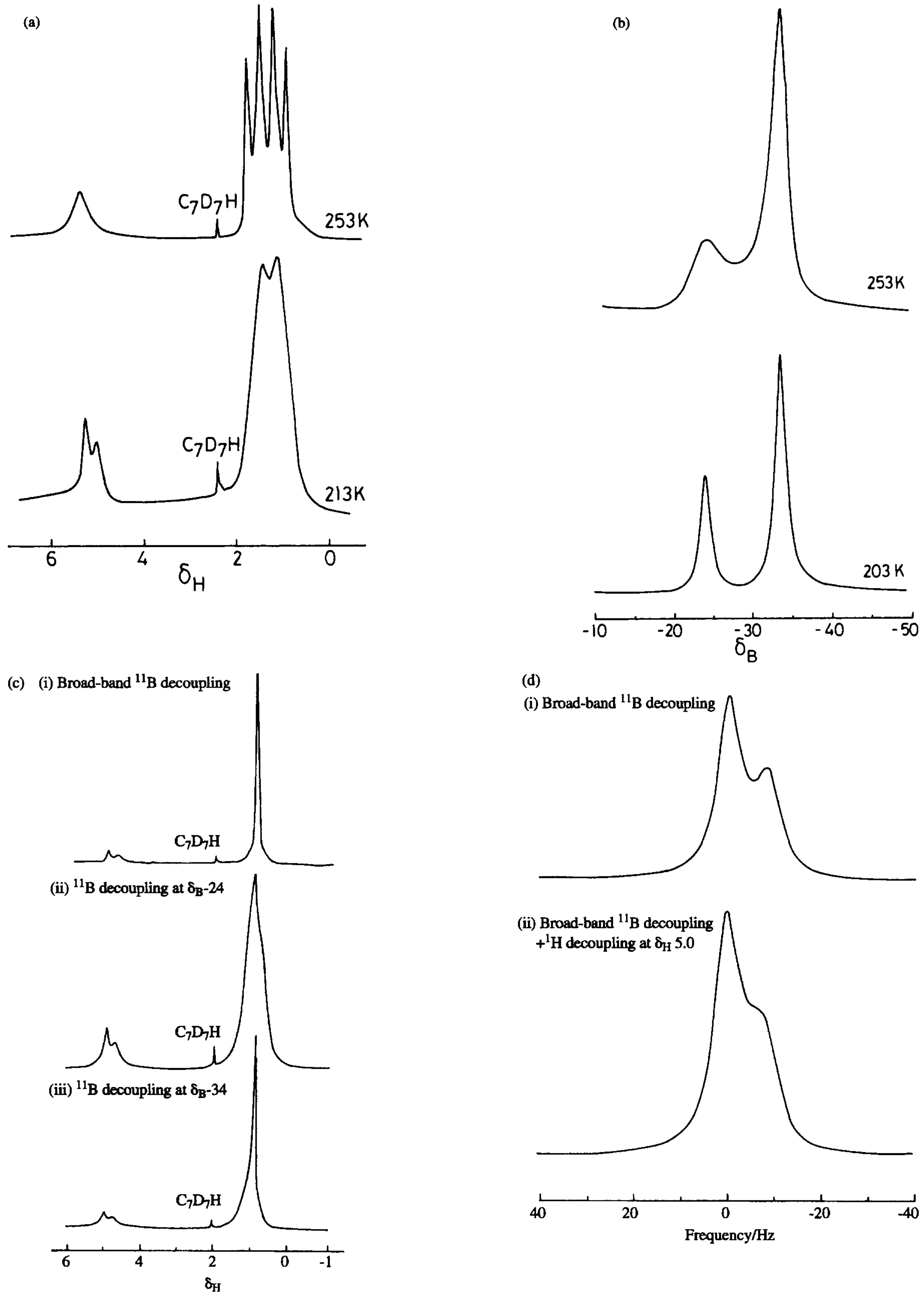
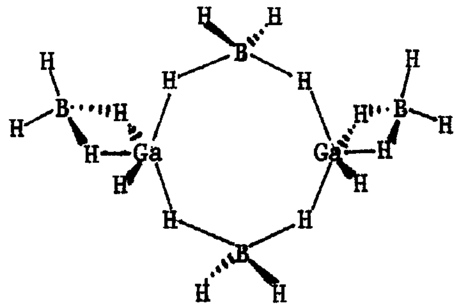


Fig. 1. NMR spectra recorded for a toluene-d_8 solution of hydridogallium bis(tetrahydroborate). (a) ^{1}H spectrum of the solution: (i) at 253 K and (ii) at 213 K; (b) ^{11}B{^{1}H} spectrum of the solution: (i) at 253 K and (ii) at 203 K; (c) ^{1}H spectrum of the solution at 213 K: (i) with broad-band and (ii) and (iii) with selective ^{11}B decoupling; (d) ^{1}H spectrum of the solution at 228 K: (i) with broad-band ^{11}B decoupling and (ii) with broad-band ^{11}B and simultaneous selective ^{1}H decoupling.

in the oligomer. The broadness of the signals makes it impossible in practice to carry out a meaningful COSY experiment to confirm the coupling of the GaH to the BH_4 protons.

Unfortunately, the spectra shed little light on the nature of the oligomer. The results are consistent with a loosely associated dimer having the cyclic structure **4** composed of alternating $GaH(BH_4)$ and BH_2 groups linked via single hydrogen bridges. A structure of this type may well be adopted by the dimer of gallaborane, $[H_2GaBH_4]_2$, under similar conditions, but there are significant differences between the NMR properties of the two oligomers,[16] and it does not necessarily follow that they have similar structures. Since the BH_4 groups remain magnetically equivalent at temperatures down to 183 K, it would be necessary to postulate rapid exchange between the bridging and terminal BH_4 groups if $[HGa(BH_4)_2]_2$ does indeed take the form of **4**. The oligomer can also be formulated in other ways, for example with Ga—H—Ga bridges. However, the GaH protons of both the monomer and the oligomer resonate at frequencies characteristic not of bridging Ga—H—Ga but of terminal GaH units,[15,16,18,25–27] and the inference is that any Ga—H···Ga interaction must be of a weak, secondary nature.



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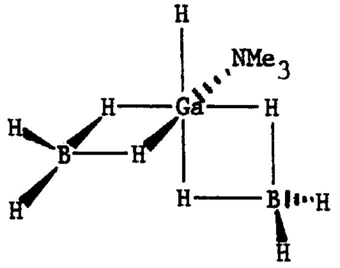
Chemical properties

Some of the chemical properties of hydridogallium bis(tetrahydroborate) have been explored, with the results summarized in Scheme 1. Reference has already been made to its decomposition at ambient temperatures. NMR studies at no stage reveal any sign of products other than elemental gallium, dihydrogen and diborane; there is, for example, no hint of any intermediates like gallaborane, H_2GaBH_4.[15,16] The most obvious mechanism therefore involves elimination of B_2H_6 and rapid decomposition of the primary co-product, gallane.[18,19]

$$\begin{array}{l} HGa(BH_4)_2 \longrightarrow \frac{1}{n}[GaH_3]_n + B_2H_6 \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad Ga + \frac{3}{2}H_2 \end{array} \quad (5)$$

In addition, our survey has explored the response of the bis(tetrahydroborate): (a) to each of three selected Lewis bases (NMe_3, NH_3 and CO), (b) to ligand exchange with Me_3Ga, (c) to protolysis by HCl or MeOH and (d) to the addition of B_2H_6 as a potential route to the tris(tetrahydroborate), $Ga(BH_4)_3$. Each of these classes of reaction will now be treated in turn.

Reactions with Lewis bases. Hydridogallium bis(tetrahydroborate) reacts with trimethylamine at 193 K to form a 1 : 1 molecular adduct, the IR spectrum of which resembles that of $Me_3N \cdot Al(H)(BH_4)_2$[8] (see Table 1) and points to the structure **5**, featuring the retention of bidentate BH_4 groups and a terminal Ga—H bond to give six-fold coordination of the gallium centre. The spectrum has been interpreted by analogy with those of the adducts $Me_3N \cdot GaH_3$[29] and $Me_3N \cdot GaMe_2(BH_4)$,[5,9] and of the uncomplexed bis(tetrahydroborate).[12] Coordination of the trimethylamine molecule appears to follow the usual pattern of increasing the energies of the $\nu(B—H_b)$ modes[30] and decreasing that of the $\nu(Ga—H_t)$ mode (b denotes a bridging and t a terminal atom) to give two more-or-less distinct sets of absorption in place of the single broad absorption displayed by the parent gallane.[12] It is also noteworthy that $\nu(Ga—H)$ is about 60 cm^{-1} higher in energy than $\nu(Al—H)$ in the corresponding aluminium compound,[8] in keeping with the trends shown by species like matrix-isolated MH_3,[31] MH_4^- [32] and $Me_3N \cdot MH_3$[29,33] (M = Al or Ga) and reflecting presumably the decreased polarity of the Ga—H compared with the Al—H bond.



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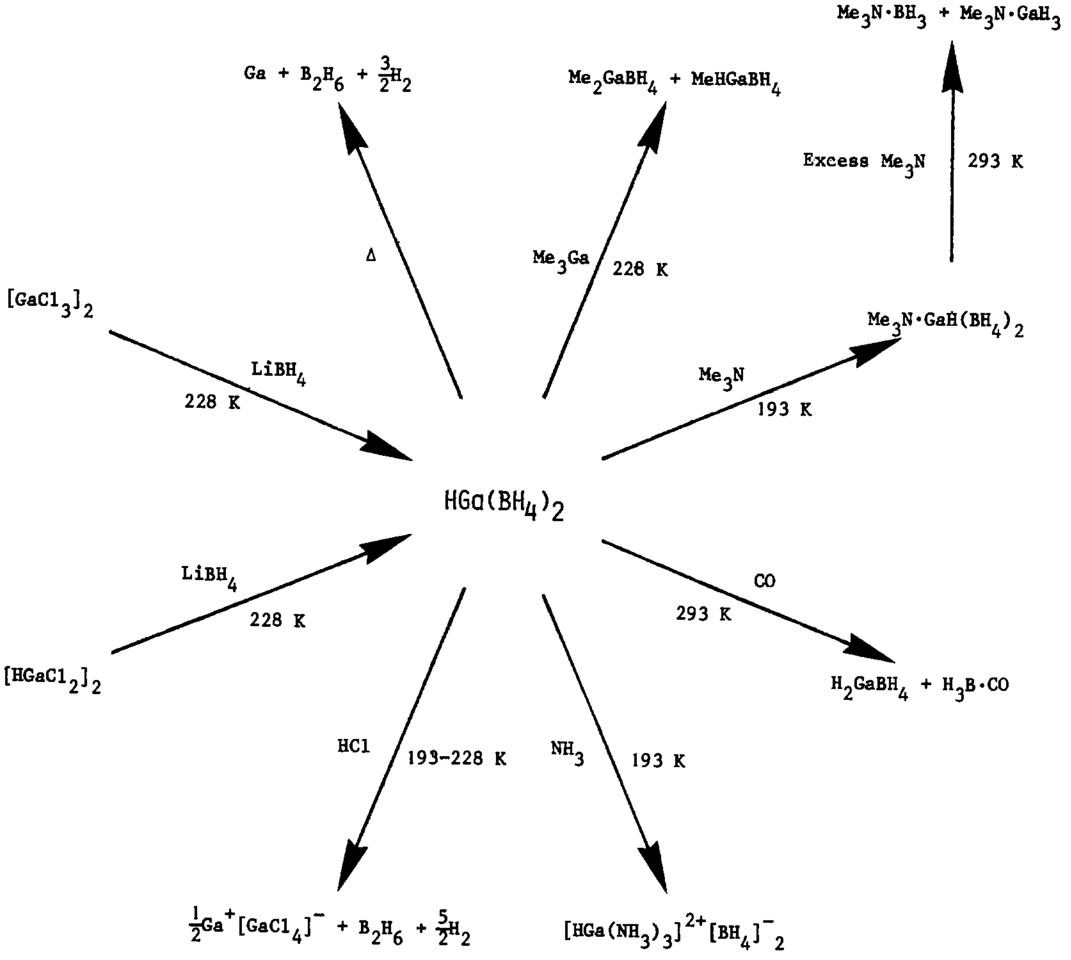

Scheme 1. Preparation and some reactions of hydridogallium bis(tetrahydroborate), $HGa(BH_4)_2$.

Warming the white solid to room temperature results in decomposition with the formation of elemental gallium, dihydrogen, diborane and a mixture of the familiar adducts $Me_3N \cdot GaH_3$ and $Me_3N \cdot BH_3$, which have been identified by their IR spectra.[29,34] On the other hand, warming in the presence of an excess of trimethylamine gives, at room temperature, a white crystalline product consisting exclusively of an equimolar mixture of the adducts $Me_3N \cdot GaH_3$ and $Me_3N \cdot BH_3$. The gallane thus resembles Me_2GaBH_4[9] in its response to trimethylamine, with the $Ga(\mu\text{-}H)_2B$ bridges being cleaved homolytically to give neutral Ga—H and B—H fragments. We note though that the stability of $Me_3N \cdot Ga(H)(BH_4)_2$ is very different from that of $Me_3N \cdot Al(H)(BH_4)_2$, which survives both dissociation and decomposition at room temperature.[8]

With an excess of ammonia at 193 K, the gallane reacts to give a white solid. Evaporation of the excess of ammonia reveals that the reacting proportions $HGa(BH_4)_2 : NH_3$ are 1 : 3. The IR spectrum of the solid shows strong, broad absorptions centred near 2270 and 1100 cm^{-1}, implying more-or-less discrete BH_4^- anions.[20,21] The other features (listed in Table 2) are consistent with the presence of the cation $[HGa(NH_3)_3]^{2+}$, finding obvious parallels in the spectra of $[H_2Ga(NH_3)_2]^+Cl^-$[27] and the isoelectronic germane Me_3GeH.[35] The formulation $[HGa(NH_3)_3][BH_4]_2$ is also endorsed by the discovery that dichlorogallane, $[HGaCl_2]_2$,[14] reacts with ammonia in a similar fashion to give a solid product presumed to be $[HGa(NH_3)_3]Cl_2$, with an IR spectrum differing significantly from that of the tetrahydroborate product only in the absence of the bands due to the BH_4^- anion (Table 2). Hence it seems that the $Ga(\mu\text{-}H)_2B$ bridges are cleaved heterolytically to give HGa^{2+} and BH_4^- fragments in accordance with eq. (6).

$$HGa(BH_4)_2 + 3NH_3 \longrightarrow [HGa(NH_3)_3]^{2+}[BH_4]_2^- \qquad (6)$$

The product decomposes slowly at room temperature to give, *inter alia*, elemental gallium, di-

Table 1. IR spectra of solid films of the complexes $Me_3N \cdot Ga(H)(BH_4)_2$ and $Me_3N \cdot Al(H)(BH_4)_2$ at 77 K

$Me_3N \cdot Ga(H)(BH_4)_2$ 250–4000 cm^{-1}		$Me_3N \cdot Al(H)(BH_4)_2$[b] 400–4000 cm^{-1}		
ν (cm^{-1})	intens.[a]	ν (cm^{-1})	intens.[a]	Assignment[c]
2972	w	2986	w	Me_3N, ν(C—H)
2918	w	2946	w	Me_3N, ν(C—H)
2452	s	2490	s	ν(B—H_t)
2413	s	2431	s	
2250	mw	2204	w,sh	ν(B—H_b)
2204	mw	2159	s	
2030	m	2110	sh	
1934	s	1861	s	ν(M—H_t)
1910	s			
1464	s	1481	s	Me_3N, $\delta_{as}(CH_3)$
1440	m	1467	s	Me_3N, $\delta_{as}(CH_3)$
1402	m	1410	mw	Me_3N, $\delta_s(CH_3)$
1251	m	1290	w,br	Me_3N, $\rho(CH_3) + \nu_{as}$(C—N)[d]
1230	mw	1244	mw	Me_3N, $\rho(CH_3) + \nu_{as}$(C—N)[d]
1166	m	1199	w	Me_3N, $\rho(CH_3)$[d]
		1179	w	
1111	s	1123	s	$\delta[B(H_t)_2]$
1098	s	1105	mw	
1000	s	990	s	Me_3N, ν_{as}(C—N) + $\rho(CH_3)$[d]
948	w	909	w	in-plane $\rho[B(H_t)_2]$
855	mw	878	w	
821	m	818	mw	Me_3N, ν_s(C—N)
		816	w	
712	m	741	s	out-of-plane $B(H_t)_2$ wag
620	sh	685	ms	δ(M—H_t)
559	w			overtone or combination
515	m	606	ms	ν(M ··· B) ring def. and ν(M—N)
500	s	536	ms	
445	w	484	s	
425	w			Me_3N, $\delta(NC_3)$
360	sh			Me_3N, $\delta(NC_3)$
315	s			

[a] s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.

[b] Ref. 8.

[c] M = Al or Ga. H_t denotes terminal, H_b denotes bridging hydrogen atom. Assignments based on analogies with the spectra of $Me_3N \cdot GaH_3$[29] and of free $HGa(BH_4)_2$.[12]

[d] Compare $Me_3N \cdot GaH_3$.[29]

hydrogen and ammonia, as well as an unidentified boron–nitrogen compound.

The ^1H and ^{11}B NMR spectra of toluene-d_8 solutions reveal that hydridogallium bis(tetrahydroborate) also reacts with carbon monoxide at an overpressure of *ca* 4 atm and ambient temperatures to produce borane carbonyl, $H_3B \cdot CO$, and gallaborane[15,16] in accordance with eq. (7).

$$HGa(BH_4)_2 + CO \longrightarrow H_2GaBH_4 + H_3B \cdot CO \quad (7)$$

Thus, after a dilute solution of the gallane has been allowed to warm up to room temperature for a few minutes under these conditions, the ^{11}B and ^1H spectra of the sample at 263 K indicate that all the bis(tetrahydroborate) has been consumed. Instead, the ^{11}B spectrum now exhibits resonances at $\delta_B -49$ (due to $H_3B \cdot CO$[36]), -23 (due to H_2GaBH_4 monomer[15,16]) and 16.8 (due to B_2H_6[34,36]), and the ^1H spectrum resonances at δ *ca* 5 and 1 (due to H_2GaBH_4[15,16]), 4.5 (due to H_2[37]), 3.9 and -0.4 (due to B_2H_6[34]), and 1.2 (due to $H_3B \cdot CO$[36]). The amounts of H_2 and B_2H_6 are relatively small, being formed presumably by the decomposition of $HGa(BH_4)_2$ and H_2GaBH_4, processes which compete with the primary reaction (7). There is a potential source of ambiguity in that the NMR properties of the bis(tetrahydroborate) and gallaborane are very similar. Indeed, gallaborane dissolved in toluene-d_8 also gives two ^{11}B resonances at δ_B *ca* -24 and -34, but the temperature- and concentration-dependence argues that these should be assigned to the monomer H_2GaBH_4 and an oligomer $[H_2GaBH_4]_n$ (where n is probably 2), respectively, i.e. in an order which is the reverse of that proposed for the corresponding features of hydridogallium bis(tetrahydroborate).[15,16] Cooling the solution to 213 K results in the appearance and growth of an ^{11}B resonance at $\delta_B - 34$ at the expense of that near $\delta_B - 24$, thereby confirming that the compound responsible is indeed gallaborane and not unchanged hydridogallium bis(tetrahydroborate). As noted already, gallaborane has not been detected as a decomposition product of the bis(tetrahydroborate), and so we must conclude that it is a product of the displacement reaction (7), in which the unusually soft base CO eliminates BH_3 from a coordinated BH_4 group.

This last reaction is not only novel but also potentially significant as a means of converting an MBH_4 to an M—H linkage in a controlled fashion and without coordination of the metal M by a base molecule. A similar reaction has been shown to occur between aluminium tris(tetrahydroborate) and carbon monoxide to afford the aluminium analogue of hydridogallium bis(tetrahydroborate) and borane carbonyl.[8]

Ligand exchange with Me_3Ga. The interaction of the gallane with trimethylgallium has been investigated by allowing an equimolar mixture of the neat reagents to warm slowly to room temperature. Melting of the compounds witnesses the evolution of some dihydrogen and the deposition of a grey solid, presumed to be gallium metal. IR measurements show that diborane and its methylated derivatives are also formed.[38,39] A less volatile component can be separated from the other products by fractional condensation *in vacuo* and shown by its vapour pressure and IR spectrum to be dimethylgallium tetrahydroborate, Me_2GaBH_4.[9] Hence it seems that exchange takes place in accordance with eq. (8), and that the decomposition of the hydridogallium compounds $HGa(BH_4)_2$ and

Table 2. IR spectra of the solid complexes $[HGa(NH_3)_3][BH_4]_2$ and $[HGa(NH_3)_3]Cl_2$ (Nujol mulls at room temperature, 400–4000 cm^{-1})

$[HGa(NH_3)]_3[BH_4]_2$		$[HGa(NH_3)_3]Cl_2$[b]		
ν (cm^{-1})	intens.[a]	ν (cm^{-1})	intens.[a]	Assignment[c]
3290	s	3300	s	ν_{as}(N—H)
3170	m	3200	s,vbr	ν_s(N—H)
2268	s			ν_3 (t_2) BH_4^-
2180	sh			
1921	s	1910	s	ν(Ga—H_t)
1615	w,br	1610	m	$\delta_{as}(NH_3)$
1331	s	1300	s	$\delta_s(NH_3)$
1296	m	1265	w	
1278	m			
1131	m			ν_4 (t_2) BH_4^-
1090	s			
793	m	787	s,br	$\rho(NH_3)$
756	s	736	s	
732	s			
645	w	648	w	$\rho(N_3GaH)$
466	w	470	w	ν(Ga—N)
443	mw	448	mw	

[a] s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder.

[b] Results taken from Ref. 27.

[c] H_t terminal hydrogen atom. The assignments are consistent with those proposed for other ammines (Ref. 45).

$MeGa(H)BH_4$ accounts for the secondary products.

$$\begin{array}{l} Me_3Ga + HGa(BH_4)_2 \longrightarrow Me_2GaBH_4 \\ \qquad\qquad\qquad + \ MeGa(H)BH_4 \\ \qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad Ga + \frac{3}{2}H_2 + \frac{1}{2}[MeBH_2]_2 \end{array} \quad (8)$$

The intermediate formation of the hydride $MeGa(H)BH_4$ finds support from an experiment in which the same reagents are co-condensed on a CsI window; warming the mixture to *ca* 193 K leads to the appearance of a new IR absorption in the region 1800–1900 cm^{-1}, suggesting the formation of a product containing a terminal Ga—H bond.[12,16,18,19]

Protolysis reactions. When a mixture of the gallane with an excess of HCl is warmed first to 193 and then to 228 K for 2 h, a white solid is formed together with dihydrogen and diborane. The solid has been identified spectroscopically as gallium 'dichloride', i.e. $Ga^+[GaCl_4]^-$, and assay of the volatile products is found to be consistent with the reaction represented by eq. (9):

$$HGa(BH_4)_2 + 2HCl \longrightarrow \tfrac{1}{2}Ga^+[GaCl_4]^- + B_2H_6 + \tfrac{5}{2}H_2. \quad (9)$$

The gallane also reacts vigorously with an excess of methanol at 193 K with the evolution of dihydrogen. Estimation of the dihydrogen shows that about 5 mol of H_2 are released per mol of $HGa(BH_4)_2$, implying that the principal reaction under these conditions is as represented by eq. (10).

$$HGa(BH_4)_2 + 5MeOH \longrightarrow \tfrac{1}{n}[MeOGaH_2]_n + 2(MeO)_2BH + 5H_2 \quad (10)$$

Warming the resulting clear solution to *ca* 253 K results in a further evolution of dihydrogen with the simultaneous deposition of a white crystalline material containing Ga—H bonds, and it appears that the intermediate products $[MeOGaH_2]_n$ and $(MeO)_2BH$ are subject to relatively slow methanolysis. Even at room temperature the reaction is slow to proceed to completion, with the ultimate formation of the tris(methoxy) derivatives $[Ga(OMe)_3]_n$ and $B(OMe)_3$ and 9 mol of H_2 for every mol of $HGa(BH_4)_2$ consumed. The volatile boron-containing compounds can be vaporized and so separated from the involatile gallium-containing solid. Following hydrolysis, the two fractions can then be analysed separately for boron (as boric acid) and gallium [as the tris(oxinate)] to afford a second method of chemical analysis of the bis(tetrahydroborate). However, the slowness of the reaction in the final phase makes this a less satisfactory alternative to thermal decomposition; by contrast, no such sluggishness seems to hamper the methanolysis of the titanium(III) compound $Ti(BH_4)_3$, which has been successfully analysed in this way.[40]

Interaction with B_2H_6. Gallium tris(tetrahydroborate), $Ga(BH_4)_3$, has been postulated as an intermediate but never isolated.[41] Since the reaction of diborane with a metal hydride offers a well established route to the corresponding tetrahydroborate,[20] as exemplified by the conversion of hydridoaluminium bis(tetrahydroborate), $[HAl(BH_4)_2]_n$, to aluminium tris(tetrahydroborate), $Al(BH_4)_3$,[8] it seemed appropriate to investigate the response of hydridogallium bis(tetrahydroborate) to diborane. In fact, there is no evidence of any interaction between the neat compounds at either 183 K or ambient temperatures, and the diborane can be recovered unchanged. Attempts to induce the reaction between gallium(III) chloride and lithium tetrahydroborate at lower temperatures by the use of toluene as a solvent for the chloride also failed to give any hint of the tris(tetrahydroborate), even at low temperatures. The ^1H and ^{11}B NMR spectra of the mixture indicated the onset of a reaction at *ca* 213 K, but the only product detectable under these conditions was hydridogallium bis(tetrahydroborate).

EXPERIMENTAL

Synthesis of hydridogallium bis(tetrahydroborate)

Hydridogallium bis(tetrahydroborate) was prepared, purified and manipulated by the procedures described previously.[12] Samples of the compound were characterized initially by chemical analysis. This involved either thermal decomposition[12] or methanolysis followed by quantitative assay of the products [(*q.v.*, see eq. (3), for example]. The purity of samples was tested subsequently by reference to the IR spectra of the vapour or of the solid condensate formed at 77 K,[12] or to the ^1H and ^{11}B NMR spectra of toluene-d_8 solutions of the compound (*q.v.*). The compound was stored *in vacuo* at 77 K in a sealed, pre-conditioned all-glass ampoule equipped with a break-seal,[18,19] until required.

Spectroscopic measurements

IR spectra were recorded using one of three spectrometers, a Perkin–Elmer 580A dispersive instrument (4000–200 cm^{-1}) or a Mattson 'Polaris' or 'Galaxy' FT-IR instrument (4000–400 cm^{-1}). Solid films of volatile materials were presented for spectroscopic analysis by causing the vapour to condense on a CsI window contained in an evacuated glass shroud and maintained at 77 K.

^1H NMR measurements on toluene-d_8 solutions at different temperatures were made at either 200 or 300 MHz with a Bruker Model AM200 or AM300, respectively; ^{11}B measurements were made at 64.17 MHz with the AM200 or 96.25 MHz with the AM300.

Mass spectrometric measurements were made with a VG SPX800 Spectromass quadrupole mass spectrometer at the University of Reading; the ionizing potential was 70 eV, and the system was controlled by a Spectrolab version 4 computer program. The ampoule containing the sample was attached directly to a glass handling line and the vapour allowed to expand into this line and thence into the ionization chamber of the spectrometer.

Chemical studies and reagents

The thermal instability of hydridogallium bis(tetrahydroborate) made it difficult to determine precisely the mass of a sample prior to any chemical reaction. Hence it was necessary normally to treat the sample with a measured quantity of the reagent, judged to be in excess, under the appropriate conditions, then to separate and identify the components of the reaction mixture (typically on the basis of their vibrational and/or NMR spectra), and, where possible, to assay one or more of these components (e.g. by manometric measurements or elemental analysis). The reaction itself was carried out in a pre-conditioned all-glass ampoule equipped with a break-seal, in accordance with the sort of procedures developed for the synthesis and isolation of the parent compound;[18,19] subsequent manipulation and analysis of the reaction mixture could usually be accomplished using a conventional vacuum line having a distillation train and greased ground-glass or, if necessary, greaseless stopcocks as well as ground-glass joints lubricated with Apiezon 'L' grease. The approach is typified by the following examples.

Reaction with NH_3. Hydridogallium bis(tetrahydroborate) (0.115 mmol) reacted with an excess of NH_3 at 193 K. After 2 h, the material volatile at this temperature (unchanged NH_3) was vaporized *in vacuo* to leave a white solid which decomposed slowly at room temperature. Hence it was found that 0.342 mmol of NH_3 had been consumed, corresponding to a stoichiometry $HGa(BH_4)_2 : NH_3 = 1 : 2.97$. The IR spectrum of the white solid supported as a Nujol mull was measured, with the results given in Table 2.

Reaction with HCl. Hydridogallium bis(tetrahydroborate) (0.27 mmol) reacted with an excess of HCl at 193 K. After 2 h, the material volatile at this temperature was removed and shown to consist of H_2 (0.67 mmol) and a mixture of B_2H_6 (0.28 mmol) and unchanged HCl. Of the HCl, 0.55 mmol had been consumed, giving the following proportions: $HGa(BH_4)_2 : HCl : H_2 : B_2H_6 = 1 : 2.04 : 2.48 : 1.04$, in keeping with eq. (9). This left a white involatile residue long-lived at room temperature and identified as gallium 'dichloride', $Ga^+[GaCl_4]^-$, on the evidence of the reacting proportions and the IR spectrum, which showed no absorption attributable to Ga—H bonds but featured a single strong band centred near 370 cm^{-1} signalling the presence of the $[GaCl_4]^-$ anion.[42]

Some reactions were monitored directly by spectroscopic measurements. Thus, the formation of the adduct $Me_3N \cdot Ga(H)(BH_4)_2$ was studied, *inter alia*, by co-condensing the gallane with an excess of Me_3N vapour on a CsI window cooled to 77 K, allowing the window to warm to 193 K, pumping off the excess of base, and then cooling the window back to 77 K before measuring the IR spectrum of the resulting solid film (Table 1). The reaction with CO was most conveniently followed by NMR measurements involving a toluene-d_8 solution of the reagents (*q.v.*).

Carbon monoxide was used as received from the British Oxygen Co. (B.O.C.). The following reagents, from the commercial sources indicated, were also used as received: gallium metal (BDH or Aldrich) and Cl_2 (BDH). The lithium salt $LiBH_4$ (BDH, Cambrian Chemicals or Aldrich) was purified by recrystallization from Et_2O. The reagents NMe_3 (BDH), NH_3 (I.C.I.) and HCl (BDH) were purified before use by fractionation *in vacuo*. Toluene-d_8 (Aldrich) and methanol (BDH, AnalaR) were dried by standard procedures and fractionated *in vacuo* prior to use. Trimethylgallium was prepared by the reaction of gallium metal with dimethylmercury[43] and diborane by the action of sulphuric acid on $NaBH_4$ (BDH).[44] The purity of volatile reagents was checked by tensimetric and/or spectroscopic (IR and NMR) measurements.

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