Gallium Borohydrides: the Synthesis and Properties of $HGa(BH_4)_2$

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Summary The novel, thermally unstable bis(tetrahydroborato) derivative of gallium hydride $HGa(BH_4)_2$ has been synthesised by two routes; it has been characterised by its physical properties, by the stoicheiometry of its thermal decomposition, and by chemical reactions entailing either adduct-formation or ligand-exchange.

SEVERAL reports of gallium tetrahydroborates exist[1] but none of the reported compounds has been well characterised. As part of our studies of the tetrahydroborato-derivatives formed by the heavier Group 3 elements, we have prepared not only the previously reported dimethylgallium compound Me_2GaBH_4, through the interaction of trimethylgallium with diborane,[2] but also the new hydridogallium compound $HGa(BH_4)_2$.

Contrary to previous indications,[1] powdered gallium(III) chloride reacts at −45 °C, in the absence of a solvent, with excess of lithium tetrahydroborate to afford, not the tris(tetrahydroborato) derivative $Ga(BH_4)_3$ to be expected by analogy with the corresponding reaction between aluminium(III) chloride and lithium tetrahydroborate,[3] but a compound with the composition GaB_2H_9 in amounts typically corresponding to 40—50% reaction according to equation (1).

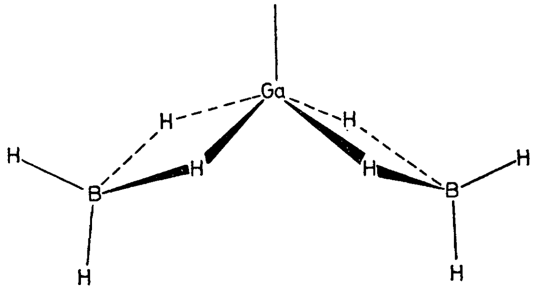
$$\tfrac{1}{2}Ga_2Cl_6 + 3LiBH_4 \longrightarrow GaB_2H_9 + 3LiCl + \tfrac{1}{2}B_2H_6 \quad (1)$$

After careful fractionation *in vacuo* to remove diborane, the product emerges as a thermally unstable, volatile liquid (m.p. *ca.* −70 °C; v.p. at −45 °C *ca.* 10 mmHg). Decomposition of the liquid, which tends to set in at temperatures much above −45 °C, is extremely sensitive to the nature and cleanliness of the container walls, and probably susceptible to auto-catalysis.

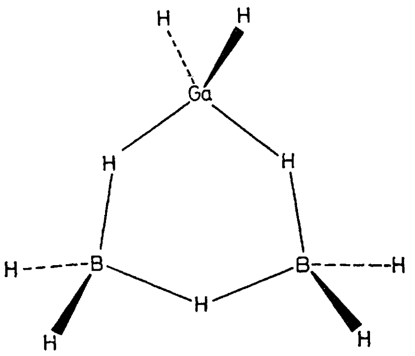
Analysis has been successfully accomplished by quantitative assay of the products formed when the vapour decomposes at room temperature, a reaction found to proceed in accordance with equation (2). Estimates of the vapour

$$GaB_2H_9 \longrightarrow Ga + \tfrac{3}{2}H_2 + B_2H_6 \quad (2)$$

density gave a molecular weight for the compound in the range 95—105 (GaB_2H_9 requires 100·4).



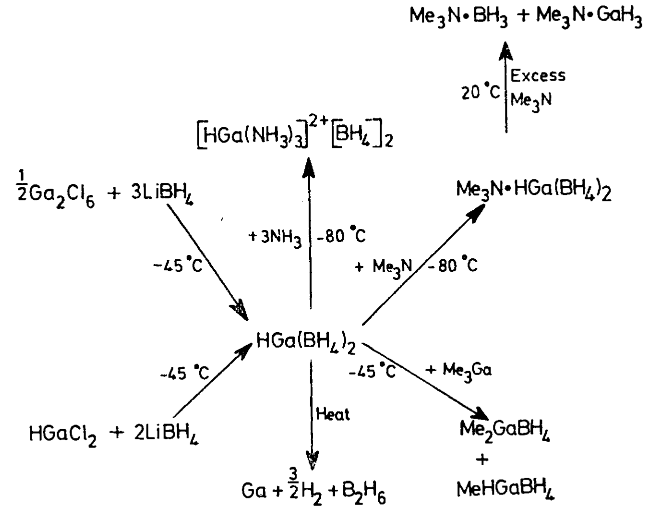
(Ia)



(Ib)

The vibrational spectra imply the presence of a molecular unit common not only to the vapour and solid phases but also to nitrogen or argon matrices held at 10—12 K. Reference to the vibrational spectra of Me_2GaBH_4, $Me_nAl(BH_4)_{3-n}$ ($n = 0$—2)[4,5] and related tetrahydroborato[6—8] and gallium hydride[9] species gives grounds for attributing each of the principal spectral features of the new compound to one or more of the skeletal fundamentals of either the di-hydrogen bridged $Ga(\mu\text{-}H)_2BH_2$ or the Ga–H unit. The partially resolved rotational structure of several bands in the vapour-phase spectrum[10] and the effects of deuteriation, together with the number of distinct i.r. absorptions brought to light with the superior definition allowed by matrix isolation, are consistent with a molecular structure possessing C_{2v} symmetry. Such evidence, taken with the absence of the sort of spectral pattern normally associated with the $-BH_2-H-BH_2-$ unit,[5,11] argues in favour of a structure containing five-co-ordinate gallium with a single terminal Ga–H bond and two doubly bridged BH_4 groups (Ia) and against a structure derived from the topologically most plausible form[12] of the hypothetical borane B_3H_9 (Ib).

Structure (Ia) finds support in the ^1H n.m.r. spectrum of the compound dissolved in $C_6D_5CD_3$ at 0 °C; this comprised (a) a broad 1:1:1:1 quartet centred at τ 8·7, and with $^4J(^{11}B\text{–}H)$ 88 Hz, arising from the protons of the BH_4 groups,[7,8,13] and (b) a broad resonance about one-eighth the intensity of this quartet at *ca.* τ 4·8 most plausibly assigned to a unique proton associated exclusively with the gallium atom.[9] Although some decomposition was unavoidable, it is noteworthy that, as with the methyl derivatives Me_2MBH_4 (M = Al or Ga),[5] lowering the temperature brought about the reversible collapse of the BH_4 multiplet; the low-field resonance simultaneously grew sharper and relatively more intense.



SCHEME. The formation and some reactions of $HGa(BH_4)_2$.

That the new compound should be formulated as $HGa(BH_4)_2$ is also implied by its ready formation, typically in about 50% yield, in the metathetical reaction between hydridogallium dichloride[14] and lithium tetrahydroborate, again in the absence of a solvent, at −45 °C [reaction (3)].

$$HGaCl_2 + 2LiBH_4 \longrightarrow HGa(BH_4)_2 + 2LiCl \qquad (3)$$

The similarity between the new compound and tris(tetrahydroborato)alane, apparent in several physical properties, extends also to the chemical behaviour of the two species. Not only is the gallium compound extremely susceptible to aerial oxidation and to hydrolysis, it suffers methanolysis with near-quantitative conversion into trimethyl borate, and reacts at low temperatures to form adducts with nitrogen-bases and to undergo ligand-exchange with trimethylgallium, as indicated in the Scheme. The uptake of 3 mol. equiv. of ammonia merits particular attention in that it gives rise to a white solid relatively long-lived at room temperature and which evidently contains the novel hydridogallium cation $[HGa(NH_3)_3]^{2+}$.

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