# 2-Galla-*arachno*-tetraborane(10), $H_2GaB_3H_8$: Synthesis, Properties and Structure of the Gaseous Molecule as determined by Electron Diffraction†

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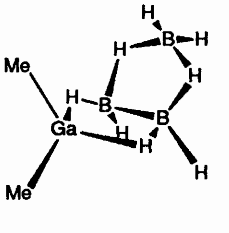
The novel mixed hydride 2-galla-*arachno*-tetraborane(10), $H_2GaB_3H_8$, has been synthesised by metathesis between neat monochlorogallane and tetra-*n*-butylammonium octahydrotriborate, $[Bu^n{}_4N]^+[B_3H_8]^-$, at temperatures near 243 K. The compound has been characterised by chemical analysis, by its vibrational, $^1H$ and $^{11}B$ NMR, and mass spectra, and by its reaction with ammonia. Electron-diffraction measurements, carried out on the vapour at *ca.* 273 K, are wholly consistent with the tetraborane(10)-like structure of the molecule with gallium replacing boron at the 2 position. The $r_a$ structure features the following parameters: $r$[Ga–B(1,3)] 231.2(0.1), $r$[B(1,3)–B(4)] 185.2(1.3), $r(Ga–H_t)$ 144.2(1.1), $r(Ga–H_b)$ 176.0(2.8) and $r(B–H_b)$ 126.4(0.7) pm; and 114.4(0.6)° for the dihedral angle between the planes GaB(1)B(3) and B(1)B(3)B(4) ($H_t$ = terminal H atom; $H_b$ = bridging H atom). The NMR spectra of solutions imply non-fluxional behaviour of the molecule in the temperature range 193–283 K. Gallatetraborane(10) decomposes at ambient temperatures to give either metallic gallium, dihydrogen and tetraborane(10) or a solid with the composition $GaB_2$, dihydrogen and diborane according to whether it is in the condensed or gaseous phase, respectively.

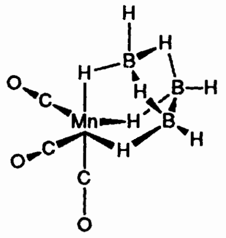
The recent synthesis of the simple base-free gallium hydrides $HGa(BH_4)_2$,[1,2] $Ga_2H_6$[3,4] and $H_2GaBH_4$[5,6] raises the question of whether GaH or $GaH_2$ moieties can also be successfully incorporated into polyborane or carborane clusters. Precedents are sparse but the compounds $Me_2GaB_3H_8$,[7,8] $Me_2GaC_2B_4H_7$,[9] $MeGaC_2B_4H_6$[10] and Tl[*commo*-3,3′-Ga(1,2-$C_2B_9H_{11})_2$][11] do provide examples of gallium-substituted *arachno*, *nido* or *closo* frameworks embodying 4–12 vertices. However, the inherent frailty of Ga–H bonds militates against high-energy methods of synthesis, requiring instead the sort of facile reaction that can be engineered at low temperatures so as to outstrip decomposition. Foremost among the precursors to gallane[3,4] and its derivatives[5,6] is monochlorogallane, $[H_2GaCl]_2$, a compound conveniently prepared by the reaction of gallium(III) chloride with an excess of trimethylsilane and which we have now characterised in some detail.[6,12,13] This has been shown to undergo metathesis with a salt of the nucleophile $GaH_4^-$[3,4] or $BH_4^-$,[5,6] typically under solvent-free conditions and at temperatures of 240–250 K, to give the elusive binary hydride, $[GaH_3]_n$, or the mixed hydride gallaborane, $[GaBH_6]_n$, respectively, in accordance with equation (1) (X = $GaH_4$ or $BH_4$).

$$\tfrac{1}{2}[H_2GaCl]_2 + Li^+X^- \longrightarrow \tfrac{1}{n}[H_2GaX]_n + Li^+Cl^- \quad (1)$$

Accordingly we were prompted to investigate whether the octahydrotriborate anion, $B_3H_8^-$, also displaces chloride from monochlorogallane. The most likely product of such a reaction is the *arachno*-gallatetraborane(10), $H_2Ga(\mu\text{-}H)_2B_3H_6$, featuring bidentate ligation of the $B_3H_8$ group and with a structure analogous to that of $Me_2GaB_3H_8$ **1**.[7,8] However, there is also the possibility of forming a four-vertex gallatetraborane $H_2Ga(\mu\text{-}H)_3B_3H_5$ featuring five-fold co-ordination of the gallium and tridentate ligation of the $B_3H_8$ group, and with a structure analogous to that of $[Mn(B_3H_8)(CO)_3]$ **2**.[14] Yet another option involves rearrangement to give a tetraborane(10) derivative with gallium replacing boron at a hinge (1) rather than an apical (2) site.



**1**



**2**

Indeed, we find that monochlorogallane reacts smoothly with freshly recrystallised tetra-*n*-butylammonium octahydrotriborate *in vacuo* at *ca.* 243 K to give a volatile product shown to be 2-galla-*arachno*-tetraborane(10), $H_2GaB_3H_8$. As reported briefly in a preliminary communication,[15] the gallane has been authenticated by chemical analysis and by its vibrational, $^1H$ and $^{11}B$ NMR, and mass spectra; the structure of the gaseous molecule has also been determined on the basis of the electron-diffraction pattern of the vapour. The present paper is concerned primarily with the synthesis, physical properties and decomposition of the compound, as well as its reaction with ammonia; a fuller account of its chemistry, now being studied, will be presented separately.[16] Our findings have already stimulated theoretical enquiries in which *ab initio* molecular orbital methods have sought to explore the equilibrium geometries open to the $GaB_3H_{10}$ molecule.[17] In a practical context, too, the gallane is noteworthy as a means of vapour transport of gallium at low temperatures (< 253 K) and also as a possible precursor to solid gallium-bearing films.[18]

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† *Non-SI unit employed:* mmHg ≈ 133 Pa.

## Results and Discussion

(*i*) *Synthesis of 2-Galla-*arachno*-tetraborane*(10).—2-Galla-*arachno*-tetraborane(10) has been synthesised by the reaction *in vacuo* between monochlorogallane, $[H_2GaCl]_2$, and powdered, freshly recrystallised tetra-*n*-butylammonium octahydrotriborate, $[Bu^n{}_4N]^+[B_3H_8]^-$, under solvent-free conditions. After co-condensation of the monochlorogallane with the octahydrotriborate, the reaction is initiated by allowing the mixture to warm to *ca.* 243 K. On the evidence of chemical and spectroscopic analysis, the main volatile product is 2-gallatetraborane(10), $H_2GaB_3H_8$. The reaction can be made to proceed with *ca.* 90% conversion of monochlorogallane into gallatetraborane in accordance with equation (2).

$$\tfrac{1}{2}[H_2GaCl]_2 + [Bu^n{}_4N]^+[B_3H_8]^- \xrightarrow[\text{neat reagents}]{243\text{–}268\ \mathrm{K}} H_2GaB_3H_8 + [Bu^n{}_4N]^+Cl^- \quad (2)$$

As with the synthesis of gallane,[3,4] scrupulous attention to practical technique is necessary for the successful synthesis and manipulation of gallatetraborane. It is imperative *rigorously* to exclude moisture, grease, or other contaminants. Operations must be carried out at pressures $<10^{-4}$ mmHg in *all-glass* apparatus designed to give short distillation paths and which has been preconditioned by heating under continuous pumping.[4] Moreover, the thermal frailty of the compound requires that all glassware to which it has access be maintained at temperatures <283 K to avoid decomposition (signalled typically by the appearance of grey deposits on the walls of the apparatus and the formation of diborane). Unlike gallane,[4] however, gaseous gallatetraborane will survive the passage through a greaseless (Teflon) valve provided that steps are taken to precondition the surfaces by preliminary exposure to a portion of the vapour which is subsequently pumped to waste. Further practical details are given in the Experimental section and ref. 4.

Gallatetraborane melts at *ca.* 178 K to give a colourless mobile liquid which, on the evidence of its rate of vaporisation, has a vapour pressure of *ca.* 1 mmHg at 210 K. Although the compound is thermally fragile, it is considerably more robust than either gallane[3,4] or gallaborane, $[GaBH_6]_n$.[5,6] Samples of the material in the condensed phase (liquid or solution) decompose rapidly at temperatures in excess of 283 K; at room temperature and a pressure of *ca.* 100 mmHg the vapour has a half-life of the order of 30 min.

(*ii*) *Decomposition and Chemical Analysis.*—Gallatetraborane(10) vapour decomposes at ambient temperatures in accordance with equation (3), as attested by quantitative assay

$$H_2GaB_3H_8 \longrightarrow GaB_2 + \tfrac{1}{2}B_2H_6 + \tfrac{7}{2}H_2 \quad (3)$$

of the products, and this provides a satisfactory means of analysis of the gallane. The involatile solid residue forms a brown film on the walls of the container; while it answers to the composition $GaB_2$, we have no definite evidence that it is a single homogeneous product. Although the aluminium boride $AlB_2$ is known, the literature does not appear to contain any reference to a gallium analogue,[19a] and, beyond the reported preparation of $GaB_{12}$,[19b] gallium borides of any description are virtually uncharted.

A potential complication arises from the existence of more than one decomposition channel. As the local concentration of the gallane increases, for example in the condensed phases, bimolecular processes compete with the unimolecular one which is presumed to be the dominant primary step at low pressures affording the products detailed above. Thus, NMR measurements reveal that the decomposition of gallatetraborane(10) in $[^2H_8]$toluene solution gives metallic gallium, dihydrogen and tetraborane(10) as the principal products, as in equation (4), although these are also accompanied by small amounts of unidentified boranes generated by secondary reactions.

$$4H_2GaB_3H_8 \longrightarrow 4Ga + 3B_4H_{10} + 5H_2 \quad (4)$$

(*iii*) *Mass Spectrum.*—The mass spectrum of the gallane vapour includes a weak peak at $m/z$ = 114 corresponding to the molecular ion $^{71}Ga^{11}B_3H_{10}{}^+$. That there is no sign of any feature at higher mass number suggests that the compound vaporises as the monomeric molecule $GaB_3H_{10}$. There is a family of peaks at $m/z$ = 107–114 but the intensities show that most of the components originate only partially in the molecular ions $^xGa^yB_3H_{10}{}^+$ ($x$ = 69 or 71, $y$ = 10 or 11), the contributions of which are augmented by the products of hydrogen loss, $GaB_3H_z{}^+$ ($z$ = 6–9). Otherwise the fragmentation pattern is dominated by successive loss of $BH_3$ giving $GaB_2H_m{}^+$, $GaBH_n{}^+$, and, ultimately, $GaH^+$ and $Ga^+$ as the most prominent ions together with an array of borane fragments containing one, two or three boron atoms.

(*iv*) *Vibrational Spectra.*—Infrared spectra have been measured for gallatetraborane with reference (*a*) to the vapour at a pressure of *ca.* 50 mmHg and ambient temperatures, (*b*) to the vapour species trapped in a solid nitrogen matrix at *ca.* 20 K, and (*c*) to the annealed solid condensate formed on a CsI window at 77 K. The Raman spectrum of the solid condensate formed on a copper block at 77 K has also been measured. The spectra are illustrated in Fig. 1 and the details itemised, with proposed assignments, in Table 1.

That the vibrational spectra are essentially independent of phase and temperature implies the presence of a molecular unit common to the vapour, matrix-isolated, and solid states. Reference to the vibrational spectra of compounds known to contain terminal $GaH_2$ groups (*e.g.* $Ga_2H_6$,[3,4] $H_2GaBH_4$[5,6] and $[H_2GaCl]_2$[12,13]) and dihydrogen-bridged octahydrotriborate groups (*e.g.* $Me_2GaB_3H_8$[7] and $B_4H_{10}$[20]) leaves little doubt that the source of our spectra is a derivative of tetraborane(10) with gallium replacing boron at the 2 position (see Fig. 2). Thus, the strong IR doublet near 2000 cm$^{-1}$ and the intense absorption near 700 cm$^{-1}$ are both characteristic of the $GaH_2$ moiety and, with due allowance for the modes localised mainly in this or in the $GaMe_2$ moiety, the spectra are virtually superimposable on those of $Me_2GaB_3H_8$ under comparable conditions.[7] Hence there is strong circumstantial evidence that the new molecule has the structure shown in Fig. 2 akin to **1**. Such a molecule, $H_2GaB_3H_8$, has $C_s$ symmetry with 36 vibrational fundamentals spanning the a′ and a″ irreducible representations and each of which is active in both IR absorption and Raman scattering. The low symmetry of the molecule, combined with the near-degeneracy of many of the fundamentals, means that there will inevitably be considerable mixing of some local, group modes. In the absence of any information about the Raman spectrum (including polarisation properties) of the compound in a fluid phase, and of experiments involving selective isotopic enrichment (*cf.* $B_4H_{10}$[20]), it is not yet feasible to carry out meaningful normal-coordinate-analysis calculations to arrive at a full vibrational assignment for the new molecule. However, analogies with the vibrational properties of related molecules, notably $Ga_2H_6$,[3,4] $H_2GaBH_4$,[5,6] $[H_2GaCl]_2$,[12,13] $[Me_2NGaH_2]_2$,[21] $B_4H_{10}$[20] and $Me_2GaB_3H_8$,[7] do provide a reasonable basis for the assignments suggested in Table 1. Although the proposals are necessarily simplified and tentative, they are consistent with the more rigorous assignments which have been advanced for molecules like $Ga_2H_6$, $H_2GaBH_4$, $[H_2GaCl]_2$ and $B_4H_{10}$, and are unlikely therefore to be too wide of the mark.

(*v*) *NMR Spectra.*—The $^1H$ and $^{11}B$ NMR spectra of the gallane, which are illustrated in Fig. 3 and itemised in Table 2, provide unequivocal evidence of its identity. The normal $^1H$ spectrum of a $[^2H_8]$toluene solution at 233 K is broad and

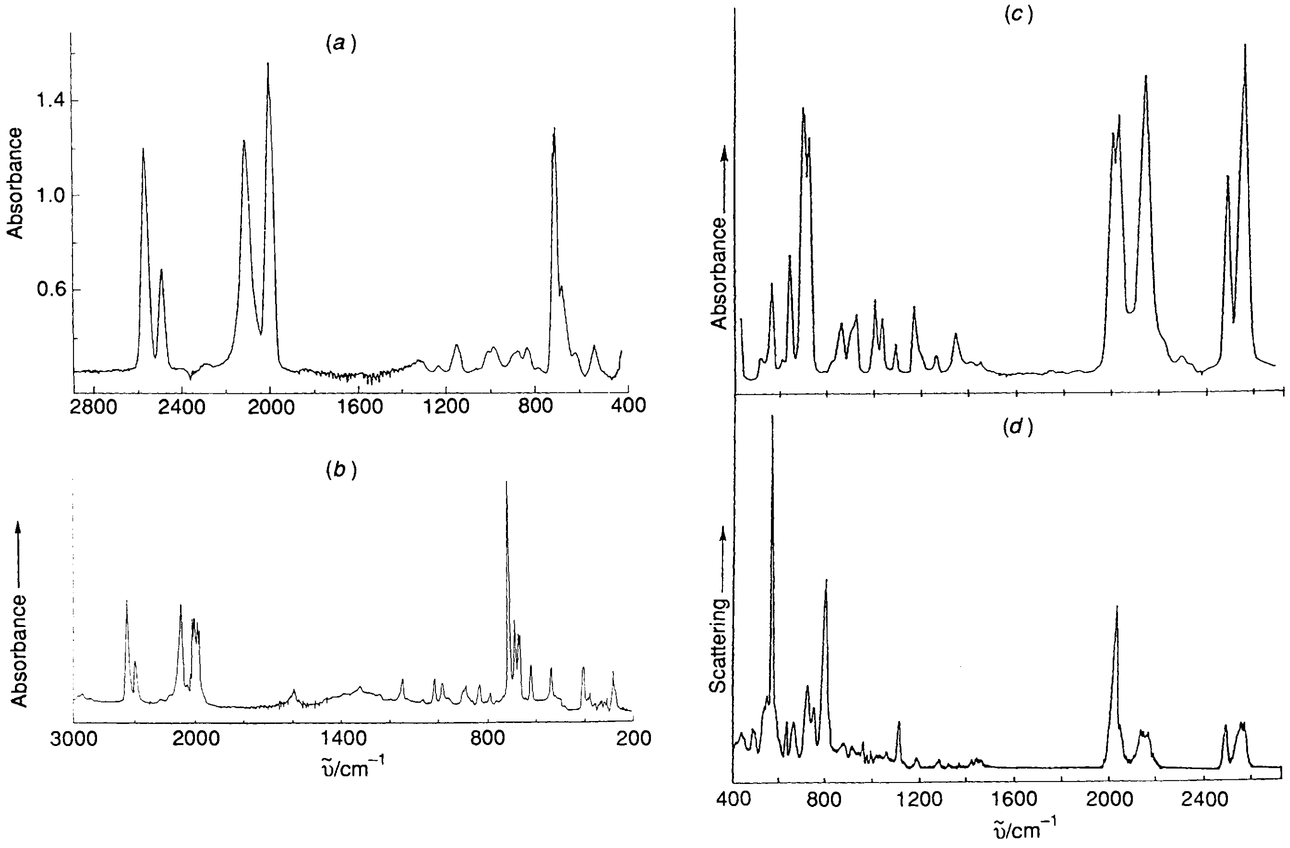

**Fig. 1** Infrared spectra of 2-gallatetraborane(10) vapour, (*a*) at a pressure of *ca.* 50 mmHg and ambient temperatures (sample contained in a cell fitted with CsI windows and having a pathlength of *ca.* 10 cm), (*b*) isolated in a solid dinitrogen matrix at *ca.* 20 K ($N_2$ : $H_2GaB_3H_8$ = *ca.* 200 : 1) and of (*c*) an annealed solid film of 2-gallatetraborane(10) condensed on a CsI window at 77 K. (*d*) Raman spectrum of an annealed solid film of 2-gallatetraborane(10) condensed on a copper block at 77 K

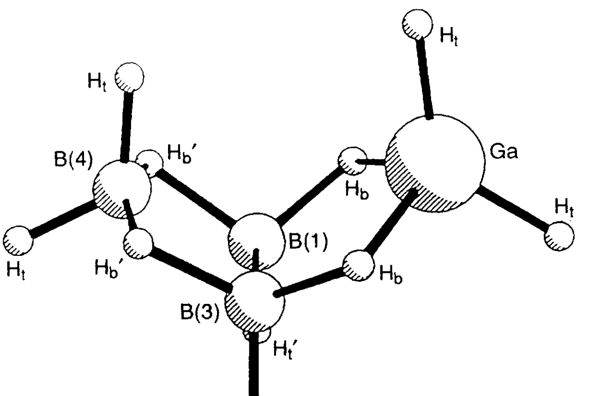

**Fig. 2** Perspective view of the 2-gallatetraborane(10) molecule in the optimum refinement of the electron-diffraction analysis

uninformative, partly as a result of the quadrupolar natures of the Ga and B nuclei, partly through the effects of correlation-time decoupling of the protons attached to boron.[23] The $^{11}B$ spectrum is much more informative [See Fig. 3(*a*)] in revealing the presence of two types of boron in the proportions 2 : 1. The triplet resonance at $\delta(^{11}B)$ −12.9 can be identified with the unique apical boron atom, B(4) in Fig. 2. The two terminal hydrogen atoms attached to B(4) are inequivalent (*exo* and *endo*) and so the $^{11}B$ resonance should take the form of a doublet of doublets; in the event the doublets overlap to give the appearance of a triplet. The resonance centred at $\delta(^{11}B)$ −44.0 is due to the boron atoms B(1) and B(3). Its splitting pattern is unusual but characteristic of the resonances emanating from hinge boron atoms in related molecules, *e.g.* $[Mn(B_3H_8)(CO)_4]$.[22]

The response of the corresponding $^1H$ NMR spectrum to broad-band and selective $^{11}B$ decoupling is shown in Fig. 3(*b*). The high-frequency signal, which is unaffected by $^{11}B$ irradiation, can be linked only to the terminal protons of the $GaH_2$ unit, the AB-type structure of the signal arising from the distinct *exo* and *endo* sites of the protons with respect to the folded $GaB_3$ ring and from the condition that *J*(H–H) is comparable in magnitude with the difference in chemical shift. The corresponding doublet which appears at $\delta_H$ 2.78/2.09 on irradiation of the sample at the resonant frequency of B(4) must originate in the apical $BH_2$ unit. In this case the difference in chemical shifts between the *exo*- and *endo*-protons appears to dwarf *J*(H–H), and no discernible H–H coupling is revealed under the conditions of our experiments. Irradiation at the resonant frequency of B(1) and B(3) sharpens the $^1H$ resonances at $\delta_H$ −0.80 and −1.49 which must therefore be correlated with the two pairs of bridging protons, $H_b$ and $H_b'$ (Fig. 2). It is impossible to deduce with certainty which of these two signals corresponds to $H_b$ and which to $H_b'$. However, the observation that the resonance at higher frequency is slightly broader when the sample is irradiated at the B(1,3) frequency than when it is subject to broad-band irradiation suggests that this originates in the protons $H_b'$ which come under the influence of B(4) as well as B(1,3). Irradiation at the resonant frequency of B(1,3) also results in decoupling of the $^1H$ resonance at $\delta_H$ 1.16 which can be attributed to the terminal protons of B(1) and B(3), $H_t'$. Support for this assignment comes from the relative intensity (2 H) and from the general observation that terminal protons attached to boron resonate at higher frequency than do bridging ones.[24]

Cooling the sample from 233 to 193 K causes the AB system of the $GaH_2$ unit in the $^1H$ NMR spectrum to sharpen but otherwise has little effect on the $^1H$-$\{^{11}B\}$ or $^{11}B$ NMR spectra.

**Table 1** Vibrational spectral data (cm$^{-1}$) for 2-gallatetraborane(10)[a]

| Solid condensate at 77 K | | IR spectrum of vapour at ambient temperatures | | |
|---|---|---|---|---|
| IR | Raman | Trapped in a nitrogen matrix at 20 K | Gaseous sample[b] | Assignment |
| 2541vs | 2547m | 2558m | 2563s | $\nu$(B–H$_t$) |
| | 2534m | 2550 (sh) | | |
| 2467ms | 2472m | 2488mw | 2486m | |
| | 2137m | | | $\nu$(B–H$_b$) |
| 2117s | 2124m | 2113m | | |
| | 2107m | | 2107s | |
| | | 2063w | | |
| | | 2036w | | |
| 2008s | 2010 (sh) | 2018m | 2007mw | $\nu_{asym}$(Ga–H$_t$) |
| | | 2004m | 1996vs | |
| | | 1998m | | |
| 1986s | 1984s | 1987m | 1989s | $\nu_{sym}$(Ga–H$_t$) |
| | | 1981m | 1983 (sh) | |
| 1314w | | 1320w | 1327vw | $\nu$(Ga–H$_b$) + out-of-phase $\delta$(BH) |
| 1231w | | 1240vw | 1235vw | |
| 1140w | | 1144w | 1153w | $\delta$(BH$_2$) |
| 1061w | 1063w | | | in-phase BH wag |
| 1007w | | 1012w | 1011w | BH$_2$ wag |
| 976w | | 980w | 984w | BH$_2$ twisting or rocking |
| 892w | 911w | 888w | 879w | |
| 834w | | 832w | 834w | |
| | | | 789vw | Bridge deformation |
| | 743s | | | |
| 701s | 704m | 712vs | 719<br>713<br>706 s[c] | $\delta$(GaH$_2$) |
| 676s | 678m | 685m<br>669m<br>664m | 678mw | GaH$_2$ wagging |
| 616m | 618w | 619mw | 620w | GaH$_2$ rocking |
| | 590w | | | Skeletal deformation? |
| 536mw | 523vs | 535mw | 529w | $\nu$(Ga–B) |
| | 502m | | | |
| 492vw | 492 (sh) | | | Skeletal deformation modes |
| 395m | 396w | 405mw | | |
| | | 375w | | |
| 270ms | 268s | 280mw | | |

[a] Abbreviations: s = strong, m = medium, w = weak, v = very, sh = shoulder, H$_t$ = terminal H atom, H$_b$ = bridging H atom. [b] Pressure *ca.* 30 mmHg in a cell with a pathlength of *ca.* 10 cm. [c] Partially resolved rotational branches.

**Table 2** Proton and $^{11}$B NMR parameters for 2-gallatetraborane(10) in [$^2$H$_8$]toluene solution at 233 K

$^1$H

| Atom[a] | Chemical shift, $\delta_H$ | Coupling constant, $^2J$(H–H)/Hz |
|---|---|---|
| H$_t$ of GaH$_2$ unit | 4.02, 4.56[b] | 48 |
| H$_b$ (or H$_b$′) | −1.49 | |
| H$_b$′ (or H$_b$) | −0.80 | |
| H$_t$′ | 1.16 | |
| H$_t$ of B(4)H$_2$ unit | 2.09, 2.78 | <40 |

$^{11}$B

| Atom[a] | Chemical shift, $\delta_B$ | Coupling constant, $^1J$(B–H)/Hz |
|---|---|---|
| B(1,3) | −44.0[c] | 69 |
| B(4) | −12.9[d] | *ca.* 125 |

[a] Labelling of atoms as in Fig. 2. [b] AB quartet. [c] Triplet of unusual form (*cf.* ref. 22). [d] Triplet due to overlapping of two doublets (see text).

Warming the sample to 273 K evokes little response from the $^1$H-{$^{11}$B} spectrum, apart from a broadening of the GaH$_2$ resonance. The $^{11}$B resonances broaden and lose their structure, a change suggesting that some proton exchange is now occurring. With the sample at temperatures above 283 K, the $^{11}$B NMR spectrum discloses the appearance and growth of a triplet centred at $\delta$($^{11}$B) −7.4 and a doublet centred at $\delta$($^{11}$B) −42.3 attributable, respectively, to B(2,4) and B(1,3) of tetraborane(10).[25] In addition, there are some weaker features which develop at this stage and signal the formation of other boranes as yet unidentified. The $^1$H NMR spectrum shows the simultaneous growth of a sharp resonance at $\delta_H$ 4.6 associated with dihydrogen[25] at the expense of the GaH$_2$ resonance. Inspection of the NMR cell at this stage shows the walls to be coated with a grey metallic film presumed to be elemental gallium.

That the NMR spectra are essentially independent of temperature in the range 193–283 K argues that fluxional processes open to the H$_2$GaB$_3$H$_8$ molecule are slow on the NMR timescale. The results naturally invite comparisons with those reported for other metallotetraboranes and related systems.[7,22,26,27] The $^{11}$B chemical shifts for the static metallotetraboranes vary only slightly with the nature of the metallo fragment, and in this respect 2-gallatetraborane is unremarkable. Rather is it the fluxional behaviour of these systems which is more remarkable. The behaviour appears to run the whole gamut from the essentially static behaviour of [Mn(B$_3$H$_8$)(CO)$_4$][22] to the rapid exchange of boron and hydrogen atoms in [Be(B$_3$H$_8$)(C$_5$H$_5$)][27a] and M$^+$[B$_3$H$_8$]$^-$ salts,[27b] even at very

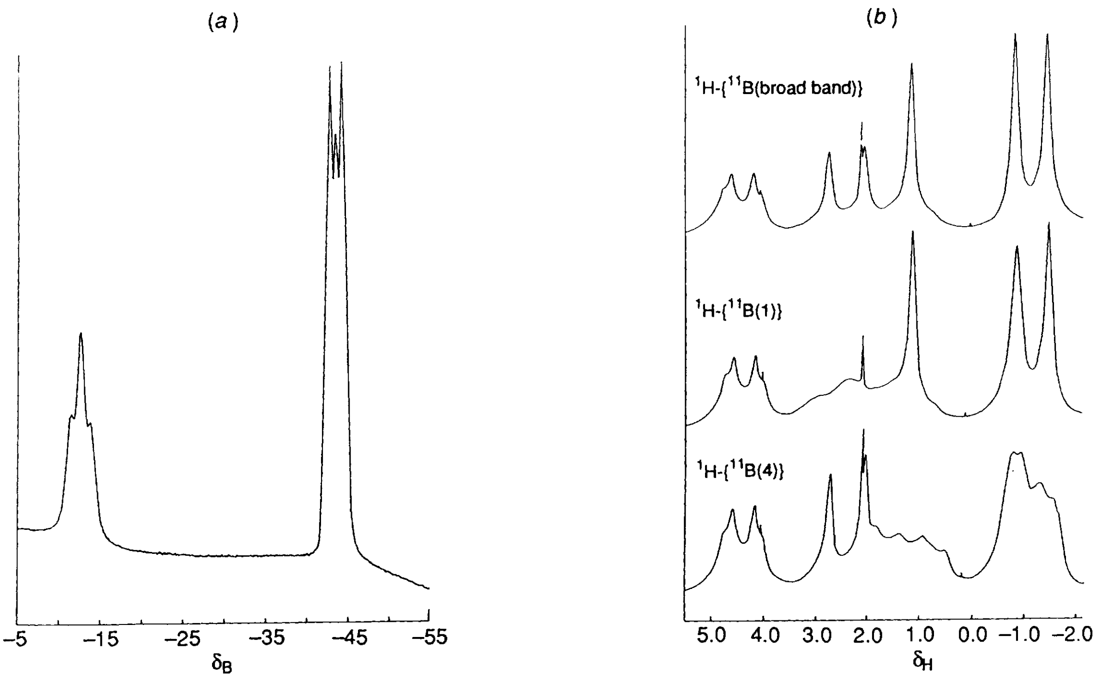

**Fig. 3** (*a*) Boron-11 NMR spectrum of a [$^2H_8$]toluene solution of 2-gallatetraborane(10) at 233 K (measured at 96.25 MHz). (*b*) Proton NMR spectrum of the same solution at 233 K (measured at 300 MHz) showing the effects of broad-band and selective $^{11}B$ decoupling. The sharp resonance in the $^1H$ spectra near $\delta_H$ 2.0 is due to the solvent

low temperatures. The factors which determine whether such compounds are fluxional or not are but poorly understood, and it seems likely in any case that traces of impurity in the sample may have a profound effect on the exchange rates and mechanisms.

(*vi*) *Structure of Gaseous* 2-*Gallatetraborane*(10) *as Determined by Electron Diffraction.*—Using the all-glass inlet system specially constructed for studies of gallane and related species[4] and maintained at a temperature near 273 K, we have succeeded in measuring the electron-diffraction pattern of the gallatetraborane vapour. The measurements have been made at two camera distances, *viz. ca.* 200 and 260 mm, at an electron wavelength of 5.67 pm to give results spanning the range 20–208 $nm^{-1}$ in the scattering variable *s*. As with similar studies of other volatile gallane[1,4–6,12,21,28] or tetrahydroborate[29] derivatives, the main obstacle to success is the propensity of the strongly reducing vapour to react with the emulsion of the photographic plates.

In the light of the evidence adduced by the vibrational and NMR spectra it seemed appropriate to adopt a structural model akin to that of $Me_2GaB_3H_8$[8] with the $GaH_2$ unit replacing $BH_2$ in the 2 position of $B_4H_{10}$[30] to give a molecule conforming overall to $C_s$ symmetry (see Fig. 2). A full specification of such a model requires the 14 independent geometrical parameters listed in Table 3. Local $C_{2v}$ symmetry has been assumed for both the apical $(H_t)_2Ga(H_b)_2$ and $(H_t)_2B(H_b)_2$ units ($H_t$ = terminal hydrogen atom, $H_b$ = bridging hydrogen atom).

The experimental molecular scattering curves for the two camera distances are shown in Fig. 4. Combination of the scaled experimental data sets yields the radial-distribution curve reproduced in Fig. 5 which exhibits no more than four well developed peaks. The broad feature centred near 130 pm plainly correlates with the scattering from all the B–$H_b$ and B–$H_t$ atom pairs. The feature at *ca.* 180 pm is also due to a blend of scattering, this time from the B(1)–B(3), Ga–$H_b$ and B(1)–B(4) atom pairs. Scattering from the Ga–B(1,3) atom pairs is responsible for the peak near 230 pm, whereas the broad feature near 320 pm reflects mainly the scattering of Ga ··· B(4) augmented by contributions from other non-bonded atom pairs, *viz.* Ga ··· H, B ··· H and H ··· H. The comparative simplicity of the radial-distribution curve, its obvious kinship to those of $B_4H_{10}$[30] and $Me_2GaB_3H_8$,[8] and the absence of any major contribution from long-range atom pairs all tend to endorse $H_2GaB_3H_8$ as the predominant, if not the sole, vapour species, and to rule out the possibility that larger molecules are present in appreciable concentrations. Tridentate ligation of the octahydrotriborate ligand, as found in $[Mn(B_3H_8)(CO)_3]$ 2,[14] would be expected to give rather different results, with significantly more scattering arising from pairs of atoms separated by *ca.* 180 (corresponding to Ga–$H_b$ bonds) and 230–250 pm (corresponding to Ga–B contacts) and less from pairs separated by *ca.* 320 pm.

Our relatively meagre knowledge of the vibrational properties characterising gallatetraborane and related molecules makes it impossible to gauge the magnitudes of 'shrinkage' corrections or to estimate on this basis any of the amplitudes of vibration. As may be expected, therefore, the analysis has been hampered by the marked correlation between several of the structural parameters, this being implicit in the composite nature of most of the peaks in the radial-distribution curve; for example, the B(1)–B(3), B(1)–B(4) and Ga–$H_b$ distances are all strongly subject to such correlation. The problems are exacerbated, moreover, by the degree to which the molecular scattering is dominated by the heavier atoms, making it particularly difficult to locate precisely the positions of the hydrogen atoms. It has been necessary therefore to assign fixed values to most of the parameters defining the structure of the $B_3H_8$ group, these being based on the corresponding dimensions of $B_4H_{10}$[30] and certified, where possible, by *R*-factor plots. The structure predicated for the molecule has been constrained by the following assumptions. (*a*) The B(1)–B(3) distance has been fixed at 174 pm on the basis of an *R*-factor plot, although values in the range 170–178 pm could be accommodated almost equally well. (*b*) The $H_t$–Ga–$H_t$ and $H_t$–B–$H_t$ bond angles have both been fixed at 115° on the basis of *R*-factor plots, but any value in the range 110–120° is found to be acceptable. (*c*) The mean B–$H_t$ distance has been fixed at 121 pm on the basis of an *R*-factor plot. (*d*) The difference between *r*[B(4)–$H_t$] and *r*[B(1,3)–$H_t$], $\Delta_1$, has been fixed at 2.8 pm in line with the dimensions of $B_4H_{10}$.[30] (*e*) The difference between the two *r*[B(1,3)–$H_b$] distances, $\Delta_3$, and between *r*[B(1,3)–$H_b$] and *r*[B(4)–$H_b$], $\Delta_2$,

**Table 3** Molecular parameters deduced from the electron-diffraction pattern of 2-gallatetraborane(10) and compared with the results of *ab initio* calculations

| Parameter | Distance/pm or angle/°<br>Experimental[a] | <br>*Ab initio* calculations[b] | Vibrational amplitude[a]/pm |
|---|---|---|---|
| (*a*) Independent parameters[c] | | | |
| r[B(1)–B(3)] | 174.0[d] | 179.2 | 4.3(2.6) |
| r[B(1,3)–B(4)] | 185.2(1.3) | 190.3 | 4.3[e] |
| r[Ga–B(1,3)] | 231.2(0.1) | 234.2 | 6.8(0.5) |
| Dihedral angle, $\alpha$[f] | 114.4(0.6) | 117.1 | — |
| r(B–H$_t$)$_{mean}$ | 121.0[d] | 118.8 | — |
| $\Delta_1$ = r[B(4)–H$_t$] – r[B(1,3)–H$_t$] | 2.8[d] | +0.4 | — |
| r(B–H$_b$)$_{mean}$ | 126.4(0.7) | 131.1 | — |
| $\Delta_2$ = r[B(4)–H$_b$′] – $\frac{1}{2}${r[B(1,3)–H$_b$′] + r[B(1,3)–H$_b$]} | 0.0[d] | 15.7 | — |
| $\Delta_3$ = r[B(1,3)–H$_b$′] – r[B(1,3)–H$_b$] | 0.0[d] | 0.2 | — |
| r(Ga–H$_b$) | 176.0(2.8) | 185.5 | 10.0[d] |
| r(Ga–H$_t$) | 144.2(1.1) | 155.7 | 9.0[d] |
| Angle H$_t$–Ga–H$_t$ | 115.0[d] | 130.2 | — |
| Angle H$_t$–B(4)–H$_t$ | 115.0[d] | 119.9 | — |
| Angle B(3)–B(1)–H$_t$′ | 110.0[d] | 107.4 | — |
| (*b*) Interatomic distances and vibrational amplitudes[c,g] | | | |
| r(Ga–H$_t$) | 144.2(1.1) | 155.7 | 9.0[d] |
| r(Ga–H$_b$) | 176.0(2.8) | 185.5 | 10.0[d] |
| r[Ga–B(1,3)] | 231.2(0.1) | 234.2 | 6.8(0.5) |
| r[Ga ··· B(4)] | 318.7(0.5) | — | 7.1(0.9) |
| r[Ga ··· H$_b$′] | 320.0(0.3) | — | 13.5(1.9) |
| r[Ga ··· H$_t$′] | 310.9(1.2) | — | 13.5[h] |
| r[B(1)–B(3)] | 174.0[d] | 179.2 | 4.3(2.6) |
| r[B(1,3)–B(4)] | 185.2(1.3) | 190.3 | 4.3[e] |
| r[B(1,3)–H$_t$′] | 122.4[d] | 118.6 | 11.4[i] |
| r[B(1,3)–H$_b$] | 126.4(0.7)[j] | 125.8 | 11.4[i] |
| r[B(1,3)–H$_b$′] | | 126.0 | 11.4[i] |
| r[B(4)–H$_b$′] | | 141.6 | 11.4[i] |
| r[B(4)–H$_t$] | 119.6[d] | 119.0 | 11.4(0.8) |

[a] This work. Figures in parentheses are the estimated standard deviations of the last digits. Although allowance has been made for systematic errors in the electron wavelength, nozzle-to-plate distances, *etc*., the values do not budget for systematic errors associated with the assumptions made about the model; to this extent they may underestimate the true margins of error. [b] Calculations use a DZP basis set (ref. 17). [c] Atoms are numbered as in Fig. 2. [d] Fixed. [e] Tied to *u*[B(1)–B(3)]. [f] Dihedral angle between the planes GaB(1)B(3) and B(1)B(3)B(4). [g] Other distances involving non-bonded atom pairs, *viz*. Ga ··· H, B ··· H and H ··· H, were included in the refinement calculations, but are not listed here. [h] Tied to *u*(Ga ··· H$_b$′). [i] Tied to *u*[B(4)–H$_t$]. [j] B–H$_b$ and B–H$_b$′ distances assumed to be equal.

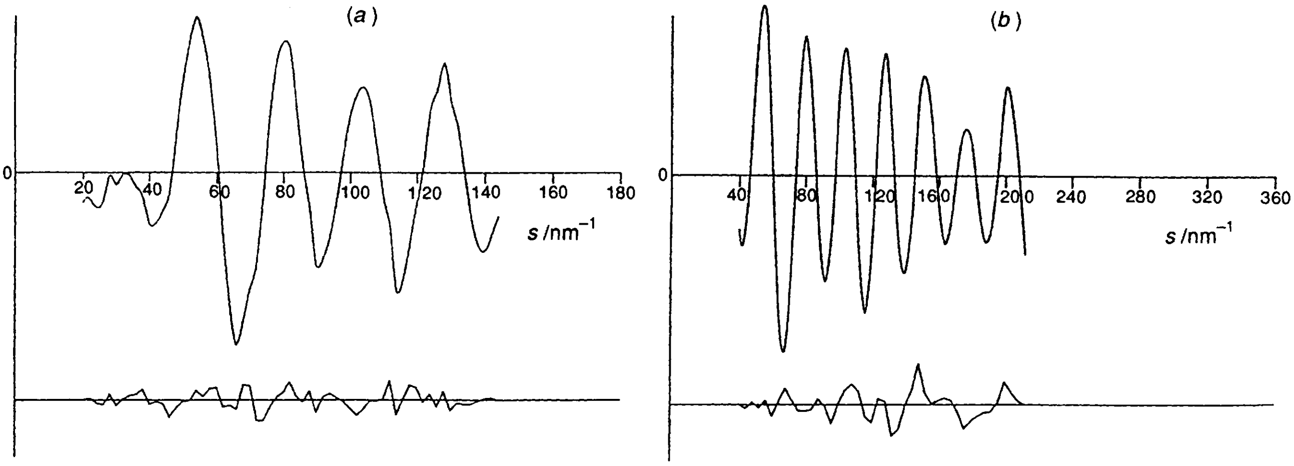

**Fig. 4** Experimental and final difference molecular-scattering intensities for 2-gallatetraborane(10) vapour; nozzle-to-plate distances (*a*) 259.48 and (*b*) 201.08 mm

have both been set at zero following checks by *R*-factor plots. (*f*) The B(3)–B(1)–H(1) angle has been assigned a value of 110°, again on the basis of an *R*-factor plot. In addition, the bridging hydrogen atoms have been taken to be coplanar with the heavy-atom planes GaB(1)B(3) and B(1)B(4)B(3); in fact this condition runs counter to the experience with $B_4H_{10}$,[30] but such is the dearth of information about the finer structural details of gallatetraborane(10) that we have little alternative.

With these provisions and simplifications, molecular-scattering intensities have been calculated and the molecular structure has been successfully refined on the basis of the model described above by full-matrix least-squares analysis.[31] It has been

**Table 4** Analysis of the electron-diffraction pattern of the $H_2GaB_3H_8$ molecule: portion of the least-squares correlation matrix listing off-diagonal elements ( × 100) with absolute values ⩾50%

| α | $r(B–H_b)_{mean}$ | $r(Ga–H_b)$ | $u[B(1)–B(3)]$ | $u[B(4)–H_t]$ | $u(Ga\cdots H_b')$ | $k_1$* | $k_2$* | |
|---|---|---|---|---|---|---|---|---|
| −90 | −50 | −90 | −91 | | | | | $r[B(1,3)–B(4)]$ |
| | | 72 | 74 | | | | | α |
| | | 57 | 51 | | | | | $r(B–H_b)_{mean}$ |
| | | | 95 | | | | | $r(Ga–H_b)$ |
| | | | | −64 | | | | $r(Ga–H_t)$ |
| | | | | | 55 | 69 | 58 | $u[Ga–B(1,3)]$ |
| | | | | | −69 | | | $u[Ga\cdots B(4)]$ |
| | | | | | | 80 | 66 | $u(Ga\cdots H_b')$ |
| | | | | | | | 75 | $k_1$ |

* Scale factor.

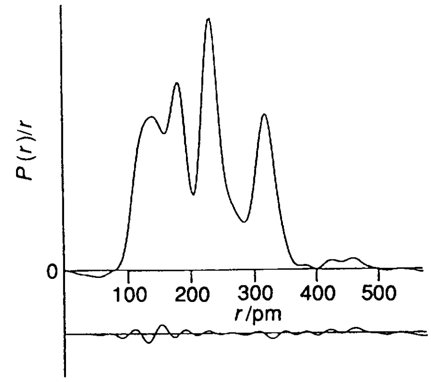

**Fig. 5** Observed and difference radial-distribution curves, $P(r)/r$ against $r$, for 2-gallatetraborane(10) vapour; before Fourier inversion the data were multiplied by $s \cdot \exp[(-0.000\,035\,s^2)/(Z_{Ga}-f_{Ga})(Z_B-f_B)]$

possible in the process to refine simultaneously six out of the 14 geometrical parameters used to specify the model. The calculations have admitted, in addition, the independent refinement of no more than five amplitudes of vibration [relating to the B(1)–B(3), Ga–B(1,3), Ga ··· B(4), B(4)–$H_t$ and Ga ··· $H_b$ vectors]; the remaining amplitudes have been assigned values in line either with these results or with corresponding parameters of the related molecules $B_4H_{10}$,[30] $Me_2GaB_3H_8$[8] and $[H_2GaCl]_2$.[6,12] The most noteworthy aspect of the final least-squares correlation matrix, reproduced in part in Table 4, is the substantial correlation involving $r$[B(1,3)–B(4)], the dihedral angle α, $r$(Ga–$H_b$) and the amplitude $u$[B(1)–B(3)]. The success of the calculations may be assessed by the differences (*a*) between the experimental and simulated radial-distribution curves (Fig. 5) and (*b*) between the experimental and simulated intensities of molecular scattering (Fig. 4). Table 3 lists the values of the geometric and vibrational parameters associated with the optimum refinement which corresponds to a value of $R_G$ = 0.089 ($R_D$ = 0.103). Fig. 2 gives a perspective view of the molecule in its ultimate form.

The detailed analysis of the electron-diffraction pattern thus supports the inferences drawn from the vibrational and NMR spectra, namely that the molecule is indeed 2-gallatetraborane(10) with the octahydrotriborate ligand bound to the $GaH_2$ fragment *via* two of its boron atoms and two single hydrogen bridges. A comparison with the dimensions of tetraborane(10) and some other octahydrotriborate derivatives whose structures have been determined by diffraction techniques is presented in Table 5. There are three aspects which merit some comment.

(*a*) $r$(Ga–B). At 231.2 pm, the Ga–B(1,3) distance is only marginally shorter than the corresponding distance (234.4 pm) in $Me_2GaB_3H_8$,[8] as well as being comparable with the M–B(1,3) distances in related molecules containing a bidentate $B_3H_8$ moiety bound to a medium-sized metal atom M {*e.g.* $[Cu(B_3H_8)(PPh_3)_2]$,[32a] $[NMe_4][Cr(B_3H_8)(CO)_4]$[32b] and $[Mn_2(B_3H_8)(\mu\text{-}Br)(CO)_6]$[32c]}. On the other hand, it is considerably longer than the Ga–B distances of 216–218 pm found in $H_2GaBH_4$,[5,6] $HGa(BH_4)_2$[1,2] and $Me_2GaBH_4$[29a] where the gallium atom is bound to boron through a *double* hydrogen bridge. It is also appreciably longer than that in the *closo*-gallacarborane $MeGaB_4C_2H_6$[10] wherein direct gallium–boron bonding must be invoked with Ga–B distances (211 and 222 pm) close to the sum of the tetrahedral covalent radii (*ca.* 214 pm).

(*b*) $r$(Ga–$H_b$). The Ga–$H_b$ distance of 176.0 pm is considerably shorter than the corresponding distance (198.9 pm) in $Me_2GaB_3H_8$,[8] and more nearly comparable with those in the gallium tetrahydroborates $H_2GaBH_4$ (182.6 pm),[5,6] $HGa(BH_4)_2$ (177.0 pm)[2] and $Me_2GaBH_4$ (179.1 pm),[29a] even allowing for the relatively large uncertainty to which this parameter is usually subject. Such a finding is particularly noteworthy in relation to the dynamics of the $H_2GaB_3H_8$ and $Me_2GaB_3H_8$ molecules. The boron environments of $Me_2GaB_3H_8$ undergo interchange which is rapid on the NMR timescale at temperatures in excess of 250 K and the molecule assumes a wholly rigid structure only at 203 K; by contrast, $H_2GaB_3H_8$ presents an essentially rigid structure throughout this temperature regime. The fluxional behaviour may well hinge on an initial bidentate ⟶ monodentate dissociative process at the $Ga(\mu\text{-}H)_2B_2$ link;[7] the shorter Ga–$H_b$ distance reflects presumably a stronger bond in $H_2GaB_3H_8$ than in $Me_2GaB_3H_8$, implying a higher activation barrier to exchange in the former molecule. The difference arises in all probability from the charge distributions in the two molecules, with the gallium atom assuming a more positive charge in $Me_2GaB_3H_8$ than in $H_2GaB_3H_8$.

(*c*) $r$(Ga–$H_t$). The Ga–$H_t$ distance is, at 144.2 pm, nominally one of the shortest to be measured so far for a gallium hydride (*cf.* $Ga_2H_6$ 151.9,[4] $H_2GaBH_4$ 158.6,[5,6] $[H_2GaCl]_2$ 155.9,[6,12] $Me_3N{\cdot}GaH_3$ 149.7[28b] and $[Me_2NGaH_2]_2$ 148.7 pm[21]). However, the vibrational spectra reveal that the ν(Ga–$H_t$) modes all occur at much the same energy (*ca.* 1980 $cm^{-1}$) in uncoordinated gallanes and 130–160 $cm^{-1}$ lower in energy in gallane complexes (*e.g.* $H_3P{\cdot}GaH_3$,[4] $Me_3N{\cdot}GaH_3$[33a] and $Me_3P{\cdot}GaH_3$[33b]). The two sets of findings are difficult to reconcile, particularly as force constants, and hence vibrational wavenumbers, tend to be more sensitive to changes in bonding than do bond distances. There is no obvious reason for any breakdown of the correlation between vibrational wavenumber and bond strength in the gallium hydrides, and the eccentric variation of the measured Ga–$H_t$ distances may reflect underestimated errors in the determination of these parameters. Such errors are likely to arise from the paucity of reliable *independent* information about the geometric and vibrational properties of the molecules. Research now under way[16] is aimed at reducing the limits of uncertainty affecting the results derived exclusively from electron-diffraction measurements. Preliminary investigations suggest that the Ga–$H_t$ distance given here for

**Table 5** Comparison of the molecular parameters of 2-gallatetraborane(10) with those of tetraborane(10) and other octahydrotriborate derivatives

| | | Distance/pm or angle/°[b] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Phase/ method[a] | B(1)–B(3) | B(1,3)–B(4) | B(1,3)–$H_b'$ | B(4)–$H_b'$ | B–$H_t$ | M–$H_b$ | B(1,3)–$H_b$ | M–B(1,3) | Dihedral angle, $\alpha$ | Ref. |
| $H_2GaB_3H_8$ | Vapour/ED | 174.0[c] | 185.2(1.3) | 126.4(0.7) | 126.4(0.7) | 119.6–122.4[c] | 176.0(2.8) | 126.4(0.7) | 231.2(0.1) | 114.4(0.6) | This work |
| $Me_2GaB_3H_8$ | Vapour/ED | 170.5[c] | 185.6[c] | 127.7(1.7) | 144.7(1.7) | 118–121(1) | 198.9(4.8) | 127.7(1.7) | 234.4(0.9) | 117.1(0.9) | 8 |
| $Me_2AlB_3H_8$ | Vapour/ED | 170.5[c] | 185.6[c] | 127.0(2.4) | 144.0(2.4) | 122–125(2) | 190.6(4.1) | 127.0(2.4) | 230.7(0.8) | 117.6(0.7) | 8 |
| $B_4H_{10}$ | Vapour/ED | 170.5(1.2) | 185.6(0.4) | 131.5(0.9) | 148.4(0.9) | 119.4(0.7),<br>122.1(1.4) | 148.4(0.9) | 131.5(0.9) | 185.6(0.4) | 117.1(0.7) | 30 |
| $Be(B_3H_8)_2$ | Solid/XRD | 176.6(0.3) | 183.4(0.4) | 105–121(2) | 130–138(2) | 105–114(2) | 150(2) | 117(2) | 197.4(0.7) | 115.0(2.0) | 32*d* |
| $[Cu(B_3H_8)(PPh_3)_2]$ | Solid/XRD | 176(1) | 182(2) | 115(9) | 152(9) | 100–130 | 185(5) | 121(6) | 230(1) | 118(2) | 32*a* |
| $[NMe_4][Cr(B_3H_8)(CO)_4]$ | Solid/XRD | 178(1) | 182(1) | 115(7) | 143(7) | 107–122 | 178(6) | 129(6) | 243(2) | 119(2) | 32*b* |
| $[Mn_2(B_3H_8)(\mu\text{-}Br)(CO)_6]$ | Solid/XRD | 171(2) | 185(2) | 112–117 | 141–150 | 126–150 | 150–176 | 89–115 | 230–236(2) | 127(3) | 32*c* |
| $[Nb(B_3H_8)(C_5H_5)_2]$ | Solid/XRD | 172.7(0.8) | 179(1)<br>180.4(0.9) | 108.8(5.8) | 143.8(2.7) | — | 182.0(4.6) | 127.9(4.6) | 255.5(0.6)<br>256.6(0.6) | 124.9 | 32*e* |

[a] ED = Electron diffraction; XRD = X-ray diffraction. [b] Figures in parentheses are the estimated standard deviations of the last digits. The labelling of atoms is in accordance with Fig. 2: M = metal atom; $H_t$ = terminal H atom; $H_b$ = bridging H atom; $\alpha$ = angle between the planes MB(1)B(3) and B(1)B(3)B(4). [c] Fixed.

**Table 6** The IR spectral data (cm$^{-1}$) of the solid (as a CsI disc) derived from the reaction of gallatetraborane with ammonia

| Species | | |
|---|---|---|
| Solid[a] | $CsB_3H_8$[b] | Assignment[c] |
| 3250s (br)<br>3177 (sh) | | $\nu$(N–H) |
| 2472s | 2465 | In-phase $\nu_{asym}(BH_2)$ of B(2),B(3) |
| 2423s | 2415 | In-phase $\nu_{sym}(BH_2)$ of B(2),B(3) + $\nu_{sym}(BH_2)$ of B(1) |
| 2366s | 2355 | $\nu_{asym}(BH_2)$ of B(1) |
| 2329m | 2320 | Out-of-phase $\nu_{sym}(BH_2)$ of B(2),B(3) |
| 2225vw | | Out-of-phase $\nu_{asym}(BH_2)$ of B(2),B(3) |
| 2125m | 2120 | $\nu_{sym}(B–H_b)$ |
| 2085m | 2080 | $\nu_{asym}(B–H_b)$ |
| 1966s | | $\nu_{asym}(GaH_2)$ |
| 1941s | | $\nu_{sym}(GaH_2)$ |
| 1606w (br) | | $\delta_{asym}(NH_3)$ |
| 1399w (br)[d] | | $\delta_{asym}(NH_4^+)$[d] |
| 1300m | | $\delta_{sym}(NH_3)$ |
| 1282m | 1255 | Sym. ring stretching, $B_3H_8^-$ |
| 1179m | 1170 | $\delta(BH_2)$ |
| 1007m | 1005 | $BH_2$ wagging or rocking |
| 772s | 775 | Ring breathing, $B_3H_8^-$ |
| 746s | | $\rho(NH_3)$ |
| 729s | | $\delta(GaH_2)$ |
| 633w | | $\rho(GaH_2)$ |
| 450m | 455 | Ring deformation, $B_3H_8^-$ |
| 433m | | $\nu$(Ga–N) |

[a] Abbreviations: s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. [b] See ref. 36. [c] For motions involving terminal hydrogen atoms of the $B_3H_8^-$ unit, the numbering scheme is such that B(2) and B(3) are directly bonded boron atoms and B(1) is linked to B(2) and B(3) *via* single hydrogen bridges. [d] $NH_4^+$ present as an impurity arising from hydrolysis of the product.

$H_2GaB_3H_8$ is closer to the mark than, say, the Ga–H$_t$ distance of 158.6 pm deduced from similar, but incomplete, electron-diffraction experiments with $H_2GaBH_4$.[5,6]

Table 3 also includes the results of some self-consistent field (SCF) *ab initio* molecular orbital calculations using a double zeta with polarisation (DZP) basis set.[17] There is reasonable agreement between the experimental and theoretical estimates of several parameters {*e.g.* *r*[Ga–B(1,3)], *r*(B–H) and the dihedral angle $\alpha$}, but two notable discrepancies are apparent. First, the Ga–H$_t$ and Ga–H$_b$ distances are calculated to be about 10 pm longer than the experimental values we have determined. Secondly, the B(4)–H$_b$ bond, with a length of 141.6 pm, is calculated to be significantly longer than the other two B–H$_b$ bonds {*r*(B(1,3)–H$_b$]}. In view of the relatively intractable correlation problems affecting the experimentally determined B–H distances, it is quite possible that the theoretical value comes closer to the truth than the experimental one, and the precedents set by related molecules, *e.g.* $B_4H_{10}$,[30] tend to bear this out. In addition, the theoretical studies imply an H$_t$–Ga–H$_t$ angle (130.2°) substantially larger than the value (115°) to which we are led, not by independent refinement, but by *R*-factor analysis. Irrespective of the precise basis set adopted, all the *ab initio* calculations reported so far[17,34] seem to point to a value near 130° for the H$_t$–Ga–H$_t$ angle of the $(H_t)_2Ga(X_b)_2$ moiety (X = H or Cl). Although this parameter cannot be determined very meaningfully from the electron-diffraction patterns of such molecules, preliminary analysis of the rovibrational spectrum of gaseous digallane[35] argues for a value close to, if not greater than, that predicted by quantum-mechanical methods. There may be scope for investigating how the incorporation of some of the theoretical parameters affects the refinement calculations for 2-gallatetraborane(10): better still would be the incorporation of independent *experimental* information relating, for example, to the vibrational properties and microwave spectrum of the gaseous molecule.

(*vii*) *Reaction with Ammonia*.—With an excess of ammonia at 195 K, 2-gallatetraborane reacts to give a white solid. Evaporation of the excess of ammonia leaves an involatile white residue which is long-lived at room temperature. At no stage is dihydrogen evolved. A mass balance of the reaction mixture reveals that the reacting proportions $H_2GaB_3H_8:NH_3$ are 1:2. Details of the IR spectrum of the solid, including suggested assignments, are itemised in Table 6. Clearly in evidence are the absorptions characteristic of the anion $B_3H_8^-$, as signalled by the close resemblance which the spectrum bears to that of the salt $CsB_3H_8$.[37] In addition, there are features diagnostic of co-ordinated ammonia,[38] leaving five bands (at 1966, 1941, 746, 633 and 433 cm$^{-1}$) which are most plausibly identified with vibrations of the $H_2GaN_2$ skeleton of the cation $[H_2Ga(NH_3)_2]^+$. The spectroscopic recognition of this cation is strongly supported by obvious parallels with the spectra of the compounds $[H_2Ga(NH_3)_2]^+Cl^-$,[13] $[H_2Ga(NH_3)_4]^+[GaH_4]^-$,[4] $[H_2Ga(NH_3)_2]^+[BH_4]^-$,[6] and $Me_2GeH_2$.[36] Hence it seems that the reaction proceeds in accordance with equation (5), with unsymmetrical cleavage of the Ga($\mu$-H)$_2$B$_2$ fragment of 2-gallatetraborane(10).

$$H_2GaB_3H_8 + 2NH_3 \xrightarrow{\text{liquid } NH_3,\ 195\ K} [H_2Ga(NH_3)_2]^+[B_3H_8]^- \quad (5)$$

(*viii*) *Further Research*.—Experiments are now under way, or are planned, to explore more fully the physical and chemical properties of 2-gallatetraborane(10). Thus, it is hoped to determine the rotational constants of the gaseous molecule in its vibrational ground state by measuring the microwave spectrum, and then to carry out a *combined* analysis of the electron-diffraction, microwave, and vibrational properties (augmented possibly by the results of quantum-mechanical calculations) with the aim of gaining a superior structural definition of the molecule. The solid may also prove amenable to useful X-ray or neutron diffraction measurements. The thermal decomposition of the compound is also likely to repay more detailed investigation: thus, rapid, controlled thermolysis could provide an expedient route to other gallium-substituted boranes, and the nature of the solid with the composition $GaB_2$ also calls for closer scrutiny. Moreover, the known reactivity of tetraborane(10)[24] holds out the promise of a rich and interesting chemistry for its 2-gallium-substituted derivative.

## Experimental

*Synthesis of* 2-*Gallatetraborane*(10).—All-glass apparatus of the sort described previously[4] was rigorously preconditioned by heating under continuous pumping. In a representative experiment, monochlorogallane (*ca.* 180 mg, 1.7 mmol of $H_2GaCl$), itself prepared by the metathesis of gallium(III) chloride with an excess of trimethylsilane at *ca.* 250 K,[12,13] was co-condensed *in vacuo* with freshly recrystallised, powdered tetra-*n*-butylammonium octahydrotriborate (*ca.* 500 mg, 1.8 mmol) at 77 K; the octahydrotriborate was prepared from $NaBH_4$ (ex BDH) by the procedure developed by Gaines *et al.*[39] Careful warming of the mixture to a temperature of *ca.* 243 K under continuous pumping resulted in effervescence and the evolution of a volatile compound. With all parts of the glassware to which the vapours had access cooled to temperatures < 283 K in a stream of cold nitrogen gas, the material was fractionated between traps held initially at 210, 147 and 77 K. The main component collected in the trap at 147 K. After *ca.* 1 h, while the reaction mixture was allowed gradually to warm to 268 K, the reaction appeared to be complete, and the various fractions were isolated by sealing the traps at the relevant constrictions.[4] The fraction condensing at 147 K, shown to be essentially pure 2-gallatetraborane(10), was kept at 77 K until required, access to it being regained by way of a suitable break-

**Table 7** Chemical analysis of 2-gallatetraborane(10)

| Found | Solid residue | Ga in solid residue | B in solid residue | $H_2$ evolved | $B_2H_6$ evolved | Total B (solid + $B_2H_6$) | Total H ($H_2$ + $B_2H_6$) |
|---|---|---|---|---|---|---|---|
| Mass/mg | 97.4 | 74.5 | 22.91 | 6.61 | 15.0 | 34.65 | 9.90 |
| mmol | — | 1.069 | 2.119 | 3.28 | 0.542 | 3.205 | 9.82 |
| Proportion | — | 1.00 | 1.98 | 3.07 | 0.51 | 3.00 | 9.19 |

seal. The authenticity of such a sample was checked by reference to its melting point (*ca.* 178 K), vapour pressure (*ca.* 1 mmHg at 210 K), the IR spectrum of the vapour or of the solid condensate it forms at 77 K, or the $^1H$ or $^{11}B$ NMR spectrum of a [$^2H_8$]toluene solution of the compound at low temperatures. The gallatetraborane(10) amounted to *ca.* 170 mg (1.5 mmol of $GaB_3H_{10}$), representing a yield of 88% based on equation (2) and the amount of monochlorogallane taken.

*Chemical Analysis.*—A sample of the gallane was allowed to decompose in a preconditioned Pyrex ampoule of known mass and volume equipped with a break-seal. It was left at room temperature for 24 h, and the temperature then raised to 333 K for 12 h to ensure complete decomposition. The volatile contents of the ampoule were withdrawn and assayed, with further gentle heating of the solid residue to secure the release of all the volatile material; this caused the appearance of the solid to change from a heterogeneous (metallic brown flecked with yellow inclusions) to a uniform brown one. The non-condensable fraction consisted only of dihydrogen which was collected and estimated by means of a Toepler pump. The only other volatile product, which condensed in a spiral trap at 77 K, was identified by its IR spectrum[40] as diborane, and this was measured tensimetrically. The solid residue was dissolved in AR concentrated nitric acid; its boron content was determined as boric acid (by titration in the presence of mannitol with standard NaOH solution) and its gallium content by atomic absorption spectroscopy. The results are presented in Table 7 (Found: H, 8.3; B, 29.1; Ga, 62.6. $GaB_3H_{10}$ requires H, 9.0; B, 28.9; Ga, 62.1%). The rather low figure for hydrogen was almost certainly caused by the retention of some elemental hydrogen by the solid residue.

*Reaction with Ammonia.*—An excess of ammonia was co-condensed with a sample of the gallane at 77 K. Warming the mixture to 195 K caused the ammonia to melt and a white solid to be precipitated. After 2 h at 195 K the mixture was warmed to 238 K over a period of 1 h to ensure that the reaction proceeded to completion. The excess of ammonia was recovered and determined tensimetrically. On the basis of the quantity of ammonia consumed (1.42 mmol) and the mass of the solid product (103 mg), the reacting proportions $GaB_3H_{10}$:$NH_3$ were found to be 1:2.02. A sample of the solid was powdered with CsI (under dry nitrogen) and a disc pressed for IR measurements.

*Spectroscopic Measurements.*—Infrared spectra were recorded using one of two spectrometers, *viz.* a Perkin-Elmer model 580A dispersive instrument for the region 4000–200 cm$^{-1}$ or a Mattson Galaxy FT-IR instrument for the region 4000–400 cm$^{-1}$. Solid nitrogen matrices, typically with compositions $N_2$:$GaB_3H_{10}$ estimated to be *ca.* 200:1, were prepared by continuous deposition of the gallane vapour (delivered *via* an appropriately cooled, preconditioned, glass inlet tube) with an excess of the matrix gas on a CsI window cooled to *ca.* 20 K by means of a Displex closed-cycle refrigerator (Air Products model CS 202); fuller details of the relevant equipment and procedures are given elsewhere.[41] Raman spectra of solid samples were excited at $\lambda$ = 514.5 nm with the output of a Spectra-Physics model 165 argon-ion laser and measured with a Spex Ramalog 5 spectrophotometer operating in conjunction with a Glen-Creston SCADAS data-handling system; the resolution was normally *ca.* 5 cm$^{-1}$. Solid films of the gallane were presented for spectroscopic analysis by allowing the vapour to condense on a CsI window (for IR measurements) or a copper block (for Raman measurements) contained in an evacuated glass shroud and maintained at 77 K. Vapour samples of the gallane for IR measurements were contained in a Pyrex-bodied cell equipped with CsI windows and having a pathlength of *ca.* 10 cm.

The NMR measurements on [$^2H_8$]toluene solutions at temperatures in the range 193–300 K were made at 300 (for $^1H$) or 96.25 MHz (for $^{11}B$) with a Bruker model AM 300 spectrometer. The mass spectrum of the gallane vapour was measured using a VG SPX800 Spectromass quadrupole mass spectrometer at the University of Reading; the ionising potential was 70 eV (*ca.* 1.12 × $10^{-17}$ J) and the system was controlled by a Spectrolab version 4 computer program. For these measurements the vapour over the sample at 238 K was admitted to a glass vacuum manifold *via* a ground-glass joint lubricated with halocarbon grease. The manifold was preconditioned by exposure for 5 min to each of two samples of the vapour; after re-evacuation, a fresh sample was admitted and from the manifold it was caused to bleed into the ionisation chamber of the spectrometer *via* a greaseless valve.

*Electron-diffraction Measurements.*—The electron-diffraction patterns of 2-gallatetraborane(10) vapour were recorded photographically on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus.[42] To accommodate the reactivity and thermal frailty of the gallane, we used the all-glass inlet assembly described previously,[4] but the more robust nature of the compound (compared, say, with $Ga_2H_6$ and $GaBH_6$) allowed some modification to be made. Thus, the assembly was fitted with a greaseless (Teflon) valve and ground-glass socket to enable samples to be changed so that the scattering of more than one sample could be recorded in a single experiment. The experience gained in manipulating gallatetraborane suggested that decomposition was slow under the conditions of the experiments provided that the glass surfaces had been adequately conditioned by prior exposure to a sample of the vapour. The ampoule containing the sample of 2-gallatetraborane(10) was kept at 253 K and the inlet system was cooled to 273 K. Before any measurements were made the inlet system was conditioned by exposing it to a slow stream of the gallane vapour for 2 min. The scattering pattern was then recorded at the two nozzle-to-plate distances listed in Table 8; also included in this table are details of the electron wavelengths, the weighting functions used to set up the off-diagonal weight matrix, the correlation parameters and the refined scale factors. The rotating sector was kept in motion until all of the sample in the diffraction chamber had been condensed in the cold trap. This prevented a 'shadow' of the stationary sector from being superimposed on the photographic plate, leaving the plate fogged (by the vapour) but with a homogeneous background. Each exposed plate was left under pumping for 4 h before removal, washed, and left in the air for 24 h before being developed. The precise nozzle-to-plate distances and electron wavelengths were determined from scattering patterns for benzene vapour recorded immediately after the sample pattern.

Details of the electron-scattering patterns were collected in

**Table 8** Nozzle-to-plate distances, weighting functions, correlation parameters, scale factors and electron wavelengths

| Nozzle-to-plate distance/mm | $\Delta s$/nm$^{-1}$ | $s_{min}$/nm$^{-1}$ | $sw_1$/nm$^{-1}$ | $sw_2$/nm$^{-1}$ | $s_{max}$/nm$^{-1}$ | Correlation, $p/h$ | Scale factor, $k$[a] | Electron wavelength[b]/pm |
|---|---|---|---|---|---|---|---|---|
| 259.48 | 2 | 20 | 40 | 140 | 160 | −0.0679 | 0.711(25) | 5.671 |
| 201.08 | 4 | 52 | 72 | 176 | 208 | 0.4494 | 0.549(26) | 5.670 |

[a] Figures in parentheses are the estimated standard deviations of the last digits. [b] Determined by reference to the scattering pattern of benzene vapour.

digital form using a computer-controlled Joyce-Loebl MDM6 microdensitometer with the scanning program described previously.[43] Calculations made use of well established programs for data reduction[43] and least-squares refinement,[31] the complex scattering factors being those listed by Fink and Ross.[44]

*Chemicals.*—Nitrogen gas (research grade) for matrix studies 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), $Cl_2$ (BDH), $NaBH_4$ (BDH), $LiAlH_4$ (BDH), $I_2$ (BDH), $Me_3SiCl$ (Aldrich) and $Bu^n{}_4NI$ (Aldrich); $NH_3$ (B.O.C.) was dried over Na and purified before use by fractionation *in vacuo*. Monochlorogallane was prepared by the interaction of gallium(III) chloride (derived from the elements and purified by vacuum sublimation) with trimethylsilane [derived from the reaction of $Me_3SiCl$ with $LiAlH_4$ in tetrahydrofuran (thf)],[45] at 250 K.[6,12,13] The solvents [$^2H_8$]toluene (Aldrich), $Et_2O$ (Fisons), thf (Fisons) and diglyme (2,5,8-trioxanonane) (Aldrich) were dried and purified by standard procedures.

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