# The Molecular Structures of the Gaseous Dimeric Molecules $Me_2Ga(\mu\text{-}H)_2GaMe_2$ and $Me_2Ga(\mu\text{-}Cl)_2GaMe_2$ as determined by Electron Diffraction†

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The structures of gaseous dimethylgallane and dimethylgallium chloride have been determined by electron diffraction. The results indicate that the predominant vapour species at low pressures and temperatures of 290—350 K are dimeric molecules with diborane-like structures, $Me_2Ga(\mu\text{-}X)_2GaMe_2$ (where X = H or Cl), with heavy-atom skeletons conforming to $D_{2h}$ symmetry. Salient structural parameters in the $r_a$ structures are: (*i*) for $[Me_2GaH]_2$, $r$(Ga · · · Ga) 261.0(0.5), $r$(Ga–C) 195.4(0.4), and $r(Ga–H_b)$ 170.8(1.4) pm; $Ga–H_b–Ga$ 99.6(1.4) and C–Ga–C 123.2(1.5)°; (*ii*) for $[Me_2GaCl]_2$, $r$(Ga · · · Ga) 330.3(1.9), $r$(Ga–C) 194.6(0.3), and $r(Ga–Cl_b)$ 237.8(0.4) pm; $Ga–Cl_b–Ga$ 88.0(0.9) and C–Ga–C 132.1 (2.7)° ('b' denotes a bridging atom). Dimethylgallane thus represents the first gallium hydride containing a $Ga(\mu\text{-}H)_2Ga$ bridging unit to be characterised structurally; it is notable for the shortness of the Ga · · · Ga distance. The two molecules invite structural comparisons with related systems like $[Me_2EH]_2$(E = B or Al), $[Me_2AlCl]_2$, and $Ga_2Cl_6$.

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For many years the chemistry of gallium hydrides appeared to be dominated by complexes in which the gallane moiety is stabilised through co-ordination to a suitable donor, with the free hydrides seldom well authenticated and typically leading a shadowy, transient existence.[1] Best characterised of these free gallanes have in the past been the disubstituted derivatives $[HGaX_2]_2$ (X = Cl or Br),[2] $Et_2GaH$,[3] $Bu^i{}_2GaH$,[4] and, $HGa(BH_4)_2$.[5] On the other hand, dimethylgallane, $[Me_2GaH]_n$, has had a rather vexed history. According to an early report,[6] a compound formulated as $[Me_2GaH]_2$ is produced by the action of an electrical discharge on a gaseous $GaMe_3$–$H_2$ mixture and through a disproportionation reaction with triethylamine, this was claimed to be a precursor to digallane. However, the failure of subsequent attempts to prepare dimethylgallane[7] prompted doubts about the authenticity of the earlier claim.

Through the reaction between trimethylgallane and freshly prepared lithium or sodium tetrahydridogallate, as represented by equation (1) (M = Li or Na), we have established a relatively

$$GaMe_3 + MGaH_4 \longrightarrow \frac{1}{n}[Me_2GaH]_n + MGaMeH_3 \quad (1)$$

efficient route to dimethylgallane. The compound has been authenticated chemically and by its vibrational, $^1H$ and $^{13}C$ n.m.r., and mass spectra. A viscous, colourless liquid at ambient temperatures, and with a vapour pressure (v.p.) at 293 K of *ca.* 1 mmHg, it resembles physically the product isolated from the discharge reactions involving $GaMe_3$ and $H_2$.[6] It resembles too the corresponding aluminium compound, $[Me_2AlH]_n$, which is reported to exist in the vapour phase as a mixture of oligomers with $n = 2$ or 3.[8-10] On the evidence of the vibrational spectra, dimethylgallane changes its degree of aggregation, $[Me_2GaH]_n$, on condensation of the vapour, with the solid being composed of either oligomeric or polymeric units where $n \geqslant 3$.

The behaviour of dimethylgallane in the condensed phases is more aptly treated, together with details of its synthesis and chemical properties, in a separate paper.[11] Here we concentrate on the nature of the vapour phase. As reported briefly in a preliminary communication,[12] the combined evidence of the mass and vibrational spectra argues for a dimeric molecule $Me_2Ga(\mu\text{-}H)_2GaMe_2$ as the predominant species, a conclusion endorsed by an analysis of the electron-diffraction pattern of the vapour at ambient temperatures. Such a structure is noteworthy for being the first validated example of a molecule in which two gallium atoms are linked *via* hydrogen bridges, and refinement calculations have afforded a relatively good definition of the central $Ga(\mu\text{-}H)_2Ga$ unit. In that the structural exploration of gallium hydrides has not previously extended beyond compounds containing terminal Ga–H bonds and/or $Ga(\mu\text{-}H)_2BH_2$ moieties, *e.g.* $Me_3N{\cdot}GaH_3$,[13a] $[Me_2NGaH_2]_2$,[13b] $HGa(BH_4)_2$,[5] and $Me_2GaBH_4$,[14] this is a significant new departure. Through its structural and spectroscopic properties, for example, $Me_2Ga(\mu\text{-}H)_2GaMe_2$ anticipates the most distinctive features of the binary hydride $Ga_2H_6$, the existence of which has been ascertained only very recently.[15,16]

With the commissioning of a new heated-inlet system as an accessory to the Edinburgh gas diffraction apparatus,[17,18] we have also determined the structure of gaseous dimethylgallium chloride by electron diffraction. Once again, the results imply the presence of a dimeric molecule, $Me_2Ga(\mu\text{-}Cl)_2GaMe_2$, with a structure closely akin to that of dimethylgallane. The dimensions of the two molecules $Me_2Ga(\mu\text{-}X)_2GaMe_2$ (X = H or Cl) invite comparisons, not only with each other, but also with those of related molecules, *e.g.* $Me_2E(\mu\text{-}H)_2EMe_2$, where E = B[19] or Al,[10] $Me_2GaBH_4$,[14] $Me_2Al(\mu\text{-}Cl)_2AlMe_2$,[20] and $Ga_2Cl_6$.[21]

## Experimental

*Synthesis.*—Dimethylgallane was prepared by the reaction between trimethylgallane and lithium or sodium tetrahydridogallate, itself freshly prepared from gallium(III) chloride and the corresponding alkali-metal hydride in diethyl ether.[22] This took

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

**Table 1.** Nozzle-to-plate distances, weighting functions, correlation parameters, scale factors, and electron wavelengths

| Molecule | 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 |
|---|---|---|---|---|---|---|---|---|---|
| $[Me_2GaH]_2$ | 285.4 | 2 | 20 | 40 | 124 | 144 | 0.2250 | 1.063(27) | 5.688 |
| | 128.4 | 4 | 60 | 80 | 260 | 320 | −0.0586 | 0.818(26) | 5.688 |
| $[Me_2GaCl]_2$ | 255.8 | 2 | 20 | 40 | 144 | 164 | −0.2665 | 0.783(13) | 5.711 |
| | 98.4 | 4 | 80 | 100 | 300 | 352 | 0.3772 | 0.637(18) | 5.712 |

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

place at room temperature [*cf.* equation (1)] under solvent-and grease-free conditions, typically in the space of 15 min, and in accordance with the details given elsewhere.[8,11,23] The volatile components of the reaction mixture were removed under continuous pumping and fractionated between traps held at 250 and 77 K. The dimethylgallane collected in the 250-K trap as a white waxy solid which melted at *ca.* 273 K and decomposed in a matter of days at room temperature, forming $Me_3Ga$, $H_2$, and an involatile methylgallium polymer approximating in composition to $[MeGa]_n$.[11] It was analysed by quantitative assay of the products formed by the reactions with ammonia and with diborane.[11,12] The authenticity of a sample was checked by reference to its m.p. and v.p., the mass spectrum of the vapour, the i.r. spectra of the vapour and solid condensate formed at 77 K, and the $^1H$ and $^{13}C$ n.m.r. spectra of the compound in $[^2H_8]$toluene solution at temperatures in the range 200—290 K. Such a sample was stored at 77 K in a glass ampoule closed by a greaseless stopcock, until required. The synthesis of the deuteriated derivative, $[Me_2GaD]_n$, followed exactly similar lines.

The interaction of stoicheiometric quantities of trimethylgallane and gallium(III) chloride at ambient temperatures afforded dimethylgallium chloride,[24] the temperature of the reaction mixture being raised ultimately to *ca.* 323 K in order to ensure that equilibrium conditions had been achieved. The product was purified by sublimation *in vacuo*, and its purity checked by reference to its m.p. (318.6 K)[25a] and i.r.[25a,b] and Raman[25c] spectra.

*Spectroscopic Measurements.*—I.r. spectra were recorded using either a Perkin-Elmer model 580A dispersive spectrophotometer or a model 1710 FT-IR instrument. Such measurements took in samples of $[Me_2GaH]_n$ and $[Me_2GaD]_n$ in the form of the vapours, of solid films at low temperatures, and of the vapour species isolated in solid argon matrices at dilutions of *ca.* 1:500. Matrices were prepared by continuous deposition of the gaseous mixture on a CsI window cooled to *ca.* 20 K by means of a 'Displex' refrigerator (Air Products model CS 202); fuller details of the relevant equipment and procedures are given elsewhere.[26] Raman spectra of solid films of $[Me_2GaH]_n$ and $[Me_2GaD]_n$ at 213 K were excited at $\lambda = 514.5$ nm with the output of a Spectra-Physics model 165 argon-ion laser and recorded with a Spex Ramalog 5 spectrophotometer.

Mass spectra were measured with the aid of an AEI MS902 instrument. Samples were admitted from an ampoule connected directly to the stainless-steel gas-inlet system of the spectrometer *via* a nozzle at ambient temperatures. The spectra were calibrated with reference to peaks due to heptacosafluorotributylamine.

Proton n.m.r. measurements on $[^2H_8]$toluene solutions of dimethylgallane at temperatures between 200 and 290 K were made at either 300 or 500 MHz using a Bruker model WH300 or AM500 Spectrometer, respectively; $^{13}C$ measurements were made at 125.78 MHz using the model AM500.

*Electron-diffraction Measurements.*—Electron-scattering patterns were recorded on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus.[17] Nozzle-to-plate distances were *ca.* 128 and 285 mm for dimethylgallane and *ca.* 98 and 256 mm for dimethylgallium chloride. The accelerating voltage approximated to 44 kV, giving an electron wavelength near 5.7 pm. The precise nozzle-to-plate distances and electron wavelengths were determined from scattering patterns for benzene vapour recorded immediately before or after the sample patterns. Details are given in Table 1, together with the weighting functions used to set up the off-diagonal weight matrices, the correlation parameters, and final scale factors.

The sample of dimethylgallane was held at room temperature (*ca.* 290 K) and the vapour gained access to the nozzle of the diffraction apparatus (also at room temperature) *via* a stainless-steel needle valve. Immediately prior to the exposure of each plate, the sample was subjected to continuous pumping for *ca.* 3 min to remove any traces of trimethylgallane which might have been formed through decomposition and also to 'condition' the interior of the apparatus. The plates were washed after exposure and left exposed to air for 24 h before being developed in order to minimise the fogging effects of the strongly reducing gallane vapour; this is a recurrent problem with hydrido derivatives of the Group 13 elements.[5,16,27,28]

The relatively low volatility of dimethylgallium chloride precluded the production of a molecular flux at ambient temperatures sufficient for electron-diffraction measurements. In this case, the ampoule containing the sample and intervening glass and stainless-steel pipework were held at *ca.* 340 K with the aid of heating tape, while a heated air stream was used to control the temperature (357 K) of the stainless-steel nozzle admitting the vapour to the diffraction chamber.

Details of the electron-scattering patterns were collected in digital form using a computer-controlled Joyce–Loebl MDM6 microdensitometer with the scanning program described previously.[29] Calculations drew on well established programs for data reduction[29] and least-squares refinement,[30] the complex scattering factors being those listed by Schäfer *et al.*[31]

## Results

(*a*) *Spectroscopic Characterisation of Dimethylgallane Vapour.* —*Mass spectrum.* The mass spectrum of dimethylgallane vapour included peaks at $m/z$ = 200, 202, and 204. These exhibited relative intensities consistent with their attribution to the parent ions associated with the dimeric molecule $[Me_2GaH]_2$, (**1**), which occurs naturally as the $^{69}Ga_2$, $^{69}Ga^{71}Ga$, and $^{71}Ga_2$ isotopomers in relative abundances of 2.33:3.05:1. The other features in the spectrum could all be interpreted by the loss of one or more hydrogen atoms from the molecular ion. There was, by contrast, no sign of any features at $m/z$ near 100 or 300 attributable to parent or fragment ions derived from the monomer $Me_2GaH$ or the trimer $[Me_2GaH]_3$, respectively. The experience of similar studies involving

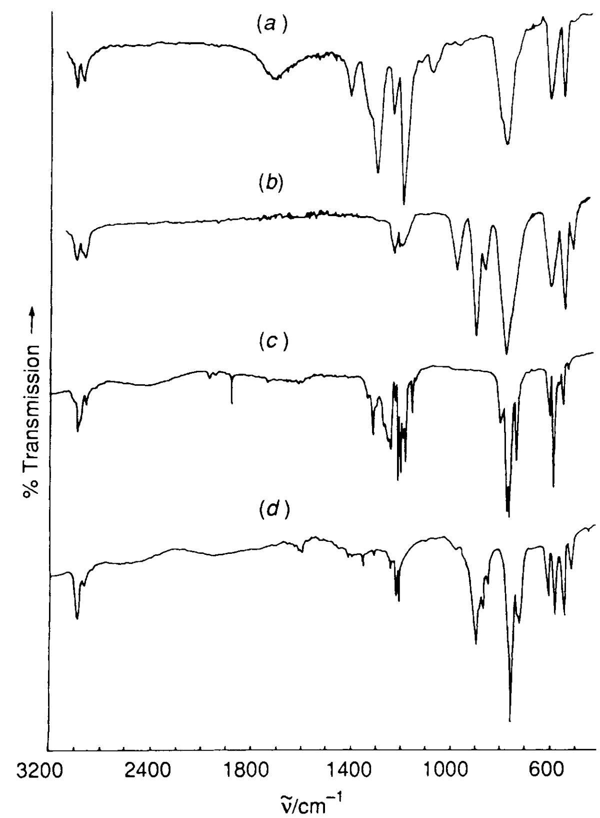
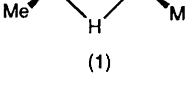


**Figure 1.** I.r. spectra in the region 400—3 200 cm$^{-1}$: (*a*) $[Me_2GaH]_n$ vapour, pressure *ca.* 1 mmHg, 290 K; (*b*) $[Me_2GaD]_n$ vapour, pressure *ca.* 1 mmHg, 290 K; (*c*) $[Me_2GaH]_n$ vapour isolated in an argon matrix at *ca.* 20 K (argon:gallane = *ca.* 500:1); and (*d*) $[Me_2GaD]_n$ vapour isolated in an argon matrix at *ca.* 20 K (argon:gallane = *ca.* 500:1)



(1)

dimethylalane demonstrates how hard it is to predict the effects of fragmentation in weakly bound molecules of this sort.[32] Hence, although the mass spectrum makes it highly unlikely that the monomer, $Me_2GaH$, is a significant constituent of dimethylgallane vapour, the results do not altogether rule out the presence of the trimer, $[Me_2GaH]_3$, or still higher oligomers. However, the obvious inference to be drawn is that $[Me_2GaH]_2$ is the predominant vapour species.

*Vibrational spectra.* I.r. spectra have been measured for $[Me_2GaH]_n$ and $[Me_2GaD]_n$, with reference to both the vapours at ambient temperatures and to the vapour species entrapped in solid argon matrices at *ca.* 20 K. The relevant results are illustrated in Figure 1 and itemised in Table 2. The results are subject to several complications and limitations. Despite every endeavour to prevent contamination, *e.g.* by conditioning the apparatus and avoiding the use of solvents and grease, the instability and reactivity of dimethylgallane made it impossible in practice to eliminate all impurities. The main problems were caused by traces of base molecules B, *e.g.* $H_2O$, which were liable to react to give adducts of the type $Me_2GaH{\cdot}B$ containing terminal Ga–H bonds. These we believe, for example, to be responsible for the absorptions of weak but variable intensity which appeared in the regions 1 850—2 000 and 1 300—1 450 cm$^{-1}$ in the spectra of matrices containing $[Me_2GaH]_n$ and $[Me_2GaD]_n$, respectively. Matrix isolation, while sharpening the absorptions and facilitating the identification of some features, resulted in the splitting of several of the bands, presumably as a result of the trapping of gallane molecules in different matrix cages. There are limitations too imposed partly by the low pressure of the vapour (*ca.* 1mmHg) and partly by the restricted wavenumber range of the measurements (200—4 000 cm$^{-1}$). Hence it follows that the spectra are necessarily incomplete.

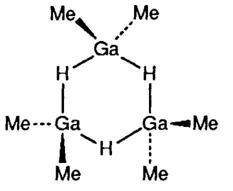
In spite of the complications and deficiencies, the spectra can be interpreted satisfactorily in terms of the group vibrations of the discrete molecules $Me_2Ga(\mu\text{-}X)_2GaMe_2$ (X = H or D), with a heavy-atom skeleton conforming to $D_{2h}$ symmetry. The proposed assignments are specified in Table 2. Our analysis has been based on three main criteria: (*i*) analogies with the vibrational properties of related molecules, including those containing $Me_2Ga$ groups,[33] *e.g.* $[Me_2GaCl]_2$[25] and $Me_2GaBH_4$,[34] and also $Me_2As{\cdot}AsMe_2$;[35] (*ii*) the selection rules expected to govern the activity in i.r. absorption of the vibrational fundamentals associated with the $[Me_2GaH]_2$ or $[Me_2GaD]_2$ molecule; and (*iii*) the effect of deuteriation at gallium on the energy of a given spectroscopic feature. Wavenumbers quoted in parentheses refer to the corresponding Ga–D compounds in the following discussion.

Most of the bands in the spectra can be identified with fundamentals which approximate to internal motions of the $Me_2Ga$ group,[25,33,34] with energies which are almost invariant with respect to deuteriation at gallium. Such is the case, for example, with the features near 2 980, 2 920, 1 210, 770, 600, and 540 cm$^{-1}$, the assignment of which is made relatively straightforward by the vibrational precedents established for the molecule $Me_2Ga(\mu\text{-}H)_2BH_2$.[34] Impurities apart, the spectra give no sign of significant absorption in the region 1 800—2 100 (1 300—1 500) cm$^{-1}$ characteristic of the stretching vibrations of terminal Ga–H (Ga–D) bonds.[1a,13b,36] On the other hand, the spectrum of $[Me_2GaH]_n$ vapour contains two prominent absorptions at 1 290 and 1 185 cm$^{-1}$, which shift to 971 and 893 cm$^{-1}$ on deuteriation at gallium. The most plausible interpretation is that these represent, respectively, antisymmetric and symmetric stretching vibrations of the Ga–H–Ga bridges in a unit of the type $Ga(\mu\text{-}H)_2Ga$ with a Ga–H–Ga bridge angle of the order of 95°.[37] Such an assignment receives strong support from the i.r. spectrum reported very recently for digallane,[15] and which includes analogous absorptions near 1 270 (910) and 1 200 (860) cm$^{-1}$. In addition, samples of dimethylgallane vapour appeared to display broad absorptions near 1 700 (1 250) and 965 (850) cm$^{-1}$; these were typically weak with the vapour at ambient temperatures but grew when attempts were made to increase the pressure by heating the closed i.r. cell including a small amount of liquid dimethylgallane contained in a cold-finger. In fact, an annealed solid film of dimethylgallane is characterised by two bands similar in their energies and relative intensities to these two features, and, although we were inclined at first to believe that they represent a second major vapour species,[12] closer scrutiny suggests that they owe their origin mainly to small amounts of the compound condensed or adsorbed on the windows of the i.r. cell. The energies of the two bands imply that they too are due to antisymmetric and symmetric stretching vibrations of Ga–H–Ga moieties, but with the Ga–H–Ga bond angle opened out to about 120°.[37] Hence it appears that the average degree of aggregation changes on condensation of the vapour, with the formation, possibly, of a trimer, (**2**), or higher oligomer. Although the spectrum of the vapour is thus open to some ambiguity, it is significant that matrix-isolated dimethylgallane gives no hint of any absorption near 1 700 (1 250) and 965 (850) cm$^{-1}$. Hence, it appears that the

**Table 2.** I.r. spectral data ($\tilde{\nu}$/cm$^{-1}$)[a] for gaseous and matrix-isolated $[Me_2GaH]_n$ and $[Me_2GaD]_n$ in the region 200—4 000 cm$^{-1}$

| $[Me_2GaH]_n$ | | $[Me_2GaD]_n$ | | |
|---|---|---|---|---|
| Vapour at *ca.* 290 K | Argon matrix at *ca.* 20 K | Vapour at *ca.* 290 K | Argon matrix at *ca.* 20 K | Assignment[b] |
| 2 981m<br>2 921m | 2 990m<br>2 975(sh)<br>2 910w | 2 982m<br>2 920m | 2 981m<br>2 925w | $\nu$(C–H) |
| | 1 961vw<br>1 937vw<br>1 870mw | | 1 414vw<br>1 397vw<br>1 349w<br>1 306w | $\nu(Ga–H_t)$ of impurities, *e.g.* $H_2O{\cdot}GaMe_2H$ |
| 1 705m(br) | | ca. 1 250w(vbr) | | $\nu(Ga–H_b)$ of $[Me_2GaH]_n$ with $n \geqslant 3$[c] |
| 1 397m | | | | $\nu(Ga–H_b)$ of $[Me_2GaH]_n$ with $n \geqslant 3$[c] |
| 1 325(sh) | 1 326(sh) | | | $\rho(CH_3) + \nu_{sym}(Ga–C)$ |
| 1 290s | 1 305ms<br>1 300(sh) | 971m | 978w(br) | $\nu(Ga–H_b)$ |
| 1 223m | 1 261(sh)<br>1 246(sh)<br>1 234s<br>1 214w<br>1 203s | 1 221m | 1 239w<br>1 214m<br>1 204m | $\delta_{sym}(CH_3)$ |
| 1 185vs | 1 194s<br>1 182s<br>1 173s<br>1 147m | 893s | 898s<br>885(sh)<br>869m<br>845mw | $\nu(Ga–H_b)$ |
| 1 115w<br>1 071w | 1 135w | 1 095vw | | $2 \times \nu_{sym}(Ga–C)$ or $\nu_{sym}(Ga–C) + \nu_{asym}(Ga–C)$ |
| 965w | | 857m | | $\nu(Ga–H_b)$ of $[Me_2GaH]_n$ with $n \geqslant 3$[c] |
| 790(sh)<br>769s | 796m<br>758vs<br>749vs<br>729s | 770s<br>745(sh) | 754vs<br>721m | $\rho(CH_3)$ |
| 590s<br>538s | 597m<br>577s<br>541mw | 598s<br>575(sh)<br>539s | 600m<br>577m<br>540m | $\nu$(Ga–C) |
| | | 508m | 508mw | Overtone or combination |

[a] s = Strong, m = medium, w = weak, v = very, br = broad, and sh = shoulder. [b] Relates to the molecule $[Me_2GaH]_2$ unless stated otherwise: $H_t$ = terminal H atom, $H_b$ = bridging H atom. [c] Probably associated with condensate or adsorbate on the windows of the i.r. cell (see text).



(2)

dimer $[Me_2GaH]_2$ is the predominant vapour species under the conditions of our experiments (pressure *ca.* 1 mmHg, temperature *ca.* 290 K). In that the i.r. and Raman spectra of dimethylgallane in the condensed phases otherwise shed little light on the vapour species, both the details and interpretation of these spectra are reserved for elaboration in a separate paper.[11]

Certain details of the i.r. spectra associated with the vapour species are less easily interpreted. For example, changes in the relative intensities of some of the bands on deuteriation at gallium suggest that the 'group vibration' approach is not wholly valid (with some modes in reality involving significant contributions from more than one internal co-ordinate) or the intervention of Fermi resonance. Moreover, the absence of any information about the low-wavenumber region of these spectra (< 200 cm$^{-1}$) denies us any details about the deformation modes of the $C_2Ga(\mu\text{-}H)_2GaC_2$ skeleton, as well as torsional motions of the $CH_3$ groups. In these circumstances it is not feasible to venture a more detailed assignment of the spectra. The essential point is that the spectra are consistent with, even if they do not prove, the identification of the dimer (**1**) as the main ingredient of dimethylgallane vapour at low pressure and ambient temperatures.

*N.m.r. spectra.* The $^1H$ n.m.r. spectrum of a $[^2H_8]$toluene solution of dimethylgallane consists of two singlet resonances, one sharp at $\delta_H$ 0.01 and the other broad at $\delta_H$ 3.06 with relative intensities 6:1. These correspond to the protons of the $Me_2Ga$ and Ga–H groups, respectively. Attempts to explore the degree of aggregation of dimethylgallane under these conditions by $^{13}C$ n.m.r. measurements yielded only a single quartet at $\delta_C$ −6.6, with $J(C–H)_{av.}$ = 125.5 Hz. Neither spectrum underwent any significant change when the solution was cooled to 200 K, although there was a pronounced sharpening of the Ga–H resonance in the $^1H$ n.m.r. spectrum. While confirming the composition of the compound and its purity, therefore, the n.m.r. spectra give no clue to its molecularity in solution, possibly because the aggregates are subject to rapid exchange which may well be catalysed by unavoidable traces of base impurity.

### (*b*) *Structural Analysis of Gaseous Dimethylgallane and Dimethylgallium Chloride by Electron Diffraction.*

—On the evidence of its mass and i.r. spectra, dimethylgallane vapour appears to consist mainly of dimeric molecules (**1**) with a diborane-like structure involving bridging hydrogen atoms and a heavy-atom framework conforming to $D_{2h}$ symmetry. Circumstantial evidence, based principally on the vibrational spectra[25]

**Table 3.** Molecular parameters deduced from the electron-diffraction patterns of $[Me_2GaH]_2$ and $[Me_2GaCl]_2$[a]

| | $[Me_2GaH]_2$ | | $[Me_2GaCl]_2$ | |
|---|---|---|---|---|
| Parameter[b] | Distance/pm or angle/° | Amplitude/pm | Distance/pm or angle/° | Amplitude/pm |
| (*a*) Independent parameters | | | | |
| $p_1$ $r$(Ga • • • Ga) | 261.0(0.5) | $u_1$ 8.2(0.8) | 330.3(1.9) | $u_1$ 10.0(1.0) |
| $p_2$ $r$(Ga–C) | 195.4(0.4) | $u_2$ 5.5(0.8) | 194.6(0.3) | $u_2$ 5.9(0.5) |
| $p_3$ $r(C–H_{Me})$ | 112.0(0.6) | $u_3$ 6.5(0.9) | 112.9(0.7) | $u_3$ 7.0[c] (0.8) |
| $p_4$ $r(Ga–X_b)$ | 170.8(1.4) | $u_4$ 5.2(1.8) | 237.8(0.4) | $u_4$ 9.3(0.2) |
| $p_5$ C–Ga–C | 123.2(1.5) | | 132.1(2.7) | |
| $p_6$ $CH_3$ 'twist' angle, $\tau$[d] | 40.8(4.5) | | 48.9(4.0) | |
| $p_7$ H–C–Ga | 101.6(1.3) | | 104.2(1.3) | |
| $p_8$ $CH_3$ 'tilt' angle, $\varphi$[d] | −6.9(3.9) | | −1.6(4.0) | |
| $p_9$ $GaC_2$ 'twist' angle, $\theta$[d] | 0.0 | | 0.0[c] | |
| $p_{10}$ Ring 'dip', $\gamma$[d] | 0.0 | | 0.0[c] | |
| (*b*) Dependent parameters | | | | |
| $r(Ga \cdots H_{Me})$ | 235.7(3.2) | $u_5$ 17.6(1.8)[e] | 246.2(3.1) | $u_5$ 12.5(2.2)[e] |
| | 241.8(1.7) | 17.6(1.8)[e] | 247.0(1.8) | 12.5(2.2)[e] |
| | 253.5(4.5) | 17.6(1.8)[e] | 250.1(5.0) | 12.5(2.2)[e] |
| $r(C \cdots X_b)$ | 302.7(1.1) | 8.4[c] | 347.2(1.5) | $u_6$ 12.2(1.2) |
| $r(C \cdots C)$[f] | 343.7(2.1) | 15.0[c] | 355.7(2.8) | 10.0[c] |
| $r(C \cdots C')$[f] | 441.0(3.5) | 27.3[c] | 482.1(5.2) | $u_7$ 13.9(3.8) |
| $Ga–X_b–Ga$ | 99.6(1.4) | | 88.0(0.9) | |

[a] Figures in parentheses are the estimated standard deviations of the last digits. [b] $H_{Me}$ methyl hydrogen atom, $X_b$ bridging X atom (X = H or Cl). [c] Fixed. [d] See text. [e] Constrained to be equal. [f] $r(C \cdots C)$ relates to the $CH_3$ groups of *each* $Me_2Ga$ unit, $r(C \cdots C')$ to the *cis*-carbon atoms attached to *different* Ga atoms.

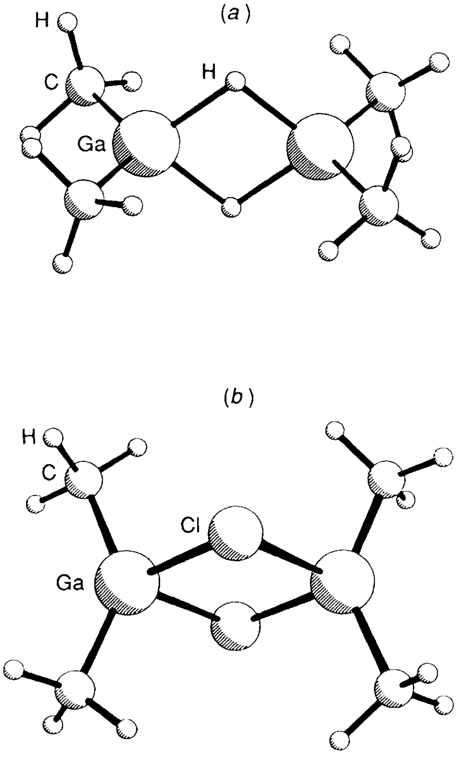
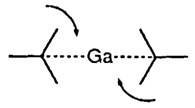


**Figure 2.** Perspective views of the molecules (*a*) $[Me_2GaH]_2$ and (*b*) $[Me_2GaCl]_2$ in the optimum refinements of the electron-diffraction data



**(3)**

and the behaviour of related molecules, *e.g.* $[Me_2AlCl]_2$,[20] suggests a similar structure for the principal component of dimethylgallium chloride vapour, *viz.* $Me_2Ga(\mu\text{-}Cl)_2GaMe_2$. Accordingly we adopted just such a model as a basis for calculating electron-scattering intensities of the molecules $Me_2Ga(\mu\text{-}X)_2GaMe_2$, drawing initially on ten independent geometrical parameters. With reference to Figure 2 and Table 3, these comprised four distances, *viz.* Ga • • •Ga, Ga–C, C–H, and Ga–X, and four angles, *viz.* C–Ga–C, H–C–Ga, and parameters defining both twisting, $\tau$, and tilting, $\varphi$, of the $CH_3$ groups. In addition, two more parameters were introduced into the calculations to check for possible distortions of the most probable structure: these defined twisting of the $GaC_2$ units, $\theta$, and puckering of the central $Ga(\mu\text{-}X)_2Ga$ ring (presumed initially to be planar) in terms of a ring 'dip,' $\gamma$. More specifically, $\tau$ describes the concerted rotation of the two $CH_3$ groups bound to a common gallium atom away from a given null position, as indicated in (3); $\varphi$ corresponds to the angle subtended by the $C_3$ axis of each $CH_3$ group (presumed to maintain local $C_{3v}$ symmetry) with respect to the Ga–C vector, positive values signifying tilting of the $CH_3$ groups of each $(CH_3)_2Ga$ moiety *away* from each other; $\theta$ measures the angle made by the normal to the $GaC_2$ plane with respect to the $GaX_2$ plane; and $\gamma$ measures the angle between the two $GaX_2$ planes of the central four-membered $Ga(\mu\text{-}X)_2Ga$ ring. Such a model was found to account satisfactorily for the experimental radial-distribution curves associated with both dimethylgallane and its chloro derivative (see Figure 3).

The experimental radial-distribution curve deduced from the scattering pattern of dimethylgallane displays prominent peaks near 110, 200, and 260 pm corresponding to scattering from C–H, Ga–C, and Ga • • • Ga atom pairs, respectively. In addition, we note a discernible shoulder near 170 pm and a broad feature near 390 pm which can be correlated with scattering from Ga–H bonded and C • • • C non-bonded pairs, respectively. Still weaker and less well defined features of the curve also take account of scattering from non-bonded $Ga \cdots H_{Me}$ and $C \cdots H_b$ pairs (where $H_{Me}$ represents a methyl hydrogen and $H_b$ a bridging hydrogen). On the other hand, the

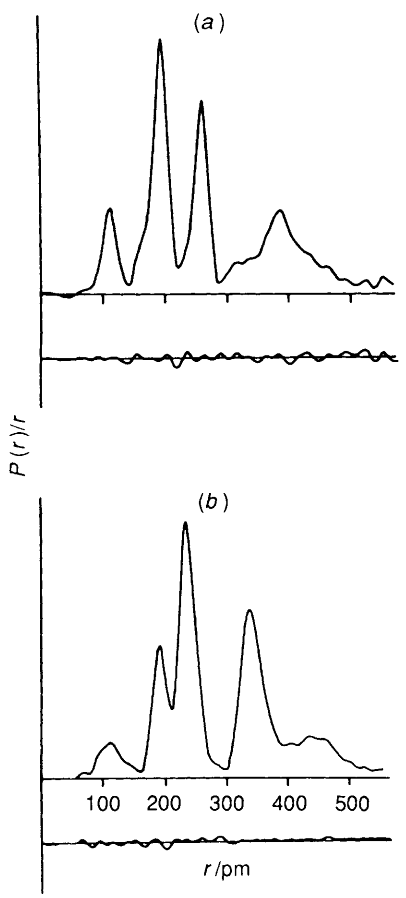


**Figure 3.** Observed and difference radial-distribution curves, $P(r)/r$ *vs.* $r$, (*a*) for $[Me_2GaH]_2$ and (*b*) for $[Me_2GaCl]_2$. Before Fourier transformation, the data were multiplied by $s\cdot\exp[(-0.000\,015\,s^2)]/(Z_{Ga}-f_{Ga})(Z_C-f_C)]$

absence of significant scattering near 150 pm attributable to terminal Ga–H bonds[5,13,27] tends to discount the presence in the vapour of more than trace amounts of the monomeric species $Me_2GaH$ or potential contaminants like $[MeGaH_2]_2$ and adducts of $Me_2GaH$ with adventitious base impurities. That atom pairs separated by more than about 500 pm do not contribute significantly to the measured scattering tends also to argue against the presence of appreciable proportions of the cyclic trimer $[Me_2GaH]_3$, (**2**). However, confirmation on this point was sought through introducing into the refinement calculations two additional parameters describing the Ga ••• Ga distance and the percentage of any such trimer in the vapour. These new parameters did not improve the refinement, leading us to conclude that the trimer is not a major constituent of dimethylgallane vapour, at least under the conditions of our experiments. The vapour density of dimethylalane implies, by contrast, that both $[Me_2AlH]_2$ and $[Me_2AlH]_3$ are present in similar circumstances.[9,10]

The experimental radial-distribution curve associated with the chloro derivative $[Me_2GaCl]_2$ resembles that associated with the hydrido derivative in several particulars. It differs, however, in the development of strong peaks near 240 and 330 pm, which can be identified with scattering from Ga–Cl and Ga ••• Ga atom pairs, respectively.

Molecular scattering intensities have been calculated, and the molecular structures refined on the basis of the model described above by full-matrix least-squares analysis.[30] For neither system are the vibrational properties sufficiently well charted to admit the possibility of 'shrinkage' corrections, but there is no reason to suppose that such corrections would alter appreciably the principal results of our calculations. All of the main geometrical parameters used to specify the $[Me_2GaH]_2$ molecule refined in a straightforward manner, with the results listed in Table 3. That no problems were experienced with correlation effects may be judged by the portion of the least-squares correlation matrix reproduced in Table 4(*a*). The angles $\tau$ and $\varphi$ relating to the positions of the hydrogen atoms in the methyl groups are subject to standard deviations approaching 5°, it is true, but this relatively large uncertainty is probably a reflection of the substantial thermal motions associated with the shallow potential wells defining the equilibrium positions of the relevant atoms. The angles $\theta$ and $\gamma$ defining the twisting of the $GaC_2$ plane relative to the central $Ga(\mu\text{-}H)_2Ga$ fragment and the puckering of that fragment, respectively, both refined to values of zero, and were fixed accordingly for the remainder of the refinement calculations.

**Table 4.** Portions of the least-squares correlation matrices (*a*) for $[Me_2GaH]_2$ and (*b*) for $[Me_2GaCl]_2$ showing off-diagonal elements greater than 50%

(*a*)

| | $p_4$ | $p_6$ | $p_7$ | $p_8$ | $u_1$ | $u_5$ | $k_1$* | $k_2$* |
|---|---|---|---|---|---|---|---|---|
| $p_2$ | 67 | | 51 | | | | | |
| $p_4$ | | | 57 | | | | −74 | −61 |
| $p_5$ | | −54 | | −80 | | −64 | | |
| $p_7$ | | | | | | | −57 | |
| $p_8$ | | | | | −62 | 73 | | |
| $u_2$ | | | | | | | 62 | 67 |
| $k_1$* | | | | | | | | 76 |

(*b*)

| | $p_5$ | $p_6$ | $p_7$ | $p_8$ | $u_1$ | $u_2$ | $u_5$ | $u_6$ | $k_1$* | $k_2$* |
|---|---|---|---|---|---|---|---|---|---|---|
| $p_1$ | 67 | | | | 76 | | | 84 | | |
| $p_2$ | | | 56 | | | | | | | |
| $p_4$ | | | | | | 53 | 86 | | | |
| $p_5$ | | 55 | 55 | −81 | 93 | | | | | |
| $p_7$ | | | | | 58 | | 58 | | 64 | |
| $p_8$ | | | | | −66 | | | | | |
| $u_2$ | | | | | | | 52 | | 70 | 52 |
| $k_1$* | | | | | | | | | | 63 |

* Scale factor

For the corresponding calculations on $[Me_2GaCl]_2$ the parameters $\theta$ and $\gamma$ were set equal to zero from the outset. Once again all the remaining geometrical parameters yielded to simultaneous refinement, with the angles $\tau$ and $\varphi$ emerging with the largest standard deviations; the details highlighted in Table 4(*b*) reveal no undue problems of correlation. With both $[Me_2GaH]_2$ and $[Me_2GaCl]_2$ independent refinement was possible for the amplitudes of vibration associated with the Ga ••• Ga, Ga–C, and Ga–$X_b$ vectors (X = H or Cl), as well as a common amplitude attributed to the various non-bonded Ga ••• $H_{Me}$ distances. With $[Me_2GaCl]_2$, moreover, the amplitudes $u$(C ••• Cl) and $u$(C ••• C′) were also amenable to refinement (where C′ denotes the *cis*-carbon atom attached to the *second* gallium centre). The amplitudes of $[Me_2GaCl]_2$ were found mostly to be larger than the corresponding properties of $[Me_2GaH]_2$, a feature attributable in part to the higher temperature of the chlorogallane vapour. The remaining amplitudes of both molecules, which made only small contributions to the overall molecular scattering, were assigned values in line with those established for related molecules, *e.g.* $Me_3Ga$[38] and $Me_2GaBH_4$.[14]

**Table 5.** Dimensions of molecules of the type $Y_2M(\mu\text{-}X)_2MY_2$ (M = B, Al, or Ga; X, Y = H, Cl, or Me) and related species

| Molecule | $r$(M···M)/pm | $r$(M–X)/pm | $r$(M–Y)/pm | Y–M–Y/° | M–X–M/° | H–C–M/° | $r$(C–H)/pm | Ref. |
|---|---|---|---|---|---|---|---|---|
| $[Me_2BH]_2$ | 184.0(1.0) | X = H, 136.4(4.5) | Y = C, 159.0(0.3) | 120.0(2.6) | 85(5) | 112(2) | 111.9(0.4) | 19 |
| $[Me_2AlH]_2$ | 261.7(0.6) | X = H, 167.6(1.9) | Y = C, 194.7(0.3) | 118.5(0.9) | 102.6(1.6) | 108.8(1.7) | 111.7(0.5) | 10 |
| $[Me_2GaH]_2$ | 261.0(0.5) | X = H, 170.8(1.4) | Y = C, 195.4(0.4) | 123.2(1.5) | 99.6(1.4) | 101.6(1.3) | 112.0(0.6) | This work |
| $[Me_2AlCl]_2$ | 327.4(1.3) | X = Cl, 230.3(0.3) | Y = C, 193.5(0.4) | 126.9(0.8) | 90.6(0.5) | 109.5(1.1) | 110.4(0.8) | 20 |
| $[Me_2GaCl]_2$ | 330.3(1.9) | X = Cl, 237.8(0.4) | Y = C, 194.6(0.3) | 132.1(2.7) | 88.0(0.9) | 106.8(1.3) | 112.9(0.7) | This work |
| $Ga_2Cl_6$ | 330.1(1.2) | X = Cl, 230.0(0.1) | Y = Cl, 209.9(0.1) | 124.6(0.9) | 91.7(0.4) | | | 21 |
| $[H_2GaCl]_2$ | 324.1(0.7) | X = Cl, 234.9(0.3) | Y = H, 155.9(1.9) | 120* | 87.2(0.8) | | | 27 |
| $Al_2Me_6$ | 261.9(0.5) | X = C, 214.0(0.4) | Y = C, 195.7(0.3) | 117.3(1.5) | 75.5(0.1) | 112.1(0.8) | 111.7(0.2) | 41 |
| $GaMe_3$ | | | Y = C, 196.7(0.2) | 118.6(0.4) | | 112.1(0.8) | 108.2(0.3) | 38 |

* Fixed

The success of the analyses may be gauged from the difference between the experimental and calculated radial-distribution curves (Figure 3). Figure 4 offers a similar comparison between the experimental and simulated molecular scattering. The structural details and vibrational amplitudes afforded by the optimum refinements, as listed in Table 3, corresponded to $R_G = 0.095$ ($R_D = 0.081$) for $[Me_2GaH]_2$ and $R_G = 0.04$ ($R_D = 0.06$) for $[Me_2GaCl]_2$. The estimated standard deviations allow for the effects of correlation and take account also of systematic errors in the electron wavelength, nozzle-to-plate distances, *etc.*

## Discussion

The findings of our experiments would seem to leave little room for doubt but that the predominant vapour species of dimethylgallane and its chloro analogue, at pressures near 1 mmHg and temperatures of *ca.* 290 and 350 K, respectively, are the dimeric molecules $Me_2Ga(\mu\text{-}X)_2GaMe_2$ (X = H or Cl), each with a diborane-like structure and a heavy-atom skeleton conforming to $D_{2h}$ symmetry. This therefore represents the first definitive structural characterisation of a compound containing two gallium atoms linked through a hydrogen bridge. Collation of the dimensions of $[Me_2GaH]_2$ and $[Me_2GaCl]_2$ with those of related boron-, aluminium-, or gallium-containing species (Table 5) is revealing for the light it sheds on some of the stereochemical details peculiar to molecules of this type. There are four aspects of some note.

(*i*) $r$(Ga···Ga).—At 261.0 pm, the Ga···Ga distance in $[Me_2GaH]_2$ is markedly shorter than that in $[Me_2GaCl]_2$ (330 pm). This dimension is to be compared, not only with twice the covalent radius of tetrahedrally co-ordinated gallium (252 pm), [39] but also with the Ga–Ga distances ranging from 247 to 307 pm in the different forms of elemental gallium.[40] In this respect, the gallane is strikingly similar to the analogous molecules $Me_2B(\mu\text{-}H)_2BMe_2$[19] and $Me_2Al(\mu\text{-}H)_2AlMe_2$,[10] and the dimensions make it hard to resist the case for direct interaction between the two Group 13 atoms linked by the hydrogen bridges. Such interaction is evidently weak in the chloro-bridged dimer, $[Me_2GaCl]_2$, but this may be a function of steric factors more than a reflection of the different donor capacity of the bridging atom. That there are secondary factors at work, even here, is revealed by the discovery that the Ga···Ga distance in different chloro-bridged gallanes varies somewhat, as evidenced by the following values (in pm): $[Me_2GaCl]_2$ 330, $Ga_2Cl_6$ 330,[21] and $[H_2GaCl]_2$ 324.1.[27]

(*ii*) $r(Ga\text{–}X_b)$.—The $Ga\text{–}H_b$ bond in dimethylgallane is, at 170.8 pm, appreciably longer than the terminal Ga–H bonds of molecules like $Me_3N{\cdot}GaH_3$ (149.7 pm),[13a] $[H_2GaNMe_2]_2$ (148.7 pm),[13b] $HGa(BH_4)_2$ (156.5 pm),[5] and $[H_2GaCl]_2$ (155.9 pm).[27] This is in keeping with the normal sacrificial behaviour shown by a metal–hydrogen bond on co-ordination to a second metal atom; it correlates too with the relatively low energies of the vibrational fundamentals approximating to Ga–H stretching modes in $[Me_2GaH]_2$ (*viz. ca.* 1 200 cm$^{-1}$). On the other hand, the $Ga\text{–}H_b$ bond is somewhat shorter than that in the molecule $Me_2Ga(\mu\text{-}H)_2BH_2$ (179 pm)[14] containing unsymmetrical Ga–H–B bridges. The $Ga\text{–}Cl_b$ bond in the chlorogallane $[Me_2GaCl]_2$ conforms to a similar pattern, being 28 pm longer than the terminal Ga–Cl bond in $Ga_2Cl_6$.[21] Molecules of the type $X_2Ga(\mu\text{-}Cl)_2GaX_2$ show a less pronounced, but none-the-less significant, dependence of the $Ga\text{–}Cl_b$ bond length on the nature of the terminal substituent X, as borne out by the following results (in pm): X = Cl 230.0,[21] H 234.9,[27] and Me 237.8. The attenuation experienced by the $Ga\text{–}Cl_b$ bond in this series reflects presumably the increasingly polar character of the $X_2Ga^{\delta+}\cdots Cl_b^{\delta-}$ interaction.

(*iii*) *The* $Me_2Ga$ *Group.*—At 194.8 ± 0.5 pm, the Ga–C distance in the three molecules $[Me_2GaH]_2$, $[Me_2GaCl]_2$, and $Me_2GaBH_4$[14] is virtually invariant, and only slightly less than the corresponding distance in $Me_3Ga$ (196.7 pm).[38] Hence it appears that this parameter is comparatively insensitive to the nature of any bridging groups and even to changes in the co-ordination geometry at gallium. On the other hand, the switch from $[Me_2GaH]_2$ to $[Me_2GaCl]_2$ is accompanied by an opening out of the C–Ga–C bond angle from 123 to 132°, a change which surpasses the comparatively wide limits of uncertainty affecting this parameter. A similar trend is displayed by the corresponding aluminium compounds with C–Al–C bond angles of 117, 118.5, and 127° for molecules of the type $Me_2Al(\mu\text{-}Y)_2AlMe_2$, where Y = $CH_3$,[41] H,[10] and Cl,[20] respectively. Such a change is consonant with a greater degree of *s* character in the metal orbitals providing the bonding to the methyl groups as the bridging unit becomes more electronegative.

(*iv*) *Orientation and Geometry of the* $CH_3$ *Groups.*—The refinement calculations explored several models describing the torsional motion of the $CH_3$ groups in $[Me_2GaH]_2$ and $[Me_2GaCl]_2$. Thus, the two $CH_3$ groups in each $(CH_3)_2Ga$ fragment were allowed independent 'twist' angles, $\tau$, but the optimum refinement was provided by the model described previously and involving concerted rotation of the $CH_3$ groups. For both molecules $\tau$ falls in the range 40—49°, but any dependence on the nature of the bridging group is masked, unfortunately, by standard deviations of 4—5°. The C–H distances, which are in line with those determined for related species,[10,19,20,38] are likewise comparatively insensitive to the nature of the molecule. More surprising, on the face of it, are the parameters defining the H–C–Ga and $CH_3$ 'tilt' angle, $\varphi$, of $[Me_2GaH]_2$. Although there is little that is untoward about

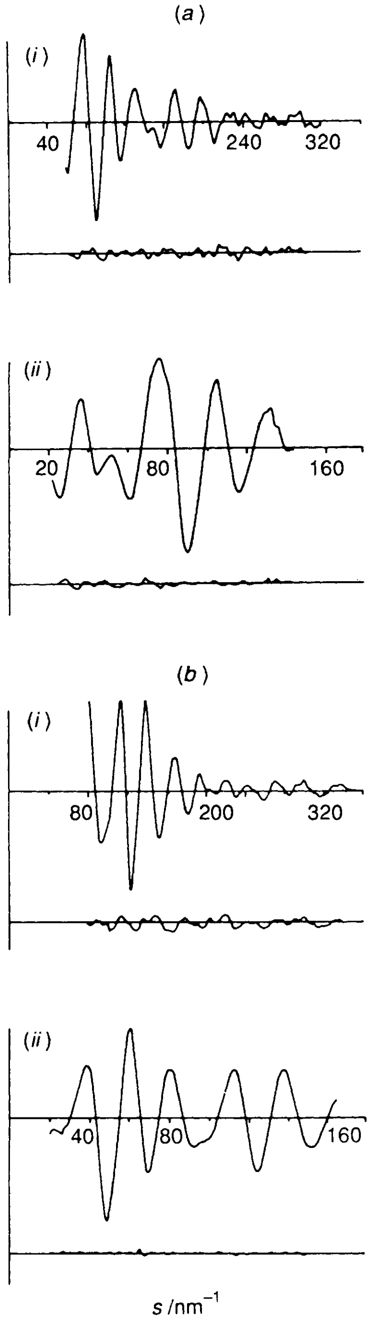


**Figure 4.** Experimental and final difference molecular-scattering intensity curves: (*a*) $[Me_2GaH]_2$ with nozzle-to-plate distances (*i*) 128.4 and (*ii*) 285.4 mm; (*b*) $[Me_2GaCl]_2$ with nozzle-to-plate distances (*i*) 98.4 and (*ii*) 255.8 mm

$[Me_2GaCl]_2$, with H–C–Ga 104.2(1.3) and $\varphi = -2(4)°$, the corresponding parameters in the hydrido derivative [*viz.* H–C–Ga 101.6(1.3) and $\varphi = -7(4)°$] may betray an anomalous orientation, in which each pair of $CH_3$ groups is tilted somewhat towards each other so that the methyl hydrogen atoms *closest* to the $Ga(\mu\text{-}H)_2Ga$ plane are drawn preferentially towards the gallium atom. No similar effect has been remarked in either of the related molecules $Me_2B(\mu\text{-}H)_2BMe_2$[19] or $Me_2Al(\mu\text{-}H)_2AlMe_2$,[10] which have been studied previously by electron diffraction, and there is nothing about the i.r. spectrum of dimethylgallane to suggest atypical orientation and coordination of the $CH_3$ groups.[42] With a compound as reactive and thermally fragile as dimethylgallane, there is no way of ruling out completely the possibility of contamination by reaction or decomposition products, *e.g.* traces of (*a*) silanes formed by the slow reaction of the gallane with glass, or (*b*) $[Me_2Ga(OH)]_n$ formed by partial hydrolysis at the hands of adsorbed moisture. Hence the tilting of the methyl groups may be real, but it may also be an artifice of contamination of the vapour being sampled by the electron beam in the electron-diffraction experiment.

How closely the dimensions of dimethylgallane presage those of the parent digallane, $Ga_2H_6$, will be revealed in a forthcoming paper.[16]

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