Molecular structure of trimethylamine–gallane, Me₃N·GaH₃: *ab initio* calculations, gas-phase electron diffraction and single-crystal X-ray diffraction studies †

Paul T. Brain,[a] Helen E. Brown,[b] Anthony J. Downs,*[b] Tim M. Greene,[b] Emma Johnsen,[b] Simon Parsons,[a] David W. H. Rankin,[a] Bruce A. Smart[a] and Christina Y. Tang[b]

[a] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*

[b] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR*

The structure of the gallane adduct Me₃N·GaH₃ has been investigated by *ab initio* quantum chemical calculations. The results of gas-phase electron-diffraction (GED) measurements, together with earlier microwave measurements, have been reanalysed using the SARACEN method to determine the most reliable structure of the gaseous molecule. Salient structural parameters (r_α^o structure) were found to be: r(Ga–H) 151.1(13), r(Ga–N) 213.4(4), r(N–C) 147.6(3), r(C–H) 108.4(4) pm; H–Ga–N 99.3(8) and Ga–N–C 108.8(2)°. Unlike the corresponding alane derivative, the adduct is monomeric in the crystalline phase with dimensions very close to those of the gaseous molecule, as confirmed by a redetermination of the structure of a single crystal at 150 K.

Gallane is not a strong Lewis acid but the adducts it forms with nitrogen, phosphorus and oxygen bases typically improve on the parent compound[1–4] in the thermal stabilities they display. For this reason the adducts rather than gallane itself are favoured for reactions seeking to exploit the facility of the gallium-bound hydrogen ligands to act as leaving groups in metathesis, reduction or elimination processes.[5–7] Herein lie significant potential applications in chemical vapour deposition (CVD) technology,[6–9] related materials science (as in the preparation of gallium nitride[10]), and chemical synthesis.[10,11] Testifying to the resurgent interest are the reported synthesis and characterisation of new amine and phosphine complexes of gallane,[2,12–18] as well as numerous quantum chemical inquiries seeking to assess the structural, vibrational and thermodynamic properties of species like H₃E·GaH₃ (E = N,[19,20] P,[20] or As[20,21]) and H₂O·GaH₃.[22]

No gallane complex has been studied more extensively than trimethylamine–gallane, Me₃N·GaH₃. Although it is not lastingly stable at ambient temperatures and dissociative adsorption prevents it from being a useful source of gallium-bearing films,[9] it is easily prepared and purified and is a convenient source material for other gallane complexes, as well as derivatives in which one or more Ga–H bonds have been replaced.[5–7,10–18] It was one of the first gallium hydrides to be characterised structurally. Incomplete X-ray studies of a single crystal confirmed the C_{3v} symmetry of the molecular skeleton but failed to locate the hydrogen atoms and yielded a poorly defined Ga–N distance of 197(9) pm;[23] a very recent study of a crystal at 173 K has improved on this to give r(Ga–N) = 207(1) pm without being able to refine the placement of the hydrogen atoms.[17] By contrast, the rotational constants derived from the microwave spectrum of the gaseous molecule imply a value of r_o(Ga–N) = 211.2(2) pm, but these too are relatively insensitive

to the location of the hydrogen atoms.[24] A more complete structure [with r_a(Ga–N) = 212.4(7) and r_a(Ga–H) = 149.7(15) pm] was subsequently determined for the gaseous molecule by electron diffraction.[25] However, there are limits to the structural details that can be established well by electron diffraction alone. Two features in particular militate against the precise positioning of the hydrogen atoms: (*i*) the distances N–C and Ga–H are very similar and the parameters defining them therefore strongly correlated, and (*ii*) the hydrogen atoms contribute relatively little to the molecular scattering which is dominated by the heavy atoms. The refinement reported originally[25] therefore gave a rather basic structure: several parameters had to be fixed at assumed values and other stipulations made to simplify the structural analysis; in keeping with normal practice at that time, moreover, no attempt was made to assess the effects of vibration other than by refinement of some amplitudes of vibration.

The limitations of the gas-phase electron-diffraction (GED) data can, to some extent, be overcome by a combined analysis incorporating geometric and vibrational information carried by the rotational constants and experimental force field,[24] respectively. A major improvement in the reliability and quality of the structural refinement is now possible with the advent of the SARACEN method[26,27] whereby parameters which cannot be refined freely are made subject to restraints derived from an array of *ab initio* calculations; all geometric parameters and significant amplitudes of vibration are then refined as a matter of principle.

Here we report the results of a series of *ab initio* molecular orbital calculations carried out on Me₃N·GaH₃. The dimensions and harmonic force field estimated in this way are then used in conjunction with the measured rotational constants and vibrational parameters[24] and the original electron-diffraction data[25] to arrive at a much more reliable structure for the gaseous molecule. This is compared with the structure of the compound in the solid phase, as redetermined by X-ray diffraction of a single crystal at 150 K. The results invite further comparisons with the corresponding alane, Me₃N·AlH₃, which

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† *Supplementary data available*: miscellaneous GED data. For direct electronic access see http://www.rsc.org/suppdata/dt/1998/3685/, otherwise available from BLDSC (No. SUP 57442, 6 pp.) or the RSC Library. See Instructions for Authors 1998, Issue 1 (http://www.rsc.org/dalton).

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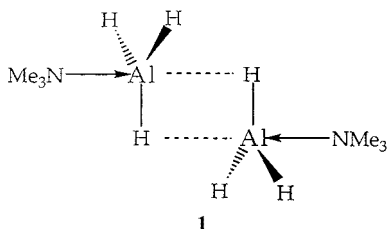
exists as a monomer in the vapour at low pressures [28] but as a dimer, **1**, in the crystalline state.[29]

Experimental

(a) *Ab initio* calculations

Theoretical methods: geometry optimisation. All *ab initio* molecular orbital calculations were carried out on a DEC Alpha APX 1000 workstation using the GAUSSIAN 94 program.[30] Geometry optimisations on trimethylamine–gallane were undertaken at the SCF and MP2 levels using the standard 6-31G(d) [31–33] and 6-311G(d,p) [34,35] basis sets. The frozen core approximation (1s frozen for C and N, 1s2s2p frozen for Ga) was employed for all correlated calculations. We sought to investigate the effect of adding diffuse functions or including a larger polarisation set by performing calculations at the 6-311 + G(d,p)/MP2 and 6-311G(df,p)/MP2 levels. The effects of including a more sophisticated treatment of electron correlation were investigated using the 6-31G(d) basis set at the MP3 and MP4SDQ levels of theory. Final, highest level estimates of geometric parameters were gained at the 6-311 + G(df,p)/MP2 level.

Frequency calculations. Vibrational frequency calculations undertaken at the 6-31G(d)/SCF and 6-31G(d)/MP2 levels were used to verify overall C_{3v} symmetry. The force field described by Cartesian force constants was transformed into one described by a set of symmetry coordinates with the aid of the program ASYM 40.[36] The resulting vibrational assignments were found to be consistent with those based on the measured infrared and Raman spectra of three isotopomers of $Me_3N \cdot GaH_3$ [24] and 16 of the *ab initio* force constants (diagonal force constants corresponding to $v > 200$ cm^{-1}) were therefore scaled to conform to the reported experimental frequencies, off-diagonal elements each being scaled as the root square product of the relevant diagonal scale factors.

(b) Gas-phase electron diffraction

GED data. The new refinement reported here is based on the original data set recorded on the Edinburgh apparatus.[25] In common with the parent compound [2] and other gallane derivatives,[3] $Me_3N \cdot GaH_3$ vapour reacted with the emulsion of the photographic plates, resulting in higher than normal noise levels in the GED measurements. Standard programs catered for the data reduction [37] with the scattering factors of Ross *et al.*[38] The weighting points used in setting up the off-diagonal weight matrix, the *s* range, scale factors, correlation parameters and electron wavelengths are listed in SUP 57442.

GED model. The molecular framework and atom numbering scheme for $Me_3N \cdot GaH_3$ are shown in Fig. 1. With the assumption of at least C_3 symmetry for the C_3NGaH_3 skeleton and local C_{3v} symmetry for the CH_3 groups, ten independent parameters are required to define the structure completely; as listed in Table 1, these comprise four distances (Ga–H, Ga–N, N–C, and C–H) and six angles [H–Ga–N, Ga–N–C, N–C–H; the H–Ga–N–C dihedral angle or 'GaN twist' (0 to 60°); the H–C–N–Ga dihedral angle or 'CH$_3$ twist' (0 to 60°); and the angle subtended by the threefold axis of each CH$_3$ group to the N–C vector or 'CH$_3$ tilt'].
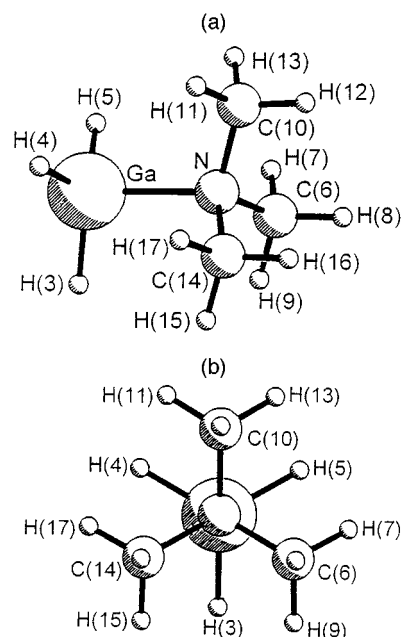

Fig. 1 Views of $Me_3N \cdot GaH_3$ in the optimum refinement of the electron-diffraction data: (a) perspective view and (b) view down the N–Ga bond.

Table 1 Experimental geometrical parameters[a] from the SARACEN[b] study of gaseous $Me_3N \cdot GaH_3$ (r_a°/pm, angles/°) and from the structure of a single crystal at 150 K as determined by X-ray diffraction

Parameter[a]	Vapour[b,c]	Single crystal[c]
Bond distances		
p_1 r(Ga–H)	151.1(13)	151(6)
p_2 r(Ga–N)	213.4(4)	208.1(4)
p_3 r(N–C)	147.6(3)	147.7(4)
p_4 r(C–H)	108.4(4)	100(3)
Bond angles		
p_5 H–Ga–N	99.3(8)	97(2)
p_6 Ga–N–C	108.8(2)	109.8(2)
p_7 N–C–H(7),H(8)	111.7(13)	107(2), 110(3)
p_8 GaN twist	60.0(f)	60(f)
p_9 CH$_3$ twist	60.0(f)	[d]
p_{10} CH$_3$ tilt	0.0(f)	[d]

[a] For definition of parameters see the text and for atom numbering see Fig. 1. [b] For details of refinement see the text and Tables 4 and SUP 57442; f = fixed. [c] Estimated standard deviations (e.s.d.s) derived from the least-squares refinement are given in parentheses. [d] In the crystal the CH$_3$ groups have local C_s symmetry with H(7)–C–H(8),H(9) 108(2), 117(2) and Ga–N–C–H(7) 63(2)°.

The rotation constants relating to an axis perpendicular to the C_3 axis of the $Me_3N \cdot GaH_3$ molecule and determined from the microwave spectra of six different isotopomers, *viz.* $Me_3^{14}N \cdot ^{69}GaH_3$, $Me_3^{15}N \cdot ^{69}GaH_3$, $Me_3^{14}N \cdot ^{69}GaD_3$, $Me_3^{14}N \cdot ^{71}GaH_3$, $Me_3^{15}N \cdot ^{71}GaH_3$ and $Me_3^{14}N \cdot ^{71}GaD_3$, were combined with the GED data. The microwave B_0 constants were corrected to B_z for the structural refinements using values calculated by ASYM 40.[36] The six corrected rotational data were presented in the refinements as the absolute value of B_z for the $Me_3^{14}N \cdot ^{69}GaH_3$ isotopomer, $B[1]$, and the five differences from this value for the other isotopomers, *i.e.* $B[1] - B[2]$, $B[1] - B[3]$, *etc.* (Table 2).

The vibrational corrections to the microwave constants ($B_0 \longrightarrow B_z$) are a summation of the corrections for each mode.[36] For the $Me_3N \cdot GaH_3$ isotopomers this sum was small, typically 0.5–0.6 MHz, but contributions from some modes were of the order 5–7 MHz. As such, the normal procedure of assuming a 10% error in the absolute value of the vibrational

Constant[a]	B_z(obs.)[b]	B_z(calc.)[c]	B_z(obs. − calc.)	Uncertainty[d]
$B[1]$	1875.31	1874.03	1.28	1.45
$B[1] - B[2]$	6.67	6.68	−0.01	0.07
$B[1] - B[3]$	59.55	59.40	0.15	1.71
$B[1] - B[4]$	17.25	17.26	−0.01	0.04
$B[1] - B[5]$	24.00	24.05	−0.05	0.06
$B[1] - B[6]$	74.85	74.84	0.01	1.69

[a] Isotopomer numbering: $[1] = Me_3{}^{14}N \cdot {}^{69}GaH_3$; $[2] = Me_3{}^{15}N \cdot {}^{69}GaH_3$; $[3] = Me_3{}^{14}N \cdot {}^{69}GaD_3$; $[4] = Me_3{}^{14}N \cdot {}^{71}GaH_3$; $[5] = Me_3{}^{15}N \cdot {}^{71}GaH_3$; $[6] = Me_3{}^{14}N \cdot {}^{71}GaD_3$. [b] From microwave spectroscopy, see ref. 24; $B_o \longrightarrow B_z$ corrections were derived from the 6-31G(d)/MP2 force field using ASYM 40. [c] From the GED analysis. [d] For details of the derivation of uncertainty estimates see the text.

correction was deemed inappropriately small. Instead, the uncertainty in the absolute correction was computed from a summation of an assumed 10% error in the correction for each mode, according to eqn. (1) below, where $c(m)_i$ is the vibrational

$$\sqrt{\sum_i \left[\frac{c(m)_i}{10} \right]^2} \qquad (1)$$

correction of the ith mode of the main isotopomer, $B[1]$. The uncertainty in the correction for a difference between the rotation constants for two isotopomers was calculated similarly, as in eqn. (2), where $c(n)_i$ is the vibrational correction of the ith

$$\sqrt{\sum_i \left[\frac{c(m)_i - c(n)_i}{10} \right]^2} \qquad (2)$$

mode of isotopomer n, $B[n]$ ($n = 2$–6). For the isotopomers, the correction terms for the ith mode are strongly correlated; thus the uncertainty in the total vibrational correction for a difference is much smaller than the uncertainties in the individual absolute values.

(c) X-Ray diffraction by a single crystal

Synthesis, crystal growth and manipulation. Trimethylamine–gallane was prepared by the reaction of $Li[GaH_4]$ with $NHMe_3Cl$ in diethyl ether[39] and purified by fractional condensation *in vacuo*; the IR spectrum of the vapour[24] and ^1H NMR spectrum of a $[^2H_8]$toluene solution[5] confirmed the identity and purity of the product. Crystals of the adduct were grown by slow sublimation *in vacuo* onto the walls of a vessel cooled to *ca.* 277 K.

A crystal suitable for study by X-ray diffraction was selected from under cold perfluoropolyether RS3000 oil. The crystals grew as rather large blocks, but attempts to cut them prior to data collection resulted in a severe deterioration in quality, perhaps because of disruption of mosaicity. The sample studied was therefore large by normal standards, although the dimensions given below partly reflect the size of the oil drop. A 1.2 mm collimator was used for data collection.

Crystal data. $C_3H_{12}GaN$, $M = 131.86$, rhombohedral, space group $R3m$, $a = 929.71(9)$, $c = 666.46(13)$ pm, $U = 498.88 \times 10^6$ pm^3, $\lambda = 71.073$ pm, $Z = 3$ (the molecule has $3m$ crystallographic symmetry), $D_c = 1.317$ Mg m^{-3}, $F(000) = 204$, $T = 150.0(2)$ K, colourless lath $0.90 \times 0.39 \times 0.31$ mm, μ(Mo-Kα) = 4.006 mm^{-1}.

Data were collected on a Stoë Stadi-4 four-circle diffractometer with graphite-monochromated Mo-Kα radiation, ω–θ mode. Of the 1932 reflections measured ($\theta_{max} = 29.90°$; $-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-9 \leq l \leq 9$) 380 were unique ($R_{int} = 0.0751$). An absorption correction was applied with ψ-scan data ($T_{min} = 0.294$, $T_{max} = 0.595$).

The structure was solved by Patterson methods and completed by iterative cycles of least-squares refinement (against F^2) and Fourier difference syntheses (SHELXTL).[40] All H atoms were readily located in difference maps and subsequently refined freely, C–H bond lengths being restrained to be similar. All non-H atoms were modelled with anisotropic displacement parameters to give a final conventional R of 0.0249 [based on F and 380 data with $F > 4\sigma(F)$] and $wR2 = 0.0639$ (based on F^2 and all 380 data). The final difference map extrema were $+0.39$ and -0.41 e Å^{-3}, and the Flack absolute structure parameter was 0.01(5).

CCDC reference number 186/1169.

See http://www.rsc.org/suppdata/dt/1998/3685/ for crystallographic files in .cif format. The structure is also available as a .mol file.

Results and discussion

(a) *Ab initio* calculations

A graded series of *ab initio* calculations was performed on trimethylamine–gallane to investigate the effects of changes in the theoretical method on the molecular geometry, with the results presented in Table 3. In general, improvements in the theoretical treatment had only a modest influence on the values of most molecular parameters, with bond lengths proving to be slightly more sensitive than bond angles to changes in the theoretical method. Bonds to gallium proved to be much the most sensitive of all the parameters, and consequently our confidence in these values is lower than that in other bond distances and angles. For example, the Ga–N bond distance was found to vary between 211.0 and 213.8 pm when correlated methods are employed, with improvements in the s,p basis and the level of electron correlation leading to longer predicted distances, while increasing the size of the polarisation set leads to smaller values. At the MP2 level the Ga–H bond distance decreased by 2.7 pm on improving the basis set from 6-31G(d) to 6-311G(d), and subsequently lengthened by 0.4 pm on the introduction of more basis functions. With the 6-31G(d) basis set the Ga–H distance lengthened at higher levels of electron correlation. The remaining bond lengths, C–N and both C–H bonds, proved to be very stable with respect to changes in the theoretical method, with variations never greater than 0.2 pm when correlated methods were employed. Variations in bond angles were similarly small and all angles exhibited ranges of less than 1° when correlated methods were employed.

(b) Gas-phase electron-diffraction study

As indicated earlier, the new structure described here depends on a re-refinement of the original GED data.[25] Various assumptions had to be made in the earlier analysis; using GED data alone, this was hampered particularly by the difficulty of locating the hydrogen atoms and by the marked correlation involving the parameters that characterise the Ga–H and N–C distances (see, for example, the radial-distribution curve shown in Fig. 2). As a result, the refined Ga–H distance was subject to a relatively large uncertainty, while the H–Ga–N, H–Ga–N–C and CH₃ tilt angles could not be refined and had to be fixed at values estimated by optimisation of the R factor. In addition to seven geometric parameters, no more than five amplitudes of vibration yielded to refinement, the remaining vibrational parameters being assigned values based not on the force field[24] but on analogies with related molecules, *e.g.* HGa(BH₄)₂ and NMe₃. The structure deduced was consistent with those of similar compounds but the geometry of the N-GaH₃ moiety was not well defined, with regard to either the H–Ga–N angle or the Ga–H distance, which at 149.7(15) pm appeared rather short compared with the corresponding distances in base-free gallane molecules.[3,25]

The rotational constants detailed above can be combined

Table 3 Molecular geometries (r_e; distances in pm, angles in °) calculated for $Me_3N\cdot GaH_3$ by a range of *ab initio* methods

Parameter[a]	6-31G(d)/ MP2	6-31G(d)/ MP3	6-31G(d)/ MP4SDQ	6-311G(d)/ MP2	6-311G(df,p)/ MP2	6-311 + G(df,p)/ MP2	GED (r_a^o)[b,c]	GED (r_a^o)[b,d]
r(Ga–N)	211.0	211.6	211.7	213.8	211.8	211.8	213.4(4)	213.9(5)
r(Ga–H)	159.3	159.8	160.0	156.6	157.1	157.1	151.1(13)	154.6(14)
r(C–N)	147.7	147.7	147.8	147.5	147.5	147.6	147.6(3)	147.5(3)
r(C–H[8])	109.8	109.8	110.0	109.9	109.9	109.9	} 108.4(4)	111.7(5)
r(C–H[7,9])	109.1	109.2	109.3	109.2	109.2	109.2		
H–Ga–N	99.7	99.7	99.7	98.9	99.0	99.0	99.3(8)	98.4(9)
C–N–Ga	109.0	109.0	109.0	109.3	109.2	109.3	108.8(2)	108.7(2)
H(8)–C–N	110.7	110.8	110.3	110.4	110.3	110.3	} 111.7(13)	109.0(15)
H(7,9)–C–N	109.1	109.1	109.1	109.1	108.9	109.0		

[a] For atom-numbering scheme, see Fig. 1. [b] Values in parentheses are the estimated standard deviations. [c] Analysis supported by ASYM 40. [d] Analysis supported by SHRINK.
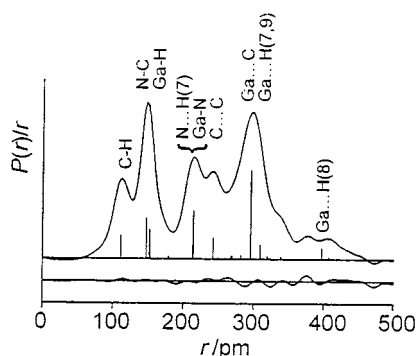

Fig. 2 Observed and final weighted difference radial-distribution curves for $Me_3N\cdot GaH_3$. Before Fourier inversion the data were multiplied by $s\cdot exp[(-0.000\,02s^2)/(Z_{Ga} - f_{Ga})(Z_N - f_N)]$.

Table 4 Selected interatomic distances (r_a/pm) and amplitudes of vibration (u/pm) derived from the SARACEN study of $Me_3N\cdot GaH_3$[a]

i	Atom pair	Distance	Amplitude[b]
1	Ga–H	152.2(13)	8.9(8)
2	Ga–N	213.9(4)	7.7(4)
3	N–C	147.9(3)	4.4(3)
4	C–H	111.1(4)	7.0(4)
5	H(3)···H(4)	259.1(24)	15.9 fixed
6	N···H(3)	280.6(16)	16.4(15)
7	Ga···C(6)	296.0(23)	10.5(4)
8	N···H(7)	214.0(16)	12.2(9)
9	C(6)···C(10)	242.1(5)	6.2(5)
10	H(7)···H(8)	178.4(19)	12.5(12)
11	C(6)···H(3,5)	319.4(69)	20.5(18)
12	C(6)···H(4)	406.2(14)	14.7(13)
13	Ga···H(7,9)	310.5(69)	17.2(14)
14	Ga···H(8)	397.4(5)	12.7(9)
15	C(6)···H(11,17)	338.7(12)	10.6(9)
16	C(6)···H(12,16)	269.7(58)	16.3(15)
17	C(6)···H(13,15)	268.4(57)	15.9(15)

[a] Estimated standard deviations, derived from the least-squares refinement, are given in parentheses. [b] Amplitudes which could not be refined are fixed at values derived from the 6-31G(d)/MP2 scaled force field.

with the GED data (Table 2) to secure more reliable estimates of some parameters. Moreover, the *ab initio* calculations we have carried out (Table 3) leave little room to doubt the values assumed by the GaN twist, CH_3 twist and CH_3 tilt angles when the molecule conforms to the global minimum prescribed by the calculated potential-energy surface. The calculations also give a harmonic vibrational force field which, after scaling to bring it into line with the experimental vibrational frequencies,[24] can be used to produce perpendicular amplitude corrections (K) for use in the electron-diffraction r_a^o refinements. The SARACEN method[26,27] then guides the refinement of the seven remaining geometric parameters as well as all the significant amplitudes of vibration, without the need for any further assumptions about the molecular model, ultimately to attain a much more reliable structure with realistic errors.

The new refinement of the structure of gaseous $Me_3N\cdot GaH_3$ affords the results listed in Tables 1 and 4. The experimental data for the shorter camera distance used in the earlier refinement have been truncated to $s = 25.2$ nm^{-1}; the resultant decrease in the standard deviations of the refining parameters indicated that the data thus excluded were superfluous.

In the final calculations all bond distances and angle parameters pertaining to C_{3v} symmetry were found to refine freely, including those associated with the hydrogen atoms. The rotation constants B are not sensitive to the value of the Ga–N twist angle, p_8. However, lowering the molecular symmetry below C_{3v} led to a poorer fit for the rotation constants as a result of changes in other refining parameters. Thus, fixing the GaN twist angle at 60° is fully justified since the B values are our most reliable source of information. At the conclusion of the analysis, however, we investigated the effects of refining the twist angles p_8 and p_9, each being restrained to $60 \pm 10°$. This allowed a more realistic gauge of the estimated standard deviations (e.s.d.s) of all the other refining parameters, particularly those defining the hydrogen atom positions. The e.s.d.s quoted for the GED results are taken from this additional refinement.

Restraints were also applied to amplitudes of vibration u that could not otherwise be refined independently. Values for the restraints (see SUP 57442) were calculated directly from the scaled force field, with uncertainty ranges of 10% of the computed values. With these restraints in place, all amplitudes, including that corresponding to H(7)···H(8) but not those for other H···H distances, were refined. Attempts to refine the other H···H amplitudes returned e.s.d.s and values very similar to those of their restraints, indicating that these were determined almost entirely by the restraints. These amplitudes were subsequently fixed in the final refinements since they were not correlated significantly with other refining parameters ($\leq 10\%$ in the correlation matrix), and thus did not contribute to their e.s.d.s.

For the distances r(Ga–H), r(Ga–N), r(N–C) and r(C–H), the final refined values were 151.1(13), 213.4(4), 147.6(3) and 108.4(4) pm, respectively, compared with the *ab initio* values [6-311 + G(df,p)/MP2] of 157.1, 211.8, 147.6 and 109.4 pm; for the angles H–Ga–N, Ga–N–C and N–C–H, the refined values were 99.3(8), 108.8(2) and 111.7(13)°, respectively, compared with the *ab initio* values of 99.0, 109.3 and 109.4°. Both the Ga–N and Ga–H distances differ from the calculated values by four or more standard deviations, a finding probably reflecting deficiencies on the part of the *ab initio* calculations, in that the parameter values are affected appreciably by basis set and electron correlation effects (see Table 3). Similar effects are found for GaH_3 itself, for which r_e(Ga–H) is computed to be 157.8 pm at 6-31G(d)/MP2, 155.3 pm at 6-311G(df,p)/MP2, and 154.8 pm at 6-311G(3df,3pd)/MP2. Following the same extrapolation

for $Me_3N \cdot GaH_3$ would predict a 6-311G(3df,3pd)/MP2 distance of 156.6 pm for $r_e(Ga–H)$. That the theoretical estimate of $r_e(Ga–H)$ should exceed appreciably the r_a^o value derived from the GED data follows the precedent of previous calculations which consistently overestimate Ga–H bond lengths.[41–43] The variation of energy with theoretical $r_e(Ga–H)$ distance at the 6-31G(d)/SCF level yields a Morse anharmonicity constant (a) of *ca.* 0.015 pm^{-1}. Applying the vibrational correction $\frac{3}{2}au_o^2$ to r_a^o gives an experimental $r_e(Ga–H)$ of 149.1(13) pm, 7.5 pm shorter than the extrapolated theoretical value. In the present circumstances the experimental values of $r(Ga–H)$ and $r(Ga–N)$ are probably better defined than the calculated ones, although there remain some doubts about the reliability of the perpendicular amplitude (K) corrections (see below). For no other structural parameter, however, do the experimental and calculated values diverge significantly.

The problem of calculating perpendicular amplitudes of vibration (K) for molecules executing large-amplitude, low-frequency vibrational motions is well documented.[44] The adoption of a rectilinear description of such motions (as in ASYM 40)[36] results in erroneously large K values for some bonding distances. In the case of $Me_3N \cdot GaH_3$ the torsional mode of the GaH_3 moiety about the N–Ga bond [predicted to lie at 172 cm^{-1} at the MP2/6-31G(d) level] has been excluded from our analysis of the vibrational force field using ASYM 40 in an attempt to negate the possibility of overestimating the K value for the Ga–H distance. Recently Sipachev[45] has made available a program called SHRINK in which vibrational motions are described by coordinates approximating more closely to true curvilinear pathways, and which should thus give rise to more realistic estimates of vibrational correction terms (equivalent to K values) than methods involving the rectilinear approximation. Although use of the program SHRINK remains in its infancy and the results need to be treated with due care, u, K and a values have been computed from the force field for $Me_3N \cdot GaH_3$, *including* the N-GaH_3 torsional mode, and have been used in a further refinement of the combined GED/MW structure.

In Table 3 geometrical parameters refined on the basis of values from Sipachev's SHRINK program are compared with those derived from the analysis employing ASYM 40. At the 1σ level only the Ga–H and C–H bond distances are significantly different, both being more than 3 pm longer in the SHRINK-supported refinement. At 154.6(14) pm, the r_a distance for Ga–H is in much better agreement with the theoretical predictions than the value of 151.1(13) pm afforded by the ASYM 40-supported refinement. However, it remains nearly 1.5 e.s.d.s shorter than the extrapolated theoretical r_e value of 156.6 pm (see above), and yields an experimental $r_e(Ga–H)$ distance of 152.6(14) pm, 4 pm shorter than the best theoretical prediction available to us. Assuming a value of 0.03 pm^{-1} for the Morse anharmonicity constant a for C–H bond distances, the experimental $r_e(C–H)$ distance is 108.9(4) pm in the SHRINK-supported refinement, very similar to the computed (6-311 + G(df,p)/MP2 level) average value of 109.4 pm. In making these comparisons with the ASYM40-supported refinements, we note that the final R_G factor for the SHRINK-supported refinements was *ca.* 3% worse and the fit to the rotational constants slightly poorer.

The final R_G factor for the new refinement was 0.10. This higher than normal value reflects in part the simultaneous fitting of the B values with the GED data and in part also the noise in these data arising from the fogging of the photographic plates by the $Me_3N \cdot GaH_3$ vapour. Nevertheless, the new structure represents the best that can be established on the basis of the experimental and theoretical information currently available; all standard deviations are realistic estimates of the errors. Several of the refined parameters now have much more reasonable values than they did previously, *e.g.* u(C–H) [7.0(4) *vs.* 5.0(8) pm[25]], implying that the data were probably over-refined

in the earlier analysis.[25] A selection of interatomic distance and vibrational amplitude values for the final structure is given in Table 4; the least-squares correlation matrix and the Cartesian coordinates are in SUP 57442, as are the molecular-scattering intensity curves.

(c) X-Ray study of a single crystal

Bond distances and angles for crystalline $Me_3N \cdot GaH_3$ are listed in Table 1; where direct comparisons are possible, the dimensions are consistent with those of Raston and co-workers.[17] The results show that the compound forms essentially molecular crystals consisting of more-or-less discrete monomeric $Me_3N \cdot GaH_3$ molecules. The shortest $Ga \cdots H$ and $Ga \cdots N$ contacts between different molecules are 338(4) and 458.4(4) pm, respectively, giving no hint of significant secondary intermolecular interactions analogous to those responsible for the dimeric units $[Me_3N \cdot AlH_3]_2$ **1** in crystals of the corresponding alane.[29] To a good approximation, therefore, the gallium centre assumes the four-fold co-ordination characteristic of the gaseous molecule and of the majority of gallium(III) complexes.[1] The increased co-ordination number of the aluminium in the solid alane derivative must reflect a difference not in size but in Lewis acidity of the co-ordinated metal centre. Testifying to this superior acidity is the uptake of a second molecule of trimethylamine to form an adduct $2Me_3N \cdot AlH_3$ which, unlike its gallane counterpart, suffers little dissociation at ambient temperatures.[1,2,5,6]

At 208.1(4) pm the Ga–N distance is substantially longer than the earliest estimate [197(9) pm],[23] although when the large standard error of the latter is taken into consideration this difference is not statistically significant. It is close to the corresponding distance in tmen·$2GaH_3$ (tmen = $Me_2NCH_2CH_2$-NMe_2),[12,13] but somewhat longer than that in the unusually stable adduct quinuclidine·GaH_3 [206.3(4) pm].[13] Within the limits of uncertainty and compatibility set by the X-ray and GED experiments, this is the only structural parameter of $Me_3N \cdot GaH_3$ to assume a value for the crystal that is significantly different from the value determined for the gaseous molecule [213.4(4) pm].

Conclusion

The present *ab initio*, GED and X-ray diffraction study provides the first reliable structural characterisation of an alane or gallane adduct to span both the vapour and condensed states and to include a reasonably precise mensuration of the L–MH_3 unit (L = donor molecule; M = Al or Ga). As noted previously,[25] the dimensions of the co-ordinated Me_3N molecule in the gaseous adduct differ only slightly and predictably from those of the free molecule, with a small increase [$\Delta r_a = 2.5(4)$ pm] in the N–C bond length and no significant opening out of the semi-vertical angle of the pyramidal NC_3 skeleton.[46,47]

On the evidence of our results, the dimensions of the $Me_3N \cdot GaH_3$ molecules alter but little with the switch from the vapour to the crystal. The one significant change attending condensation is a 5.3(6) pm contraction of the Ga–N distance, suggesting an increased degree of charge transfer in the solid state. This effect is commonly found for adduct structures on changing from the gas phase to the solid state. An increasing dipole moment allows intermolecular interactions in the crystal to provide the energetic incentive needed to compress bonds.[48] It has been claimed elsewhere[29] that the increased co-ordination number of the metal atom in tertiary amine complexes of alane results in an Al–N distance that is *longer* in the solid than in the isolated monomer. In fact, only for $Me_3N \cdot AlH_3$ can a direct test be made, with results hinting at, but insufficiently well defined to establish, the reverse behaviour; certainly *ab initio* studies of the model complexes $H_3N \cdot MH_3$ (M = B, Al or Ga) point to a shrinkage of the M–N distance on dimerisation.[49]

From the first structural studies to be carried out on gallium hydrides, accurate measures of Ga–H bond lengths have proved elusive, with reported values[3] for terminal units extending over a range of more than 14 pm and showing no clear correlation with the composition or form of the co-ordination geometry about the metal centre. Co-ordination of a gallane by an amine results typically in a decrease in average frequency of 130–160 cm^{-1} for the stretching fundamentals of terminal Ga–H bonds,[50] yet the implied elongation of these bonds cannot be discerned at the level of precision carried by the structural data currently available. Quantum chemical calculations certainly indicate that co-ordination by a Lewis base causes lengthening of the bonds in the GaH$_3$ monomer (by up to 2 pm),[6,19–22] although the force of the arguments is weakened by the persistent overestimation of all such distances. The best estimate of the Ga–H distance (r_a) in gaseous Me$_3$N·GaH$_3$, at 152.2(13) pm [r_a^o = 151.1(13) pm], is 2.5 pm longer than the earlier estimate.[25] This is still comparable with the terminal Ga–H distance reported for the base-free molecule Ga$_2$H$_6$ [151.9(35) pm][2] and rather shorter than the corresponding distance in GaBH$_6$ [158.6(8) pm],[51,52] although the v(Ga–H) modes of both these molecules occur near 2000 cm^{-1},[2,53] some 100 cm^{-1} *higher* than in Me$_3$N·GaH$_3$.[24] On the other hand, the new estimate is consistent with the shorter terminal Ga–H distances displayed by the molecules HGa(BH$_4$)$_2$ [r_a(Ga–H) = 149(4) pm][42] and H$_2$GaB$_3$H$_8$ [r_a(Ga–H) = 149.3(14) pm][41] on the evidence of recent combined analyses of their GED properties, thereby furnishing the makings of a pattern conforming with the vibrational frequencies. It seems likely therefore that some of the other Ga–H distances reported previously will prove, on closer examination, to require revision. Clearly there is experimental and theoretical work still to be done in this area.

Perhaps the most notable feature of the N-GaH$_3$ unit now revealed by our analysis is the large semi-vertical angle of the GaH$_3$ moiety implied by the H–Ga–N angle of 99.3(8)° in the gaseous molecule. With H–Ga–H interbond angles of 117.5(4)°, the GaH$_3$ unit is thus seen to be a decidedly flattened pyramid not far removed from the planar skeleton of the base-free GaH$_3$ molecule.[54] The corresponding parameters for the gaseous Me$_3$N·AlH$_3$ molecule are H–Al–N 104.3(11)° and H–Al–H 114.1(9)°.[28] The angular structures are well reproduced here and elsewhere[54] by *ab initio* calculations. On the evidence of both experimental and theoretical studies of complexes of the type L·MH$_3$ formed by a Group 13 element M, the semi-vertical angle of the MH$_3$ component varies with the donor properties of the ligand L, approaching the tetrahedral value of 70.5° when M and L bind strongly and 90° when they bind only weakly.[47] Hence our results confirm that GaH$_3$ is a comparatively weak Lewis acid, inferior in its acceptor power to either AlH$_3$ or GaCl$_3$.

The same conclusion comes from quantum chemical estimates of the binding energy as given by the energy change accompanying reaction (3). Using a DZP or TZP basis set and

$$\text{Me}_3\text{N·MH}_3(g) \longrightarrow \text{Me}_3\text{N}(g) + \text{MH}_3(g) \qquad (3)$$
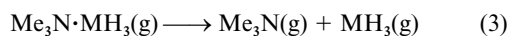
the single- and double-excitation coupled-cluster (CCSD) method, Marsh and Schaefer[54] have computed a binding energy of *ca.* 130 kJ mol^{-1} for M = Al. At the MP2 level of theory we predict a binding energy of 164 [6-31G(d)] or 167 kJ mol^{-1} [6-311G(d,p)] for Me$_3$N·GaH$_3$, with some confidence that these values will not be found far wide of the mark. Since the energy change for the dissociation reaction (4) appears to be

$$\tfrac{1}{2}\text{Ga}_2\text{H}_6(g) \longrightarrow \text{GaH}_3(g) \qquad (4)$$
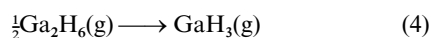
about 50 kJ mol^{-1},[43] it follows that Me$_3$N·GaH$_3$ enjoys a reasonable measure of stability with respect to free Me$_3$N and Ga$_2$H$_6$ at temperatures low enough to overcome the entropic advantage of dissociation. That Me$_3$N is a stronger base than

NH$_3$ is reflected by MP2 estimates in the order of 90 kJ mol^{-1} for the binding energy of the ammonia complex H$_3$N·GaH$_3$.[19,20] By contrast, PH$_3$ and AsH$_3$ form gallane complexes with binding energies variously calculated to lie between 20 and 70 kJ mol^{-1},[20,21] values which would greatly reduce their range of stable existence, possibly to vanishing point. In fact, H$_3$P·GaH$_3$ can be trapped but only in a matrix at low temperatures,[2] whereas attempts to prepare H$_3$As·GaH$_3$ by these or other means have failed.[55] The relative weakness of the coordinate links formed by gallane with the Group 15 atom E of donor molecules like these means that the Ga–E bond is prone to be the first to break, thereby defeating the use of the adducts as possible single-source precursors to III–V semiconductors. The Ga–E bond can be strengthened by boosting the basicity of the donor, as with the replacement of trimethylamine by quinuclidine,[6,7] for example, or by exchanging H for more electron-withdrawing substituents at the gallium centre, but these changes will be of practical use only if low-energy pathways exist for the quantitative elimination of all the substituents, whether attached to the gallium or to the Group 15 atom.

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