

# Organometallic Precursors for the Formation of GaN by Metal-organic Chemical Vapour Deposition: A Study of $[(\text{CH}_3)_2\text{GaNH}_2]_3$ \*

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The reaction of  $\text{Ga}(\text{CH}_3)_3$  with an excess of ammonia leads to the formation of  $(\text{CH}_3)_3\text{Ga}\cdot\text{NH}_3$ , which, when heated at 120 °C under 450 Torr nitrogen, decomposes to yield  $\text{CH}_4$  and the trimer  $[(\text{CH}_3)_2\text{GaNH}_2]_3$  **1** and not, as previously stated, a dimeric species. A single-crystal X-ray study of **1** revealed that it is a molecular species containing a  $(\text{GaN})_3$  ring [Ga–N 1.93(2)–2.05(2) Å] in which four consecutive ring atoms are coplanar. The remaining two atoms of the ring are on the same side of the plane so the ring has the sofa conformation. The internal ring angles range from 93.8(8) to 101.3(8)° (for N–Ga–N) and 119.5(9) to 125.3(9)° (for Ga–N–Ga). Compound **1** is monoclinic, space group  $P2_1/c$ ,  $Z = 4$ . 985 Independent reflections have been measured on a diffractometer and the structure refined to  $R = 0.076$ . Spectroscopic evidence shows that **1** retains its trimeric nature in the gas phase. Thus, in the mass spectrum the parent ion is seen while infrared spectra of mulls of solid **1**, of gaseous **1** condensed onto CsI windows and of matrix-isolated **1** are in agreement with the same species being in both solid and gas phases.

Thin layers of the wide band-gap semiconductor gallium nitride GaN, which has applications in optoelectronic devices, are grown by metal-organic chemical vapour deposition (MOCVD). Commonly in MOCVD two species are allowed to react over a heated crystalline substrate upon which the desired binary compound grows as an epitaxial layer. For GaN production the reactants are trimethylgallium and an amine.<sup>1</sup> The most frequently employed reagents are  $\text{Ga}(\text{CH}_3)_3$  and  $\text{NH}_3$ . These are allowed to mix in the gas phase prior to their being passed over a heated substrate which is held at about 1000 °C.<sup>2</sup> Obviously it would aid in designing modifications to improve the production of pure crystalline GaN if the reactions that take place in the  $\text{Ga}(\text{CH}_3)_3\text{--NH}_3$  system were fully understood. The mechanism leading to GaN is a complex one involving as it does both gas-phase and surface reactions, and it is unlikely that the near future it will be completely established. However, we have started to investigate the reaction mechanism concentrating on the early part of the reaction scheme, *i.e.* that which takes place in the gas phase.

The first product formed on mixing  $\text{Ga}(\text{CH}_3)_3$  and  $\text{NH}_3$  is  $(\text{CH}_3)_3\text{Ga}\cdot\text{NH}_3$ <sup>3</sup> and we now present a study of its thermal decomposition. The likely initial thermal reaction of  $(\text{CH}_3)_3\text{Ga}\cdot\text{NH}_3$  is the elimination of methane; a similar reaction has been postulated to take place in the production of GaAs from  $\text{Ga}(\text{CH}_3)_3$  and  $\text{AsH}_3$  mixtures.<sup>4</sup> Such methane-elimination reactions have been observed with the nitrogen-donor ligand adducts of gallane.<sup>5</sup> However, while the gaseous product is always methane, the oligomeric nature of the products is said to be dependent upon a range of factors which includes ring strain, steric interactions, entropy factors and phase.<sup>6</sup> For example,  $[(\text{CH}_3)\text{HNGaH}_2]_n$  is a trimer ( $n = 3$ ) in benzene solution<sup>7</sup> while a similar compound  $[(\text{CH}_3)_2\text{NGaH}_2]_n$  is a dimer ( $n = 2$ ) in the gas phase.<sup>8</sup> It has been suggested that  $[(\text{CH}_3)_2\text{GaNH}_2]_2$  is the initial product formed by heating  $(\text{CH}_3)_3\text{Ga}\cdot\text{NH}_3$ .<sup>9</sup> Because of the commercial importance of the  $\text{Ga}(\text{CH}_3)_3\text{--NH}_3$  reaction, we decided to determine the initial product formed by

the thermal reaction of  $(\text{CH}_3)_3\text{Ga}\cdot\text{NH}_3$  and characterise it by structural and spectroscopic methods. From the study we have shown that this product is not  $[(\text{CH}_3)_2\text{GaNH}_2]_2$  but is trimeric in nature, *i.e.*  $[(\text{CH}_3)_2\text{GaNH}_2]_3$  **1**. Now presented are the results of a single-crystal X-ray study that provides unequivocal evidence of the nature of the product and spectroscopic data for **1** which can be used to monitor its occurrence and its reactions in the processes that lead to the formation of GaN from  $\text{Ga}(\text{CH}_3)_3\text{--NH}_3$  mixtures.

## Experimental

**General Procedures.**—Standard high-vacuum-line techniques and an oxygen-free, nitrogen-filled dry-box were employed in the storing and handling of samples. Trimethylgallium was kindly supplied by Professor D. J. Cole-Hamilton and was distilled *in vacuo* before use. Ammonia gas (BOC) was dried over sodium metal prior to use.

**Physical Methods.**—Infrared spectra of thin films of compound **1** and argon matrices containing **1** were deposited under vacuum onto CsI windows, held at 77 or 20 K respectively. The spectra were recorded between 4000 and 180  $\text{cm}^{-1}$  using a Perkin-Elmer model 983 dispersive spectrophotometer. A normal co-ordinate analysis<sup>10</sup> was carried out using force constants obtained from related molecules.<sup>3</sup> Proton NMR spectra of the compounds encapsulated in sealed tubes and dissolved in sodium-dried  $\text{C}_6\text{D}_6$  (Aldrich) were obtained by using a JEOL FX 90Q Fourier-transform spectrometer. All chemical shifts are measured relative to benzene at  $\delta$  7.13 and are quoted in the normal way. The mass spectrum of the sample vapour was recorded by using a Vacuum Generator SXP800 Spectramass quadrupole spectrometer, with an ionising potential of 70 eV, and controlled by a Spectralab version 4 computer program.

**Preparation of  $[(\text{CH}_3)_2\text{GaNH}_2]_3$  **1**.**—The adduct  $(\text{CH}_3)_3\text{Ga}\cdot\text{NH}_3$  was prepared by condensation of an excess of ammonia onto trimethylgallium at  $-196$  °C. The excess of ammonia was removed at the pump with the sample being held at room temperature. The white solid that formed was subsequently heated at 120 °C for 1 h under a pressure of 450 Torr of dry

\* Tri- $\mu$ -amido-1:2 $\kappa^2$ N; 1:3 $\kappa^2$ N; 2:3 $\kappa^2$ N-tris(dimethylgallium).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

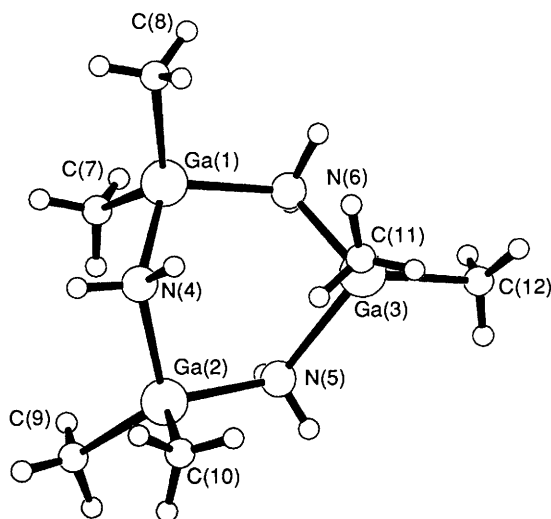
Non-SI units employed: eV  $\approx 1.60 \times 10^{-19}$  J, Torr  $\approx 133$  Pa.

**Table 1** Atomic coordinates ( $\times 10^4$ ) with estimated standard deviations in parentheses for compound **1**

Atom	x	y	z
Ga(1)	2796(2)	4949(3)	2269(2)
Ga(2)	1722(2)	5314(3)	4325(2)
Ga(3)	2931(2)	1996(3)	3917(2)
N(4)	2844(10)	5857(20)	3637(11)
N(5)	1564(15)	3150(21)	4057(16)
N(6)	2813(18)	2845(23)	2578(13)
C(7)	1315(23)	5368(28)	1287(20)
C(8)	4249(19)	5475(28)	2033(19)
C(9)	246(18)	6272(32)	3688(20)
C(10)	2551(19)	5758(33)	5735(21)
C(11)	4368(20)	2788(26)	4910(16)
C(12)	2506(15)	-200(31)	3828(24)

**Table 2** Molecular dimensions (distances in Å, angles in °)

Ga(1)–N(4)	2.05(2)	Ga(3)–N(5)	2.00(2)
Ga(1)–N(6)	1.93(2)	Ga(3)–N(6)	1.98(2)
Ga(1)–C(7)	1.92(3)	Ga(3)–C(11)	1.99(2)
Ga(1)–C(8)	1.93(2)	Ga(3)–C(12)	2.02(3)
Ga(2)–N(4)	1.93(2)	Ga(1)···Ga(2)	3.488(4)
Ga(2)–N(5)	1.97(2)	Ga(1)···Ga(3)	3.469(4)
Ga(2)–C(9)	1.93(2)	Ga(2)···Ga(3)	3.422(4)
Ga(2)–C(10)	1.96(3)		
N(4)–Ga(1)–N(6)	100.6(6)	C(9)–Ga(2)–C(10)	119.4(10)
N(4)–Ga(1)–C(7)	110.1(9)	N(5)–Ga(3)–N(6)	93.8(8)
N(6)–Ga(1)–C(7)	107.1(8)	N(5)–Ga(3)–C(11)	108.3(8)
N(4)–Ga(1)–C(8)	106.6(9)	N(6)–Ga(3)–C(11)	108.6(9)
N(6)–Ga(1)–C(8)	109.0(9)	N(5)–Ga(3)–C(12)	108.0(7)
C(7)–Ga(1)–C(8)	121.4(10)	N(6)–Ga(3)–C(12)	111.7(10)
N(4)–Ga(2)–N(5)	101.3(8)	C(11)–Ga(3)–C(12)	122.6(9)
N(4)–Ga(2)–C(9)	109.9(8)	Ga(1)–N(4)–Ga(2)	122.0(8)
N(5)–Ga(2)–C(9)	109.1(8)	Ga(2)–N(5)–Ga(3)	119.5(9)
N(4)–Ga(2)–C(10)	103.1(7)	Ga(1)–N(6)–Ga(3)	125.3(9)
N(5)–Ga(2)–C(10)	112.4(9)		

**Fig. 1** Molecular structure of  $[(\text{CH}_3)_2\text{GaNH}_2]_3$ 

nitrogen which led to the formation of  $[(\text{CH}_3)_2\text{GaNH}_2]_3$  **1** in high yield. The gaseous mixture over the trimer was examined by infrared spectroscopy and gas-chromatographic analysis. The only gaseous product formed during the thermal decomposition was shown to be methane.

*Single-crystal X-Ray Determination of  $[(\text{CH}_3)_2\text{GaNH}_2]_3$  **1**.*—Crystal data.  $\text{C}_6\text{H}_{24}\text{Ga}_3\text{N}_3$ ,  $M = 347.4$ , monoclinic, space group  $P2_1/c$ ,  $a = 11.985(9)$ ,  $b = 8.937(7)$ ,  $c = 13.908(12)$  Å,  $\beta = 107.5(1)^\circ$ ,  $U = 1420.7$  Å<sup>3</sup>,  $F(000) = 696$ ,  $Z = 4$ ,  $D_c = 1.61$

$\text{g cm}^{-3}$  Mo-K $\alpha$  radiation ( $\lambda = 0.7107$  Å),  $\mu(\text{Mo-K}\alpha) = 59.2$   $\text{cm}^{-1}$ .

A crystal, of approximate size  $0.3 \times 0.2 \times 0.2$  mm, was mounted upon a STOE-2 diffractometer to rotate around the  $b$  axis. 1603 Independent reflections were measured with a  $2\theta$  maximum of  $50^\circ$ . Background counts were for 20 s and a scan rate of  $0.0333^\circ \text{ s}^{-1}$  was applied to a width of  $1.5 + \sin \mu/\tan \theta$ . No decay in intensity was observed for the standard reflections. 985 Reflections with  $I \geq 2\sigma(I)$  were used in subsequent calculations. The structure was determined by direct methods using SHELX 76.<sup>11</sup> All non-hydrogen atoms in the molecule were given anisotropic thermal parameters. Hydrogen atoms bonded to nitrogen were included in calculated tetrahedral positions. Hydrogen atoms in methyl groups were included as rigid groups. Common refined thermal parameters were applied to hydrogen atoms bonded to the same atom.

An empirical absorption correction was applied.<sup>12</sup> Parameters were refined using full-matrix least-squares methods with a weighting scheme  $w = 1/[\sigma^2(F) + 0.003F^2]$ . In the calculations we used SHELX 76<sup>11</sup> and some of our own programs on the Amdahl 5870 Computer at the University of Reading. The final  $R$  value was 0.076 ( $R' = 0.083$ ). In the final cycle of refinement no shift was  $> 0.2\sigma$ . Maximum and minimum peaks in the final difference map were 1.3 and  $-1.2$  e Å<sup>-3</sup>, both close to gallium atoms. Positional coordinates are given in Table 1 and molecular dimensions in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

## Results and Discussion

Thermal decomposition of the adduct  $(\text{CH}_3)_3\text{Ga}\cdot\text{NH}_3$  at  $120^\circ\text{C}$  under *ca.* 450 Torr pressure of nitrogen results in the evolution of methane and the formation of a solid material which we have shown, by a single-crystal X-ray study, to be the trimer  $[(\text{CH}_3)_2\text{GaNH}_2]_3$  **1**.

*Single-crystal X-Ray Study of  $[(\text{CH}_3)_2\text{GaNH}_2]_3$  **1**.*—The molecular form of compound **1** is apparent from Fig. 1, which also contains the atom numbering scheme, while selected bond lengths and angles are given in Table 2. The isolation of a trimer is interesting. We have found that similar treatment of  $(\text{CH}_3)_3\text{Ga}\cdot\text{NHR}_2$  ( $\text{R} = \text{CH}_3$  or  $\text{C}_2\text{H}_5$ ) to that which led to the formation of **1** from  $(\text{CH}_3)_3\text{Ga}\cdot\text{NH}_3$  gives dimers of the type  $[(\text{CH}_3)_2\text{GaNR}_2]_2$ .<sup>3</sup> This behaviour we ascribe to steric effects as the non-bonded alkyl distances between  $\text{CH}_3$ –Ga and N–R are greater in a dimeric than a trimeric species for a given R and given Ga–N distance.

The nature of the  $(\text{GaN})_3$  ring in **1** is similar to that found in the isomorphous aluminium compound  $[(\text{CH}_3)_2\text{AlNH}_2]_3$ .<sup>13</sup> The torsion angles of the ring in **1** are given in Table 3(a) and compared to those in  $[(\text{CH}_3)_2\text{AlNH}_2]_3$ . The angles in Table 3(a) for the aluminium compound differ from those published and are the result of a recalculation using published coordinates, which was undertaken when it was noticed that  $[(\text{CH}_3)_2\text{AlNH}_2]_3$  is isomorphous with **1** but all the published torsion angles had a positive sign. It is clear from the value of the torsion angle  $\text{N}(4)\text{Ga}(1)\text{N}(6)\text{Ga}(3) - 2.7^\circ$  that four consecutive atoms in the ring, N(4), Ga(1), N(6) and Ga(3), form an approximate plane. The result of the least-squares plane calculation for the four atoms is shown in Table 3(b) and the maximum deviation of an atom from that plane is 0.02 Å. The two atoms not in the plane, Ga(2) and N(5), both lie on the same side of the  $\text{Ga}(3)\text{N}(6)\text{Ga}(1)\text{N}(4)$  plane at 1.37 and 1.57 Å above it respectively. Therefore the ring in **1** is neither of the two commonly found regular six-membered rings, *i.e.* 'boat' or 'chair', and is perhaps best described as a 'twisted sofa'. The only other structural study of a species containing a  $(\text{GaN})_3$  ring is of the trimer  $[(\text{CH}_2)_2\text{NGaH}_2]_3$  which is formed from aziridinylligallane. This latter trimer was shown to contain a chair  $(\text{GaN})_3$

**Table 3** (a) Torsion angles of the (GaN)<sub>3</sub> ring in compound **1** and comparable values for [(CH<sub>3</sub>)<sub>2</sub>AlNH<sub>2</sub>]<sub>3</sub> and (b) least-square planes for **1**

(a) Dihedral angle (°)		[(CH <sub>3</sub> ) <sub>2</sub> AlNH <sub>2</sub> ] <sub>3</sub> <sup>a</sup>	
<b>1</b>			
N(5)Ga(2)N(4)Ga(1)	39.6	N(2)Al(1)N(1)Al(3)	36.3
N(4)Ga(2)N(5)Ga(3)	31.4	N(1)Al(1)N(2)Al(3)	30.9
N(6)Ga(3)N(5)Ga(2)	-72.9	N(3)Al(2)N(2)Al(1)	-69.6
N(5)Ga(3)N(6)Ga(1)	54.4	N(2)Al(2)N(3)Al(3)	49.8
N(6)Ga(1)N(4)Ga(2)	-54.0	N(3)Al(3)N(1)Al(1)	-51.6
N(4)Ga(1)N(6)Ga(3)	-2.7	N(1)Al(3)N(3)Al(2)	0.5

(b) Least-squares planes	
Atom (starred atom used to define the plane)	Distance from the plane/Å
Ga(1)*	-0.02
Ga(2)	1.37
Ga(3)*	-0.01
N(4)*	0.01
N(5)	1.57
N(6)*	0.02

<sup>a</sup> Recalculated from data given in ref. 12.**Table 4** Mass spectral data for [(CH<sub>3</sub>)<sub>2</sub>GaNh<sub>2</sub>]<sub>3</sub>, *I* = 70 eV

<i>m/z</i> *		Fragment
A	B	
345	345	[(CH <sub>3</sub> ) <sub>2</sub> GaNh <sub>2</sub> ] <sub>3</sub> <sup>+</sup>
329		[(CH <sub>3</sub> ) <sub>2</sub> GaNh <sub>2</sub> ] <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> Ga <sup>+</sup>
	315	[(CH <sub>3</sub> ) <sub>2</sub> GaNh <sub>2</sub> ] <sub>2</sub> GaNh <sub>2</sub> <sup>+</sup>
299		[(CH <sub>3</sub> ) <sub>2</sub> GaNh <sub>2</sub> ] <sub>2</sub> Ga <sup>+</sup>
	246	[(CH <sub>3</sub> ) <sub>2</sub> GaNh <sub>2</sub> ] <sub>2</sub> Nh <sub>2</sub> <sup>+</sup>
230	230	[(CH <sub>3</sub> ) <sub>2</sub> GaNh <sub>2</sub> ] <sub>2</sub> <sup>+</sup>
214		[(CH <sub>3</sub> ) <sub>2</sub> GaNh <sub>2</sub> ](CH <sub>3</sub> ) <sub>2</sub> Ga <sup>+</sup>
	200	[(CH <sub>3</sub> ) <sub>2</sub> GaNh <sub>2</sub> ](GaNh <sub>2</sub> ) <sup>+</sup>
184		[(CH <sub>3</sub> ) <sub>2</sub> GaNh <sub>2</sub> ] <sub>2</sub> Ga <sup>+</sup>
	130	[(CH <sub>3</sub> ) <sub>2</sub> GaNh <sub>2</sub> ] <sub>2</sub> Nh <sub>2</sub> <sup>+</sup>
115	115	[(CH <sub>3</sub> ) <sub>2</sub> GaNh <sub>2</sub> ] <sub>2</sub> <sup>+</sup>
	99	(CH <sub>3</sub> ) <sub>2</sub> Ga <sup>+</sup>
	69	Ga <sup>+</sup>

\* See text for discussion of the two fragmentation routes. For simplicity only the masses of ions containing <sup>69</sup>Ga are given.

ring<sup>14</sup> with the modulus of the torsion angles being in the range 59–61°. There have, however, been published at least six structural studies of the isoelectronic systems that contain (AlN)<sub>3</sub> rings which are isoelectronic with the (GaN)<sub>3</sub> ring. These exhibit a variety of ring type. A planar ring was shown for [(*tert*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>AlNH<sub>2</sub>]<sub>3</sub>,<sup>13</sup> no doubt because of the steric effect from the bulky *tert*-C<sub>4</sub>H<sub>9</sub> groups. Isomers have been found to form non-planar rings with each isomer exhibiting a different ring structure. For example, [*cis*-(CH<sub>3</sub>)<sub>2</sub>AlNH(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub> has a chair ring (torsion angles 53, -53, 53, -53, 53, -53°) while the other isomer [*trans*-(CH<sub>3</sub>)<sub>2</sub>AlNH(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>, having torsion angles 35, -61, 20, 31, -62 and 33°, has a ring related to that seen in **1**.<sup>15</sup> The isomeric pair [(CH<sub>3</sub>)<sub>2</sub>AlNH<sub>2</sub>]<sub>3</sub><sup>13</sup> and [H<sub>2</sub>AlN(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub><sup>16</sup> have different ring structures, the first having a ring of the type seen in **1** while the latter has a chair conformation. Attempts have been made to rationalise the nature of the rings obtained by considering the endocyclic bond angles. This statement is supported by the endocyclic angles in **1** being similar to those in [(CH<sub>3</sub>)<sub>2</sub>AlNH<sub>2</sub>]<sub>3</sub>, [Al-N-Al 118.6(2)–125.3(2), N-Al-N 99.7(2)–102.7(2)°]. However, these bond angles alone cannot determine the nature of the ring as the *cis* and *trans* isomers of [(CH<sub>3</sub>)<sub>2</sub>AlNH(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub> have closely related endocyclic bond angles but different ring structures.<sup>13</sup> The energy difference between one form of ring and another is small

and so packing and steric repulsion forces are likely to be the dominant factors.

The length of the Ga–N bonds in compound **1** range from 1.93(2) [Ga(2)–N(4)] to 2.05(2) Å [Ga(1)–N(4)] which covers the range found in [(CH<sub>2</sub>)<sub>2</sub>NGaH<sub>2</sub>]<sub>3</sub> [1.93(1)–1.99(2) Å]<sup>14</sup> and in crystalline GaN (1.94 Å).<sup>17</sup> However, the Ga–N ring bonds in **1** are shorter than that found in its precursor (CH<sub>3</sub>)<sub>3</sub>Ga·NH<sub>3</sub> [2.17(2) Å]<sup>3</sup> thus suggesting that there could be some multiple-bond nature associated with the ring which would imply some participation of the lone pairs on the nitrogen atoms in ring binding.

From the evidence provided by structural studies on Lewis-base adducts of Al(CH<sub>3</sub>)<sub>3</sub><sup>18,19</sup> and Ga(CH<sub>3</sub>)<sub>3</sub><sup>20</sup> it is apparent that there is a tendency for the M(CH<sub>3</sub>)<sub>3</sub> fragment to be planar with the lone pair being accepted into the p<sub>z</sub> orbital of the metal atom. Thus the metal atoms exhibit sp<sup>2</sup> hybridisation. In the present structure the C–Ga–C angles are 121.4(10), 119.4(10) and 122.6(9)°; thus the metal atoms could be envisaged as exhibiting sp<sup>2</sup> hybridisation with two of the sp<sup>2</sup> lobes being used in Ga–C bonding and the third in ring formation. As previously stated, from a consideration of the Ga–N distances [1.93(2)–2.05(2) Å] it appears likely that the lone pairs on the nitrogen atoms take part in bonding. It is most probable that these lone pairs are accepted, *via* a σ-type interaction, into the p orbitals on the metal atoms that are not involved in hybridisation. From the structural parameters it is impossible to define the nature of the bonding around the nitrogen atoms as the positions of the NH hydrogen atoms were not determined.

*Spectroscopic Study of [(CH<sub>3</sub>)<sub>2</sub>GaNh<sub>2</sub>]<sub>3</sub> 1.*—It has been shown that compound **1** is trimeric in the solid state and spectroscopic evidence on solid and gaseous samples indicates that it is trimeric in the gas phase. Thus the mass spectrum of the vapour over a heated sample of **1** clearly demonstrates that the compound is transported as a trimer. The parent ion was observed as a cluster of peaks around *m/z* = 345, corresponding to the molecular ion [(CH<sub>3</sub>)<sub>2</sub>GaNh<sub>2</sub>]<sub>3</sub><sup>+</sup> and showing the isotopic pattern expected for a fragment containing three gallium atoms (relative abundances of the two isotopes of gallium: <sup>69</sup>Ga, 60; <sup>71</sup>Ga, 40%). The observed pattern of peaks can be explained by the occurrence of two fragmentation routes, both of which correspond to the loss in three steps of a (CH<sub>3</sub>)<sub>2</sub>GaNh<sub>2</sub> moiety. In the first, labelled A in Table 4, there is initial loss of NH<sub>2</sub>, followed by two methyl groups, and then a gallium atom. In the second, labelled B in Table 4, first two methyl groups are removed, followed by a metal atom and finally NH<sub>2</sub>. Both routes lead to the formation of [(CH<sub>3</sub>)<sub>2</sub>GaNh<sub>2</sub>]<sub>2</sub><sup>+</sup> which also fragments by routes A and B. In contrast, in the mass spectrum of (CH<sub>3</sub>)<sub>3</sub>Ga·NH<sub>3</sub>, measured under identical conditions, the parent ion was not observed and no evidence was obtained for any species containing a Ga–N bond, thus indicating that the Ga–N bond in the monomer is weaker than those in the trimer.

The features, seen in the IR spectra of both a frozen solid film of compound **1** at 77 K and of **1** when isolated in an argon matrix at 20 K, are listed in Table 5. In this Table are also given the approximate descriptions of the vibrations which have been obtained from a normal co-ordinate analysis<sup>10</sup> of the molecule using modified force constants obtained from the related molecules (CH<sub>3</sub>)<sub>3</sub>Ga·NH<sub>3</sub> and [(CH<sub>3</sub>)<sub>2</sub>GaN(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.<sup>3</sup> The film was obtained by condensation, at 77 K, of **1** onto a CsI infrared window, while the matrix was produced by co-condensation, at 20 K, of the vapour over a sample of **1** held at 40 °C with a large excess of argon. Similar spectra were obtained in each case (see Fig. 2). Likewise a similar, but not so well resolved, spectrum was obtained from a mull made from solid **1**. In two respects these results have a particular significance. First, though the mass spectral data do not in themselves rule out the possibility that there is some dimeric [(CH<sub>3</sub>)<sub>2</sub>GaNh<sub>2</sub>]<sub>2</sub> in the vapour, when taken in conjunction with the infrared data it seems certain that only one species, the trimer, does exist in the

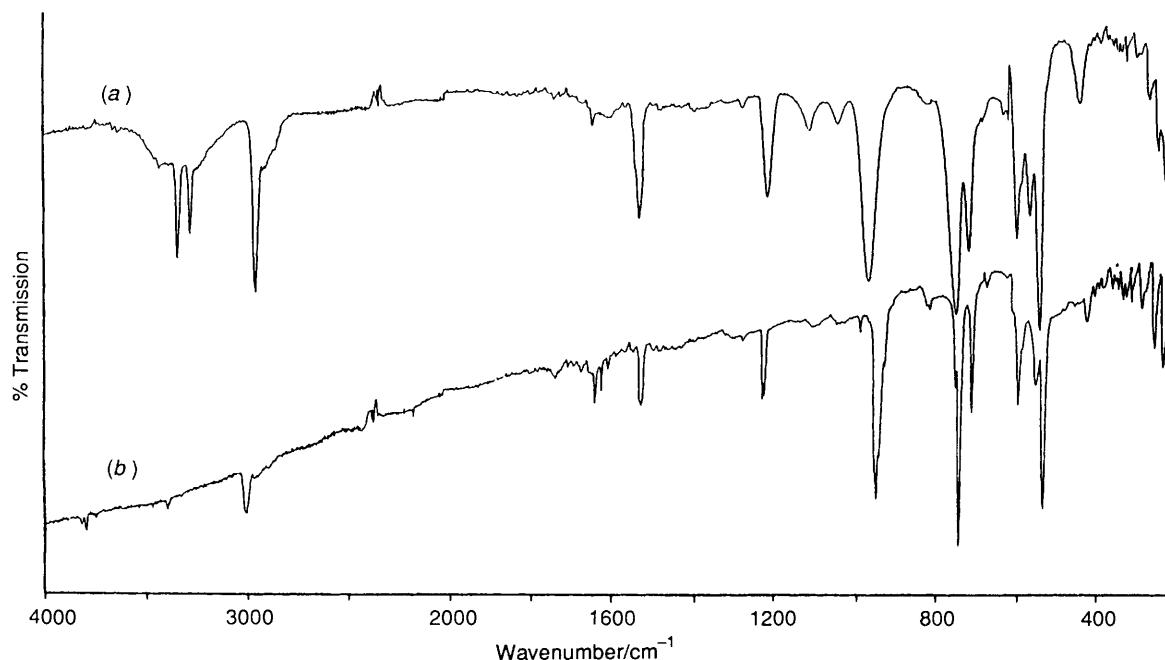


Fig. 2 Infrared spectra of  $[(\text{CH}_3)_2\text{GaNH}_2]_3$ . (a) at 77 K; (b) matrix-isolated sample

Table 5 Infrared absorptions ( $\text{cm}^{-1}$ ) of the trimer  $[(\text{CH}_3)_2\text{GaNH}_2]_3$

Observed		Calc.	Assignment
Solid (77 K)	Argon matrix		
3342m	3357wm	3342	$\nu_{\text{asym}}(\text{N-H})$
3278m	3280wm	3270	$\nu_{\text{sym}}(\text{N-H})$
2950s	2966s	2977	$\nu(\text{C-H})$
2890wm		2848	$\nu(\text{C-H})$
1514m	1507m	1504	$\delta(\text{NH}_2)$
		1433	$\delta(\text{CH}_3)$
1200m	1213m	1208	$\delta(\text{CH}_3)$
	1208m		
1027vw	1033w	1076	$\delta(\text{CH}_3)$
949s	930s	956	$\delta(\text{GaNH})$
813vw	802vw (br)	836	$\delta(\text{GaNH})$
731s	738m (sh)	724	$\rho(\text{CH}_3)$
	727vs		
700ms	697ms	700	$\rho(\text{CH}_3)$
581ms	582ms	587	$\nu(\text{Ga-N})$
		574	$\nu(\text{Ga-C})$
548ms	540ms	531	$\nu(\text{Ga-C})$
524vs	520vs	519	$\nu(\text{Ga-N})$
		517	$\nu(\text{Ga-C})$
422wm	413wm	423	$\nu(\text{Ga-N})$

vapour over a sample of **1**. Secondly, the similarity between matrix and solid mull spectra shows that the same species is present in the solid. Thus it appears that the only species present in the solid is also the trimer and this result shows that the crystal selected for study is representative of the solid as a whole.

In the infrared spectrum of compound **1**, obtained at 77 K, the lowest-energy Ga-N mode occurs at  $422 \text{ cm}^{-1}$  which is a significant increase in frequency from the position of the Ga-N stretching vibration ( $357 \text{ cm}^{-1}$ ) of the adduct  $(\text{CH}_3)_3\text{Ga-NH}_3$ ,<sup>21</sup> reflecting, at least in part, an increase in Ga-N bond order in the trimer with respect to the corresponding monomeric adduct. The assignment of the other major Ga-N mode is problematical as the bands observed at 581 and  $524 \text{ cm}^{-1}$  are mixtures of Ga-N and Ga-C vibrations.

Finally the  $^1\text{H}$  NMR spectrum of compound **1** in  $\text{C}_6\text{D}_6$  solution contained one singlet arising from the methyl protons at  $\delta -0.55$ , a shift to lower frequency from the signal arising

from the methyl protons in the adduct  $(\text{CH}_3)_3\text{Ga-NH}_3$ , at  $\delta -0.22$ . This difference implies better shielding of the methyl protons in **1** and hence gives further evidence for a stronger Ga-N bond in **1** than in the simple adduct  $(\text{CH}_3)_3\text{Ga-NH}_3$ . We ascribe the failure to detect a signal from the  $\text{NH}_2$  protons to the influence of nitrogen nuclear quadrupole broadening. An alternative explanation is that the protons are exchanging between different sites. Unfortunately the necessary variable-temperature facilities to investigate this hypothesis are not available.

### Conclusion

The thermolysis of  $(\text{CH}_3)_3\text{Ga-NH}_3$  at  $120^\circ\text{C}$  under 450 Torr of nitrogen, which results in loss of methane, produces compound **1** that exists in both the solid and gas states as a trimer, and not as previously proposed a dimer.<sup>7</sup> The conditions used to make **1** are very similar to those used in MOCVD methods for GaN production and thus the results of the study suggest that **1** is an intermediate in the formation of GaN and so shed some light on the mechanism by which gallium nitride is formed by MOCVD from these precursors.

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