

# Organometallic precursors for the formation of GaN by MOCVD: the spectroscopic and gas-phase electron diffraction structural characterisation of $\text{Me}_3\text{Ga}\cdot\text{NHMe}_2$ and $[\text{Me}_2\text{Ga}(\mu\text{-NMe}_2)]_2$ <sup>☆</sup>

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## Abstract

The reaction of  $\text{Me}_3\text{Ga}$  with  $\text{Me}_2\text{NH}$  (1:1.1 molar ratio) led to the formation of  $\text{Me}_3\text{Ga}\cdot\text{NHMe}_2$ , **I**, as a white crystalline compound which had a vapour pressure of approximately 1 Torr at room temperature. Mass spectrometric and vibrational spectroscopic measurements showed that at room temperature **I** was transported in the gas phase without decomposition. The structure of **I** was determined from gas-phase electron diffraction data, combined with ab initio molecular orbital calculations (HF/LANL1DZ). **I** was assumed to have a mirror plane defined by the C(3)–Ga–N–H(23) fragment ( $C_s$  symmetry). The results for the bond distances ( $r_g$ ) and valence angles ( $\angle_\alpha$ ) from this combined ED/ab initio investigation are as follows:  $r(\text{Ga–N}) = 2.170(13)$ ,  $r(\text{C–N}) = 1.473(6)$ ,  $r(\text{C–H}) = 1.115(5)$ ,  $r(\text{Ga–C}) = 1.991(4)$ ,  $r(\text{N–H}) = 1.023$  Å (ab initio value),  $\langle\angle\text{N–Ga–C}\rangle = 101.5(10)^\circ$ ,  $\Delta\angle\text{N–Ga–C} = \angle\text{N–Ga–C}(3) - \angle\text{N–Ga–C}(4) = 2.55^\circ$  (ab initio value),  $\Delta\angle\text{C–Ga–C} = \angle\text{C}(3)\text{–Ga–C}(4) - \angle\text{C}(4)\text{–Ga–C}(5) = 1.94^\circ$  (ab initio value),  $\angle\text{Ga–N–C} = 113.8(11)^\circ$ ,  $\angle\text{C–N–C} = 108.5(43)^\circ$ ,  $\angle\text{Ga–C–H} = 111.0(13)^\circ$ ,  $\angle\text{Ga–N–H} = 101.6^\circ$  (ab initio value),  $\angle\text{N–C–H} = 110.0^\circ$  (ab initio value).

Heating of **I** (160–180°C) under an atmosphere of argon or nitrogen led to the formation of  $\text{CH}_4$  and  $[\text{Me}_2\text{Ga}(\mu\text{-NMe}_2)]_2$ , **II**. The mass spectrum and infrared spectra (in the gas phase and in matrices) of **II** show that it is transported in the gas phase without decomposition and so the structure of **II** was determined by gas-phase electron diffraction. **II** contains a (Ga–N)<sub>2</sub> ring. The model that gave the best fit to the data was that in which the ring was allowed to deviate from planarity by bending about the gallium–gallium vector. The angle between the Ga–N–Ga planes refined to  $160.1(11)^\circ$  (the dependent angle between the N–Ga–N planes was found to be  $159.7(13)^\circ$ ). The apparent deviation from planarity may be ascribed to vibrational motion with the equilibrium structure being planar with **II** having overall  $D_{2h}$  symmetry. The major distances ( $r_g$ ) and angles ( $\angle_\alpha$ ) found for **II** are:  $r(\text{Ga–N}) = 2.061(7)$ ,  $r(\text{N–C}) = 1.473(5)$ ,  $r(\text{Ga–C}) = 1.971(10)$ ,  $r(\text{C–H}) = 1.120(7)$  Å,  $\angle\text{N–Ga–N} = 88.0(5)^\circ$ ,  $\angle\text{Ga–N–Ga} = 90.2(5)^\circ$ ,  $\angle\text{N–Ga–C} = 110.4(5)^\circ$ ,  $\angle\text{Ga–N–C} = 114.3(6)^\circ$ ,  $\angle\text{C–N–C} = 108.9(19)^\circ$ ,  $\angle\text{C–Ga–C} = 122.0(15)^\circ$ ,  $\angle\text{N–C–H} = 103.7(49)^\circ$ , and  $\angle\text{Ga–C–H} = 106.8(27)^\circ$ . The thermolysis of **II** was studied from which it was concluded that **II** is not a suitable precursor for the production of GaN by MOCVD.

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## 1. Introduction

There is considerable current interest in the role

of complexes that contain bonds between atoms from group 13 and 15 in the growth of III/V semi-conductor compounds by metal organic chemical vapour deposition (MOCVD). Such complexes are formed as intermediates during MOCVD and recently the species that are likely to be formed during the synthesis of GaN from  $\text{Me}_3\text{Ga}$  and  $\text{NH}_3$  have been studied [1,2]. The use, as precursors for MOCVD, of complexes containing a M–X bond (M = group 13 element and X = P or As) has also been studied [3]. For example, compounds of the type  $\text{Me}_3\text{Ga} \cdot \text{L}$  where L is a bulky amine, e.g. dicyclohexylamine [4] or 2,6-dimethylpiperidine [4], have been prepared and their structures determined. It was hoped that such compounds, while being less reactive and therefore easier to handle than  $\text{Me}_3\text{Ga}$ , would still have some volatility and so be suitable for use in MOCVD. Recently the solid state structure of the dimer  $[\text{Bu}_2^i\text{Ga}(\mu\text{-NHPh})]_2$ , prepared from the reaction of  $\text{Bu}_2^i\text{GaCl}$  with  $\text{LiNHPh}$ , has been determined [5]. Such dimeric products are likely to be formed during the reaction of  $\text{R}_3\text{Ga}$  with  $\text{HNR}'_2$  during MOCVD and over 40 years ago it was claimed that compounds of the type  $[\text{Me}_2\text{Ga}(\mu\text{-NR}_2)]_2$  were formed by the elimination of methane from  $\text{Me}_3\text{GaNH}_x\text{Me}_y$  ( $x = 1, y = 2$ ;  $x = 2, y = 1$ ;  $x = 3, y = 0$ ). Mixtures of  $\text{Me}_3\text{Ga}$  and  $\text{NH}_3$  are used, at high temperatures, to grow GaN by MOCVD and recently we have shown by single crystal X-ray methods, that the elimination of methane from  $\text{Me}_2\text{Ga} \cdot \text{NH}_3$  leads to the formation of the fairly involatile trimer,  $[\text{Me}_2\text{Ga}(\mu\text{-NH}_2)]_3$ , rather than a dimer [2].

The major use of the trimethylgallium amine adducts is in the synthesis of semi-conductor materials. The processes of greatest current interest require the transport of the adducts in the gas phase. It was therefore decided to study the reaction of trimethylgallium with a range of simple amines  $\text{H}_{3-x}\text{NR}_x$  ( $x = 1$  or  $2$  R = alkyl group) and to study the stability of the adducts in the gas phase and, by selecting suitable R groups, the role, if any, of  $\beta$ -elimination. Presented here are the results of gas-phase electron diffraction and spectroscopic studies of  $\text{Me}_3\text{Ga} \cdot \text{NHMe}_2$ , **I**, and the dimer  $[\text{Me}_2\text{Ga}(\mu\text{-NMe}_2)]_2$ , **II**, which is formed from **I** by thermal decomposition.

## 2. Experimental

### 2.1. 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. Dimethyl amine (Aldrich) was dried over sodium metal prior to use.

### 2.2. Preparation of $\text{Me}_3\text{Ga} \cdot \text{NHMe}_2$ (**I**) and $[\text{Me}_2\text{Ga}(\mu\text{-NMe}_2)]_2$ (**II**)

**I** was prepared on an all-glass vacuum line by distilling onto  $\text{Me}_3\text{Ga}$  a slight molar excess of dry  $\text{NHMe}_2$ . **I** was formed as a white crystalline solid and the excess of  $\text{NHMe}_2$  was removed at the pump. Care had to be taken to avoid removal of the product **I** as it has a vapour pressure at room temperature of approximately 1 Torr. Samples of **II** were prepared from **I**. Ampoules containing **I** were opened to a mercury manometer on a vacuum line. With an over-pressure of approximately 500 Torr of nitrogen or argon, the ampoules of **I** were heated to 413–423 K for 1 h during which time methane and **II** were formed.

### 2.3. Physical methods

Infrared spectra of **I** and **II** were measured in the gas phase at room temperature in a 10 cm path-length cell fitted with CsI windows. For these measurements and for those of samples sublimed onto and held at 77 K on a CsI window a Perkin–Elmer 1720X Fourier transform instrument was used. Spectra of **I** and **II** in argon matrices at 20 K were obtained with a Perkin–Elmer 983 dispersive spectrometer; both instruments gave a resolution of  $\pm 1 \text{ cm}^{-1}$ . Mass spectra of **I** and **II** were obtained by means of a quadrupole Vacuum Generators SXP800 Spectramass instrument, with an ionising potential of 70 eV, and controlled by a SPECTRALAB version 4 computer program.

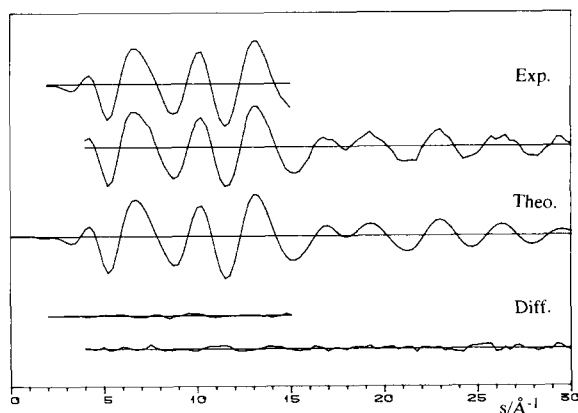


Fig. 1. Experimental, theoretical and difference intensity curves,  $sI_m(s)$ , for  $\text{Me}_3\text{Ga} \cdot \text{NHMe}_2$ , **I**. The theoretical curve was calculated from the structural parameters shown in Table 1.

#### 2.4. Gas-phase electron diffraction

Gas-phase electron diffraction data of **I** and **II** were obtained from the Balzers Eldigraph KDG-2 apparatus at the University of Oslo [6]. The nozzle-to-plate distances were 496.65 and 246.86 mm and the data were obtained with the nozzle and samples at room temperature. The electron wavelength (0.058720 Å) was calibrated against diffraction patterns of benzene.

Six plates from each camera distance for each compound, traced on the microdensitometer of the University of Oslo, were used in the

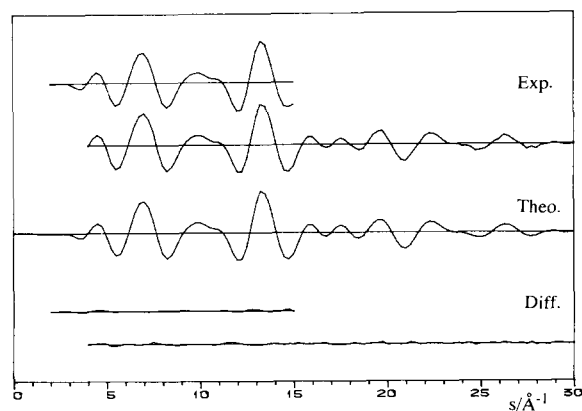


Fig. 2. Experimental, theoretical and difference intensity curves,  $sI_m(s)$ , for  $[\text{Me}_2\text{Ga}(\mu\text{-NMe}_2)]_2$ , **II**. The theoretical curve was calculated from the structural parameters shown in Table 3.

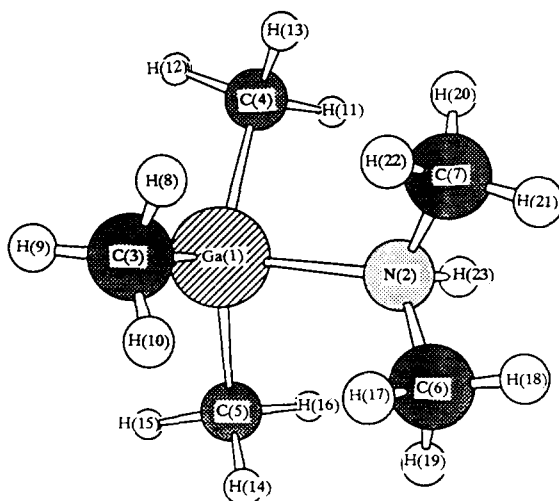


Fig. 3. Diagram of  $\text{Me}_3\text{Ga} \cdot \text{NHMe}_2$ , **I**, with atom numbering scheme.

final analysis. The data, covering the ranges  $2.00 \leq s \leq 15.00 \text{ \AA}^{-1}$  and  $4.00 \leq s \leq 30.00 \text{ \AA}^{-1}$  at intervals of  $\Delta s = 0.25 \text{ \AA}^{-1}$ , were processed as previously described [7] with scattering factors taken from Ref. [8]. The average intensity curves for each compound, produced for each camera distance, together with the theoretical intensity curves for the final models and the difference curves for **I** and **II**, are shown in Figs. 1 and 2, respectively.

The refinements of the structures were based upon the molecular models of **I** and **II** illustrated in Figs. 3 and 4, respectively, in which are given the atom numbering schemes. A number of common assumptions were made in the determination of the structures of **I** and **II** and these were as follows:

- (i) it was assumed that all the methyl groups were identical and had local  $C_{3v}$  symmetry, with the axes of symmetry being along the Ga–C bonds or the N–C bonds as appropriate;
- (ii) all C–H bond distances were assumed equal.

#### 2.5. Refinement of the electron diffraction data for **I**

For **I** a model which was based upon 15 parameters was constructed. The parameters consisted of the bond distances  $r(\text{Ga–N})$ ,  $r(\text{C–N})$ ,  $r(\text{N–H})$ ,  $r(\text{C–H})$ ,  $r(\text{Ga–C})$ , the valence angles  $\angle \text{Ga–N–C}$ ,

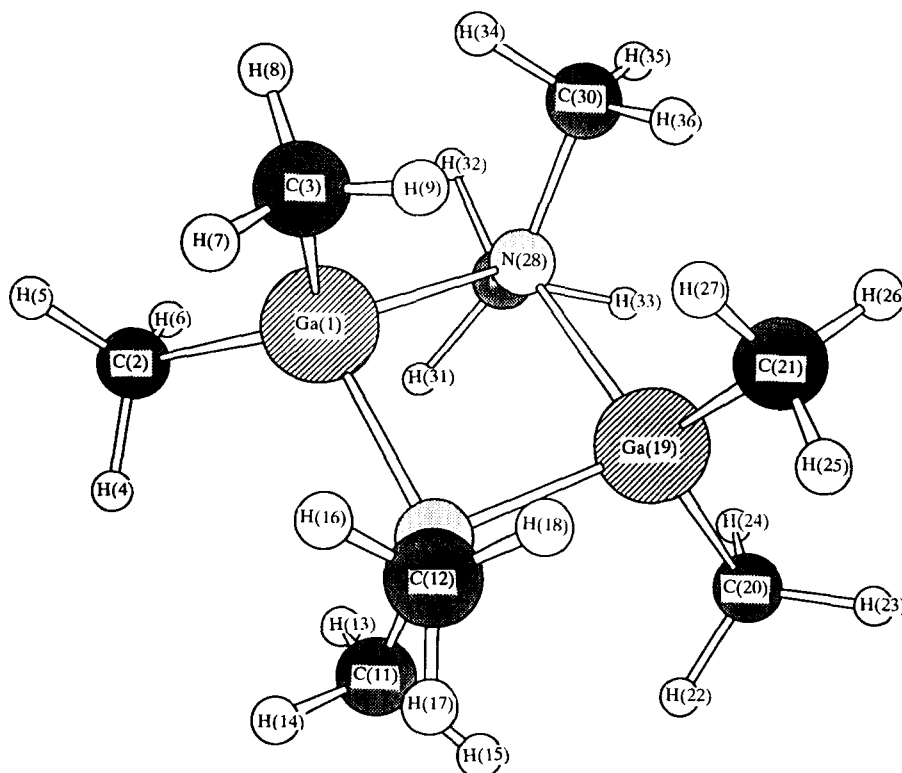


Fig. 4. Diagram of  $[\text{Me}_2\text{Ga}(\mu\text{-NMe}_2)]_2$ , **II**, with atom numbering scheme.

$\angle\text{Ga-N-H}$ ,  $\angle\text{N-C-H}$ ,  $\langle\angle\text{N-Ga-C}\rangle = 0.5 \times (\angle\text{N-Ga-C(3)} + \angle\text{N-Ga-C(4)})$ ,  $\Delta\angle\text{N-Ga-C} = \angle\text{N-Ga-C(3)} - \angle\text{N-Ga-C(4)}$ ,  $\angle\text{C-N-C}$ ,  $\angle\text{Ga-C-H}$ , torsion angles  $\phi_1(\angle\text{H-C-Ga-N})$ , and  $\phi_2(\angle\text{H-C-N-Ga})$ . The starting values for the independent parameters were taken from related molecules.

Not all the independent parameters for **I** could be determined from the electron diffraction data alone, and we therefore made some *ab initio* molecular orbital calculations. The geometry of **I** was fully optimized at the HF/LANL1DZ level with the program GAUSSIAN 92 [9]. The results of these calculations were used as constraints in our least-squares refinements.  $r(\text{N-H})$ ,  $\angle\text{Ga-N-H}$ ,  $\angle\text{N-C-H}$ ,  $\Delta\angle\text{C-Ga-C}$ ,  $\Delta\angle\text{N-Ga-C}$ ,  $\phi_1$ , and  $\phi_2$  were kept constant at the calculated values.

The structure was defined in terms of the geometrically consistent  $r_\alpha$ -type distances. These were converted to the  $r_\alpha$ -type required by the formula for the scattered intensities by using values of

the centrifugal distortion constants ( $\delta r$ ), perpendicular amplitude corrections ( $K$ ) and root-mean square amplitudes of vibration ( $l$ ) calculated from a harmonic force field ( $r_a = r_\alpha - (l^2/r) + K + \delta r = r_g - (l^2/r)$ ). The force constants used were derived from  $\text{Me}_3\text{Ga} \cdot \text{NH}_3^1$  and other related molecules.

Not all the vibrational amplitudes could be determined from the experimental data. Some of the amplitudes were refined together as groups. The amplitudes which could not be refined were kept constant at the values calculated in the normal coordinate analysis. In the final least-squares refinement 12 independent parameters were refined together: four distance parameters, four angle parameters and four amplitude parameters.

The angle  $\langle\angle\text{N-Ga-C}\rangle$  was initially set at  $107^\circ$  and it refined to a value of  $101.0(13)^\circ$ . When the starting value was set at around  $110^\circ$ , a second minimum was found at  $112^\circ$ . However, the model

Table 1

Final structural parameters for  $\text{Me}_3\text{Ga} \cdot \text{NHMe}_2^a$ , **I**

Parameter	Electron diffraction				Ab initio
	$r_a/\text{\AA}$	$r_g$	$l_{\text{refined}}$	$l_{\text{calc}}$	$r/\text{\AA}$
$r(\text{Ga}-\text{N})$	2.169(13)	2.170	0.057(5)	0.055	2.182
$r(\text{Ga}-\text{C})$	1.988(4)	1.991	0.053(5)	0.052	2.007
$r(\text{C}-\text{N})$	1.466(6)	1.473	0.060(6)	0.050	1.486
$r(\text{N}-\text{H})$	1.006 <sup>b</sup>	1.023	0.076(6)	0.077	1.006
$r(\text{C}-\text{H})$	1.091(5)	1.115	0.081(6)	0.078	1.087
$\angle \text{Ga}-\text{N}-\text{C}$	113.8(11)				111.9
$\angle \text{Ga}-\text{N}-\text{H}$	101.6 <sup>b</sup>				101.6
$\angle \text{N}-\text{C}-\text{H}$	110.0 <sup>b</sup>				110.0
$\langle \angle \text{N}-\text{Ga}-\text{C} \rangle$	101.5(10)				101.35
$\Delta \angle \text{N}-\text{Ga}-\text{C}$	2.55 <sup>b</sup>				2.55
$\Delta \angle \text{C}-\text{Ga}-\text{C}$	1.94 <sup>b</sup>				
$\angle \text{Ga}-\text{C}-\text{H}$	111.0(13)				111.3
$\angle \text{C}-\text{N}-\text{C}$	108.5(43)				112.3
$\phi_1^c$	180.0 <sup>b</sup>				180.0
$\phi_2^c$	180.0 <sup>b</sup>				180.0
<i>Selected dependent parameters</i>					
$r(\text{C}(3) \cdot \text{C}(4))$	3.390(15)	3.393		0.129	
$r(\text{C}(3) \cdot \text{C}(6))$	3.660(45)	3.663		0.264	
$r(\text{C}(6) \cdot \text{C}(7))$	2.379(63)	2.387		0.079	
$r(\text{C}(5) \cdot \text{C}(6))$	3.547(42)	3.550		0.266	
$r(\text{C}(5) \cdot \text{C}(7))$	4.534(18)	4.536		0.127	
$r(\text{Ga} \cdot \text{H}(23))$	2.569(12)	2.574		0.112	
$r(\text{Ga} \cdot \text{H}(8))$	2.587(17)	2.599	0.141(18)	0.133	
$r(\text{Ga} \cdot \text{C}(6))$	3.069(15)	3.071		0.115	
$r(\text{C}(3) \cdot \text{N}(2))$	3.251(24)	3.253		0.129	
$r(\text{N}(2) \cdot \text{H}(17))$	2.105(7)	2.121		0.120	
$\angle \text{C}(4)-\text{Ga}-\text{C}(3)$	117.0(7)				117.1
$\angle \text{C}(4)-\text{Ga}-\text{C}(5)$	115.1(6)				115.2
$\angle \text{N}(2)-\text{Ga}-\text{C}(3)$	102.8(10)				102.6
$\angle \text{N}(2)-\text{Ga}-\text{C}(4)$	100.3(10)				100.1
$R$	0.099				

<sup>a</sup> Distances ( $r$ ) and vibrational amplitudes ( $l$ ) are in angstroms, angles ( $\angle$ ) are in degrees.<sup>b</sup> Fixed in the final refinement at ab initio values.<sup>c</sup>  $\phi_1 = \angle \text{H}-\text{C}(3)-\text{Ga}-\text{N}$ ,  $\phi_2 = \angle \text{H}-\text{C}-\text{N}-\text{Ga}$  torsion angles.

in which  $\langle \angle \text{N}-\text{Ga}-\text{C} \rangle$  had the lower value was preferred on the basis of a better fit to the experimental data and the preferred structure reported for  $\text{Me}_3\text{Ga} \cdot \text{NH}_3$ , and because the ab initio value for this average angle was  $101.3^\circ$ . The final  $R$  factor was 0.099. The bond distances, angles and amplitudes from the final refinement are given in Table 1 together with some of the ab initio values. The correlation matrix is shown in Table 2. Fig. 5 contains the experimental, theoretical and difference radial distribution curves for **I**.

## 2.6. Refinement of the electron diffraction data for **II**

A model based upon 12 parameters was constructed, consisting of the distances  $r(\text{Ga}-\text{N})$ ,  $r(\text{N}-\text{C})$ ,  $r(\text{Ga}-\text{C})$ ,  $r(\text{C}-\text{H})$ , the angles  $\angle \text{Ga} \cdot \text{Ga}-\text{C}$ ,  $\angle \text{N}-\text{C}-\text{H}$ ,  $\angle \text{Ga}-\text{C}-\text{H}$ ,  $\angle \text{N}-\text{N}-\text{C}$ ,  $\angle \text{N}-\text{Ga}-\text{C}$ , torsion angle  $\phi_1(\angle \text{H}-\text{C}-\text{N}-\text{Ga})$ ,  $\phi_2(\angle \text{H}-\text{C}-\text{Ga}-\text{N})$ , and  $\alpha$ , a ring bend. Refinement of  $\alpha$ , which is defined as a bend of the  $\text{Ga}_2\text{N}_2$  ring about the  $\text{Ga} \cdot \text{Ga}$  vector, allowed refinement of the angle between the two  $\text{Ga}-\text{N}-\text{Ga}$  planes. If  $\alpha$  is  $180^\circ$ ,

Table 2

Correlation matrix ( $\times 100$ ) for  $\text{Me}_3\text{Ga} \cdot \text{NHMe}_2$ , **I**

Parameter	$\sigma_{\text{LS}}^a$	$r_1$	$r_2$	$r_3$	$r_4$	$\angle_5$	$\angle_6$	$\angle_7$	$\angle_8$	$\angle_9$	$\angle_{10}$	$\angle_{11}$	$\angle_{12}$
1 $r(\text{Ga}-\text{N})$	0.0044	100	-8	0	70	-51	-27	-1	55	58	17	32	14
2 $r(\text{C}-\text{N})$	0.0020		100	9	-21	-21	1	4	-23	7	-1	12	-1
3 $r(\text{C}-\text{H})$	0.0018			100	-3	-1	-3	-16	1	2	-5	-9	1
4 $r(\text{Ga}-\text{C})$	0.0011				100	-20	-23	-19	52	31	4	17	19
5 $\angle(\text{GaNC})$	0.38					100	-17	16	22	-39	-14	-26	37
6 $\angle(\text{NGaC})$	0.37						100	-10	-30	-8	0	-2	-15
7 $\angle(\text{GaCH})$	0.44							100	13	8	2	4	11
8 $\phi_{\text{CNC}}$	2.14								100	34	5	12	58
9 $l(\text{Ga}-\text{N})$	0.0016									100	19	36	12
10 $l(\text{C}-\text{N})$	0.0019										100	22	5
11 $l(\text{N}-\text{H})$	0.0018											100	9
12 $l(\text{Ga} \cdot \text{H}(8))$	0.0061												100

<sup>a</sup> Standard deviations from least-squares refinement. Distances ( $r$ ) and amplitudes ( $l$ ) are in angstroms, angles ( $\angle$ ) are in degrees.

the overall symmetry of **II** (ignoring the hydrogen atoms) is  $D_{2h}$ .

The root-mean square amplitudes of vibration ( $l$ ), the perpendicular amplitude corrections ( $K$ ), and the centrifugal distortion constants ( $\delta r$ ), were calculated from an assumed force field, using values for the force constants derived from related molecules combined with the gas-phase vibrational spectroscopic data reported here.

The least-squares refinements were based upon the 12 geometrical parameters defined above. In the initial refinement the torsion angles  $\phi_1$  and  $\phi_2$

were fixed. Having obtained initial values for most of the major parameters,  $\phi_1$  and  $\phi_2$  were refined in a systematic manner. The final values obtained for the torsion angles were  $19^\circ$  and  $60^\circ$  for  $\phi_1$  and  $\phi_2$ , respectively. Since the uncertainties on the values for the torsion angles were very large,  $\phi_1$  and  $\phi_2$  were fixed at the refined values during the final refinements. Thus in the final refinement all the independent parameters, except the two torsion angles, were allowed to refine as were the vibrational amplitudes of all the bonded distances and

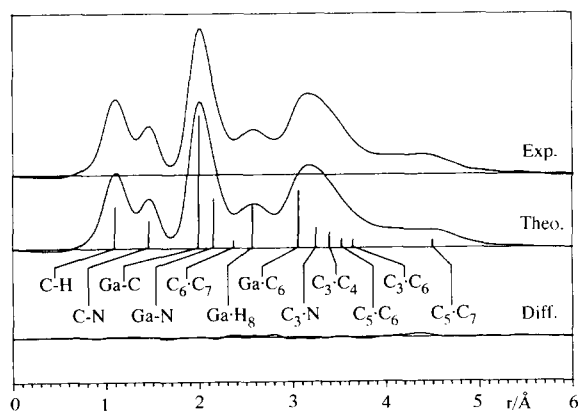


Fig. 5. Experimental, theoretical and difference radial distribution curves for  $\text{Me}_3\text{Ga} \cdot \text{NHMe}_2$ , **I**. These curves were obtained by Fourier inversion of the curves shown in Fig. 1 after multiplication by  $Z_{\text{Ga}}Z_{\text{N}}(f_{\text{Ga}}f_{\text{N}})^{-1} \exp(-0.0025s^2)$  and using theoretical data for the unobserved area  $s < 2.00 \text{ \AA}^{-1}$ .

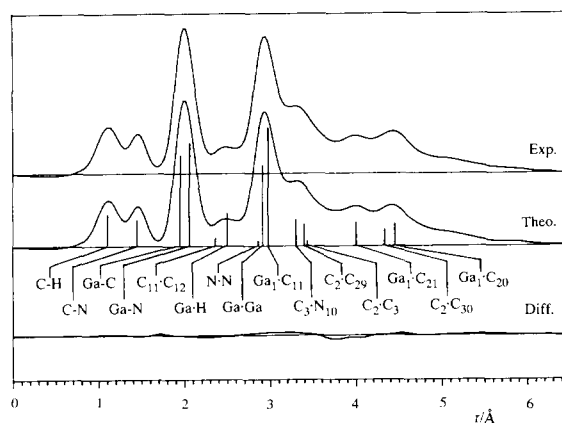


Fig. 6. Experimental, theoretical and difference radial distribution curves for  $[\text{Me}_2\text{Ga}(\mu\text{-NHMe}_2)]_2$ , **II**. These curves were obtained by Fourier inversion of the curves shown in Fig. 2 after multiplication by  $Z_{\text{Ga}}Z_{\text{N}}(f_{\text{Ga}}f_{\text{N}})^{-1} \exp(-0.0025s^2)$  and using theoretical data for the unobserved area  $s < 2.00 \text{ \AA}^{-1}$ .

Table 3  
Final structural parameters for  $[\text{Me}_2\text{Ga}(\mu\text{-NMe}_2)]_2^{\text{a}}$ , **II**

Parameter	$r_o/\angle_o$	$r_g$	$l_{\text{refined}}$	$l_{\text{calc}}$
$r(\text{Ga-N})$	2.058(7)	2.061	0.066(13)	0.053
$r(\text{N-C})$	1.463(5)	1.473	0.054(6)	0.047
$r(\text{Ga-C})$	1.958(10)	1.971	0.044(12)	0.054
$r(\text{C-H})$	1.080(7)	1.120	0.088(8)	0.078
$\angle\text{Ga}\cdot\text{Ga-C}$	119.0(7)			
$\angle\text{N-C-H}$	103.7(49)			
$\angle\text{Ga-C-H}$	106.8(27)			
$\phi_1^c$	19.0 <sup>b</sup>			
$\phi_2^c$	60.0 <sup>b</sup>			
$\angle\text{N}\cdot\text{N-C}$	125.5(10)			
$\alpha^d$	160.1(11)			
$\angle\text{N-Ga-N}$	88.0(5)			
<i>Selected dependent parameters</i>				
$r(\text{Ga}\cdot\text{Ga})$	2.957(7)	2.916	0.072(4)	0.079
$r(\text{N}\cdot\text{N})$	2.860(23)	2.862	0.079(4)	0.086
$r(\text{C}(2)\cdot\text{C}(3))$	3.425(38)	3.438		0.119
$r(\text{C}(11)\cdot\text{C}(12))$	2.381(29)	2.392		0.091
$r(\text{C}(2)\cdot\text{C}(30))$	4.313(11)	4.320		0.144
$r(\text{C}(2)\cdot\text{C}(29))$	3.389(23)	3.396		0.203
$r(\text{Ga}(1)\cdot\text{C}(11))$	2.976(9)	2.981	0.108(9)	0.102
$r(\text{C}(3)\cdot\text{N}(10))$	3.299(10)	3.305	0.098(8)	0.120
$r(\text{Ga}(1)\cdot\text{C}(20))$	4.417(15)	4.421	0.096(10)	0.124
$r(\text{Ga}(1)\cdot\text{C}(21))$	4.008(18)	4.012	0.092(10)	0.124
$\angle\text{C-Ga-C}$	122.0(15)			
$\angle\text{C-N-C}$	108.9(19)			
$\angle\text{N-Ga-C}$	110.4(5)			
$\angle\text{Ga-N-C}$	114.3(6)			
$\angle\text{Ga-N-Ga}$	90.2(5)			
$R$	0.055			

<sup>a</sup> Distances ( $r$ ) and vibrational amplitudes ( $l$ ) are in angstroms, angles ( $\angle$ ) are in degrees.

<sup>b</sup> Not refined in the final refinement.

<sup>c</sup>  $\phi_1 = \angle\text{H-C-Ga-N}$ ,  $\phi_2 = \angle\text{H-C-Ga-N}$ .

<sup>d</sup> Angle between the two GaNGa planes of the  $(\text{GaN})_2$  ring.

those of the six non-bonded distances that were thought to be most influential e.g.  $l(\text{Ga}\cdot\text{Ga})$  and  $l(\text{N}\cdot\text{N})$ . The remaining amplitudes were held constant at their calculated values.

A good fit between the data calculated for the final model and the experimental data was obtained as can be seen from the radial distribution curves shown in Fig. 6 and from the value of the  $R$  factor (0.055). Values for the bond distances, angles and vibrational amplitudes as obtained from the final least-squares refinement are given in Table 3 and the correlation matrix for the refined parameters is shown in Table 4.

### 3. Results and discussions

#### 3.1. Gas-phase studies of $\text{Me}_3\text{Ga}\cdot\text{NHMe}_2$ **I**

The compound **I** is readily prepared from the reaction of trimethylgallium and dimethylamine. It has a vapour pressure at room temperature of approximately 1 Torr and thus it was possible to execute a number of measurements on the vapour. The mass spectrum of **I** contained no parent peak but did show peaks at 144 ( $\text{Me}_2\text{Ga}\cdot\text{NMe}_2\text{H}^+$ ), 128 ( $\text{MeGa}\cdot\text{NMe}_2^+$ ), 99 ( $\text{Me}_2\text{Ga}^+$ ), 84 ( $\text{MeGa}^+$ ), 69 ( $\text{Ga}^+$ ) and 45 ( $\text{NMe}_2^+$ ) (NB for simplicity only peaks for  $^{69}\text{Ga}$  are reported; all the peaks assigned as containing a Ga atom consisted of two peaks separated by two mass numbers and in the intensity ratio 100:63). The results clearly indicate that **I** can be vaporised and that **II** is not formed by room temperature vaporisation of **I** at low pressure. The infrared spectra of **I**, obtained in the gas and solid phases, as well as in an argon matrix, are given in Table 5. There is good correlation between the three spectra but significant differences from the spectra of **II** (see Table 6) confirming the conclusion obtained from the mass spectrometry investigation that room temperature vaporisation of **I** under reduced pressure does not lead to the formation of **II**. In all the infrared spectra of **I** that are recorded in Table 5, both the  $\nu_{\text{as}}(\text{Ga-C})$  and  $\nu_{\text{s}}(\text{Ga-C})$  were observed, as was  $\nu(\text{Ga-N})$ . The latter two, having the same symmetry and being relatively close together, are heavily mixed as was revealed by the normal coordinate analysis. The Raman spectrum obtained of **I** was extremely poor and only  $\nu_{\text{as}}(\text{Ga-C})$  and  $\nu_{\text{s}}(\text{Ga-C})$  were observed.

It was against this background that the structure of **I** was determined by gas-phase electron diffraction with use being made of the infrared spectra recorded in Table 5 to calculate vibrational amplitudes. The major bond distances and angles determined for **I** are given in Table 1. The model, in which  $\text{C}(3)\text{-Ga}(1)\text{-N}(2)\text{-H}(23)$  are on a mirror plane, was found to give a good fit to the data. The Ga-N distance ( $r_g(\text{Ga-N}) = 2.170(13)$  Å) is comparable to that found for  $\text{Me}_3\text{Ga}\cdot\text{NH}_3$  (2.161(22) Å). Interestingly, in the mass spectrum of **I**, a number of fragments were detected that

Table 4

Correlation matrix ( $\times 100$ ) for  $[\text{Me}_2\text{Ga}(\mu\text{-NMe}_2)]_2$ 

Parameter	$\sigma_{\text{LS}}^a$	$r_1$	$r_2$	$r_3$	$\angle_4$	$\angle_5$	$\angle_6$	$\angle_7$	$\angle_8$	$\angle_9$	$\angle_{10}$	$\angle_{11}$	$\angle_{12}$	$\angle_{13}$	$\angle_{14}$	$\angle_{15}$	$\angle_{16}$	$\angle_{17}$	$\angle_{18}$
1 $r(\text{Ga-N})$	0.0025	100	-37	-30	-9	19	-32	-15	-50	4	82	-33	-64	10	-1	6	-10	14	-1
2 $r(\text{N-C})$	0.0016		100	11	10	1	10	7	5	-5	-23	19	31	-5	13	-5	3	-7	1
3 $r(\text{Ga-C})$	0.0035			100	4	-59	-64	-66	-5	-14	-25	95	73	11	19	18	-3	6	-3
4 $r(\text{C-H})$	0.0023				100	-4	-6	13	3	-1	-5	6	8	-7	-5	1	-5	2	1
5 $\angle(\text{GaGaC})$	0.26					100	28	44	37	19	28	-56	-42	-9	-10	-22	-13	-17	-13
6 $\angle(\text{NCH})$	1.74						100	77	22	1	-33	-55	-31	-10	-12	-14	34	-13	13
7 $\angle(\text{GaCH})$	0.94							100	39	9	-7	-60	-39	-14	-14	-24	-1	-25	1
8 $\angle(\text{NNC})$	0.34								100	24	-29	-5	19	-12	-9	-37	-19	-43	-20
9 $a^b$	0.40									100	-24	-14	-9	-3	-4	-15	-12	-11	32
10 $\angle(\text{NGaN})$	0.19										100	-30	-55	2	-3	13	-42	4	-25
11 $l(\text{Ga-N})$	0.0043											100	78	17	22	20	9	7	1
12 $l(\text{Ga-C})$	0.0030												100	7	18	13	12	1	2
13 $l(\text{C-N})$	0.0016													100	14	12	17	7	5
14 $l(\text{C-H})$	0.0021														100	9	12	3	5
15 $l(\text{Ga-Ga})$	0.0012															100	-19	10	-8
16 $l(\text{Ga-C}_N)^c$	0.0029																100	21	-1
17 $l(\text{C-N})$	0.0038																	100	1
18 $l(\text{Ga-C}_{Ga})^d$	0.0048																		100

<sup>a</sup> Standard deviations from least-squares refinement. Distances ( $r$ ) and amplitudes ( $l$ ) are in angstroms, angles ( $\angle$ ) are in degrees.<sup>b</sup> Angle between the two GaNGa planes of the  $(\text{GaN})_2$  ring.<sup>c</sup> C atoms of methyl groups bound to a nitrogen atom.<sup>d</sup> C atoms of methyl groups bound to a gallium atom.

contained the Ga–N fragment (see above). This is in contrast to the results obtained for  $\text{Me}_3\text{Ga} \cdot \text{NH}_3$  measured with the same instrument under the same conditions, where no such fragments were seen. The Ga–C distances ( $r_g(\text{Ga-C}) = 1.991(4) \text{ \AA}$ ) are equivalent to those found in  $\text{Me}_3\text{Ga} \cdot \text{NH}_2\text{Bu}^t$  ( $r_g(\text{Ga-C}) = 1.990(3) \text{ \AA}$ ) and  $\text{Me}_3\text{Ga} \cdot \text{NHEt}_2$  ( $r_g(\text{Ga-C}) = 1.991(4) \text{ \AA}$  [10]) and slightly longer than those found in  $\text{Me}_3\text{Ga} \cdot \text{NH}_3$  ( $r_g(\text{Ga-C}) = 1.979(3) \text{ \AA}$  [1]). All these Ga–C distances are longer than those of the trimethyl gallium ( $r_g(\text{Ga-C}) = 1.967(2) \text{ \AA}$  [11]). The observation that the Ga–C bonds are longer in coordination compounds of  $\text{Me}_3\text{Ga}$  than in the parent alkyl is as expected.

The agreement between the ab initio values for the geometrical parameters and those determined from electron diffraction is quite good. The calculated value for  $\angle\text{Ga-N-C}$  is larger and the value for  $\angle\text{C-N-C}$  is smaller than the experimental values, but these two parameters are correlated in the least-squares refinements. For both the C–Ga–C and the N–Ga–C valence angles, there is excellent agreement between the values

from ab initio calculations and those determined from electron diffraction. The average experimental value of  $\angle\text{N-Ga-C}$  ( $101.5(10)^\circ$ ) is smaller than the tetrahedral angle; an observation that is in common with those made for a whole range of  $\text{Me}_3\text{M} \cdot \text{L}$  ( $\text{M} = \text{Al}$  or  $\text{Ga}$ ,  $\text{L} = \text{NMe}_3$  or  $\text{PMe}_3$  [12,13]).

### 3.2. Gas-phase studies of $[\text{Me}_2\text{Ga}(\mu\text{-NMe}_2)]_2$ II

II was prepared from I by heating a sample under a pressure of nitrogen (approximately 500 mmHg) in a tapped glass ampoule which was open to a mercury manometer on a vacuum line. The temperature of the sample was gradually increased until a small rise in pressure (above that expected as a consequence of the rise in temperature) was observed and heating was then continued at this temperature until evolution of gas ceased. A sample of the gas was taken into an evacuated gas cell and analysed using infrared spectroscopy and mass spectrometry and shown to be methane. II, which was isolated as a white, crystalline solid, has a similar vapour pressure to that of I. The existence



Table 5

The infrared spectra of  $\text{Me}_3\text{Ga} \cdot \text{NMe}_2\text{H}$ , **I** in the gas and solid phases (77 K) and in an argon matrix<sup>a</sup> at 14 K plus the low frequency Raman spectrum

Gas phase $\nu$ ( $\text{cm}^{-1}$ )	77 K $\nu$ ( $\text{cm}^{-1}$ )	Raman <sup>b</sup> $\nu$ ( $\text{cm}^{-1}$ )	Argon matrix <sup>a</sup> $\nu$ ( $\text{cm}^{-1}$ )	Approximate assignment
3329 (w)	3264 (vs)		3271 (m)	$\nu(\text{N-H})$
	3000 (wm)		3003 (w)	$\nu(\text{C-H})$
2979 (wm)	2975 (m)		2971 (w)	$\nu(\text{C-H})$
2948 (vs)	2950 (sh)			$\nu(\text{C-H})$
2917 (m)	2934 (s)		2936 (s)	$\nu(\text{C-H})$
2857 (wm)	2850 (wm)		2864 (w)	$\nu(\text{C-H})$
2814 (w)	2804 (w)			
1473 (wm)	1471 (m)		1467 (s)	$\delta_{\text{as}}(\text{CH}_3)$ (N)
			1408 (w)	$\delta_{\text{s}}(\text{CH}_3)$ (N)
	1256 (w)			$\rho(\text{CH}_3)$ (N)
1022 (m)	1218 (wm)		1214 (s)	$\rho(\text{CH}_3)$ (N)
	1193 (wm)			$\delta_{\text{s}}(\text{CH}_3)$ (Ga)
	1185 (ms)		1185 (ms)	$\delta_{\text{s}}(\text{CH}_3)$ (Ga)
	1177 (ms)			
1129 (w)	1127 (m)		1124 (m)	$\rho(\text{CH}_3)$ (N)
	1063 (w)			
1025 (w)	1023 (s)		1021 (s)	$\nu_{\text{as}}(\text{C-N})$
971 (wm)				
900 (m)	904 (s)		903 (s)	$\nu_{\text{s}}(\text{C-N})$
	757 (m)			$\delta(\text{NH})$
726 (m,br)	732 (s,br)		722 (vs)	$\rho(\text{CH}_3)$ (Ga)
	664 (w)			
647 (w)	652 (w)		657 (w)	$\rho(\text{CH}_3)$ (Ga)
552 (s)	546 (vs)	537 (s)	543 (vs)	$\nu_{\text{as}}(\text{Ga-C})$
516 (vw)	516 (w)	511 (s)	515 (w)	$\nu_{\text{s}}(\text{Ga-C})$
429 (vw)	431 (w)		433 (w)	$\nu(\text{Ga-N})$
	398 (w)		393 (vw)	$\delta(\text{C}_2\text{N})$

<sup>a</sup> Ref. [22].

<sup>b</sup> Adduct studies as a solid in a glass capillary.

of the starting material as a dimer in the solid phase has been reported previously: Coates reported its formation and carried out vapour pressure measurements upon it [14], Beachley et al. published the infrared spectrum of the sample in Nujol, measured its degree of association in benzene, carried out a preliminary X-ray study and provided evidence for the existence of the compound in a glassy, polymeric, strain-free form at higher temperatures [15], and Storr recorded the  $^1\text{H}$  NMR spectrum of **I** [16]. Thus, although the compound has already been isolated and studied, it has not been characterised fully in the gas phase. The mass spectrum of **II** was measured. No parent ion was detected; however, the peaks observed at highest  $m/e$  values (NB  $m/e$  values are quoted only

for  $^{69}\text{Ga}$  containing ions; 271 [**II** – Me]<sup>+</sup>, 241 [**II** – 3Me]<sup>+</sup>, 227 [**II** – NMe<sub>2</sub> – Me]) have isotopic patterns indicating that they contain two gallium atoms. The infrared spectra of **II** are given in Table 6 and as these spectra, which were obtained by condensing **II** from the gas phase, are in accord with the null spectrum previously reported [15], it is clear that **II** is transported in the gas phase without decomposition. The assignments given in Table 6 were derived from a normal coordinate analysis carried out as part of this study and they are in accord with those previously reported [15]. From a comparison of the vibrational spectra of **II** with those of **I** it is evident that the bands assigned to  $\nu(\text{Ga-N})$  are of much stronger intensity in the former spectra, in all phases. Additionally a shift

Table 6

Bands observed in the infrared spectrum of gas-phase and matrix-isolated  $[\text{Me}_2\text{Ga}(\mu\text{-NMe}_2)]_2$  and in the Raman spectrum of the solid dimer

Gas phase $\nu$ ( $\text{cm}^{-1}$ )	Argon matrix $\nu$ ( $\text{cm}^{-1}$ )	Raman $\nu$ ( $\text{cm}^{-1}$ )	Approximate assignment <sup>a</sup>
2988 (m)	2974 (wm)	2974 (w)	$\nu(\text{C-H})$
2962 (m)	2951 (m)	2957 (w)	$\nu(\text{C-H})$
		2945 (w)	$\nu(\text{C-H})$
		2936 (w)	$\nu(\text{C-H})$
2921 (s)	2915 (m)	2912 (wm)	$\nu(\text{C-H})$
2893 (vs)	2882 (m)	2883 (wm)	$\nu(\text{C-H})$
2849 (m)	2840 (wm)	2840 (w)	$\nu(\text{C-H})$
2801 (m)	2794 (wm)	2790 (wm)	
1464 (wm)	1459 (m)	1474 (wm)	$\delta_{\text{as}}(\text{CH}_3)$ (N)
		1441 (w)	$\delta_{\text{s}}(\text{CH}_3)$ (N)
		1426 (w)	$\delta_{\text{as}}(\text{CG}_3)$ (Ga)
1231 (w)	1232 (wm)		$\rho(\text{CH}_3)$ (N)
1211 (ms)	1204 (m)		$\rho(\text{CH}_3)$ (Ga)
	1193 (m)		$\rho(\text{CH}_3)$ (N)
1167 (vw)	1166 (vw)		
1140 (m)	1137 (s)		$\nu_{\text{as}}(\text{C-N})$
1948 (wm)	1045 (m)		$\nu_{\text{s}}(\text{C-N})$
955 (w,br)			
906 (m)	906 (s)		$\rho(\text{CH}_3)$ (N)
	742 (m)	754 (wm)	$\rho(\text{CH}_3)$ (Ga)
728 (m,br)	727 (s)		$\rho(\text{CH}_3)$ (Ga)
685 (w)	679 (wm)		$\rho(\text{CH}_3)$ (Ga)
574 (m)	574 (m)	565 (m)	$\nu_{\text{as}}(\text{Ga-C})$
535 (m)	537 (m)	539 (vs)	$\nu_{\text{s}}(\text{Ga-C})$
502 (vs)	502 (m)	489 (ms)	$\nu(\text{Ga-N})$
	480 (w)		

<sup>a</sup> In making the assignments the mode that, from the normal coordinate analysis, makes a contribution of more than 80% is given.

in  $\nu(\text{Ga-N})$  to higher frequency is observed in the dimer spectrum (502 and  $480\text{ cm}^{-1}$ ) from that in the monomer ( $433\text{ cm}^{-1}$ ). Although the bands at 502 and  $480\text{ cm}^{-1}$  do not arise purely from  $\nu(\text{Ga-N})$  (the normal coordinate analysis showed that there is a small amount of mixing of the  $\nu(\text{Ga-C})$  and  $\nu(\text{Ga-N})$  modes), no band at a lower frequency which could be assigned to  $\nu(\text{Ga-N})$  was observed. These values indicate that the Ga-N bonding in the dimer is stronger and different from that in the monomer. The values obtained for **II** compare favourably with those observed in the dimer  $[\text{H}_2\text{Ga}(\mu\text{-NMe}_2)]_2$  ( $512$  and  $477\text{ cm}^{-1}$  [17]). It is against this spectroscopic background that the structure of **II** was determined by gas-phase electron diffraction.

Analysis of the electron diffraction data obtained for **II** reveals that under the conditions of the

electron diffraction experiment, **II** is transported with no decomposition. At the core of **II** is a four-membered  $(\text{Ga-N})_2$  ring ( $r_{\text{g}}(\text{Ga-N}) = 2.061(7)\text{ \AA}$ ). Similar rings have been found in a number of compounds. An example from gas-phase studies is provided by  $[\text{H}_2\text{Ga}(\mu\text{-NMe}_2)]_2$  ( $r_{\text{g}}(\text{Ga-N}) = 2.060(7)\text{ \AA}$  [17]) and there are a number of examples arising from solid state e.g.  $[\text{Bu}^1_2\text{Ga}(\mu\text{-NHPh})]_2$  ( $\text{Ga-N}$  2.103(9) and 2.018(9) $\text{ \AA}$  [5]),  $[\text{Me}_2\text{Ga}(\mu\text{-NHPh})]_2$  ( $\text{Ga-N}$  = 2.039(3) $\text{ \AA}$  [18]),  $[\text{Me}_2\text{Ga}(\mu\text{-NHDipp})]_2$  (where  $\text{Dipp} = 2, 6\text{-Pr}^1_2 - \text{C}_6\text{H}_3$ ) ( $\text{Ga-N}$  = 2.024(11), 2.026(11) $\text{ \AA}$  [16]) and  $[\text{Me}_2\text{Ga}(\mu\text{-HNBu}^1)]_2$  ( $\text{Ga-N}$  = 2.022(4), 2.024(4) $\text{ \AA}$  [19]; 2.012(4) $\text{ \AA}$  [20]). In **II** the ring is approximately square ( $r_{\text{g}}(\text{Ga-Ga}) = 2.916(7)\text{ \AA}$ ,  $r_{\text{g}}(\text{N-N}) = 2.862(23)\text{ \AA}$  and the angles in the ring are  $\angle\text{N-Ga-N} = 88.0(5)^\circ$  and  $\angle\text{Ga-N-Ga} = 90.2(5)^\circ$ ). In crystallographic studies on three

related compounds of the type  $[\text{Me}_2\text{Ga}(\mu\text{-NHR})]_2$ , where R is a bulky group, the N–Ga–N angles range between  $83.6(4)$  to  $86.4(1)^\circ$  and the Ga–N–Ga angles span  $93.6(1)$  to  $94.7(1)^\circ$  [18]. Thus the  $(\text{Ga}-\text{N})_2$  ring in **II** is closer to a square than in the  $[\text{Me}_2\text{Ga}(\mu\text{-NHR})]_2$  (where R is a bulky group) and this is readily seen by comparing the differences in the length of the diagonals of the rings which are  $r_g(\text{Ga}\cdot\text{Ga}) = 2.916(7)$  Å,  $r_g(\text{N}\cdot\text{N}) = 2.862(23)$  Å in **II** while of the three solid state structures the closest agreement between the diagonals was seen with R = 1-adamantyl ( $2.977$  Å ( $\text{Ga}\cdot\text{Ga}$ ) and  $2.744$  Å ( $\text{N}\cdot\text{N}$ )). However, for **II** the best fit to the data, especially in the area of the radial distribution curve where  $r_g(\text{Ga}\cdot\text{Ga})$  and  $r_g(\text{N}\cdot\text{N})$  occur, was obtained with a model in which the  $(\text{Ga}-\text{N})_2$  ring was allowed to fold around the Ga·Ga vector. With such a model, the best fit was found with an angle between the Ga–N–Ga planes of  $160.1(11)^\circ$  (the dependent angle between the N–Ga–N planes was found to be  $159.7(13)^\circ$ ). The apparent deviation from planarity may be ascribed to vibrational motion with the equilibrium structure being planar where **II** has overall  $D_{2h}$  symmetry. In the three solid state structures referenced above [16] one of them was found to have a non-planar ring, namely  $[\text{Me}_2\text{Ga}(\mu\text{-NHDipp})]_2$  (Dipp = 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$ ), where the inter-Ga–N–Ga plane angle was found to be  $154.2^\circ$ .

While the Ga–N bond in **II** is comparable to those seen in other compounds having a  $(\text{Ga}-\text{N})_2$  ring it is shorter than that seen in **I** ( $2.061(7)$  compared with  $2.170(13)$  Å). For ring binding, there are eight electrons available (one from each gallium atom and three from each nitrogen atom). Five of the angles around the nitrogen atom are close to the tetrahedral angle  $\angle\text{C}-\text{N}-\text{C} = 108.9(19)^\circ$ ,  $\angle\text{C}-\text{N}-\text{Ga} = 114.3(6)^\circ$  (there are four such angles), while the size of the sixth angle,  $\angle\text{Ga}-\text{N}-\text{Ga}$  at  $90.2(5)^\circ$ , is influenced by the fact that it is part of the four-membered ring. Thus it is clear that all five valence electrons from each nitrogen atom are involved in bonding and three are used in ring binding. The C–Ga–C angle at  $122.0(15)^\circ$  is similar to that seen in the gas-phase structure of  $[\text{Me}_2\text{GaH}_2]_2$  ( $123.2(15)^\circ$  [21]) and values ranging from  $118.5(3)$  to

$121.9(2)^\circ$  have been observed in the solid state. Thus it could be envisaged that the gallium atoms form  $\text{sp}^2$  hybrids in a plane which is orthogonal to the  $(\text{Ga}-\text{N})_2$  ring with one lobe and the remaining p orbital being used for ring binding.

### 3.3. The thermolysis of $[\text{Me}_2\text{Ga}(\mu\text{-NMe}_2)]_2$ **II**

Having obtained **II** by the thermolysis of **I** the thermal properties of **II** were investigated to see if **II** is a suitable precursor for GaN. When heated under an atmosphere of inert gas in the temperature range 503 to 523 K, **II** began to yield methane and a trace of dimethylamine. Extensive decomposition of the compound occurred at 673 K, with the evolution of methane, dimethylamine and a trace of ethene taking place. The products were identified by the measurement of gas-phase FTIR spectra. Prolonged heating at 673 K resulted in a decrease in the methane/dimethylamine ratio. After the evolution of both gaseous products had ceased the residue consisted of metallic gallium, a black tar and an orange-brown organic liquid.

The decomposition pathway may begin with the breakage of a Ga–C bond followed by the abstraction of a hydrogen atom (possibly from another Ga–Me methyl group) to form methane, since methane was the predominant product in the early stages of the decomposition. The absence of ethane amongst the gaseous products suggests that the Ga–C rupture must be coincident with H abstraction. The subsequent fracture of the Ga–N bond and the abstraction of a hydrogen atom would allow  $\text{NMe}_2\text{H}$  to be released. Obviously the most notable point is that the extensive loss of nitrogen in the form of  $\text{NMe}_2\text{H}$  reveals that rupture of the Ga–N bond occurs and thus **II**, and presumably **I** from which it is made, are not feasible precursors for the production of gallium nitride.

## 4. Conclusions

The gas-phase structure and reactivity of the adduct formed between trimethylgallium and dimethylamine have been studied. The dimer formed from the adduct is quite volatile. Its gas-

phase structure and spectroscopic properties have been measured. The dimer is quite stable and does not readily decompose to yield gallium nitride. The results suggest that a study of compounds formed by  $\text{Me}_3\text{Ga}$  and  $\text{HNet}_2$ , where  $\beta$ -elimination is possible, may be profitable and yield a route to gallium nitride.

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