

## Chemical Vapor Deposition of Gallium Nitride from the GaCl<sub>3</sub>+NH<sub>3</sub> System. Theoretical Study of the Structure and Thermodynamics of Potential Intermediates Formed in the Gaseous Phase

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Quantum chemical calculations at the B3P86/6-311G(d,p) level have been performed on potential intermediate molecules in the chemical vapor deposition (CVD) of GaN from the GaCl<sub>3</sub> + NH<sub>3</sub> system. The investigated molecules included the monomer (Cl<sub>x</sub>GaNH<sub>x</sub>, x = 1–3) and oligomer species (Cl<sub>2</sub>GaNH<sub>2</sub>)<sub>n</sub> with n = 1–3 and (ClGaNH)<sub>n</sub> with n = 1–4 as well as the respective chain dimers and trimers. The calculations revealed the importance of intramolecular Cl···H hydrogen bonding and dipole–dipole interactions in determining the conformational properties of the larger species. Except for the ClGaNH monomer, the Ga–N bonding has a single bond character with a strong ionic contribution. Our thermodynamic study of the composition of the gaseous phase supported the predominance of the Cl<sub>3</sub>GaNH<sub>3</sub> complex under equilibrium conditions. Additionally, the calculated Gibbs free energies of various GaCl<sub>3</sub> + NH<sub>3</sub> reactions imply the favored formation of “saturated” chain and cyclic oligomers below 1000 K.

### Introduction

The binary group 13 nitrides AlN and GaN, and their ternary mixed phases with In, are very important materials for advanced microelectronic and optoelectronic devices such as light emitting diodes and lasers and high temperature and high power devices, as well as chemical sensors and acoustic surface-wave conductors.<sup>1–4</sup> Production of these materials in the necessary form of thin films or nanocrystals embedded into various matrixes is usually done by the chemical vapor deposition (CVD) technique.<sup>5</sup>

The chemistry of Ga–N compounds has been summarized recently in a 1996 special issue of Gmelin’s Handbook.<sup>6</sup> Despite the extensive experimental investigations, the detailed mechanism of the GaN CVD process is still unclear,

and the thermodynamic properties of many gas-phase precursors and possible intermediates are unknown. To the reasons belong the difficulties arising at the experimental detection and characterization of the intermediates formed in this complex reaction. A good alternative to investigate the large variety of potential species in the CVD process is offered by theoretical computations. The reliability of present advanced quantum chemical methods to obtain molecular (among them thermodynamic) data has been proved on various systems.<sup>7,8</sup> Recently, the CVD of GaN from organometallic precursors was studied by Timoshkin et al.<sup>9,10</sup> Their theoretical analysis covered the species formed in the GaH<sub>3</sub> + NH<sub>3</sub>, Ga(CH<sub>3</sub>)<sub>3</sub> + NH<sub>3</sub>, and GaH<sub>3</sub> + N(CH<sub>3</sub>)<sub>3</sub> systems and predicted the importance of larger oligomers (tetramer, hexamer) as intermediate in the formation of GaN.

Besides organometallic precursors the Cl<sub>3</sub>MNH<sub>3</sub> complexes (obtained from a mixture of MCl<sub>3</sub> and NH<sub>3</sub>, where M = Al, Ga) belong to the most suitable starting materials

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in the CVD process for producing high purity nitrides.<sup>2,11–13</sup> The importance of the  $\text{MCl}_3 + \text{NH}_3$  reaction initiated several experimental and theoretical studies, focused mostly on the formation of AlN.<sup>11,12,14,15</sup> Less attention has been paid to the CVD of GaN from  $\text{Cl}_3\text{GaNH}_3$ ; thus our knowledge about the nature of the various possible intermediates in the  $\text{GaCl}_3 + \text{NH}_3$  system is incomplete. In addition to limited experimental investigations,<sup>16–20</sup> a single theoretical study was published recently.<sup>21</sup> This latter study, however, was restricted to a couple of species only, lacking any comprehensive structural and thermodynamic analysis. Moreover, Okamoto used simple Hartree–Fock (and MP2 for the smaller species) calculations, while these exotic structures would require advanced computational techniques for obtaining reliable structural and thermodynamic data.

In this paper we present our computational results on the HCl elimination from  $\text{Cl}_3\text{GaNH}_3$  and the gas-phase polymerization of the intermediates. We analyzed the structure, energetics, and bonding of the monomers and cyclic oligomer species  $(\text{Cl}_2\text{GaNH}_2)_n$  with  $n = 1–3$  and  $(\text{ClGaNH})_n$  with  $n = 1–4$  as well as those of the respective chain-type dimers and trimers.

### Computational Details

In a series of test calculations we surveyed the performance of various computational levels for  $\text{Cl}_3\text{GaNH}_3$ , for which reliable experimental gas-phase structural data are available.<sup>22</sup> The tested theories included the traditional Hartree–Fock (HF) and second-order Møller–Plesset perturbation theories (MP2)<sup>23</sup> as well as two density functional approaches, those with the Becke3–Lee–Yang–Parr (B3LYP)<sup>24,25</sup> and Becke3–Perdew86 (B3P86)<sup>24,26</sup> exchange–correlation functionals. The basis sets were gradually extended from valence double- $\zeta$  6-31G(d,p) up to the diffuse polarized valence triple- $\zeta$  6-311+G(2df, 2pd) basis. Although  $\text{Cl}_3\text{GaNH}_3$  has been studied previously by different computational approaches,<sup>21,27–30</sup> those approaches did not provide consistent information on the electron correlation and basis set effects.

On the basis of these test calculations (detailed results given as Supporting Information), we selected the B3P86/6-311G(d,p) level for our overall study of the  $\text{Cl}_3\text{GaNH}_3$  derivatives. The B3P86 density functional gave a very good performance, being only slightly worse than that of MP2 for the molecular geometry, while the HF and B3LYP methods performed poorly. Selection of the 6-311G(d,p) basis was reasoned by its satisfactory approach to saturation when used in conjunction with the B3P86 functional, while at the MP2 level this is not the case even for the largest basis sets tested here. Another support for the 6-311G(d,p) basis was that it is also affordable for the larger molecular species.

The calculations were carried out with the Gaussian 98 suite of programs.<sup>31</sup> Full geometry optimizations were carried out, the found stationary points being characterized by frequency analysis. The thermodynamic data and the relative energies of the isomers were calculated from the absolute energies corrected by unscaled zero-point vibrational energies (ZPE). The computed bonding properties, viz., natural charges,<sup>32</sup> Wiberg bond indices,<sup>33</sup> and topological properties of the electron density distribution<sup>34</sup> (obtained by the AIM2000 program<sup>35</sup>), are given in the Supporting Information.

### Results and Discussion

**GaN.** There is little information on the GaN molecule, although its existence has been predicted and its electronic structure has been investigated by fourth-order multireference coupled pair approximation (MRCPA-4) calculations.<sup>36</sup> In agreement with these previous results we found  $^3\Sigma^-$  as the ground state of GaN, but the energy difference between the ground and first excited ( $^3\Pi$ ) states was considerably smaller (7 kJ/mol versus 48 kJ/mol<sup>36</sup>) at our less sophisticated computational level. At the same time, the bond length from the two studies agree well, 2.003 and 1.990 Å from the B3P86/6-311G(d,p) and MRCPA-4 calculations, respectively.

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**Table 1.** Geometric Parameters<sup>a</sup> of NH<sub>x</sub> and GaCl<sub>x</sub> (x = 1–3) Fragments

	N–H	H–N–H	Ga–Cl	Cl–Ga–Cl
		NH <sub>x</sub>		
NH	1.042			
NH <sub>2</sub>	1.029	102.1		
NH <sub>3</sub>	1.014	106.5		
NH <sub>3</sub> (expt) <sup>b</sup>	1.012	106.7		
		GaCl <sub>x</sub>		
GaCl			2.234	
GaCl <sub>2</sub>			2.171	119.0
GaCl <sub>3</sub>			2.115	120.0
GaCl <sub>3</sub> (expt) <sup>c</sup>			2.101(2)	120.0

<sup>a</sup> The calculated data were obtained at the B3P86/6-311(d,p) level. Bond distances are given in angstroms, bond angles in degrees. <sup>b</sup> Experimental equilibrium geometry from ref 41. <sup>c</sup> Experimental equilibrium geometry from refs 43 and 44.

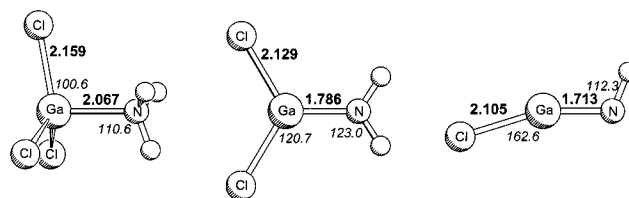
**NH<sub>x</sub>, GaCl<sub>x</sub> (x = 1–3).** The fragments of the Cl<sub>x</sub>GaNH<sub>x</sub> molecules, NH<sub>x</sub> and GaCl<sub>x</sub>, x = 1–3, have been the targets of several studies in the past.<sup>37–40</sup> The calculated and available experimental geometric parameters are compared in Table 1.

The most important point in the calculations of the fragments is to reproduce the lowest electronic state for the species with unsaturated valence shell. Our B3P86 calculations gave correctly the <sup>2</sup>B<sub>1</sub> ground state for the NH<sub>2</sub> radical<sup>38</sup> and the well-known <sup>3</sup>Σ<sup>-</sup> ground state<sup>37</sup> for NH. The singlet electronic state (<sup>1</sup>Σ<sup>+</sup>) of NH was calculated to be higher in energy by 227.4 kJ/mol. We note the very good agreement between our calculated and the experimental<sup>41</sup> molecular geometry of NH<sub>3</sub> (cf. Table 1).

Calculations on the GaCl<sub>2</sub> radical resulted in the <sup>2</sup>A<sub>1</sub> ground state.<sup>40</sup> Similarly to AlCl,<sup>42</sup> the GaCl molecule has a singlet ground state (<sup>1</sup>Σ<sup>+</sup>).<sup>39</sup> The triplet electronic state (<sup>3</sup>Σ<sup>-</sup>) was calculated to be higher in energy by 345.0 kJ/mol. We note that the B3P86/6-311(d,p) level slightly overestimates the experimentally determined Ga–Cl bond distance<sup>43,44</sup> of GaCl<sub>3</sub>, probably a systematic error of the computational level.

**Cl<sub>x</sub>GaNH<sub>x</sub> (x = 1–3).** The molecular geometry and bonding properties of the Cl<sub>3</sub>GaNH<sub>3</sub> complex have been investigated in several experimental and theoretical studies.<sup>21,22,27–30</sup> In the present section we intend to perform a comparative analysis with the other two Cl<sub>x</sub>GaNH<sub>x</sub> molecules (cf. Figure 1). The monomeric Cl<sub>2</sub>GaNH<sub>2</sub> and ClGaNH species have not been investigated before; thus our study provides the first structural and bonding information on these molecules.

While the Cl<sub>3</sub>GaNH<sub>3</sub> molecule is characterized by a classical donor–acceptor bonding, in Cl<sub>2</sub>GaNH<sub>2</sub> both Ga and N are three-coordinated and a single bond is established

**Figure 1.** Structures and selected geometric parameters of monomeric Cl<sub>x</sub>GaNH<sub>x</sub> species (x = 1–3). Bond distances (bold) are given in angstroms, bond angles (italic) in degrees.

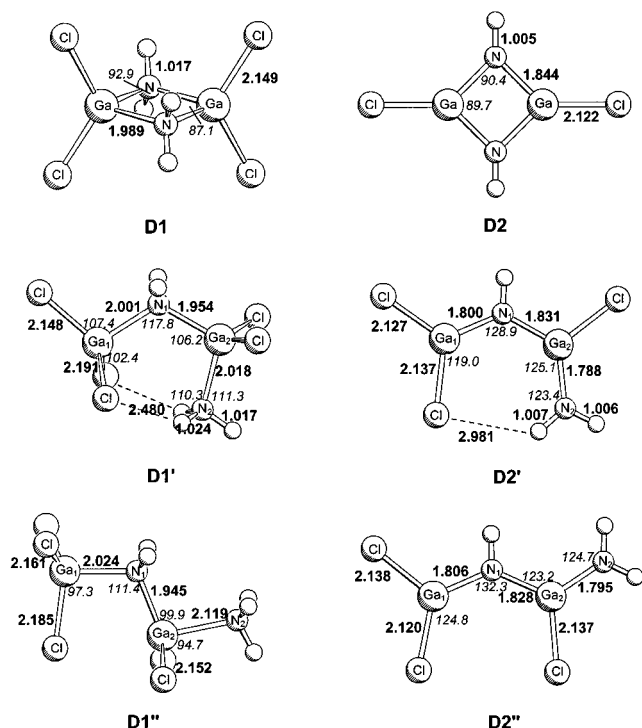
between the two atoms. According to the calculations the molecule is planar and possesses C<sub>2v</sub> symmetry. For ClGaNH two possible structures were considered: the singlet state with a formal Ga=N double bond and the triplet structure with a Ga–N single bond. From the two structures the singlet one was identified as the electronic ground state of ClGaNH. It has a bent planar (C<sub>s</sub>) geometry with a near-linear Cl–Ga–N moiety (cf. Figure 1). The triplet state lies higher in energy by 83.4 kJ/mol. Its structure is planar (in contrast to the nonplanar Al analogue<sup>15</sup>) with a considerably bent Cl–Ga–N angle (113°) and a longer Ga–N bond (by 0.24 Å) as compared to the singlet state geometry.

The most characteristic geometric parameter of the Cl<sub>x</sub>GaNH<sub>x</sub> molecules is the Ga–N bond reflecting the different type of bonding between the GaCl<sub>x</sub> and NH<sub>x</sub> moieties. In agreement with the weaker donor–acceptor interaction, it is the longest in Cl<sub>3</sub>GaNH<sub>3</sub> and shortens considerably (by 0.28 Å) in Cl<sub>2</sub>GaNH<sub>2</sub>. We note that this latter bond distance (1.786 Å) is well below the sum of the covalent radii of the two atoms (1.92 Å).<sup>45</sup> A further decrease, though to a much smaller degree (by 0.07 Å), appears in ClGaNH. Both these parameters and the nonlinearity of the Cl–Ga–N bond angle (162.6°) indicate a partial double bond character of Ga–N in ClGaNH. The planar NH<sub>2</sub> group in Cl<sub>2</sub>GaNH<sub>2</sub> points to the delocalization of the N lone pair. The properties of the Ga–N bond critical points are in agreement with pronounced π interactions between the two atoms in Cl<sub>2</sub>GaNH<sub>2</sub> (ellipticity 0.150) and ClGaNH (ellipticity 0.128).

**Oligomers. Dimers.** Experimental studies on related derivatives indicated that association reactions are important for Ga–N systems.<sup>46</sup> In the CVD process HCl elimination from Cl<sub>3</sub>MnNH<sub>3</sub> and subsequent polymerization may result in various association products among which cyclic and chain structures can be distinguished. Several analogous cyclic structures (containing mostly bulky substituents) have been synthesized.<sup>47–54</sup> Therefore, we start our discussion with the

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**Figure 2.** Structures and selected geometric parameters of cyclic and chain dimers. Bond distances (bold) are given in angstroms, bond angles (italic) in degrees.

cyclic dimers of  $\text{Cl}_2\text{GaNH}_2$  and  $\text{ClGaNH}$  (**D1**<sup>55</sup> and **D2**, cf. Figure 2). On the basis of the analogy with organic compounds, **D1** containing tetracoordinated Ga and N can be considered as “saturated”, while **D2** containing tricoordinated Ga and N is “unsaturated”.

Both **D1** and **D2** are planar and have  $D_{2h}$  symmetry in agreement with previous results on related aluminum<sup>42,49</sup> and gallium derivatives.<sup>21,50,56</sup> The  $\text{Ga}\cdots\text{Ga}$  distances in the dimers are quite short (2.882 and 2.616 Å in **D1** and **D2**, respectively) being well within the sum of the nonbonded atomic radii of Ga (3.44 Å).<sup>45</sup> The proximity of the two gallium atoms, however, can be attributed to the geometric constraints of the ring structure, rather than to a Ga–Ga bonding. The absence of a Ga–Ga bond is supported by our AIM analysis locating no bond but a ring critical point in the middle of the rings.

Contrary to the extensive data on cyclic adducts, only a few studies about noncyclic associates are available and even they report the formation of polymeric chains.<sup>57–59</sup> On the other hand, a close stability of the chain and cyclic dimers and trimers was predicted recently.<sup>21</sup>

Due to the three Ga–N rotational axes, several stable conformers can be expected for the chain  $\text{Cl}(\text{Cl}_2\text{GaNH}_2)_2\text{H}$

dimer. We searched systematically the potential energy surface (PES) of the molecule and found (only) two minimum structures, both having  $C_s$  symmetry (cf. Figure 2). Additionally, six saddle points (of first and second order) were located on the PES, derived from the minimum structures by rotation of the terminal  $\text{GaCl}_3$  and  $\text{NH}_3$  groups. Generally, the saddle points derived by  $\text{NH}_3$  rotation lie closer in energy to the respective minima ( $\Delta E = 1\text{--}6$  kJ/mol) than the saddle points corresponding to  $\text{GaCl}_3$  rotation ( $\Delta E = 10\text{--}20$  kJ/mol).

In contrast to the results of Okamoto,<sup>21</sup> the global minimum of  $\text{Cl}(\text{Cl}_2\text{GaNH}_2)_2\text{H}$  is bent and there is a local minimum chain conformer (**D1'**) lying higher in energy by 51.0 kJ/mol (cf. Figure 2). This large energy difference can mainly be attributed to the double  $\text{Cl}\cdots\text{H}$  hydrogen bond in **D1'**, while only weak attractive dipole–dipole interactions (between the syn-periplanar  $\text{N}_1\text{--Ga}_2$  and  $\text{Ga}_1\text{--Cl}$  bonds) can be assumed in **D1''**. The length of the  $\text{Cl}\cdots\text{H}$  hydrogen bond in **D1'** is 2.480 Å, well below the sum of the van der Waals radii of the two atoms (3.00 Å<sup>45</sup>). Its strength is demonstrated by the pronounced lengthening of the affected  $\text{Ga}_1\text{--Cl}$  (0.043 Å) and  $\text{N}_2\text{--H}$  (0.007 Å) bonds with respect to the third, terminal  $\text{Ga}_1\text{--Cl}$  and  $\text{N}_2\text{--H}$  bonds. Similarly, the  $\text{Cl}\text{--Ga}_1\text{--N}_1$  and  $\text{H}\text{--N}_2\text{--Ga}_2$  angles indicate a significant tilt of the two groups toward each other. We note, however, that the above geometric characteristics cannot be attributed solely to the intramolecular hydrogen bond. As the geometric parameters of the **D1''** conformer show, the strong dipole–dipole interactions in such structures also exert nonnegligible impacts on the molecular geometry.

Our systematic search on the PES of the  $\text{Cl}(\text{ClGaNH})_2\text{H}$  dimer found again two minimum conformers. The structures are the “unsaturated” analogues of the stable  $\text{Cl}(\text{Cl}_2\text{GaNH}_2)_2\text{H}$  ones, both being planar (**D2'** and **D2''** in Figure 2). Again, a structure with a short attractive  $\text{Cl}\cdots\text{H}$  contact (**D2'**) is favored (by 8.2 kJ/mol) over **D2''**, that latter one containing a repulsive dipole–dipole interaction of peri Ga–Cl bonds. The calculated  $\text{Cl}\cdots\text{H}$  nonbonded distance in **D2'** (2.981 Å) corresponds to the sum of the van der Waals radii of the two atoms. However, there are signs of a very weak bonding interaction between Cl and H, viz., the slight increase of the  $\text{Ga}_1\text{--Cl}$  and  $\text{N}_2\text{--H}$  bonds of the interacting atoms. Additionally, a bond critical point was located along the  $\text{Cl}\cdots\text{H}$  path with characteristics of very weak bonding interactions.

All the dimer Ga–N bond distances show a single bond character (cf. Figure 2) indicating that these species are not weakly bonded adducts of the respective monomers but well-defined compact molecules. The Ga–N bonds in the “saturated” and “unsaturated” dimers resemble in magnitude those in the  $\text{Cl}_3\text{GaNH}_3$  and  $\text{Cl}_2\text{GaNH}_2$  monomers, respectively. They are somewhat decreased in the “saturated” while

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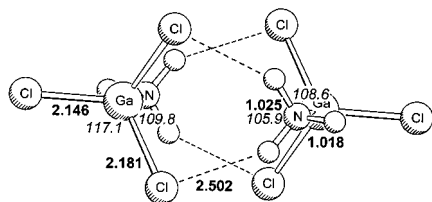
(55) Designation of the oligomers throughout the paper obeys the following scheme: **D**, **T**, and **Q** mean dimer, trimer, and tetramer, respectively; **1** and **2** are assigned to “saturated” and “unsaturated” skeletons, respectively, while the chain structures are indicated additionally by primes.

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**Figure 3.** Structure of hydrogen-bonded dimer of Cl<sub>3</sub>GaNH<sub>3</sub>. Bond distances (bold) are given in angstroms, bond angles (italic) in degrees.

somewhat increased in the “unsaturated” dimers as compared to the Ga–N bond in the respective monomer derivatives.

Though its formation under the conditions of the high-temperature CVD process is improbable, the hydrogen-bonded dimer of Cl<sub>3</sub>GaNH<sub>3</sub> is interesting from a structural point of view. We investigated three possible structures: one structure built up from two staggered monomer units (three Cl···H contacts) and two structures built up from eclipsed monomer units (two and four Cl···H contacts, respectively). Among these structures only the one with four Cl···H hydrogen bonds (presented in Figure 3) proved to be a minimum on the PES. It has *C*<sub>2h</sub> symmetry and a dimerization energy of –48.3 kJ/mol. Normalized to one hydrogen bond, we get a hydrogen bonding energy of 12.1 kJ/mol for the Cl···H interaction. The Cl···H distance in (Cl<sub>3</sub>GaNH<sub>3</sub>)<sub>2</sub>, 2.502 Å, is close to the ones found in **D1'**, indicating a similar stabilization effect of the latter intramolecular hydrogen bonds. We note that this strong exothermic character of dimerization is accompanied by a negative entropy contribution; hence the (Cl<sub>3</sub>GaNH<sub>3</sub>)<sub>2</sub> dimer cannot be expected in the vapor phase.

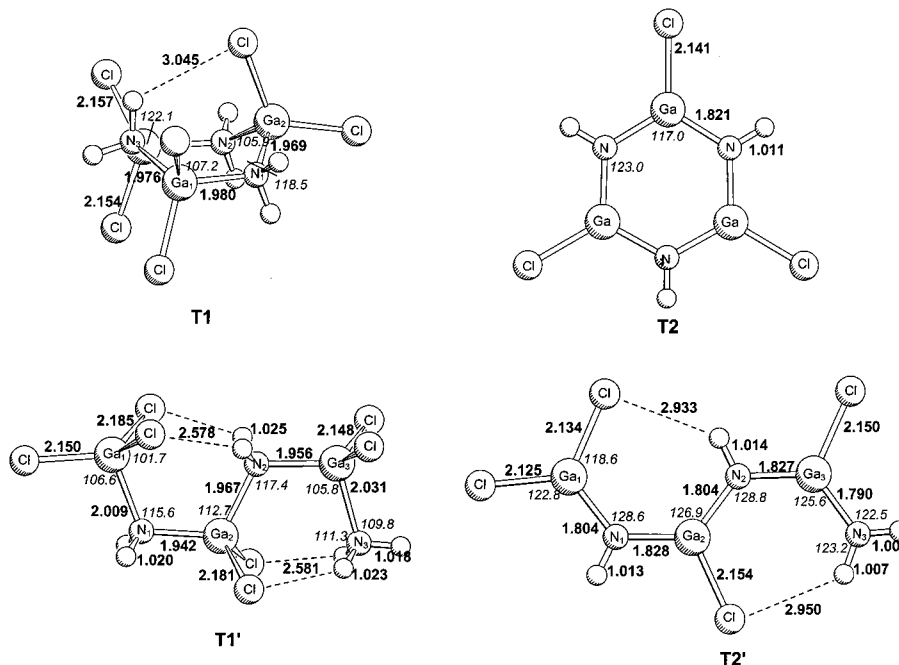
**Trimers and Tetramers.** The cyclic trimers have a larger conformational freedom than the more compact analogous dimers. Saturated organic six-membered rings are known to exist in chair, boat, or twist-boat conformations, but in the

case of exotic molecules a planar arrangement cannot be excluded either. The conformational properties may also depend on the substituents of the (GaN)<sub>3</sub> skeleton. On the basis of X-ray structural data of (H<sub>2</sub>GaNH<sub>2</sub>)<sub>3</sub> and neutron powder diffraction of (D<sub>2</sub>GaND<sub>2</sub>)<sub>3</sub>, Gladfelter and co-workers established a chair conformation of the compounds in the solid state. However, they found that the twist-boat conformation of (H<sub>2</sub>GaNH<sub>2</sub>)<sub>3</sub> is more stable (by 11 kJ/mol) than the chair conformation at the MP2/VDZ level.<sup>60</sup> Also, the [(CH<sub>3</sub>)<sub>2</sub>GaNH<sub>2</sub>]<sub>3</sub> compound exists in a “twisted chair” form in the solid state,<sup>61</sup> while quantum chemical computations found again the twist-boat conformation as only minimum on the PES.<sup>9</sup>

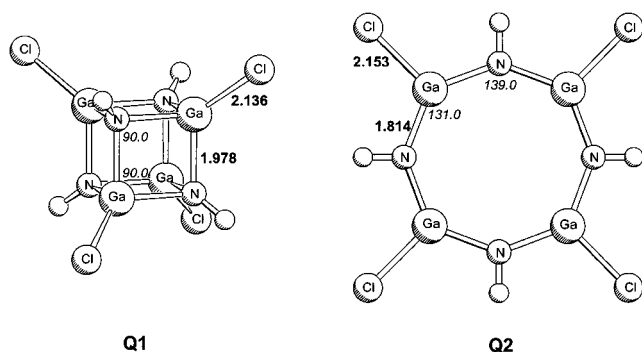
Previously, Okamoto reported only a planar *D*<sub>3h</sub> structure for (GaCl<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>.<sup>21</sup> According to our more sophisticated calculations the planar structure is a second-order saddle point on the PES. The chair conformer, the generally favored minimum in saturated organic cyclic structures, is a first-order saddle point lying higher in energy by 8.5 kJ/mol than the global (and only) minimum boat conformer (**T1**, cf. Figure 4). This strongly favored boat arrangement can be reasoned by attractive dipole–dipole interactions between the nearly parallel N–H and Ga–Cl dipoles in this structure. The distance between the bowl positioned H and Cl (3.045 Å, cf. Figure 4) may be too large for any appreciated stabilizing interaction.

Similarly, a single minimum structure was found for (GaClNH)<sub>3</sub>. The equilibrium geometry of the molecule is planar and has *D*<sub>3h</sub> symmetry (**T2**, cf. Figure 4). Analogous benzene-like structures have been reported for related imino trimers, viz., for (AlClNH)<sub>3</sub>,<sup>15</sup> (AlHNH)<sub>3</sub>,<sup>62</sup> and (HGaNH)<sub>3</sub>.<sup>9</sup>

Due to the five Ga–N rotational axes numerous stable conformers may be possible for the chain trimers. On the basis of our results on the smaller dimer derivatives, a



**Figure 4.** Structures and selected geometric parameters of the most important cyclic and chain trimers. Bond distances (bold) are given in angstroms, bond angles (italic) in degrees.



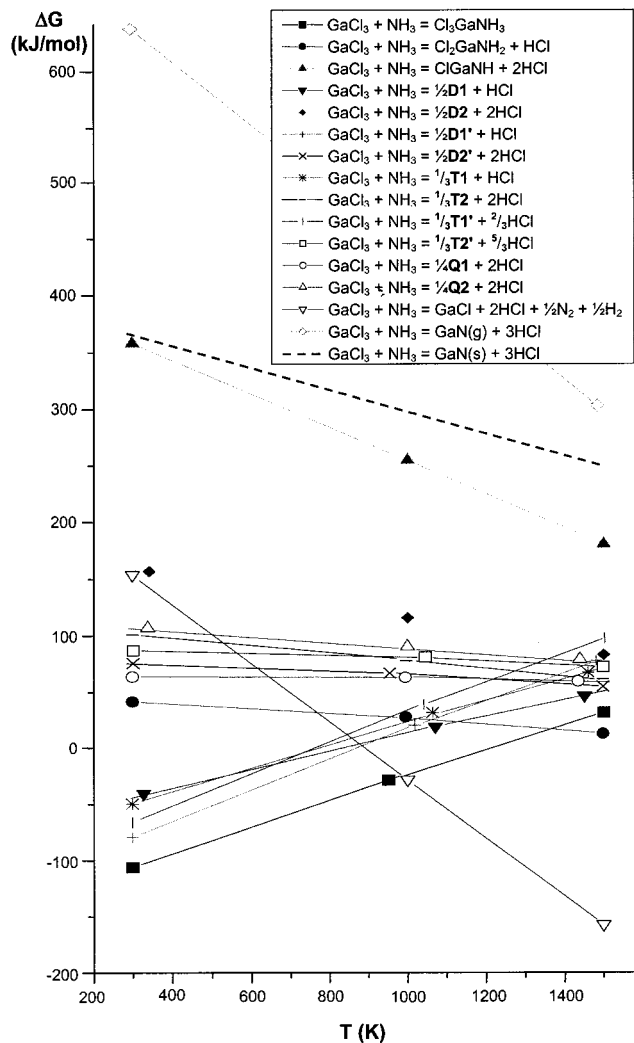
**Figure 5.** Structures and selected geometric parameters of cube and planar tetramers. Bond distances (bold) are given in angstroms, bond angles (italic) in degrees.

multiple hydrogen-bonded arrangement can be expected as the global minimum on the PES. Therefore, we neglected a complete analysis of the conformational space of the chain trimers and performed only a couple of test calculations with other structures. The most favored conformers for “saturated” (**T1'**) and “unsaturated” (**T2'**) chain trimers are shown in Figure 4. Each structure has two slightly different Cl...H attractive interactions forming weakly bound six rings. We note the slightly out-of-plane position of the terminal NH<sub>2</sub> group (by 2°) in **T2'**, in disagreement with the rigorously planar structure of the **D2'** dimer.

From the possible numerous tetramer oligomers only the most interesting symmetric (GaClNH)<sub>4</sub> structures were considered in the present study (Figure 5). The global minimum is the cubic *T<sub>d</sub>* structure (**Q1**) while the planar *D<sub>4h</sub>* one (**Q2**, local minimum) lies higher in energy by 187.5 kJ/mol. The cubic skeleton is well-known among iminoalanes and gallanes, and several derivatives with alkyl and aryl substituents have been synthesized.<sup>42,63–68</sup> Moreover, previous theoretical studies suggested an important role for these species as intermediates in the CVD processes from NH<sub>3</sub> + AlCl<sub>3</sub>,<sup>15</sup> GaH<sub>3</sub> + NH<sub>3</sub>, Ga(CH<sub>3</sub>)<sub>3</sub> + NH<sub>3</sub>, and GaH<sub>3</sub> + N(CH<sub>3</sub>)<sub>3</sub>.<sup>9</sup>

The bonding in the above chain and cyclic trimers and tetramers is analogous to that of the respective dimers. There are only marginal differences in the bond distances, atomic charges, and properties of the bond critical points. In the cubic tetramer, however, the atomic charges of Ga and N reflected a considerably increased ionic character of the Ga–N bond. These stronger attractive electrostatic forces are probably compensated by the geometric constraints,

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**Figure 6.** Gibbs free energies for reactions resulting in formation of monomers and selected oligomers from a 1:1 mixture of GaCl<sub>3</sub> and NH<sub>3</sub>.

which hinder a considerable shortening of the Ga–N bond (cf. Figures 4 and 5).

**Thermodynamics.** The reliability of the B3P86/6-311G-(d,p) level for a thermodynamic analysis of the GaCl<sub>3</sub> + NH<sub>3</sub> system can be assessed by comparing the computed and experimental thermodynamic properties of the Cl<sub>3</sub>GaNH<sub>3</sub>(g) = GaCl<sub>3</sub>(g) + NH<sub>3</sub>(g) dissociation. The computed dissociation enthalpy at 743 K, 137.6 kJ/mol, agrees excellently with the experimental value of 134.2 ± 0.8 kJ/mol.<sup>69</sup> On the other hand, the computations seem to underestimate the entropy change of the dissociation (computed 117.5 J/mol·K; experimental 141.3 ± 2.5 J/mol·K<sup>69</sup>). Nevertheless, the above data indicate a good performance of the B3P86/6-311G(d,p) level for the thermodynamic properties, especially at lower temperatures.

The theoretical enthalpies ( $\Delta H$ ), entropies ( $\Delta S$ ), and Gibbs free energies ( $\Delta G$ ) of various association and dissociation reactions in the GaCl<sub>3</sub> + NH<sub>3</sub> system at 1300 K, the usual temperature of CVD using Cl<sub>3</sub>GaNH<sub>3</sub> precursor,<sup>70</sup> are compiled in Table 2. The Gibbs free energies of the reactions producing the most important species from a 1:1 mixture of GaCl<sub>3</sub> and NH<sub>3</sub> are depicted in Figure 6 as a function of the temperature. The  $\Delta G$  for the formation of solid GaN(s) was

**Table 2.** Computed Enthalpies ( $\Delta H$ , kJ/mol) Entropies ( $\Delta S$ , J/mol·K), and Gibbs Free Energies ( $\Delta G$ , kJ/mol) for Selected Gas-Phase Reactions at 298 and 1300 K

	298 K			1300 K		
	$\Delta H$	$\Delta S$	$\Delta G$	$\Delta H$	$\Delta S$	$\Delta G$
Cl <sub>3</sub> GaNH <sub>3</sub> = GaCl + 2HCl + (1/2)N <sub>2</sub> + (1/2)H <sub>2</sub>	373.2	380.8	259.7	358.8	365.6	-116.4
Cl <sub>3</sub> GaNH <sub>3</sub> = GaCl <sub>2</sub> + NH <sub>2</sub> + HCl	547.0	290.8	460.3	531.2	272.3	177.3
Cl <sub>3</sub> GaNH <sub>3</sub> = GaCl + NH + 2HCl	712.4	401.0	593.0	697.9	385.5	196.7
Cl <sub>2</sub> GaNH <sub>2</sub> = GaCl + HCl + (1/2)N <sub>2</sub> + (1/2)H <sub>2</sub>	184.1	241.8	112.1	173.8	229.8	-125.0
(1/2) <b>D1</b> = GaCl + HCl + (1/2)N <sub>2</sub> + (1/2)H <sub>2</sub>	301.7	347.6	198.1	286.1	329.5	-142.2
(1/2) <b>D1'</b> = GaCl + (3/2)HCl + (1/2)N <sub>2</sub> + (1/2)H <sub>2</sub>	352.9	403.2	232.7	360.5	401.7	-161.6
(1/2) <b>D2</b> = GaCl + (1/2)N <sub>2</sub> + (1/2)H <sub>2</sub>	56.1	203.5	-4.5	46.0	191.2	-202.6
(1/2) <b>D2'</b> = GaCl + (1/2)HCl + (1/2)N <sub>2</sub> + (1/2)H <sub>2</sub>	153.6	252.5	78.4	139.8	235.1	-165.8
(1/3) <b>T1</b> = GaCl + HCl + (1/2)N <sub>2</sub> + (1/2)H <sub>2</sub>	313.8	371.0	203.2	296.2	350.2	-159.0
(1/3) <b>T1'</b> = GaCl + (4/3)HCl + (1/2)N <sub>2</sub> + (1/2)H <sub>2</sub>	341.7	409.2	219.7	321.8	385.1	-178.9
(1/3) <b>T2</b> = GaCl + (1/2)N <sub>2</sub> + (1/2)H <sub>2</sub>	123.0	235.7	52.8	111.2	218.5	-172.8
(1/3) <b>T2'</b> = GaCl + (1/3)HCl + (1/2)N <sub>2</sub> + (1/2)H <sub>2</sub>	143.9	258.1	67.0	129.0	239.0	-181.8
(1/4) <b>Q1</b> = GaCl + (1/2)N <sub>2</sub> + (1/2)H <sub>2</sub>	168.3	263.7	89.7	155.1	247.6	-166.8
Cl <sub>3</sub> GaNH <sub>3</sub> = Cl <sub>2</sub> GaNH <sub>2</sub> + HCl	189.0	139.0	147.6	185.1	135.7	8.6
Cl <sub>3</sub> GaNH <sub>3</sub> = ClGaNH + 2HCl	544.1	268.2	464.2	533.4	256.6	199.9
Cl <sub>3</sub> GaNH <sub>3</sub> = (1/2) <b>D1</b> + HCl	71.5	33.2	61.6	72.7	36.1	25.8
Cl <sub>3</sub> GaNH <sub>3</sub> = (1/2) <b>D1'</b> + (1/2)HCl	20.3	-22.4	27.0	-1.7	-36.1	45.2
Cl <sub>3</sub> GaNH <sub>3</sub> = (1/3) <b>T1</b> + HCl	59.4	9.9	56.5	62.6	15.4	42.6
Cl <sub>3</sub> GaNH <sub>3</sub> = (1/3) <b>T1</b> + (2/3)HCl	31.5	-28.4	40.0	37.1	-19.5	62.5
Cl <sub>3</sub> GaNH <sub>3</sub> = (1/2) <b>D2</b> + 2HCl	317.1	177.4	264.2	312.8	174.4	86.2
Cl <sub>3</sub> GaNH <sub>3</sub> = (1/2) <b>D2'</b> + (3/2)HCl	219.5	128.3	181.3	219.1	130.5	49.4
Cl <sub>3</sub> GaNH <sub>3</sub> = (1/3) <b>T2</b> + 2HCl	250.1	145.1	206.9	247.6	147.1	56.4
Cl <sub>3</sub> GaNH <sub>3</sub> = (1/3) <b>T2'</b> + (5/3)HCl	229.3	122.7	192.7	229.9	126.6	65.4
Cl <sub>2</sub> GaNH <sub>2</sub> = (1/2) <b>D1</b>	-117.5	-105.8	-86.0	-112.3	-99.6	17.2
Cl <sub>2</sub> GaNH <sub>2</sub> = (1/2) <b>D2</b> + HCl	128.0	38.4	116.6	127.8	38.6	77.6
Cl <sub>2</sub> GaNH <sub>2</sub> = (1/2) <b>D2'</b> + (1/2)HCl	30.5	-10.7	33.7	34.0	5.2	40.8
Cl <sub>2</sub> GaNH <sub>2</sub> = (1/3) <b>T1</b>	-129.6	-129.1	-91.2	-122.5	-120.3	34.0
Cl <sub>2</sub> GaNH <sub>2</sub> = (1/3) <b>T2</b> + HCl	61.1	6.1	59.3	62.5	11.3	47.8
Cl <sub>2</sub> GaNH <sub>2</sub> = (1/3) <b>T2'</b> + (2/3)HCl	40.2	-16.2	45.1	44.8	-9.2	56.8
Cl <sub>2</sub> GaNH <sub>2</sub> = (1/4) <b>Q1</b> + HCl	15.9	-21.9	22.4	18.7	-17.7	41.8
ClGaNH = (1/2) <b>D2</b>	-227.0	-90.8	-199.9	-220.6	-82.2	-113.7
ClGaNH = (1/3) <b>T2</b>	-293.9	-123.1	-257.3	-285.8	-109.5	-143.5
ClGaNH = (1/4) <b>Q1</b>	-339.2	-151.1	-294.1	-329.7	-138.6	-149.5
GaCl <sub>3</sub> + NH <sub>3</sub> = GaN(g) + 3HCl	732.4	278.2	649.5	730.6	279.0	367.9
Cl <sub>3</sub> GaNH <sub>3</sub> = GaN(g) + 3HCl	875.7	403.1	755.6	861.1	387.2	357.8
Cl <sub>2</sub> GaNH <sub>2</sub> = GaN(g) + 2HCl	686.7	264.1	607.9	676.0	251.4	349.2
ClGaNH = GaN(g) + HCl	331.6	134.9	291.4	327.6	130.6	157.9
(1/2) <b>D1</b> = GaN(g) + 2HCl	804.2	370.0	694.0	788.3	351.0	332.0
(1/2) <b>D1'</b> = GaN(g) + (5/2)HCl	855.4	425.5	728.6	862.8	423.2	312.6
(1/2) <b>D2</b> = GaN(g) + HCl	558.6	225.8	491.4	548.3	212.8	271.6
(1/2) <b>D2'</b> = GaN(g) + (3/2)HCl	656.2	274.8	574.3	642.0	256.7	308.4
(1/3) <b>T1</b> = GaN(g) + 2HCl	816.3	393.3	699.1	798.5	371.7	315.2
(1/3) <b>T1'</b> = GaN(g) + (7/3)HCl	844.2	431.5	715.6	824.0	406.7	295.3
(1/3) <b>T2</b> = GaN(g) + HCl	625.6	258.0	548.7	613.5	240.1	301.4
(1/3) <b>T2'</b> = GaN(g) + (4/3)HCl	646.4	280.4	562.9	631.2	260.6	292.4
(1/4) <b>Q1</b> = GaN(g) + HCl	670.8	286.0	585.6	657.3	269.2	307.4

obtained by combining the respective  $\Delta G$  value for gaseous GaN(g) and the  $\Delta G$  of sublimation ( $\Delta G_{\text{sub}}$ ) of GaN.  $\Delta G_{\text{sub}}$  was calculated within the required temperature range using the thermodynamic data given in ref 71. Details on the sublimation of GaN are given as Supporting Information.

We emphasize that our calculated thermodynamic data refer to equilibrium conditions of the 1:1 GaCl<sub>3</sub> + NH<sub>3</sub> system. In practice, however, CVD is a nonequilibrium process involving effects of nonstoichiometric vapor composition, quality of carrier gas, flow rate of the gas stream, and surface reactions.<sup>16</sup> Moreover, the growth rate was indicated to be controlled kinetically over a wide temperature range.<sup>18</sup> On the other hand, a thermodynamic analysis may be important to understanding and optimizing the selective

epitaxial growth processes, because in many cases the film composition is determined by the thermodynamics. Our results can also give useful guidelines for gas-phase experiments on the association products.

First we discuss the thermodynamic probability of the formation of various structures from a 1:1 mixture of GaCl<sub>3</sub> and NH<sub>3</sub>. As Figure 6 shows, below 1000 K the formation of the Cl<sub>3</sub>GaNH<sub>3</sub> complex is the most probable. Additionally to Cl<sub>3</sub>GaNH<sub>3</sub> the “saturated” dimers and trimers **D1**, **D1'**, **T1**, and **T1'** have negative  $\Delta G$  values in this range with the chain forms slightly more favored. However, the thermodynamic stability of these molecules decreases with increasing temperature, and above 800–1000 K the  $\Delta G$  values (that of the Cl<sub>3</sub>GaNH<sub>3</sub> complex above 1300 K) become positive. The temperature dependence is near parallel for all five species. The close thermodynamic stability of **D1** and **T1** is in agreement with the dimer ↔ trimer equilibrium of [Cl<sub>2</sub>-GaN(H)Si(CH<sub>3</sub>)<sub>3</sub>]<sub>n</sub> observed in toluene solution.<sup>72</sup> Moreover, the computations and observations agree in the interchanging

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stability order of the dimer and trimer with increasing temperature (cf. Figure 6 and ref 72).

Above 1000 K the decomposition to small fragments (GaCl, HCl, N<sub>2</sub>, H<sub>2</sub>) dominates, showing a steep slope with increasing temperature. This is in agreement with experience that the GaN deposition ceases above 1300 K.<sup>70</sup>

According to our calculations, the GaCl<sub>3</sub> + NH<sub>3</sub> = GaN(g) + 3HCl reaction has a large positive Δ*G* value which decreases steeply with increasing temperature. Taking into account the calculated Gibbs free energies of sublimation (Δ*G*<sub>sub</sub>), the Δ*G* of the reaction drops between 300 and 400 kJ/mol but the slope of the curve moderates. We should note the rather large deviation between the calculated and experimental standard enthalpies of the above deposition reaction (396.7 and 106.4 kJ/mol,<sup>73</sup> respectively). This large deviation could not be removed by trying another theoretical level, MP2/6-311G(d,p), either. Taking into account the previously shown good performance of the B3P86/6-311G-(d,p) method for the Cl<sub>3</sub>GaNH<sub>3</sub> dissociation, the reason for the above discrepancy may lie in an underestimation of the absolute energy of GaN (as a systematic error) by these less sophisticated theoretical levels. Nevertheless, both the present theoretical results and experimental observations imply that the formation of GaN films is not favored under equilibrium conditions from a 1:1 mixture of GaCl<sub>3</sub> and NH<sub>3</sub>. In fact, starting from the GaCl<sub>3</sub> + HCl + NH<sub>3</sub> system, Tshagnov et al. found a better yield for GaN deposition.<sup>74</sup>

A major point in the stability of the various monomers and oligomers is their decomposition to the small fragments which becomes important at higher temperatures. Among the three decomposition routes (see lines 1–3 in Table 2) the one resulting in GaCl, HCl, N<sub>2</sub>, and H<sub>2</sub> is favored, while the ones with GaCl<sub>2</sub>, GaCl, NH<sub>2</sub>, and NH products are thermodynamically less probable. The large endothermic character of the latter two reactions can be explained by the relative instability of the dissociation products, especially that of the GaCl<sub>2</sub>, NH<sub>2</sub>, and NH radicals. As Table 2 shows, the “saturated” oligomers are slightly more stable against decomposition than the respective “unsaturated” derivatives.

According to the data in Table 2, Cl<sub>2</sub>GaNH<sub>2</sub> may be formed from Cl<sub>3</sub>GaNH<sub>3</sub> at higher temperatures. The formation of the “saturated” **D1**, **D1'**, **T1**, and **T1'** species from the Cl<sub>3</sub>GaNH<sub>3</sub> complex is unlikely: the oligomers may be directly formed from the GaCl<sub>3</sub> + NH<sub>3</sub> mixture (cf. Figure 6). On the other hand, the association of Cl<sub>2</sub>GaNH<sub>2</sub> to the cyclic **D1** and **T1** structures is highly exothermic, which makes this monomer a very suitable intermediate for cyclic “saturated” oligomers. Due to the negative entropy, however, the temperature increase may prevent this reaction, a trend opposite the predicted population of Cl<sub>2</sub>GaNH<sub>2</sub> in the gaseous phase. The most probable intermediate for the “unsaturated” oligomers **D2**, **T2**, and **Q1** would be ClGaNH, which species, however, is thermodynamically strongly unfavored.

The third section of Table 2 contains the thermodynamic data for various reactions producing GaN(g). All these reactions are highly endothermic with close Δ*G* values. Only the formation from ClGaNH has a considerably lower Δ*G*, but just this species appears with the least probability in the gaseous phase. The differences between the other Δ*G* data are not significant enough to make predictions on the possible intermediates under nonequilibrium conditions.

## Conclusions

Test calculations on the performance of HF, MP2, B3LYP, and B3P86 theories proved the superior character of the MP2 and B3P86 methods for the Cl<sub>3</sub>GaNH<sub>3</sub> complex. From the two methods B3P86 showed better convergence to basis set saturation; hence this level in conjunction with a 6-311G-(d,p) basis set was selected for our systematic study of the GaCl<sub>3</sub> + NH<sub>3</sub> system in the gaseous phase. We calculated various molecular properties (geometries, bonding properties, thermodynamic data) of the possible species from the very small fragments up to tetramer oligomers.

Our general conclusions on the geometry and bonding in the title compounds can be summarized as follows:

(i) In the oligomer species possessing conformational freedom, strong intramolecular Cl···H hydrogen bonding and dipole–dipole interactions determine the most stable conformers.

(ii) The Ga–N bond distances in the “saturated” oligomers (tetracoordinated Ga and N) are around 2.0 Å, while those in the “unsaturated” oligomers (tricoordinated Ga and N) are around 1.8 Å. These distances are in agreement with the single bond character of Ga–N. The only compound that shows a well-defined double bond character is ClGaNH.

(iii) The Ga–N–Ga angles in the cyclic oligomers are consistently larger than the N–Ga–N ones, with the difference increasing with ring size. The smaller value for N–Ga–N is in agreement with the larger size and the lower valence density around Ga (due to its positive partial charge) and the consequently arising smaller repulsion between the bonding electron densities.

The thermodynamic analysis of the GaCl<sub>3</sub> + NH<sub>3</sub> reaction under equilibrium conditions reproduced the generally observed predominance of the Cl<sub>3</sub>GaNH<sub>3</sub> complex in the gaseous phase.<sup>18,22</sup> The computations indicate additionally the probable appearance of the “saturated” chain and cyclic oligomers below 1000 K. According to the calculated Gibbs free energies, these species may be directly formed from the GaCl<sub>3</sub> + NH<sub>3</sub> mixture. For the cyclic “saturated” oligomers additionally the Cl<sub>2</sub>GaNH<sub>2</sub> molecule seems to be a suitable intermediate. According to our computations the deposition of GaN from a GaCl<sub>3</sub> + NH<sub>3</sub> mixture may be achieved only under nonequilibrium conditions.

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**Supporting Information Available:** Computed geometric parameters and absolute energies of Cl<sub>3</sub>GaNH<sub>3</sub> using HF, MP2, B3LYP, and B3P86 theories and basis sets extended gradually from 6-31G(d,p) up to 6-311+G(2df, 2pd); computed natural atomic charges, Wiberg bond indices, and topological properties of the electron density distribution; harmonic vibrational frequencies and IR intensities (for assistance in experimental identification of

possible intermediates in the GaN CVD process); Gibbs free energies of the sublimation of GaN in the range 298–2000 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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