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Article

Ring, Chain, and Cluster Compounds in the Cl–Ga–N–H System

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The formation of gas-phase oligomer compounds in the Cl–Ga–N–H system is considered using hybrid Hartree–Fock/density functional theory and a polarized double-ζ quality basis set. Geometric parameters, vibrational frequencies, and thermodynamic characteristics for the Cl_3GaNH_3 adduct, its dissociation products $GaCl_n$, NH_n, ($n = 1$–3), the amidochlorogallanes $[Cl_2GaNH_2]_n$ ($n = 1$–3), their donor–acceptor complexes with $GaCl_3$ and NH_3, and the imidochlorogallanes $[ClGaNH]_n$ ($n = 1$–4,6) have been obtained. Generation of amidochlorogallanes is expected to be viable during laser assisted chemical vapor deposition (CVD) at low temperatures. High-temperature association processes in the gas phase during the CVD of GaN from the Cl_3GaNH_3 adduct are predicted to be less important, in contrast to previous findings for the aluminum analogue. This difference may be explained in terms of a much lower Ga–N bond energy compared to Al–N in the ring and cluster compounds.

Introduction

Gallium nitride is one of the prospective materials for micro- and optoelectronics. There is a rapidly growing interest in GaN chemistry, which has resulted in a special volume of Gmelin's Handbook[1] and several special issues of *Semiconductors and Semimetals*.[2,3] One of the most common routes to GaN synthesis is the metal organic chemical vapor deposition (MOCVD) from trimethylgallium and ammonia. However, this method results in carbon contamination which cannot be completely avoided even in excess ammonia at high temperatures.[1] To eliminate the possibility of carbon inclusion, new inorganic precursors, such as $[H_2GaNH_2]_3$,[4] $[Cl_2GaN_3]_3$,[5a] and $[HClGaN_3]_4$[5b] have been recently proposed and examined. However, the role of the N_3 azido group as the source of nitrogen is questionable, since, e.g., the N_3 group does not play a key role as a nitrogen source in ammonia atmosphere.[6]

According to the thermodynamic analysis by Tchegnov et al.,[7] the GaCl−HCl−NH_3 system is the most promising one for GaN production, and the gallium trichloride−ammonia adduct is one of the most suitable precursors. The Cl_3GaNH_3 adduct has been extensively studied experimentally, and its structural[8] and thermodynamic[9] characteristics are well-known. At 820−1320 K the source complex decomposes to produce HCl and the binary nitride:[10−12]

$$GaCl_3NH_3(g) = GaN(s) + 3HCl(g)$$

By varying the experimental conditions, monocrystalline

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GaN was obtained. Despite the intensive experimental investigations, the chemical nature of the intermediates involved in the GaN chemical vapor deposition (CVD) process is still unclear. The knowledge of the mechanism is expected to be essential for finding optimal growing conditions. Experiments indicate that the GaN deposition velocity is lowered at T beyond 1180 K because of side processes. The GaN growth rate is increased with increasing NH_3 partial pressure, which, according to Grekov,[12] indicates the existence of a dissociation pathway.

In 1997, employing the B3LYP/DZP level of theory, we demonstrated that formation of gas-phase clusters as intermediates is thermodynamically feasible[13] and association processes in the gas phase play major roles for AlN CVD from $AlCl_3NH_3$. However, in 1998 Okamoto[14] investigated the cyclic $[Cl_2MNH_2]_n$ and chain $M_nCl_{2n+1}N_nH_{2n+1}$ structures ($n = 1-3$, M = Al, Ga, In) at the MP2/cc-pVDZ [with effective core potentials (ECP) on Ga and In] level of theory and found that chain structures of the dimers were more stable than the cyclic structures. He also concluded that "the monomer was the most stable in these species irrespective of the metal element" in contradiction with experimental indications of the key role of higher mass associates during the chlorine-vapor-phase epitaxy (ClVPE) of AlN.[15]

Although the gallium−nitrogen bond dissociation enthalpy is the lowest among the group 13 metals (Al > Ga < In),[16] the experimentally derived Ga−N bond dissociation enthalpy of Cl_3GaNH_3 is lower by only 3 kJ mol^{-1} compared to the aluminum analogue[9b] (theoretical methods predict a 12−19 kJ mol^{-1} difference[16]). Hence, one should expect that association processes might also be important for GaN CVD.

The operation of association processes in condensed phase is well-known for galliumorganic compounds.[17] Amido- and imidogallanes can be produced by the reaction of substituted gallanes with primary amines:

$$GaR_3 + NH_2R' \rightarrow \underset{\text{amidogallanes}}{{}^1/_n[R_2GaNHR']_n} \rightarrow \underset{\text{imidogallanes}}{{}^1/_m[RGaNR']_m}$$

Both amido- and imidogallanes are associated in the solid state and in nonaqueous solutions with the association degree n, m, depending on the steric demand of organic substituents R, R′. The chemistry of chlorogallanes (R = Cl) is much less explored, but recently structural data for mixed metal complex $[Cl_2GaN{=}N{-}R]_2$, R = $WCl(PMe_2Ph)_4$,[18] which contains the $[(Cl_2Ga)N]_2$ skeleton, have been reported. These types of compounds may be promising starting materials for the synthesis of transition metal doped GaN. The dimers $[Cl_2GaN(H)SiMe_3]_2$ and $[Cl_2GaN(Me)SiMe_3]_2$ have been prepared and structurally characterized by Nutt and coworkers.[19a] In toluene solution both complexes exist as a mixture of cis and trans isomers, with the trans isomer being 2.4 kJ mol^{-1} more stable. Substitution of toluene for CH_2Cl_2 results in additional stabilization of the cis form due to higher solvation of the more polar cis isomer. In solutions of $[Cl_2GaN(H)SiMe_3]_2$ the trimer species $[Cl_2GaN(H)SiMe_3]_3$ is present, while for $[Cl_2GaN(Me)SiMe_3]_2$ trimerization was not evidenced. This observation is in line with the high sensitivity of the nitrogen center toward substituents, observed earlier for the organogallium compounds: trimer forms are formed with H substituents on the nitrogen center ($[Me_2GaNH_2]_3$ [20] and $[H_2GaNH_2]_3$ [4]) but only dimer species $[H_2GaNMe_2]_2$ [21] are formed in the case of methyl substituents.

Experimental thermodynamic data for the oligomerization processes of amido- and imidogallanes are very rare, with the notable exceptions being the studies of Nutt et al.[19] The equilibrium constant and thermodynamic characteristics of the trimer−dimer equilibrium have been obtained for the 313−366 K temperature interval from the temperature dependence of the ^1H NMR spectrum:

$$2[Cl_2GaN(H)SiMe_3]_3 = 3[Cl_2GaN(H)SiMe_3]_2$$

for which $\Delta H = 68 \pm 3$ kJ mol^{-1} and $\Delta S = 206 \pm 9$ J mol^{-1} K^{-1}. These experimental results indicate that the process of rearrangement of dimeric amidochlorogallanes into trimeric rings is energetically favorable at low temperatures.

There are no thermodynamic data available for the gas-phase amido- and imidochlorogallanes. To clarify the role of oligomers as possible intermediates in the GaN CVD process from the Cl_3GaNH_3 adduct, here we computationally investigate amidochlorogallanes $[Cl_2GaNH_2]_n$ ($n = 1-3$), their donor−acceptor complexes with $GaCl_3$ and NH_3, and the imidochlorogallanes $[ClGaNH]_n$ ($n = 1-4,6$). Unlike our previous report on aluminum analogues,[13] not only ring and cluster but also some chain structures are considered. The knowledge of thermodynamic properties is necessary to predict the conditions of the operation of the thermodynamically most favorable reactions in the gas phase during ClVPE. We here report structural characteristics of the individual compounds, as well as thermodynamic analyses of the major processes in the gas phase. Vibrational frequencies and IR intensities are given as Supporting Information and may facilitate the experimental observation of these species via the IR matrix isolation technique.

Computational Details

All computations were performed using the Gaussian 94 program package.[22] All geometries were fully optimized using the three-

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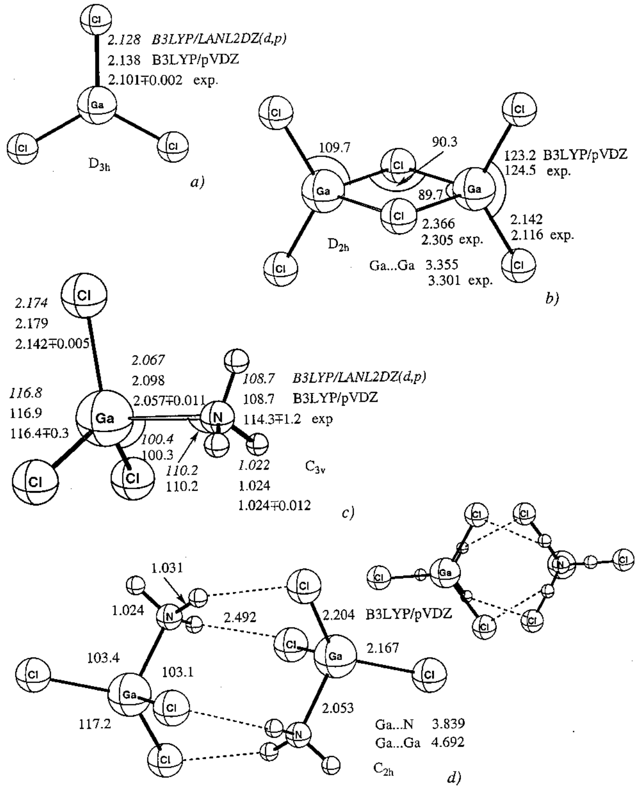

Figure 1. Optimized geometries of $GaCl_3$ (a), Ga_2Cl_6 (b), the $GaCl_3NH_3$ adduct (c), and the dimer $(Cl_3GaNH_3)_2$ (d). Bond lengths are in angstroms; bond angles are in degrees. Data are from the B3LYP/pVDZ level of theory, with data from B3LYP/LANL2DZ(d,p) level given in italics. Experimental values for $GaCl_3$, Ga_2Cl_6, and $GaCl_3NH_3$ are taken from refs 28c,d, 28b, and 8, respectively.

parameter exchange functional of Becke[23] with the gradient-corrected correlation functional of Lee, Yang, and Parr[24] (B3LYP). Since our goal was to study mostly large oligomeric species, the all electron polarized valence double-ζ (pVDZ) basis set of Ahlrichs and co-workers[25] was used throughout. Performance of the ECP basis set of Hay and Wadt,[26] augemented by *d* polarization functions on heavy atoms (orbital exponents 0.16 for Ga, 0.56 for Cl, 0.8 for N) and *p* polarization functions on hydrogen (orbital exponent 1.0), denoted as LANL2DZ(d,p) has also been tested. All stationary points on the potential energy surface (PES) were characterized by the computation of analytic second derivatives for the pVDZ basis set and by numeric evaluation of analytic first derivatives with the ECP basis sets.

For the simple species $GaCl_x$, NH_x there is satisfactory agreement between computed and experimental vibrational frequencies if usual scaling factors are applied[13] (see Table 1, Supporting Information), but the Ga−Cl bond lengths are slightly overestimated (Figure 1a). We also considered the Ga_2Cl_6 dimer as a test system for the performance of the level of theory employed, since the correct description of the bridging region is known to be sensitive to the quality of the approximation employed. Ga_2Cl_6 was earlier studied computationally by Duke et al. at self-consisted field SCF/DZP and SCF/ECP levels of theory.[27] We find that both terminal and bridging Ga−Cl bond distances are slightly overestimated compared to experiment, but the Ga···Ga distance of 3.355 Å (B3LYP/pVDZ) agrees better with the experimental value of 3.301 Å[28a] and 3.260 Å[28b] than does the SCF/DZP result of 3.385 Å (Figure 1b). The SCF/DZP dimerization energy of 40.6 kJ mol^{-1} was suggested to lie 20−40 kJ mol^{-1} lower than the experimental value.[27] Indeed, our B3LYP/pVDZ result of 83.1 kJ mol^{-1} agrees much better with the experimental 79.9 kJ mol^{-1}.[29] Therefore, we conclude that B3LYP/pVDZ method can successfully reproduce experimental thermodynamic parameters for the systems studied here.

Results and Discussion

(I) Cl_3GaNH_3 Donor−Acceptor Complex and Its Dimer. (A) Cl_3GaNH_3 Adduct. The staggered conformation was found to be a minimum on the PES at the SCF/LANL2DZ(d,p) level of theory. However, at the B3LYP level of theory, the eclipsed conformation of C_{3v} symmetry (Figure 1c) is a minimum for both the pVDZ and LANL2DZ(d,p) basis sets. It has intramolecular Cl···H contacts of 3.075 Å (compared to 3.37 Å in the staggered conformation). The Ga−N and Ga−Cl bond distances are slightly overestimated compared to experimental findings.[8] Calculated thermodynamic parameters ($\Delta H°_{(298)} = 137.2$ kJ mol^{-1}; $\Delta S°_{(298)} = 133.7$ J mol^{-1} K^{-1}) are in agreement with high-temperature data reported by Trusov et al.[9] ($\Delta H°_{(743)} = 134.3 \pm 0.8$ kJ mol^{-1}; $\Delta S°_{(743)} = 141.4 \pm 2.5$ J mol^{-1} K^{-1}). Taking into account that basis set superposition error (BSSE) will lead to higher values, and assuming the value of BSSE obtained previously for the $AlCl_3NH_3$ adduct (14 kJ mol^{-1}),[16] our BSSE corrected value of $\Delta H°_{(298)} = 123.2$ kJ mol^{-1} is in excellent agreement with the accepted standard value of $\Delta H°_{(298)} = 124.1$ kJ mol^{-1}.[29] The staggered conformation of Cl_3GaNH_3 is a transition state for the internal rotation around the Ga−N bond at the B3LYP/pVDZ level of theory. The rotational barrier is low (3.4 kJ mol^{-1} compared to 0.6 kJ mol^{-1} for Cl_3AlNH_3, B3LYP/DZP),[13] and the vibrational frequency corresponding to the internal rotation (104.3 cm^{-1}) is somewhat higher than in the aluminum analogue (47 cm^{-1}). Changes in bond lengths between the minimum and TS are marginal (less than 0.002 Å).

(B) $[Cl_3GaNH_3]_2$. Dimerization of the source adduct Cl_3GaNH_3 due to electrostatic intermolecular interactions may be a good starting point for association processes. The structure of the optimized dimer of C_{2h} symmetry is given in Figure 1d. For the hydrogen analogue, H_3GaNH_3 Cramer and Gladfelter[30] predicted a dimerization energy of 41 kJ

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Table 1. Selected Parameters for Donor−Acceptor Monomer X_3GaNH_3 and Dimer $[X_3GaNH_3]_2$ Compounds (All Distances, Å; Dipole Moment, D; Dimerization Enthalpy $\Delta_{dim}H°_{(298)}$ (per Mole of Dimer), kJ mol^{-1}) at the B3LYP/pVDZ Level of Theory

param	H_3GaNH_3[a]	$[H_3GaNH_3]_2$[a]	Cl_3GaNH_3	$[Cl_3GaNH_3]_2$
Ga−N	2.184	2.140	2.096	2.053
Ga−X[b]	1.585	1.581	2.179	2.204
NH[b]	1.023	1.034	1.024	1.031
X···H[b]		1.784		2.492
$\Delta_{dim}H°_{(298)}$		−41.4		−66.4

[a] Reference 30. [b] For the terminal N−H and Ga−X bonds values are given for hydrogen and chlorine atoms which are involved in H···H or H···Cl intermolecular contacts in dimers.

mol^{-1} at the B3LYP/pVDZ level of theory. They attributed this to the formation of a new type of bond, the so-called "dihydrogen bond" with an H···H intermolecular distance of 1.784 Å. They also predict that the Ga−N distance in the C_2 symmetric head-to-tail dimer $[H_3GaNH_3]_2$ is shorter by 0.044 Å than in the C_{3v} symmetric monomer (Table 1). There are some minor changes in geometric parameters for hydrogen atoms involved in dihydrogen bond formation; e.g., the N−H distance is increasing by 0.011 Å, while the Ga−H distance is slightly decreased (by 0.004 Å). Similar trends in bond lengths are observed for H···Cl intermolecular interactions in $[Cl_3GaNH_3]_2$ ($r_{H\cdots Cl} = 2.492$ Å): while the Ga−N distance shortens by 0.043 Å during dimer formation, the terminal Ga−Cl and N−H distances are elongated by 0.023 and 0.007 Å, respectively. In contrast, the Ga−Cl terminal bonds uninvolved in intermolecular bonding are shortened by 0.011 Å. Head-to-tail dimerization of Cl_3GaNH_3 leads decrease of the dipole moment from 6.3 D in the monomer to zero (by symmetry) in the dimer.

We predict a dimerization enthalpy of −66 kJ mol^{-1} for Cl_3GaNH_3 at B3LYP/pVDZ level of theory (per mole of dimer). Since the dimerization process is strongly unfavored by entropy, the temperature at which the equilibrium constant of the dimerization process equals one, $K^{dim} = 1$ ($T = 399$ K), is too low to stabilize dimeric $[Cl_3GaNH_3]_2$ species in the gas phase.

The observed Ga−N bond shortening in the dimeric structure is consistent with the fact that in single-crystal X-ray studies Ga−N bonds are usually shorter than those found in the gas phase. For example, for solid H_3GaNMe_3 $r_{Ga-N} = 2.081(4)$ Å, but $r_{Ga-N} = 2.134(4)$ Å in the gas-phase.[31] The 0.053(8) Å difference is close to the difference of the Ga−N bond lengths between H_3GaNH_3[30] and Cl_3GaNH_3 monomers and dimers (0.044 and 0.048 Å, respectively).

The shortening of the Ga−N bond in the dimer may be rationalized in terms of the "dipolar enhancement" mechanism presented by Leopold et al.[32] Significant bond shortening between the gas phase and condensed phase has been observed for "partially bonded" molecules, such as BF_3–NCH. Note that the large B−N bond distance difference (0.835 Å) between solid (1.638 Å) and gas (2.473 Å) phase for the weak BF_3–NCH adduct (dissociation energy 23.4 kJ mol^{-1}) cannot be reproduced using a dimeric unit $(BF_3$–$NCH)_2$ (it accounts for only 0.152 Å or 18%).[33] Rather modeling of the "crystal" using a dielectric continuum is necessary as the self-consistent reaction field approximation was found to reproduce the bond shortening (0.746 Å or 89% of the bond shortening).[34] For the stronger complexes, such as the Cl_3GaNH_3 species studied in the present work, a dimeric model already accounts for 0.048 Å (about 80%) of the shortening of the donor−acceptor bond. Our present results indicate that even the simple dimeric model may provide a good estimate of the magnitude of the expected bond shortening effect between the gas phase and the crystal structure.

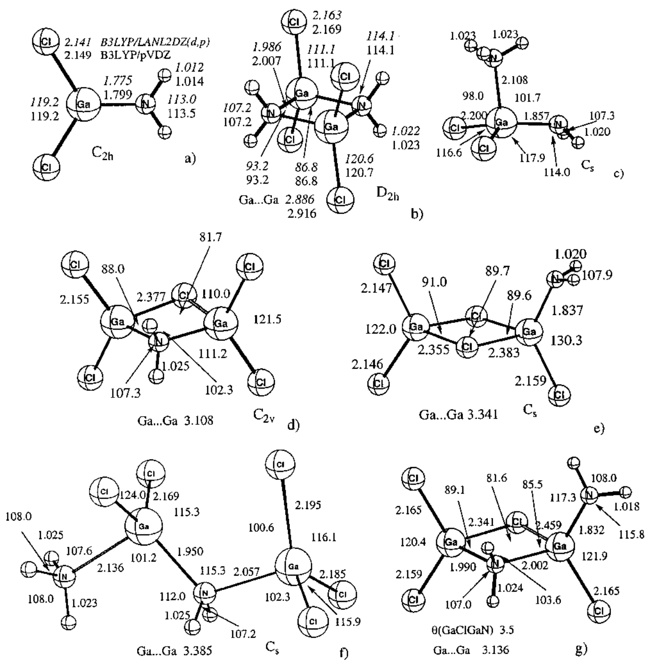

Figure 2. Optimized geometries of Cl_2GaNH_2 (a), the cyclic dimer $[Cl_2GaNH_2]_2$ (b), and the donor−acceptor complexes of monoamidochlorogallane: $NH_3{\cdot}Cl_2GaNH_2$ (c), $Cl_2GaNH_2{\cdot}GaCl_3$ or $Ga_2Cl_5NH_2$ (d, e), $NH_3{\cdot}Cl_2GaNH_2{\cdot}GaCl_3$ (f), and the Cl-bridged cyclic dimer $Cl_2Ga(\mu$-Cl)-(μ-NH_2)GaClNH$_2$ (g). Bond lengths are in angstroms; bond angles are in degrees. Data are from the B3LYP/pVDZ level of theory, with data from the B3LYP/LANL2DZ(d,p) level given in italics.

(II) Amidochlorogallanes $[Cl_2GaNH_2]_n$ ($n = 1−3$) and Their Donor−Acceptor Complexes. Cl_2GaNH_2 is a planar molecule of C_{2v} symmetry (Figure 2a). It has a Ga−N bond 0.299 Å shorter than the Cl_3GaNH_3 adduct. This bond shortening is slightly greater than in the aluminum analogue (0.267 Å) which may indicate bond strengthening. However, the Ga−N bond dissociation enthalpy, yielding $GaCl_2$ and NH_2 radicals (345 kJ mol^{-1}), is 75 kJ mol^{-1} *lower* than for the aluminum analogue (420 kJ mol^{-1}),[13] indicating a weaker Ga−N bond. Note that only a 12 kJ mol^{-1} difference between Ga and Al was predicted for the donor−acceptor bond in the Cl_3MNH_3 adducts.

Both donor and acceptor centers in Cl_2GaNH_2 are unsaturated (coordination number 3). In terms of the donor−acceptor properties, Cl_2GaNH_2 is an ambivalent compound,

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as it bears one donor and one acceptor center directly bonded to each other. Due to the low coordination number, head-to tail dimerization is expected to be very favorable energetically. Indeed, formation of the dimeric $[Cl_2GaNH_2]_2$ D_{2h} structure (Figure 2b) is highly exothermic (-117 kJ mol^{-1}/(mol of monomer)). Since the CVD process is usually carried out in an excess of ammonia, further coordination of ammonia molecules also is possible. Therefore, we considered donor−acceptor properties of Cl_2GaNH_2 toward both $GaCl_3$ and NH_3 in more detail.

The structure of the $H_3N{\cdot}Cl_2GaNH_2$ adduct is presented in Figure 2c. The energy of the formation of the donor−acceptor bond is -111.4 kJ mol^{-1}, which is by 26 kJ mol^{-1} less than that for to the $GaCl_3$–NH_3 interaction. This indicates lower acceptor ability of Cl_2GaNH_2, as would be expected due to the closely bonded donor and acceptor centers.

During optimization of the $Cl_2GaNH_2{\cdot}GaCl_3$ adduct a C_{2v} symmetric cyclic structure is obtained with two gallium, chlorine, and nitrogen atoms in the ring. This $Ga_2Cl_5NH_2$ compound (Figure 2d) may be viewed as a Ga_2Cl_6 dimer with substitution of the one bridging chlorine atom for the μ_2-amino group. This rearrangement allows both gallium and nitrogen atoms to have the very favorable coordination number 4. Thus, the enthalpy change for the $GaCl_3$ addition to Cl_2GaNH_2 is found to be much more exothermic (-168 kJ mol^{-1}) than the $GaCl_3$ addition to NH_3 (-137 kJ mol^{-1}) due to the stabilizing bridging effect of the chlorine atom. The rearrangement of the $Cl_2GaNH_2{\cdot}GaCl_3$ adduct precludes a comparison of the donor properties of chloroamidogallane and ammonia. Another possible $Ga_2Cl_5NH_2$ isomer with a terminal amino group is expected to be less stable, since the coordination number of the nitrogen center is only 3. Indeed, the optimized structure (Figure 2e) lies 105 kJ mol^{-1} higher in energy than the μ_2-NH_2 isomer. Therefore, it is concluded that the NH_2 group will preferentially occupy the bridging position.

The donor−acceptor interaction of Cl_2GaNH_2 both with NH_3 and $GaCl_3$ at the same time results in the formation of a linear chain unit. We optimized two possible isomers of C_s symmetry and found that one of them is a true minimum on the PES (Figure 2f), while another (with rotated $GaCl_3$ and NH_3 moieties) turns out to be second-order stationary point lying 13 kJ mol^{-1} higher in energy. From the enthalpy of formation of the two donor−acceptor bonds in $NH_3{\cdot}GaCl_2NH_2{\cdot}GaCl_3$ and the enthalpy of formation of the $H_3N{\cdot}Cl_2GaNH_2$ adduct we conclude that the donor ability of the NH_2 group in Cl_2GaNH_2 toward $GaCl_3$ (-126.2 kJ mol^{-1}) is lower by 11 kJ mol^{-1} than that of ammonia toward $GaCl_3$. Similarly, a stabilization energy of 46 kJ mol^{-1} can be estimated for the Cl-bridged structure $Ga_2Cl_5NH_2$.

The formation of donor−acceptor bonds between monomer amidogallane may be compared to the head-to-tail dimerization process, in which two additional donor−acceptor bonds are formed. The dimerization enthalpy of Cl_2GaNH_2 is -234 kJ mol^{-1}, while formation of two donor−acceptor bonds with $GaCl_3$ and NH_3 yields -238 kJ mol^{-1}. Therefore, the two processes are energetically equivalent, but the entropy factor slightly favors dimerization over the additional DA interactions. We also can compare the enthalpies of formation of such species from the source donor−acceptor adduct:

Table 2. Calculated and Experimental Subsequent Oligomerization Enthalpies (per Mole of Monomer) of Amido Compounds, kJ mol^{-1}

monomer	monomer = $^1/_2$ dimer	$^1/_2$ dimer = $^1/_3$ trimer	method	ref
Cl_2GaNH_2	-117	-14.1	B3LYP/pVDZ	this work
$Cl_2GaNH(SiMe_3)$		-11.3 ± 0.5[a]	exp (^{1}H NMR)	19
Cl_2AlNH_2	-127		B3LYP/DZP	13
H_2GaNH_2	-97	-7	B3LYP/pVDZ	35
Me_2GaNH_2	-91	-4	B3LYP/pVDZ	35

[a] Experimental value obtained in toluene solution for the 313−366 K temperature interval.

$$Cl_3GaNH_3 = {}^1/_2[Cl_2GaNH_2]_2 + HCl \qquad \Delta H^\circ_{(298)} = 77.5\ \text{kJ mol}^{-1}$$

$$Cl_3GaNH_3 = {}^1/_2NH_3GaCl_2NH_2GaCl_3 + {}^1/_2HCl \qquad \Delta H^\circ_{(298)} = 45.8\ \text{kJ mol}^{-1}$$

But as the amount of HCl eliminated is different, the entropy factor favors formation of the cyclic dimer over the chain adduct ($\Delta S^\circ_{(298)}$ are $+41.6$ and -3.5 J mol^{-1} K^{-1}, respectively) at temperatures higher than 703 K.

The cyclic dimeric structure $[Cl_2GaNH_2]_2$ may be compared to the linear chain isomer $Cl_2GaNH_2Cl_2GaNH_2$. However, attempts to optimize the chain structure resulted either in cyclization into $[Cl_2GaNH_2]_2$ or in the bridged $GaCl_2(\mu\text{-}Cl,\mu\text{-}NH_2)GaCl(NH_2)$ (Figure 2g). The latter asymmetric compound has a terminal NH_2 group and lies 85 kJ mol^{-1} higher in energy than $[Cl_2GaNH_2]_2$. The GaClGaN atoms in the cycle are almost coplanar (the deviation from planarity is only 3.5°).

$[Cl_2GaNH_2]_3$. Okamoto[14] reported a D_{3h} symmetric structure for the trimeric aminochlorogallane. However, in the present study the D_{3h} symmetric structure turned out to be second-order stationary point with two low imaginary vibrational frequencies (14i cm^{-1}) at the SCF/pVDZ level. Optimization without symmetry constrains resulted in a C_s symmetric boat conformation (Figure 1a). However, the energetic difference between the boat conformation and the D_{3h} symmetric structure is only 6 kJ mol^{-1} at the B3LYP/pVDZ level of theory, which suggests a rather flat PES. The dimer−trimer reorganization enthalpy of -14 kJ mol^{-1} (per mole of monomer) is in good agreement with experimental data obtained for the dimer−trimer equilibrium of $Cl_2GaN(H)SiMe_3$ (Table 2). Oligomerization of inorganic derivatives of amidogallanes is more favorable than that of organometallic systems.

An alternative chain structure of the trimer $GaCl_2NH_2$-$GaCl_2NH_2GaCl_2NH_2$ has been optimized. By analogy with linear $GaCl_2NH_2GaCl_2NH_2$, a C_s symmetric chain was found to be a second-order stationary point on the PES. Removing symmetry constrains resulted in cyclization process with formation of a Cl bridged structure.

The process of cyclization is extremely favorable due to unsaturated Ga and N centers, but it may be blocked in principle by additional donor−acceptor interactions. We

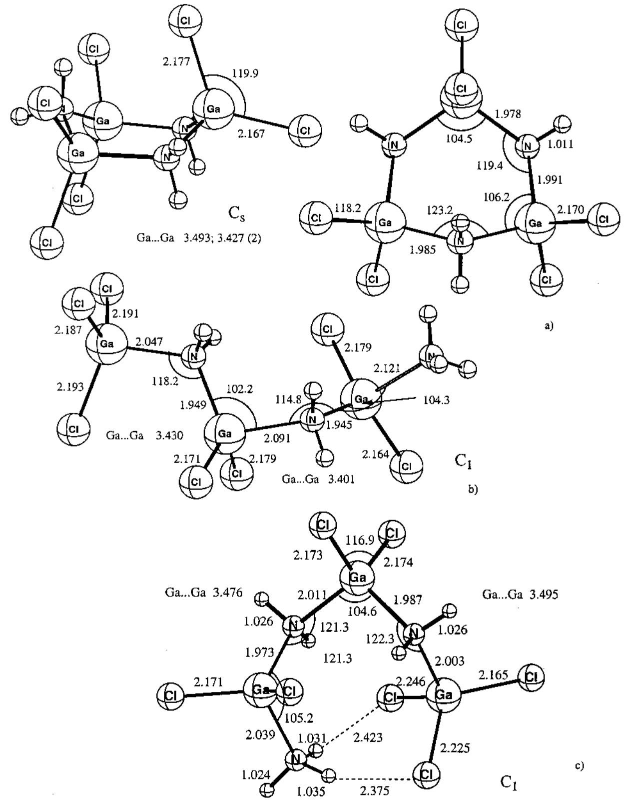

Figure 3. Optimized geometries of the cyclic trimer $[Cl_2GaNH_2]_3$ (a), and the $Ga_3Cl_7N_3H_7$ (donor−acceptor stabilized monoamidochlorogallane dimer): linear (b) and cyclic (c) isomers. Bond lengths are in angstroms; bond angles are in degrees. Data are from the B3LYP/pVDZ level of theory.

considered the two isomers of the $NH_3{\cdot}(GaCl_2NH_2)_2{\cdot}GaCl_3$ compound (Figure 3b,c). One of these is a chain with separated terminal $GaCl_3$ and NH_3 moieties, while the other one has close intramolecular contacts between terminal groups and is a precursor of the $[Cl_2GaNH_2]_3$ trimer. The H···Cl stabilized chain trimer $NH_3{\cdot}(GaCl_2NH_2)_2{\cdot}GaCl_3$ (Figure 3c) is predicted to lie 91 kJ mol^{-1} lower in energy than the unstabilized structure (Figure 3b). The two chain compounds have almost the same Ga···Ga distances (3.476−3.495 Å) as the cyclic trimer $[Cl_2GaNH_2]_3$ (3.427−3.493 Å), which indicates the absence of strain in the cyclic compound.

(III) Imidochlorogallanes $[ClGaNH]_n$ ($n = 1−4, 6$). For ClGaNH we considered only structures which are monomer building blocks for the oligomer species, with Cl−Ga and N−H connectivity of substituents (Figure 4a). In qualitative agreement with the aluminum analogue,[13] the ClGaNH triplet structure has a longer Ga−N bond by 0.251 Å and lies 79 kJ mol^{-1} higher in energy. Note that the situation is reversed for the GaN molecule, where the triplet structure($^3\Pi$) state also has a longer Ga−N distance (by 0.144 Å) but lies 123 kJ mol^{-1} *lower* in energy compared to singlet ($^1\Sigma^+$) state (See Table 1s).

Subsequent oligomerization steps lead to the structures of dimer, trimer, tetramer, and hexamer compounds (Figure 4b−e). The oligomerization energy (Table 3) decreases successively with increasing oligomerization degree *n* (per unit of monomer), but changes from the tetramer to hexamer are still considerable. These energy changes may be compared to changes in the Ga−N, Ga−Cl, and Ga···Ga distances (Figure 5). For the hexamer species values for the four- and six-membered rings, as well as mean values of the Ga−N and Ga···Ga distances are given (values for the aluminum analogues[13] are presented for comparison). The metal−nitrogen bond is shorter in the trimers than in the dimers, and the metal−metal distance is considerably larger both for Al and Ga, reflecting the electrostatic repulsion of M−M and N−N atoms and resulting in the high exothermicity of the dimer−trimer reorganization energy (Table 3) when all bonds are preserved and all atoms are coplanar. A shorter Al−N bond, found for all *n*, agrees well with the higher oligomerization energies of formation of imidochloroalanes (Table 3). The M−Cl bond lengths are increasing with oligomerization degree *n*, but this trend is much less pronounced.

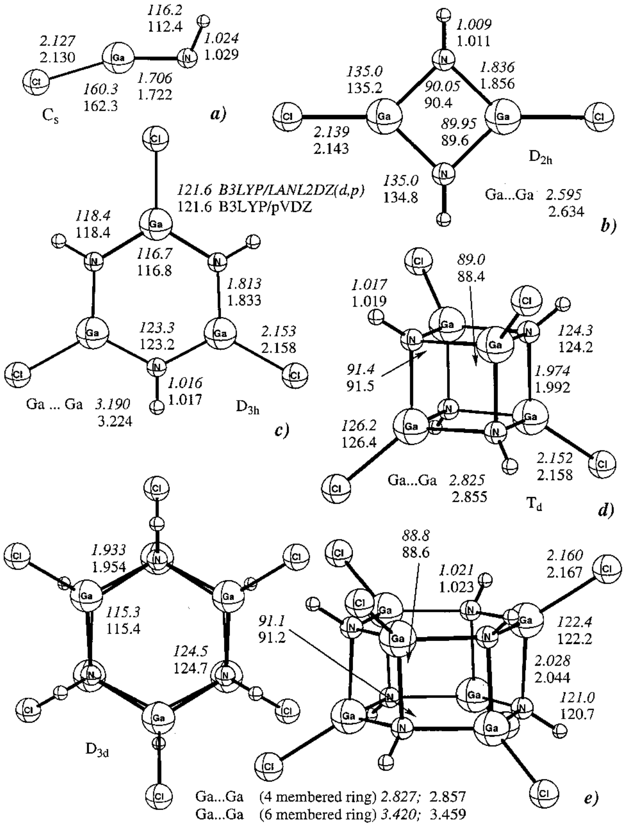

Figure 4. Optimized geometries of imidochlorogallanes: singlet ClGaNH (a), cyclic dimer $[ClGaNH]_2$ (b), cyclic trimer $[ClGaNH]_3$ (c), cube tetramer $[ClGaNH]_4$ (d), and cage hexamer $[ClGaNH]_6$ (e). Bond lengths are in angstroms; bond angles are in degrees. Data are from the B3LYP/pVDZ level of theory, with data from B3LYP/LANL2DZ(d,p) level given in italics.

Table 3. Calculated Subsequent Oligomerization Enthalpies of Imido Compounds: $^1/_{n-1}[XMNH]_{n-1} = {}^1/_n[XMNH]_n$, kJ mol^{-1}

compd	$n = 2$	$n = 3$	$n = 4$	$n = 6^a$	method	ref
ClGaNH	−221	−68	−42	−26	B3LYP/pVDZ	this work
	−246	−69	−37	−26	B3LYP/LANL2DZ(d,p)	this work
HGaNH	−207	−59	−41	−20	B3LYP/pVDZ	35
	−228	−60	−38	−21	B3LYP/LANL2DZ(d,p)	this work
MeGaNH	−201	−55	−42	−19	B3LYP/pVDZ	35
ClAlNH	−301	−63	−56	−26	B3LYP/DZP	13
	−312	−64	−61	−27	B3LYP/LANL2DZ(d,p)	this work
HAlNH	−282	−58	−57	−24	B3LYP/LANL2DZ(d,p)	this work

[a] Oligomerization enthalpy is that for the reaction $^1/_4[XMNH]_4 = {}^1/_6[XMNH]_6$.

Table 4. Calculated Standard (298.15 K, 1 atm) Enthalpies (kJ mol^{-1}) and Entropies (J mol^{-1} K^{-1}) for Several Reactions at the B3LYP/LANL2DZ(d,p) and B3LYP/PVDZ Levels of Theory

	B3LYP/LANL2DZ(d,p)		B3LYP/pVDZ			
reaction	$\Delta H°_{(298)}$	$\Delta S°_{(298)}$	$\Delta H°_{(298)}$	$\Delta S°_{(298)}$	$\Delta\Delta H$[a]	$\Delta\Delta S$[a]
$Cl_3GaNH_3 = GaCl_3 + NH_3$	136.0	127.9	137.2	133.7	1.2	5.8
$Cl_3GaNH_3 = Cl_2GaNH_2 + HCl$	180.7	133.9	194.5	146.7	13.8	12.8
$Cl_2GaNH_2 = GaCl_2 + NH_2$	366.5	160.1	345.0	153.2	−21.5	−6.9
$Cl_2GaNH_2 = {}^1/_2[Cl_2GaNH_2]_2$	−111.8	−97.8	−117.0	−105.2	−5.2	−7.4
$Cl_3GaNH_3 = ClGaNH + 2HCl$	555.3	272.8	550.8	278.0	−4.5	5.2
$ClGaNH = GaCl + NH$	170.4	131.4	150.2	131.6	−20.2	0.2
$ClGaNH = {}^1/_2[ClGaNH]_2$	−245.6	−96.1	−221.4	−93.4	24.2	2.7
$ClGaNH = {}^1/_3[ClGaNH]_3$	−314.7	−126.5	−288.9	−121.5	25.8	5.0
$ClGaNH = {}^1/_4[ClGaNH]_4$	−351.5	−155.1	−330.6	−154.2	20.9	0.9
$ClGaNH = {}^1/_6[ClGaNH]_6$	−378.1	−167.7	−356.7	−166.3	21.4	1.4
$GaCl_3NH_3 = 2HCl + {}^1/_2N_2 + GaCl + {}^1/_2H_2$	410.6	384.0	356.4	389.6	−54.2	5.6
|mean|					19.4	4.9

[a] ΔΔ denotes the difference between the B3LYP/pVDZ and B3LYP/LANL2DZ(d,p) results.

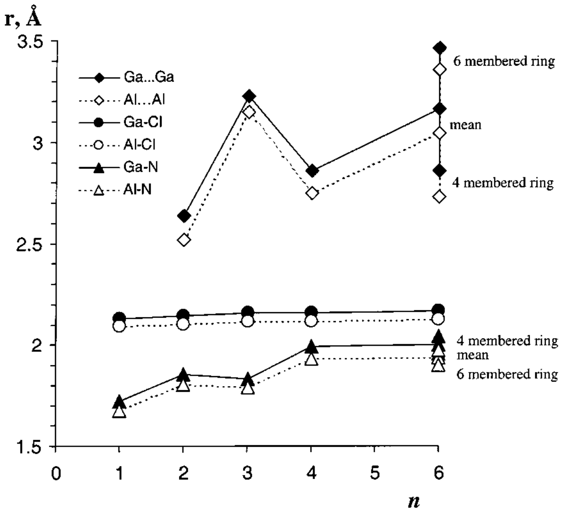

Figure 5. Trends in structural parameters for imidochlorogallanes and imidochloroalanes $[ClMNH]_n$. Lines are drawn to guide the eye only. Data for Al compounds are taken from ref 13.

We did not consider alternative chain structures for the imidochlorogallanes since they would have coordination number 3, which is highly unfavorable, as indicated by the very high dimerization enthalpies of dimer and trimer species:

$$2[ClGaNH]_2 = [ClGaNH]_4 \qquad \Delta H°_{(298)} = -436.8\ \mathrm{kJ\ mol^{-1}}$$

$$2[ClGaNH]_3 = [ClGaNH]_6 \qquad \Delta H°_{(298)} = -406.8\ \mathrm{kJ\ mol^{-1}}$$

While oligomerization reactions are more favorable for Cl derivatives compared to H and Me (Table 3), the overall Gibbs energies for the processes of their formation from the $GaCl_3NH_3$ adduct are greater than zero, i.e., endothermic, in contrast to the formation of $[HGaNH]_n$ and $[(CH_3)GaNH]_n$ species.[35] Thus, HCl is a poor leaving group, which is probably due to the stronger Ga−Cl bonding compared to the Ga−H and Ga−C bonds. In fact, the mean Ga−Cl, Ga−H, and Ga−C bond dissociation energies in $GaCl_3$, GaH_3, and $Ga(CH_3)_3$ are 363,[29] 271,[39] and 237[40] kJ mol^{-1}, respectively.

(IV) Thermodynamics of the Gas-Phase Reactions. Standard enthalpies and entropies of major gas-phase reactions are given in Table 4. Comparing the results obtained with LANL2DZ(d,p) and pVDZ basis sets shows reasonable agreement. The average discrepancies between the two approaches are no more than 20 kJ mol^{-1} in standard enthalpy and 5 J mol^{-1} K^{-1} in standard entropy of the reaction.

An important aspect of the reaction pathways considered is the height of the potential energy barriers. Since adduct formation proceeds without an activation barrier,[36] the enthalpy of the dissociation into free components is equal to the dissociation energy. Okamoto[14] obtained transition states (TS) for the reaction $Cl_3MNH_3 = Cl_2MNH_2 + HCl$ (M = Al, Ga) at the SCF level of theory but could not obtain the TS's at the MP2 level. For M = In, a TS could not be found by Okamoto even at the SCF level.[14] He thus concluded that the activation energy is "not much larger than the reaction energy" even if transition states actually exist.[14] For the boron analogues, however, it was shown that the activation energy of the process $Cl_3BNH_3 = Cl_2BNH_2 + HCl$ is 130 kJ mol^{-1}, which is 76 kJ mol^{-1} higher than the reaction enthalpy of 54 kJ mol^{-1} (all data from RI-MP2/TZVP level of theory).[37]

We find that the TS for HCl elimination from Cl_3AlNH_3 lies 10 kJ mol^{-1} (SCF/D95**) higher than the reaction energy, while for the gallium analogue the barrier is only 1 kJ mol^{-1} (SCF/pVDZ level). At the B3LYP level, we could not obtain the TS for either Al or Ga compounds, in line with Okamoto's results at the MP2 level of theory.

On the other hand, we did locate a TS at the B3LYP/pVDZ level for the HCl elimination from the dimer $[Cl_3GaNH_3]_2$ to yield $Cl_3GaNH_3 + HCl + Cl_2GaNH_2$. As

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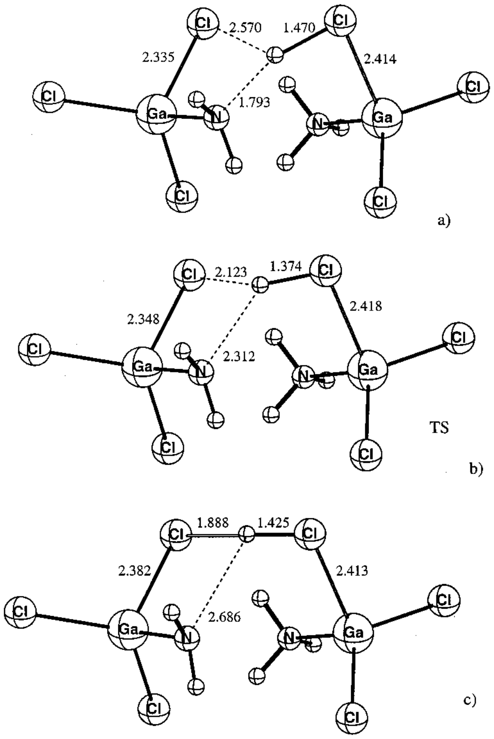

Figure 6. Optimized geometry of the transition state for the adduct-assisted HCl elimination (b) and structures on the intrinsic reaction path in the forward (c) and reverse (a) directions. Bond lengths are in angstroms. Data are from the B3LYP/pVDZ level of theory.

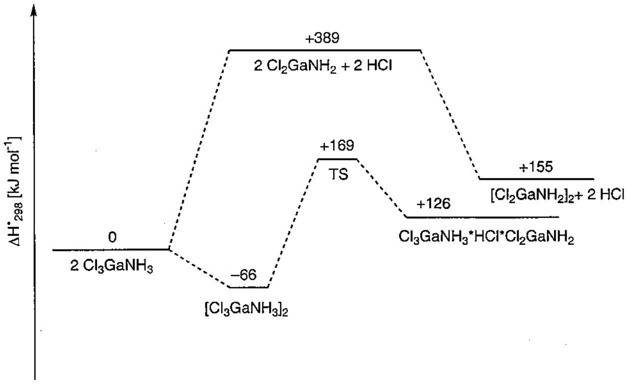

Figure 7. Enthalpy profiles of initial reactions of the Cl_3GaNH_3 adduct. Not drawn to scale.

can be seen in Figure 6, a chlorine atom of one Cl_3GaNH_3 moiety assists in the hydrogen transfer from the nitrogen to the chlorine atom within the second Cl_3GaNH_3 moiety. The overall classical barrier for this process is lower by 25 kJ mol^{-1} than the enthalpy of the reaction $Cl_3GaNH_3 = HCl + Cl_2GaNH_2$. Hence, the initial elimination of HCl from the primary Cl_3GaNH_3 adduct (Figure 7) does not involve significant barriers beyond the reaction endothermicity, in agreement with Okamoto's assessment.[14]

Once formed, the Cl_2GaNH_2 molecules can dimerize in a head-to-tail fashion, but again we could not locate a TS for this reaction at the B3LYP/pVDZ level of theory. Note that the dimerization of the boron analogue Cl_2BNH_2 was found to be a stepwise process involving an intermediate with only one additional B−N bond. According to the RI-MP2 computations by Reinhardt et al. the formation of this intermediate involves a barrier of 25 kJ mol^{-1} with respect to separated reactants.[37]

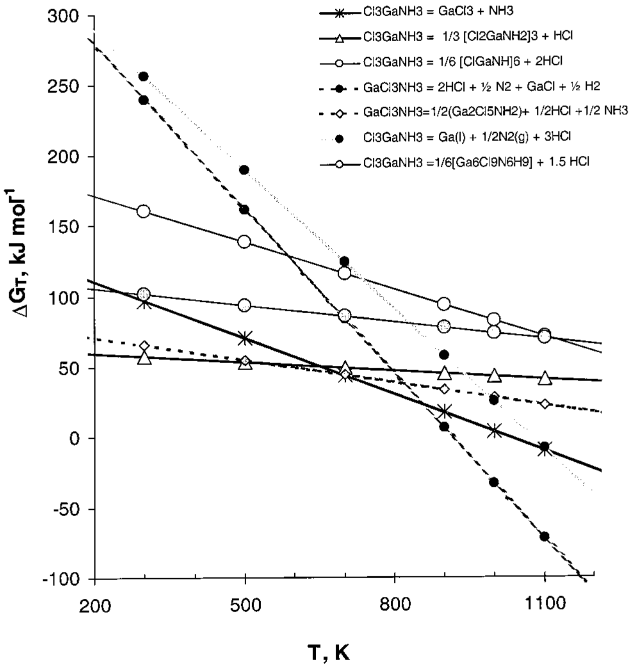

Figure 8. Gibbs energy−temperature dependence diagram for selected gas-phase reactions.

While in the case of Cl_3BNH_3 barriers for HCl elimination and for dimerization of the resulting Cl_2BNH_2 have to be overcome, this is not the case for Cl_3GaNH_3. Accordingly, an analysis of the first steps toward oligomer formation based on the thermodynamics of these reactions is possible. We will use a Gibbs energy−temperature dependence diagram for this thermodynamic analysis.

The Gibbs energy−T dependence diagram of major gas-phase processes is presented in Figure 8 (a diagram of the energetics of all gas-phase reactions is given as Supporting Information). As may be concluded, the Cl_3GaNH_3 adduct is quite stable in the gas phase. The dissociation of the Cl_3GaNH_3 adduct into free components is favorable above 680 K, while at lower temperatures formation of other species, such as the trimeric amidochlorogallane $[Cl_2GaNH_2]_3$ and cyclic $Ga_2Cl_5NH_2$ are thermodynamically preferable to the dissociation into components. Note that the Gibbs energies of all imidocompounds $[ClGaNH]_n$ lie much higher (only the most favorable process of hexamer formation is shown in Figure 8), and these species are thermodynamically not accessible, in contrast to the Al analogues.[13]

Therefore it is of interest to compare the behavior of the Ga and Al systems in more detail. Earlier[13] we predicted that oligomer forms may be intermediates in CVD of AlN from Cl_3AlNH_3. Analysis of the Gibbs energy−temperature diagram (Figure 8) shows that this is not the case with the gallium imido compounds. The difference may be rationalized in terms of the lower Ga−N bond energy compared to that of Al−N. From the standard enthalpies of reactions with M−N bond formation (Table 5) a difference in mean bond energies may be estimated assuming that all other changes in the course of the reaction (such as distortion of fragments

Table 5. Estimation of the Difference of Al−N and Ga−N Bond Energies from the Standard Reaction Enthalpies ($\Delta E = E_{\text{Al-N}} - E_{\text{Ga-N}}$ per One Bond Formed), kJ mol^{-1}, and Coordination Numbers (CN) of Reagents and Products

reaction	M = Al^a	M = Ga^b	ΔE per MN bond	CN product	CN reagent
$MCl_3 + NH_3 = Cl_3MNH_3$	−149.0	−137.2	11.8	4	3
$Cl_2MNH_2 = {}^1/_2[Cl_2MNH_2]_2$	−126.5	−117.0	9.5	4	3
${}^1/_2[ClMNH]_2 = {}^1/_4[ClMNH]_4$	−119.4	−109.2	10.2	4	3
${}^1/_3[ClMNH]_3 = {}^1/_6[ClMNH]_6$	−82.7	−67.8	14.9	4	3
$MCl_2 + NH_2 = Cl_2MNH_2$	−420.2	−345.0	75.2	3	2
$ClMNH = {}^1/_2[ClMNH]_2$	−300.9	−221.4	79.5	3	2
$ClMNH = {}^1/_3[ClMNH]_3$	−363.8	−288.9	74.9	3	2
$MCl + NH = ClMNH$	−229.5	−150.2	79.3	2	1

[a] Reference 13, B3LYP/DZP level of theory. [b] Present work, B3LYP/pVDZ level of theory.

and terminal bond relaxation) are the same for the Al and Ga cases. The results obtained (Table 5) indicate, first, that the Ga−N bond is always weaker than the Al−N bond and, second, that the bond energy difference for a given type of reaction depends on the coordination number of the M center in products and reagents (see Table 5). The difference in Al−N and Ga−N bond energies is found to be 10−15 kJ mol^{-1} for the formation of tetracoordinated atoms from tri-coordinated ones, but it rises to 75−80 kJ mol^{-1} for the formation of tri-coordinated atoms from di-coordinated ones. Clearly, it is the lower GaN bond energy of the unsaturated gallium species that makes formation of gas-phase oligomers in the case of gallium much less favorable than for Al−N species. Note that, in the case of organometallic and hydride derivatives, formation of cluster imidogallanes is exothermic, due to the more favorable leaving groups CH_4 and H_2.

At temperatures of about 850 K decomposition processes become much more important than Cl_3GaNH_3 formation. Herein we consider formation of GaCl, N_2, HCl, and H_2 as major products in the gas phase. These small species start to dominate in the reaction volume at temperatures above 850 K, and it is expected that radical mechanisms for GaN growth will be predominant in the case of ClVPE, in contrast to MOVPE. Another important side reaction is formation of liquid gallium metal, N_2, and HCl, which according to our analysis (using literature data for the liquid gallium) becomes important at 1100 K. Indeed, GaN deposition is not observed experimentally above 1180 K.[12]

It was repeatedly shown by Koplitz and co-workers[38] that laser irradiation may be the best choice to activate the generation of clusters at low temperatures. Among the other products, hexamer species $Me_9Ga_6N_6H_9$ have been observed in the gas phase.[38c] The stability of amidochlorogallanes suggests that similar products may be formed under laser irradiation at low temperatures in Cl_3GaNH_3 systems. The optimized structure of the C_{3v} symmetric $Cl_9Ga_6N_6H_9$ compound is given in Figure 9. It has two Ga_3N_3 rings in a chair conformation bonded to each other by three additional Ga−N bonds. The standard enthalpy of the process

$$2[Cl_2GaNH_2]_3 = Cl_9Ga_6N_6H_9 + 3HCl$$

is 300 kJ mol^{-1}, but the entropy factor favors HCl elimination with increasing temperature ($\Delta S°_{(298)} = 114.2$ J mol^{-1} K^{-1}).

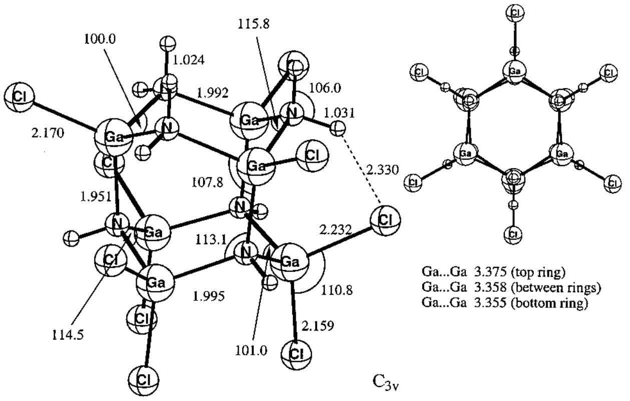

Figure 9. Optimized geometry of the $Cl_9Ga_3N_6H_9$ cluster compound. Bond lengths are in angstroms; bond angles are in degrees. Data are from the B3LYP/pVDZ level of theory.

The overall enthalpy of formation of this compound from the source adduct is 113.4 kJ mol^{-1}, which is comparable to the adduct dissociation enthalpy.

(V) Calculation of the Standard Enthalpies of Formation of All Compounds. The results obtained in this research allow us to calculate the standard gas-phase enthalpies of formation ($\Delta_f H°_{(298)}$) of all investigated compounds. However, there are different ways to evaluate $\Delta_f H°_{(298)}$. One of the ways is to use computed atomization enthalpies together with experimental values of the standard enthalpies of formation of free atoms. This approach was recently employed for the calculation of formation enthalpies of the $GaCl_x$ species ($x = 1−3$).[41] However, the accuracy of the computed thermochemical properties of radicals is much lower compared to that of closed shell species. Moreover, the description of isolated atoms is a known problem for density functional theory (DFT) methods.[43] Therefore, our goal was to find a way of predicting standard enthalpies of formation without taking into account atomization enthalpies.

The approach used will be illustrated by deriving standard enthalpies of formation of the Cl_xGaNH_x compounds ($x = 1−3$) and $Ga_2Cl_5NH_2$ (Table 6). Two independent reactions of decomposition of Cl_3GaNH_3 were considered. The calculated B3LYP/pVDZ dissociation enthalpy and literature values of the enthalpies of formation of $GaCl_3$, NH_3, GaCl, and HCl (−447.7, −46.1, −79.9, and −92.3 kJ mol^{-1}, respectively)[29] were used to obtain two independent values of $\Delta_f H°_{(298)}(Cl_3GaNH_3)$ (see Table 6, processes 1 and 2). The mean value of −626 ± 5 kJ mol^{-1} is in excellent agreement with the literature value of −628 kJ mol^{-1}.[29] This gives us confidence in deriving standard enthalpies of formation for other compounds.

By analogy, $\Delta_f H°_{(298)}(Cl_2GaNH_2)$ may be deduced from the B3LYP/pVDZ enthalpies of three independent reactions (3−5) and the literature values of $\Delta_f H°_{(298)}$ of Cl_3GaNH_3 (−628 kJ mol^{-1}) and NH_2 (185 kJ mol^{-1}).[29] The two values obtained for reaction 3 have a large deviation due to

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(41) Bauschlicher, C. W. *J. Phys. Chem. A* **1998**, *102*, 10424.
(42) Pankratz, L. B. *Thermodynamic Properties of Halides*; U.S. Bureau of Mines, Bulletin 674; Superintendent of Documents: Washington, DC, 1984, as cited in ref 41.
(43) Galbraith, J. M.; Schaefer, H. F. *J. Chem. Phys.* **1996**, *105*, 862.

Table 6. Calculation of $\Delta_f H°_{(298)}$ (kJ mol^{-1}) for Italic Species

process	reaction enthalpy	$\Delta_f H°_{(298)}$
(1) $\mathit{Cl_3GaNH_3} = \mathrm{GaCl_3} + \mathrm{NH_3}$	137.2	−631.0
(2) $\mathit{Cl_3GaNH_3} = \mathrm{GaCl} + {}^1/_2\mathrm{H_2} + {}^1/_2\mathrm{N_2} + 2\mathrm{HCl}$	356.4	−620.9
	mean value	−626.0
	lit. value[29]	−628.0
(3) $\mathit{Cl_2GaNH_2} = \mathrm{GaCl_2} + \mathrm{NH_2}$	345.0	−303.7;[a] −401.3[b]
(4) $\mathrm{Cl_3GaNH_3} = \mathit{Cl_2GaNH_2} + \mathrm{HCl}$	194.5	−341.2
(5) $\mathit{Cl_2GaNH_2} = \mathrm{GaCl} + \mathrm{HCl} + {}^1/_2\mathrm{H_2} + {}^1/_2\mathrm{N_2}$	161.9	−339.1
	mean value[c]	−340.2
(6) $\mathit{ClGaNH} = \mathrm{GaCl} + \mathrm{NH}$	150.2	121.4
(7) $\mathrm{Cl_3GaNH_3} = \mathit{ClGaNH} + 2\mathrm{HCl}$	550.8	107.4
(8) $\mathit{ClGaNH} = \mathrm{GaCl} + {}^1/_2\mathrm{H_2} + {}^1/_2\mathrm{N_2}$	194.3	114.4
	mean value[d]	110.9
(9) $\mathrm{Cl_2GaNH_2} + \mathrm{GaCl_3} = \mathit{Ga_2Cl_5NH_2}$	168.4	−954.7
(10) $\mathrm{Ga_2Cl_6} + \mathrm{NH_3} = \mathit{Ga_2Cl_5NH_2} + \mathrm{HCl}$	28.0	−957.1
(11) $\mathit{Ga_2Cl_5NH_2} = \mathrm{GaCl} + \mathrm{GaCl_3} + \mathrm{HCl} + {}^1/_2\mathrm{H_2} + {}^1/_2\mathrm{N_2}$	330.3	−950.2
	mean value	−954.0

[a] Using $\Delta_f H°_{(298)}(\mathrm{GaCl_2})$ from ref 41. [b] Using $\Delta_f H°_{(298)}(\mathrm{GaCl_2})$ from ref 42. [c] Process 3 is excluded. [d] Process 6 is excluded.

Table 7. Standard Enthalpies of Formation and Standard Entropies of Gas-Phase Species Studied in the Present Work (All Data from the B3LYP/PVDZ Level of Theory If Not Otherwise Indicated)

compd	point group	$\Delta_f H°_{(298)}$, kJ mol^{-1}	$S°_{(298)}$, J mol^{-1} K^{-1}
$\mathrm{Cl_3GaNH_3}$	C_{3v}	−628.0[a]	384.7
$\mathrm{(Cl_3GaNH_3)_2}$	C_{2h}	−1322.4	603.0
$\mathrm{Cl_2GaNH_2}$	C_{2v}	−340.2	344.7
$\mathrm{NH_3 \cdot Cl_2GaNH_2}$	C_s	−496.4	397.0
$\mathrm{Ga_2Cl_5NH_2}$	C_{2v}	−954.0	498.2
$\mathrm{NH_3 \cdot Cl_2GaNH_2 \cdot GaCl_3}$	C_s	−1071.6	575.6
$\mathrm{Cl_3GaNH_3 \cdot HCl \cdot Cl_2GaNH_2}$	$\mathrm{C_1}$	−1129.8	649.7
$\mathrm{[Cl_2GaNH_2]_2}$	D_{2h}	−914.4	479.1
$\mathrm{[Cl_2GaNH_2]_3}$	C_s	−1413.9	656.4
ClGaNH	C_s	110.9	289.3
$\mathrm{[ClGaNH]_2}$	D_{2h}	−221.0	391.8
$\mathrm{[ClGaNH]_3}$	D_{3h}	−534.0	503.4
$\mathrm{[ClGaNH]_4}$	T_d	−878.8	540.7
$\mathrm{[ClGaNH]_6}$	D_{3d}	−1474.8	738.4
$\mathrm{[Cl_9Ga_6N_6H_9]}$	C_{3v}	−2251.7	867.1
GaCl	$C_{\infty v}$	−79.9[a]	239.8; 240.3[a]
$\mathrm{GaCl_2}$	C_{2v}	−180.1	303.1
$\mathrm{GaCl_3}$	D_{3h}	−447.7[a]	325.8
$\mathrm{Ga_2Cl_6}$	D_{2h}	−975.3[a]	510.5
NH	$C_{\infty v}$	351.5[a]	181.2; 181.2[a]
$\mathrm{NH_2}$	C_{2v}	184.9[a]	194.9; 195.0[a]
$\mathrm{NH_3}$	C_{3v}	−46.1[a]	192.5; 192.5[a]
HCl	$C_{\infty v}$	−92.3[a]	186.7; 186.9[a]

[a] Experimental value, ref 29.

uncertainties in the literature values of $\Delta_f H°_{(298)}(\mathrm{GaCl_2})$. Note that the values obtained from reactions 4 and 5 agree well with each other, and therefore, the mean value of −340 kJ mol^{-1} will be recommended as $\Delta_f H°_{(298)}(\mathrm{Cl_2GaNH_2})$. Using this value, the standard enthalpy of formation of the $\mathrm{GaCl_2}$ radical may be revisited according to the first equation, and it is equal to −180 kJ mol^{-1}, which falls in the range of previously reported values of −144 kJ mol^{-1} (computed by Bauschlicher)[41] and the experimentally derived −241 kJ mol^{-1} value of Pankratz.[42]

The standard enthalpy of formation of ClGaNH may be derived in three different ways (reactions 6−8, Table 6). The value obtained for the process 6 is slightly overestimated due to the diradical nature of NH ($^3\Sigma^-$) and will be excluded. Therefore, the mean value of the eqs 7 and 8, +111 kJ mol^{-1} is recommended as standard gas-phase enthalpy of ClGaNH. For the $\mathrm{Ga_2Cl_5NH_2}$ compound with Cl and $\mathrm{NH_2}$ bridges, a $\Delta_f H°_{(298)}$ was estimated from three different processes (9−11), and the values obtained agree well with each other.

The calculation of the standard enthalpies of formation of oligomer species is now straightforward by using derived $\Delta_f H°_{(298)}(\mathrm{Cl}_x\mathrm{GaNH}_x)$ values for the monomer species and enthalpies of oligomerization reactions. The standard enthalpies of formation and standard entropies obtained for all gas-phase species studied in the present work are summarized in Table 7.

Conclusions

We find that the cyclic dimeric forms of $\mathrm{Cl_2GaNH_2}$ possess the same stability as chain forms, in contradiction to previous theoretical assessments.[14] The thermodynamic analysis indicates high favorability of oligomerization processes of chloroimidogallanes, and the synthesis of $[\mathrm{ClGaNR'}]_n$ analogues with bulky ligands R′ is feasible in principle. Gas-phase generation of clusters in the course of ClVPE of GaN is not possible. This is due to the lower stability of the Ga−N bond (vs Al−N) and the small temperature window for operation of gas-phase association reactions due to side processes. However, laser-induced generation of chloroamidogallanes at low temperatures is possible both thermodynamically and kinetically. Analysis of the potential energy surfaces revealed that the first steps toward oligomer formation, HCl elimination and subsequent dimerization, proceed without barriers. Assistance of a second $\mathrm{Cl_3GaNH_3}$ monomer is found to lower the energy required for HCl elimination below the dissociation limit for the $\mathrm{Cl_3GaNH_3} = \mathrm{Cl_2GaNH_2} + \mathrm{HCl}$ reaction. Finally, we conclude that the stability of oligomer imido and amido compounds with respect to dissociation processes makes them suitable precursors for GaN production.

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Supporting Information Available: Tables giving structural and thermodynamic properties of simple NH_x and GaCl_x species, theoretical vibrational frequencies and IR intensities for all studied compounds (B3LYP/pVDZ level of theory, unscaled), and total energies and zero-point vibrational energies for all compounds and figures showing full Gibbs energy−temperature diagrams for the gas-phase processes. This material is available free of charge via the Internet at http://pubs.acs.org.

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