Triazidogallium and Derivatives: New Precursors to Thin Films and Nanoparticles of GaN**

Roland A. Fischer,* Alexander Miehr, Eberhardt Herdtweck, Michael R. Mattner, Oliver Ambacher, Thomas Metzger, Eberhard Born, Sevil Weinkauf, Colin R. Pulham, and Simon Parsons

Dedicated to Professor Kurt Dehnicke on the occasion of his 65th birthday

Abstract: The synthesis and properties of $[Ga(N_3)_3]_\infty$ (**1**) and the related derivatives $[(Do)_nGa(N_3)_3]$ (**2a–d**: Do = THF, NEt_3, NMe_3, quinuclidine, $n = 1$; **2e**: Do = pyridine; $n = 3$), $Li[(CH_3)Ga(N_3)_3]$ (**3**), $[(N_3)_2Ga\{(CH_2)_3NMe_2\}]$ (**4**), $[Cp(CO)_2Fe{-}Ga(N_3)_2(py)]$ (**5**), and $[(CO)_4Co{-}Ga(N_3)_2(NMe_3)]$ (**6**) are reported. Compounds **2e** and **4** were characterized by single-crystal X-ray diffraction. The deposition of polycrystalline GaN thin films from **2a–e** by solution methods (spin-on pyrolysis) and the solid-state pyrolysis of **1** to give GaN nanoparticles are described.

Keywords
azides · chemical vapor deposition · gallium compounds · materials science · thin films

Introduction

Gallium nitride (GaN) and its ternary mixed phases with Al and In are currently the most promising systems for advanced microelectronic and optoelectronic devices. Interesting applications of these materials, some of which have already come to commercial fruition, include blue light-emitting diodes and lasers (large direct band gaps: $Al_xGa_{1-x}N$, 3.4–6.2 eV; $Ga_xIn_{1-x}N$, 1.9–3.4 eV; for $x = 0–1$), high-temperature and high-power devices, chemical sensors, and acoustic surface-wave conductors.[1] Usually, the metal-organic chemical vapor deposition (MOCVD) of GaN from GaR_3 (R = Me, Et) and NH_3 requires very drastic conditions (>950 °C), a high molar excess of ammonia (>2000:1), and the perfect control of complex fluid-dynamic transport processes (minimizing parasitic prereactions in the gas phase).[2] The inefficient activation of ammonia at lower temperatures causes N vacancies in the thin films leading to highly n-type materials, which are difficult to p-dope in a controlled fashion. The onset of the decomposition of GaN in vacuo is at around 850–900 °C. The maximum substrate temperature for the growth of stoichiometric GaN by molecular beam methods using independent sources (e.g., GaR_3 and NH_3) lies between 960–1040 °C, provided that the flux of N-*radicals* to the growth surface is on the order of 10^{15}–$10^{16}\,cm^{-2}s^{-1}$ (typical values for conventional radical sources).[3] The search for alternative precursors for the growth of stoichiometric GaN (with the goal of mass-producing devices) largely aims at lowering the required temperatures and reducing the complexity of the process. A rather new strategy to this end is based on gallium azide compounds as single-source precursors for GaN, such as $[\{R_2Ga(\mu^2\text{-}N_3)\}_3]$ ($R = CH_3$, C_2H_5)[4] and $[\{(R_2N)_2Ga(\eta^1\text{-}N_3)\}_2]$,[5] although the dimeric or trimeric molecular structure of these precursors considerably lowers the vapor pressure and consequently the achievable growth rates. An ideal GaN single-source precursor would be a non-pyrophoric, air-stable liquid with a high vapor pressure, which contains the necessary nitrogen in chemically activated form already bound to gallium and without or at least with only a few Ga–C, N–C, and N–H bonds. This is important because carbon impurities reduce the electron mobility, and hydrogen compensates the p-dopant magnesium.[6] Nitrogen-rich compounds are preferable with respect to stoichiometric growth to overcome the intrinsic thermal instability of GaN above 800 °C. The parent compound, $[Ga(N_3)_3]_\infty$ (**1**), first described by E. Wiberg et al. in 1954 as an insoluble, white solid and merely characterized by elemental analysis,[7] but since then almost forgotten,[8] would be of interest in this respect. It would be particularly desirable to prepare a volatile, monomeric derivative that is easy to transfer safely and decompses under mild conditions to give pure, stoichiometric GaN.

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[*] Prof. Dr. R. A. Fischer, Dr. E. Herdtweck, Dr. A. Miehr, Dr. M. R. Mattner
Anorganisch-chemisches Institut der Ruprecht-Karls Universität
Im Neuenheimer Feld 270, D-69120 Heidelberg (Germany)
Fax: Int. code + (6221) 54-6617
Prof. Dr. E. Born, Dipl.-Min. T. Metzger
Lehrstuhl für Angewandte Mineralogie und Geochemie
Dr. S. Weinkauf
Institut für Technische Chemie der Technischen Universität München
Lichtenbergstrasse 4, D-85747 Garching (Germany)
Dr. O. Ambacher
Walter-Schottky-Institut, Technische Universität München
Am Coulombwall, D-85748 Garching (Germany)
Dr. C. R. Pulham, Dr. S. Parsons
Dept. of Chemistry, The University of Edinburgh
King's Buildings, West Mains Road, Edinburgh EH9 3JJ (UK)

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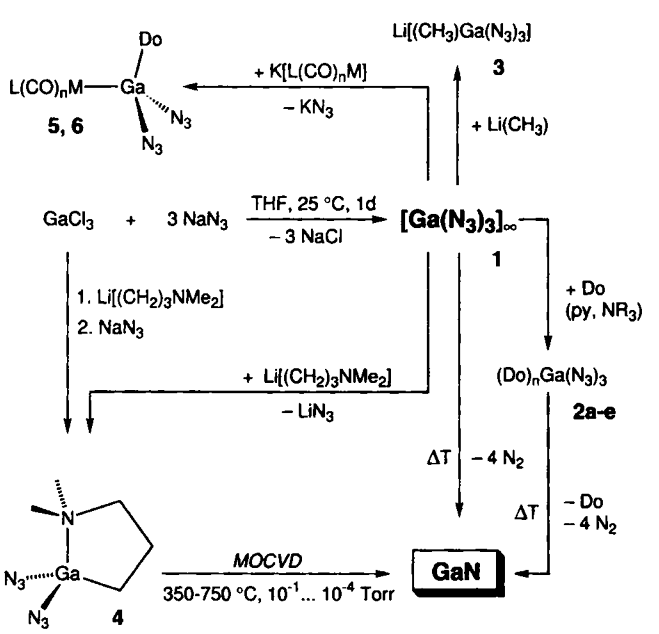
Results and Discussion

Synthesis and Properties: Solvent-free $[Ga(N_3)_3]_\infty$ (**1**) is an insoluble coordination polymer and detonates violently on rapid heating ($\approx 1\,°s^{-1}$) at temperatures above 280–300 °C. It is prepared as an analytically pure white, microcrystalline powder according to Scheme 1, by removing the solvent from THF solutions and drying the residue at high-vacuum. It melts reversibly at 232 °C with slow nitrogen evolution (TG/MS) as a clear colorless liquid and is *not* volatile. Attempts to sublime the compound (200–500 mg) under high vacuum (25–180 °C, 10^{-3} to 10^{-8} Torr) led to detonation! Compound **1** is also sensitive to (intense) mechanical shock; a glass capillary was filled with ca. 5 mg of **1** and hit with a hammer: a sharp loud noise indicated that **1** had detonated.



Scheme 1. Synthesis and reactivity of $[Ga(N_3)_3]_x$ (**1**). Pyrolysis of **1**, **2a–e**, and **4** to give GaN (powder or thin films). **2a–d**: Do = THF, NEt_3, NMe_3, quinuclidine, $n = 1$; **2e**: Do = py; $n = 3$. **5**: $L(CO)_nM = Cp(CO)_2Fe$, Do = py. **6**: $L(CO)_nM = (CO)_4Co$, Do = NMe_3.

Compound **1** is insoluble in noncoordinating, aprotic organic solvents (e.g., toluene, *n*-pentane, dichloromethane). However, in THF or in the presence of a Lewis base as donor in toluene, it dissolves as a monomeric Lewis-base adduct (**2a–e**). The pyridino derivative $[(C_5H_5N)_3Ga(N_3)_3]$ (**2e**) was crystallized from benzene, and the structure was determined by single-crystal X-ray diffraction (see below). Pseudo-C_{3v} symmetry of the complexes $[(Do)Ga(N_3)_3]$ (**2a–d**) in solution was deduced from the IR and NMR spectra by comparison with literature data.[8] The ^{71}Ga NMR data of a THF solution of **1** indicate the existence of a rather symmetrical species, probably $[(THF)Ga(N_3)_3]$ (**2a**), because of the comparably small line-width of 750 Hz.[9] On treatment of **1** with methyllithium the complex salt $Li[(Me)Ga(N_3)_3]$ (**3**) was isolated. The IR data, the ^{71}Ga NMR shift of $\delta = 215$, and the narrow line-width of 350 Hz agree with a tetracoordinate trigonal pyramidal geometry, similar to that proposed for **2a**. The complexes $[(Do)Ga(N_3)_3]$ (**2b–d**: Do = NEt_3, NMe_3, quinuclidine) dissolved in toluene or THF show similar ^{71}Ga NMR spectra. Compound **2e** shows a signal at $\delta = 192$ (THF solution; insufficiently soluble in toluene), which could only be detected as a very broad signal (7.2 kHz) on cooling to 165 K. The relative IR intensities of the N_3 absorptions of **1** dissolved in THF are independent of concentration (0.05 to 0.001 $mol\,L^{-1}$) and are consistent with the postulated structure of **2a**. It is therefore unlikely that **1** dissociates into ion pairs (i.e., $[(THF)_2Ga(N_3)]^+$ and $[Ga(N_3)_4]^-$), as might have been expected by analogy with the dissociation behavior of Al and Ga halogenides in ethereal solvents.[10] It should also be noted that **1** is quantitatively synthesized from $GaCl_3$ and *excess* NaN_3 in THF without the formation of "ate" complexes, such as $Na[Ga(N_3)_4]$.

If one azido substituent of **1** is replaced by the 3-dimethylaminopropyl group, which is capable of *intramolecular* coordination, the bisazide **4** is obtained as a colorless, nonexplosive, and volatile liquid, properties which qualify it for use as a precursor for MOCVD of GaN.[11] We recently reported a somewhat different synthesis and the spectroscopic properties of compound **4** and related derivatives. Temperature-dependent NMR studies (^{14}N, ^{15}N, and ^{13}C) have shown, that a concentration-dependent (intermolecular) dynamic exchange of the azido substituents of **4** occurs in solution (residual Lewis acidity at the Ga center!).[12] The single-crystal structural data of **4** nicely agree with these solution properties and are reported below.

The selective and quantitative substitution of azide groups by transition metal nucleophiles $[L(CO)_nM]^-$ is possible (Scheme 1). From the analytical data it is clear that the molecular structure of the resulting compounds is similar to that of the known congeners with halide and alkyl substituents at the gallium center.[13] Certain volatile representatives of this class of compound may be interesting as single-source precursors for novel ternary metal nitrides, $M_xGa_yN_z$.

Structure: Structural data of azidogallium compounds are very scarce. Examples are azido(octaethylporphyrinato)gallium(III),[14] $[(CH_3)_2Ga(N_3)]_\infty$,[15] $[(R_2N)_2Ga(\eta^1\text{-}N_3)]_2$,[5] and $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Ga(N_3)_2]$.[16] The structure of polymeric $[Ga(N_3)_3]_\infty$ (**1**) would be rather interesting, but we have not yet obtained single crystals of sufficient quality. The X-ray powder diffraction pattern of **1** exhibits a high background and only very few and comparably broad reflection signals. We report here the solid-state structures of the two new gallium azides **2e** and **4**.

*Tripyridino(triazido)gallium (**2e**)*: The molecular structure of **2e** in the solid state is shown in Figure 1. It is the first example of a structurally characterized triazidogallium compound. The Ga center is coordinated in an octahedral fashion with the azido groups in the *mer* configuration. The $Ga-N_{azide}$ bonds range from 200.8(4) to 201.7(4) pm and are rather similar to the related values of 191.4(4) and 192.8(4) pm found for $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Ga(N_3)_2]$.[16] The somewhat longer $Ga-N_{azide}$ bonds of **2e** are a consequence of the increased coordination number. The donor–acceptor bonds to the three pyridine ligands range between 212.1(4) and 215.1(3) pm and are, as expected, longer than the $Ga-N_{azide}$ bonds. The Ga-N-N angles of between 119 and 125° are also similar to those of other (covalent) metal azides and indicate sp^2 hybridization at the N_{ipso} atoms. The alternation of the N–N bond lengths—a long N_a-N_b bond (118–120 pm) and a short N_b-N_c bond (113–116 pm)—is also a typical feature of covalent azides.[7b] The pyridine ligands are twisted with respect to each other, minimizing steric interactions between the *ortho* hydrogen substituents. There are no unusually short intermolecular distances. The closest analoguous structure to **2c** is that of $[Cl_3Ga(2,2':6',2''\text{-terpyridine})]$.[17]

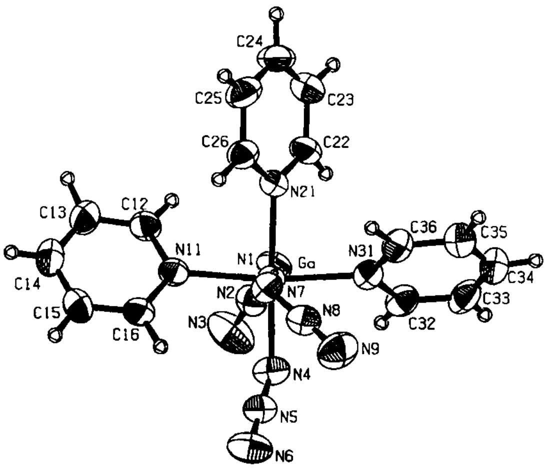


Fig. 1. Molecular structure of [$(py)_3Ga(N_3)_3$] (**2e**) in the solid state (Platon drawing; thermal ellipsoids at the 50% probability level). Selected bond lengths [pm] und angles [°]: Ga–N1 200.8(4), Ga–N4 201.7(4), Ga–N7 201.2(4), Ga–N11 212.1(4), Ga–N21 213.0(4), Ga–N31 215.1(3), N1–N2 118.3(5), N2–N3 115.0(6), N1-Ga-N4 89.25(16), N1-Ga-N7 176.27(16), N1-Ga-N11 90.59(15), N1-Ga-N21 86.37(14), N1-Ga-N31 89.32(14), N4-Ga-N7 94.41(16), N4-Ga-N11 94.55(15), N4-Ga-N21 175.24(13), N4-Ga-N31 92.67(15), N7-Ga-N11 88.39(15), N7-Ga-N21 90.00(14), N7-Ga-N31 91.24(14), N11-Ga-N21 87.36(13), N11-Ga-N31 172.78(15), N21-Ga-N31 85.42(13), N1-N2-N3 176.2(4), N4-N5-N6 176.2(5), N7-N8-N9 177.8(5).

*Bisazido[N,N-dimethylaminopropyl]gallium (**4**)*: The crystals of the low-melting compound **4** (m.p. = – 28 °C) were grown from the melt in a sealed capillary mounted directly on the diffractometer. The data collection was performed at 150.0(2) K. The quality of the crystal grown was poor, and this limited the quality of the data. Nevertheless, the principal structural features of **4** can be discerned without ambiguity. The compound crystallizes as a centrosymmetric dimer with two $\eta^1:\mu^2$-N_3 bridging units (Fig. 2). The dimeric solid-state structure of **4** agrees nicely with the observation of residual Lewis acidity of **4** in solution (concentration- and solvent-dependent association and azide exchange equilibria).[12] As a consequence of symmetry, the four-membered ring Ga_2N_2 involving the gallium centers Ga and GaA and the terminal N_{azide} atoms N1A and N1A′ is strictly planar. It exhibits a short Ga–N1A bond of 194(2) pm, which compares to the related values found for [$\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Ga(N_3)_2$], and a distinctly longer distance for Ga–N1A′ of 245(2) pm. The coordination geometry at the gallium center can be described as trigonal bipyramidal. The apical positions of the coordination polyhedron are occupied by N4 and N1A′ with an N4-Ga-N1A′ angle of 175.7(7)°. A five-membered heterocycle (in an envelope conformation) is formed by intramolecular coordination of N4 to Ga; the donor–acceptor bond is 213(2) pm. These structural features are similar to those of other compounds containing the [$Ga\{(CH_2)_3NMe_2\}$] moiety.[18] While the angles N4-Ga-C1 and N4-Ga-N1B are close to 90°, as required for an ideal trigonal bipyramidal structure, the angle N4-Ga-N1A is distorted to 104.5(7) by the weak intermolecular donor–acceptor interaction N1A–GaA. Consequently, the Ga atom lies 20 pm above the "equatorial plane" defined by C1, N1A, and N1B. The equatorial angles C1-Ga-N1B and C1-Ga-N1A are close to the ideal value of 120°, while the angle N1A-Ga-N1B of 109.4(7)° is somewhat smaller due to the coordinative bond N1A–GaA. The known compound [$\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Ga(N_3)_2$] also exhibits a pentacoordinate Ga center, but intermolecular contacts are absent. Interestingly, the angle N_{azide}-Ga-N_{azide} of 108.2(2)° is quite similar to the corresponding angle in **4**. The bridging angle Ga-N1A-GaA of 106.7° is rather smaller than expected for an sp^2 N atom, a possible consequence of dimer formation. Polymeric $[Me_2Ga(N_3)]_\infty$ also contains $\eta^1:\mu^2$-N_3 bridging units; here, the basic structural element, $Me_2Ga(N_3)$, forms a spiral chain along the *a* axis of the orthorhombic unit cell of the crystal.[19] Because of the different steric requirements to dimer **4**, the bridging angle Ga-N-Ga′ of $[Me_2Ga(N_3)]_\infty$ is enlarged to 131.5(1)°. The angle N1A-Ga-N1A′ of 73.2° is rather small. Interestingly, the atoms of the terminal azide groups N1B, N2B, and N3B and their symmetric equivalents as well as the metal centers Ga and GaA are almost coplanar. N3B and N3B′ point to the GaA and Ga with a clearly nonbonding distance of 413 pm. The angle between the planes defined by the atoms Ga, N1A, GaA (the Ga_2N_2 core) and N1B, Ga, GaA is 72° (Fig. 3). These structural properties may be regarded as being a consequence of a minimization of the steric hindrance between the terminal azide substituents and the heterocyclus. An analysis of the nonbonding intramolecular contacts (e.g., C4–N1B 300 pm) indicates the importance of such steric interactions.

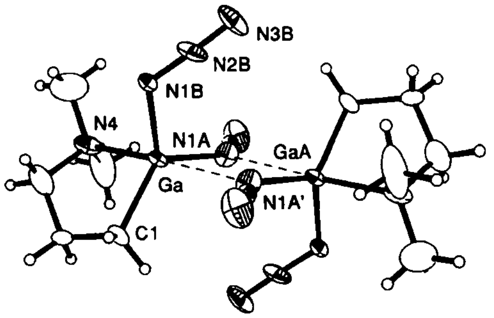


Fig. 2. Molecular structure of [$(N_3)_2Ga\{(CH_2)_3NMe_2\}$] (**4**) in the solid state (ORTEP drawing; thermal ellipsoids at the 50% probability level). Selected distances [pm] und angles [°]: Ga–N1A 194(2), Ga–N1B 190(2), Ga–N4 213(2), Ga–N1A′ 245(2), Ga–C1 197(2), N4-Ga-N1A′ 175.7(7), N4-Ga-C1 89.1(8), N4-Ga-N1B 95.3(7), N4-Ga-N1A 104.5(7), N1B-Ga-N1A 109.4(7), N1B-Ga-C1 122.7(8), N1A-Ga-C1 124.5(8), N1A-Ga-N1A′ 73.2(8), N1B-Ga-N1A′ 88.8(7), N2A-N1A-Ga 132(2), N2B-N1B-Ga 122(1).

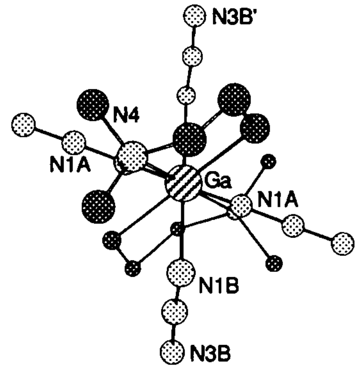


Fig. 3. Projection of the molecular structure of **4** along the Ga–GaA bond vector (CSC-CHEM 3D drawing).

Material Synthesis

*Pyrolysis of $[Ga(N_3)_3]_\infty$ (**1**) to GaN*: None of the Lewis base stabilized derivates of **1** proved to be sublimable, but the donor stabilization of **1** offers interesting possibilities for the safe handling of the $Ga(N_3)_3$ unit as a building block for GaN in the condensed phase (solution, melt, polymer matrix). The variety of the potential ligands available as donors can be used to exert a strong influence on the properties of the GaN precursors (e.g., solubility, melting point, viscosity of the melt). This is of crucial importance for thin-film deposition and coating techniques, which are based on aerosol transport methods[20] or on the pyrolysis of very thin liquid films (spin-on pyrolysis[21]). Compounds **1** and **2e** were characterized by thermal analysis (Fig. 4).

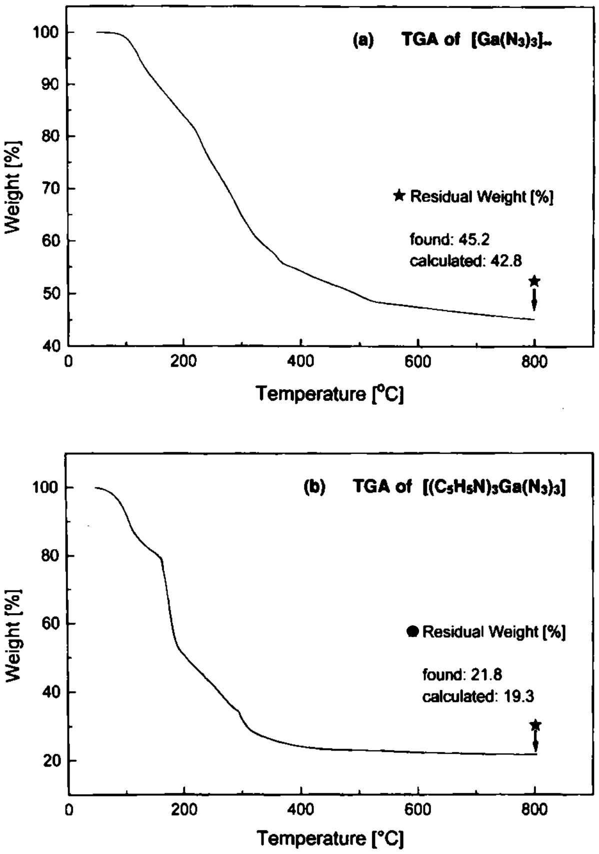


Fig. 4. Thermogravimetric analysis (TGA) of compounds **1** (a) and **2e** (b).

The pyrolysis was almost quantitative at around 400 °C in both cases. The notable difference is that **2e** decomposes in several steps, while **1** shows an nonspecific, gradual loss of weight. This finding indicates it is possible to rationally control the thermal decomposition process by the choice of ancillary ligand.

The prolonged tempering of a melt of **1** at 250–280 °C led to formation of an off-white to grey, nonexplosive powder, which was identified as polycrystalline GaN by elemental analysis and by X-ray diffraction. The IR azido absorptions disappeared during the pyrolysis. After a short time at 700–900 °C under Ar as inert gas, the pyrolysate gave an X-ray diffraction pattern (Fig. 5) clearly showing the typical pattern of the hexagonal GaN phase (Wurzite-type). By controlling the pyrolysis conditions (heating rate and time) it was possible to obtain nanocrystalline hexagonal GaN with particle sizes of approximately 5–10 nm (Fig. 6). Recently, Gladfelter et al. reported the solid-state conversion of cyclotrigallazane into nanocrystalline GaN.[22] In this case, the particles obtained (ca. 6 nm) were found to consist of a mixture of cubic and hexagonal GaN.

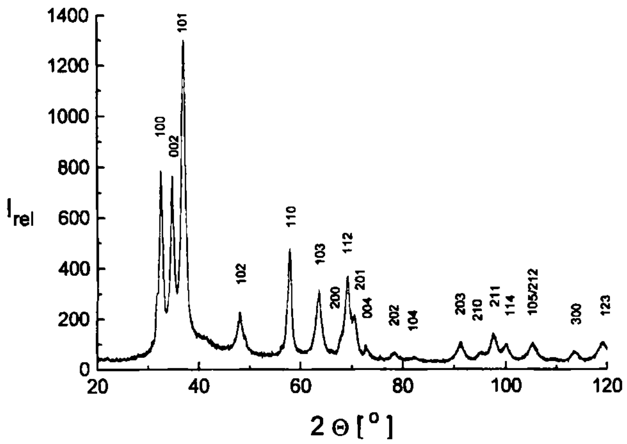


Fig. 5. X-ray diffraction pattern of a representative sample of nanocrystalline GaN powder obtained from the controlled pyrolysis of $[Ga(N_3)_3]_\infty$ (**1**).

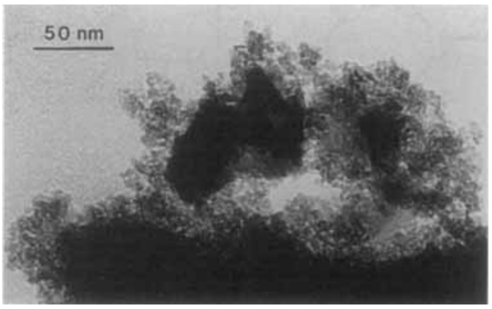


Fig. 6. Transmission electron micrograph (JEOL 100CX spectrometer operating at 100 kV) of GaN nanoparticle agglomerates. The GaN powder sample was suspended in H_2O/EtOH and placed on the carrier nets (coated with Formwar/carbon). The dimensions of the agglomerates are several microns. The nanoparticultate structures of 50–100 Å can clearly be seen at the more transparent peripheries of the agglomerates.

With the donor-stabilized precursors **2a–e** GaN layers were produced by a simple dip-coating procedure. The quality of the materials obtained allowed them to be characterized by photoluminescence spectroscopy (level of impurities <0.1 atom%). The photoluminescence (5 K; argon ion laser, 333 nm, 10 mW) of a GaN thin film deposited from **2a** is dominated by a very broad signal, which reaches its maximum intensity at 3.1 eV (Fig. 7). These photoluminescence peaks can be attributed to donor–acceptor recombination, which is most likely caused by the fact that the growth is not perfectly stoichiometric. Optical transitions occur at energies between 3.16 and 3.34 eV, probably due to oxygen and carbon impurities of the crystallites. These features of the spectrum are thought to be caused by an imperfect purification of the precursor to ≤99.8 %, as well as to the presence of a large number of grain boundaries and surface-adsorbed contaminants. The narrow luminescence peak at 3.47 eV may be caused by a donor-bound exciton, whose energetic position lies 30 meV below the conduction band edge of hexagonal GaN.

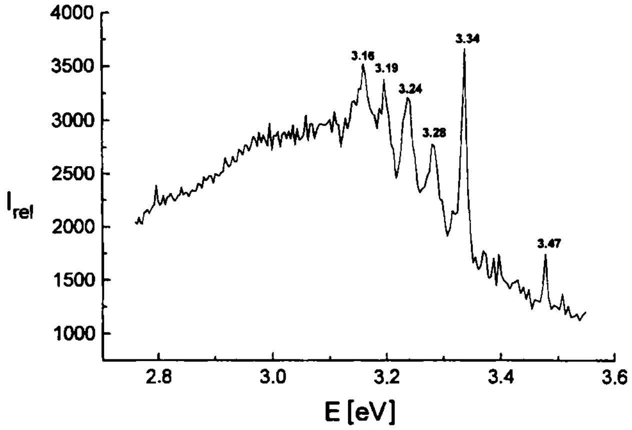


Fig. 7. Photoluminescence spectrum of a crystalline GaN thin film obtained by a simple dip-coating pyrolysis process.

Chemical Vapor Deposition of GaN Thin Films from ***4***: Using compound **4** as precursor and a simple horizontal isothermal hot-wall quartz tube reactor,[23] we have deposited highly oriented crystalline GaN films on sapphire substrates without ammonia in vacuo (10^{-3} Torr) at 650–750 °C. This study has been reported in some detail elsewhere.[11]

Conclusions

The synthetic potential of insoluble, polymeric, and explosive $[Ga(N_3)_3]_\infty$ (**1**) was studied. The inherent explosiveness of **1** can be reduced by the formation of a Lewis base adduct at the gallium center. The resulting soluble nonexplosive derivatives can be used as starting materials for further reactions. A selective substitution of one azide substituent with alkyl groups or transition metal nucleophiles is possible. The compounds **1** and **2a–e** serve as single-molecule precursors for the deposition of polycrystalline GaN thin films or for the production of GaN nanoparticles by pyrolysis (both Wurzite phase). Compound **4** represents the first liquid and volatile bisazido organogallium compound that is suitable as precursor for metal-organic vapor phase epitaxi of GaN in the *absence* of ammonia.

Experimental Section

All reactions were performed with standard Schlenk techniques in an oxygen-free, dry nitrogen atmosphere. Solvents were dried by standard methods and distilled under N_2. Infrared spectra were recorded in solution between carefully dried CaF_2 plates on a Perkin-Elmer 1600 series FT-IR instrument (resolution 4 cm^{-1}). ^{1}H (400.13 MHz), ^{13}C (100.85 MHz), ^{14}N (28.91 MHz), and ^{71}Ga (122.05 MHz) NMR spectra were recorded on a Bruker DPX400 instrument and calibrated against residual protons of the deuterated solvents. All NMR solvents were carefully dried, degassed and stored over K/Na alloy before use. Elemental analyses were carried out at the microanalytical laboratory of the Technical University Munich. A Phillips PW 3040 $\omega-2\theta$ two-circle diffractometer equipped with a graphite monochromator (Cu$_{K_\alpha}$ radiation) was used for X-ray powder diffraction. The crystallite size was determined by the Scherrer formula. Transmission electron micrographs were recorded with a JEOL 100CX instrument at 100 kV.

$[Ga(N_3)_3]_\infty$ (1): Freshly sublimed $GaCl_3$ (2.5 g, 14.2 mmol) was dissolved in dry THF (30 mL) and added to a slurry of dry NaN_3 (5.5 g, 85.2 mmol) in THF (30 mL). The mixture was stirred at room temperature for 24 h. Filtration and removal of the solvent in vacuo gave **1** as a white microcrystalline solid. Yield 99% (2.8 g): m.p. 232 °C; decomp. > 250 °C. ^{71}Ga NMR (122.05 MHz, [D$_8$]THF, 300 K): $\delta = 213$ (750 Hz); IR (THF): $\tilde{\nu} = 2131$ vs (N_3, asym.), 2104 vs (N_3, asym.), 1344 m (N_3, sym.), 1294 m (N_3, sym.) cm^{-1}; GaN_9 (195.78): calcd. C 0, H 0, N 64.39, Cl 0; found C 0, H 0, N 62.07, Cl 0.1.

$[(Et_3N)Ga(N_3)_3]$ (2b), **$[(Me_3N)Ga(N_3)_3]$ (2c)**, **[(quinuclidine)Ga$(N_3)_3$] (2d)**, and **$[(py)_3Ga(N_3)_3]$ (2e)**: A mixture of pyridine (0.4 mL, 4.9 mmol) with THF (10 mL) was slowly added to a solution of $[Ga(N_3)_3]_\alpha$ (0.32 g, 1.63 mmol) in THF (30 mL) at − 78 °C. After warming up to room temperature, the mixture was stirred for 5 h. Removal of the solvent gave a white residue which was dissolved again in benzene (40 mL). Filtration gave a clear, colorless solution. Colorless, very hard crystals of **2e** crystallized from saturated benzene solutions in 85% yield (0.6 g). Compound **2b–d** were prepared analogously.

2b: pale brownish solid (90% yield, 0.44 g), m.p. 33–35 °C. ^{1}H NMR (400.13 MHz, C_6D_6, 300 K): $\delta = 1.15$ (t, 3H, CH_3), 2.98 (q, 2H, NCH_2); ^{13}C NMR (100.85 MHz, C_6D_6, 300 K): $\delta = 10.1$ (CH_3), 49.1 (NCH_2); ^{71}Ga NMR (122.05 MHz, [D$_8$]THF, 300 K): $\delta = 215$ (4000 Hz); IR (THF): $\tilde{\nu} = 2131$ vs (N_3, asym.), 2105 vs (N_3, asym.), 1344 m (N_3, sym.), 1291 m (N_3, sym.) cm^{-1}; $C_6H_{15}N_{10}Ga$ (296.97): calcd. C 24.27, H 5.09, N 47.17, Ga 23.47; found C 23.80, H 4.99, N 46.63, Ga 24.58.

2c: white powder; yield 83%. IR (THF): $\tilde{\nu} = 2130$ s (N_3, asym.), 2098 vs cm^{-1}; $C_1H_9N_{10}Ga$ (240.88): calcd. C 14.97, H 3.77, N 52.33; found C 15.00, H 3.40, N 53.90.

2d: pale brownish crystals, yield 70%. ^{1}H NMR (400.13 MHz, C_6D_6, 300 K): 1.37 (m, broad, 6H, CH_2), 2.69 (t, 6H, NCH_2); 3.20 (s, broad, 1H, CH). ^{13}C NMR (100.85 MHz, C_6D_6, 300 K): $\delta = 1.4$ (CH_2), 21.3 (NCH_2), 47.8 (CH); ^{14}N NMR (28.91 MHz, [D$_8$]THF, 300 K): $\delta = -139.3$ (50 Hz), − 271.6 (300 Hz); IR (THF): $\tilde{\nu} = 2118$ s (N_3, asym.), 2094 vs (N_3, asym.), 1345 m (N_3, sym.), 1294 m (N_3, sym.) cm^{-1}. $C_{11}H_{21}N_{10}O_1Ga$ (**2d**·THF) (379.07): calcd. C 34.85, H 5.58, N 36.95, Ga 18.39; found C 34.10, H 5.86, N 37.03, Ga 17.80.

2e: m.p. (decomp.): 133 °C. ^{1}H NMR (400.13 MHz, C_6D_6, 300 K): 7.52 (m, 2H, CH), 7.96 (t, 1H, CH), 8.34 (d, 2H, NCH) ^{13}C NMR (100.85 MHz, C_6D_6, 300 K): $\delta = 126.7$ (CH), 142.9 (CH), 146.8 (NCH); ^{71}Ga NMR (122.05 MHz, [D$_8$]THF, 165 K): $\delta = 192$ (7180 Hz); IR (THF): $\tilde{\nu} = 2132$ vs (N_3, asym.), 2117 vs (N_3, asym.), 1296 m (N_3, sym.), 1261 m (N_3, sym.) cm^{-1}; $C_{15}H_{15}N_{12}Ga$ (433.1): calcd. C 41.60, H 3.49, N 38.81, Ga 16.10; found C 41.53, H 3.52, N 38.79, Ga 18.3.

Li$[(CH_3)Ga(N_3)_3]$ (3): A solution of **1** (0.3 g, 1.53 mmol) in THF (20 mL) was added to MeLi (0.034 g, 1.53 mmol; hexane solution) at − 78 °C. The reaction mixture was warmed up to room temperature and stirred for 2 h. Filtration and removal of the solvent gave **3** as white solid in 99% yield (0.33 g): ^{1}H NMR (400.13 MHz, C_6D_6, 300 K): − 0.40 (s, 3H, CH_3); ^{13}C NMR (100.85 MHz, C_6D_6, 300 K): 1.3 (CH_3); ^{71}Ga NMR (122.05 MHz, [D$_8$]THF, 300 K): $\delta = 215$ (350 Hz); ^{14}N NMR (28.91 MHz, [D$_8$]THF, 300 K): $\delta = -320.3$ (358 Hz), − 232.3 (86 Hz), − 138.3 (94 Hz); IR (THF): $\tilde{\nu} = 2130$ vs (N_3, asym.), 2097 vs (N_3, asym.), 1344 m (N_3, sym.), 1296 m (N_3, sym.) cm^{-1}; CH_3N_9LiGa (217.76): calcd. C 5.52, H 1.39, N 57.89, Li 3.18, Ga 32.02; found C 5.69, H 1.39, N 56.9, Li 3.0, Ga 33.3.

$[(N_3)_2Ga\{(CH_2)_3NMe_2\}]$ (4): A solution of **1** (1.2 g, 6.12 mmol) in THF (50 mL) was added to Li$[(CH_2)_3NMe_2]$ (0.570 g, 6.12 mmol; hexane solution) at − 78 °C. After warming up to room temperature the reaction mixture was heated to reflux for 12 h to complete the reaction. After filtration and removal of the solvent in vacuo, the product was recovered from the white waxy residue by flask-to-flask distillation (150 °C and 10^{-3} Torr, dynamic vacuum). After additional purification by short-path distillation in vacuo, the product was obtained as colorless oil in 71% yield (1.0 g): m.p. − 28(+ 2) °C; ^{1}H NMR (400.13 MHz, C_6D_6, 300 K): $\delta = 0.34$ (t, 2H, $GaCH_2$), 1.05 (quin., 2H, CH_2), 1.44 (t, 2H, NCH_2), 1.67 (s, 6H, NCH_3); ^{13}C NMR (100.85 MHz, C_6D_6, 300 K): 3.3 ($GaCH_2$), 21.9 (CH_2), 45.3 (NCH_3), 62.5 (NCH_2); IR (toluene): $\tilde{\nu} = 2111$ vs (N_3, asym.), 2091 vs (N_3, asym.), 1342 m (N_3, sym.), 1290 m (N_3, sym.) cm^{-1}; $C_5H_{12}N_7Ga$ (239.92): calcd. C 25.03, H 5.04, N 40.87; found C 25.38, H 5.19, N 41.15.

$[Cp(CO)_2Fe-Ga(N_3)_2(py)]$ (5) and **$[(CO)_4Co-Ga(N_3)_2(NMe_3)]$ (6)**: A solution of K$[Cp(CO)_2Fe]$ (6.13 mmol) was freshly prepared by reduction of $[Cp(CO)_2Fe]_2$ with KC_8 in THF (30 mL). A solution of **1** (1.2 g, 6.13 mmol) in THF (20 mL) at − 78 °C was then added. After having been stirred at room temperature for 2 h, the mixture was cooled down again, and pyridine (0.5 mL, 6.13 mmol) was added slowly. After removal of the solvent and extraction with toluene (40 mL) **5** was obtained as orange crystals at − 30 °C in 70% yield (2.13 g). Complex $[(CO)_4Co-Ga(N_3)_3(NMe_3)]$ (**6**) was obtained analogously.

5: m.p. (decomp.) 94 °C. ^{1}H NMR (400.13 MHz, C_6D_6, 300 K): $\delta = 4.51$ (s, 5H, C_5H_5), 6.31 (s, 2H, py), 6.59 (s, 2H, py), 8.35 (s, 2H, py); ^{13}C NMR (100.85 MHz, C_6D_6, 300 K): $\delta = 81.1$ (C_5H_5), 125.4 (py), 140.5 (py), 146.5 (py); IR (toluene): $\tilde{\nu} = 2099$ vs (N_3, asym.), 2075 vs (N_3, asym.), 1985 vs (CO), 1935 vs (CO), 1338 m (N_3, sym.), 1289 m (N_3, sym.) cm^{-1}; $C_{12}H_{10}N_7O_2FeGa$ (400.83): calcd. C 35.17, H 2.46, N 23.92; found C 35.32, H 2.59, N 24.12.

6: m.p. 87 °C. ^{1}H NMR (400.13 MHz, C_6D_6, 300 K): $\delta = 1.66$ (s, 9H, CH_3); ^{13}C NMR (100.85 MHz, C_6D_6, 300 K): $\delta = 198.1$ (s, CO), 47,7 (q, CH_3); IR (toluene): $\tilde{\nu} = 2115$ s (N_3, asym.), 2090 vs (N_3, asym.), 2029 m (CO), 1989 vs (CO), 1340 m (N_3, sym.), 1280 m (N_3, sym.) cm^{-1}; $C_7H_9N_7O_4CoGa$ (383.85): calcd. C 21.90, H 2.36, N 25.54; found C 21.99, H 2.53, N 25.56.

X-ray analysis for 2e and 4 (Table 1) [28]: Complex **2e**: All data were collected on an IPDS IPDS (STOE & Cie.), rotating anode with oscillation; 2.5 min per image [24]. Corrections for absorption or decomposition were not necessary and not applied. The structure was solved by combination of direct methods, difference-Fourier synthesis, and least-squares refinements (STRUX-V; SIR-92; SHELXS-93; full matrix; F^2). Aniosotropic vibrational parameters were used for all non-hydrogen atoms. Hydrogen atoms were placed in ideal positions with isotropic vibrational parameters and included into the structure factor calculations. A final DF synthesis showed no unusual features (e(min/max) = + 0.54/ − 0.80 e Å^{-3}). For further information see ref. [24] or contact E. H.

Complex **4**: A sample of **4** held in a 0.1 mm (o.d.) capillary was mounted on a Stadi-4 four-circle diffractometer equipped with an Oxford cryosystems low-temperature device [25]. A stable solid–liquid boundary was established at 287 K, and crystal growth occurred spontaneously at this temperature. Intensity data were collected using Cu$_{K_\alpha}$ X-radiation ($\lambda = 1.54184$°) at 150.0(2) K. Following data reduction and the application of an absorption correction (based on ψ scans, $T_{min} = 0.431$, $T_{max} = 0.714$) the structure was solved by direct methods (SIR 92) [26]. Hydrogen atoms were placed in calculated positions, and the structure refined with anisotropic displacement parameters on all non-H atoms. (Shelxtl v.5.) [27]. The refinement converged to a conventional $R1$ of 10.67% [based on F and 688 data with $F > 4\sigma(F)$] and $wR2$ of 30.16% (based on F^2 and all 1439 unique data). The high values of these parameters are a consequence of low crystal quality. The final

Table 1. Crystallographic data for **2e** and **4** [28].

	2e	**4**
empirical formula	$C_{15}H_{15}GaN$	$C_5H_{12}N_7Ga$
formula weight	433.09	239.94
T (K)	300	150
λ (pm)	71.070	154.184
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (pm)	895.4(2)	694.1(3)
b (pm)	993.5(2)	837.7(4)
c (pm)	1261.3(3)	915.4(5)
α (°)	99.84(2)	93.29(4)
β (°)	103.58(2)	100.29(2)
γ (°)	115.77(2)	107.53(4)
V (10^6 pm^3)	933.2(4)	495.9(4)
Z	2	2
ρ_{calcd} (Mg m^{-3})	1.541	1.607
μ (mm^{-1})	15.0	3.573
F_{000}	440	244
crystal dimensions (mm)	0.25 × 0.25 × 0.08	0.16 × 0.10 × 0.10
θ range (°)	–	4.95–60.07
index ranges		$-7 \leq h \leq 7$ $-9 \leq k \leq 8$ $0 \leq l \leq 10$
refections collected	7900	2185
independent reflections	2911	1450
refinement method	full-matrix least-squares on F^2	
data/restraints/parameters	2911/0/311	1439/0/121
goodness-of-fit on F^2		1.054
final R indices	$R1 = 0.051$ $wR2 = 0.117$	$R1 = 0.1067$ $wR2 = 0.301$
largest diff. peak/hole	+0.54/−0.80	+0.989/−1.072

DF synthesis max. and min. were + 0.99 and − 1.07 e Å^{-3}, respectively. Details on the crystal growth and the structure determination can be obtained directly by the authors (C. R. P. and S. P.) [28].

Pyrolysis of 1: A small quartz crucible was filled with a sample of compound **1** (0.50 g), placed into a quartz tube and was slowly heated to 250 °C (rate 5 °C min^{-1}) with a flux of dry nitrogen (10 sccm). After 3 h the temperature of the oven was raised to 800 °C (25 °C min^{-1}), and the material was annealed at this temperature for 10 min. The off-white to gray GaN material (220 mg, 56% weight loss) obtained was characterized by X-ray diffraction (Fig. 5). Elemental analysis: GaN (83.73), calcd. N 16.73, Ga 83.27; found N 15.98, Ga 82.9.

Thin Films of GaN Obtained by Dip-Coating: A degreased (0001)sapphire substrate was dipped into a concentrated THF solution of **1** and blown dry with Ar. Under a flux of dry nitrogen atmosphere (10 sccm) the coated substrate was then placed into a quartz tube and was stepwise and slowly heated to 800 °C following the same temperature program as above. The thin film obtained exhibited the characteristic reflections of polycrystalline GaN and gave the PL spectrum of Figure 7.

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Note added in proof (August 9, 1996): After the submission of this manuscript, a communication by A. H. Cowley et al. appeared (ref. [29], received: March 18, 1996) describing a different synthesis of the title compound **2e** together with the results of a single-crystal X-ray diffraction analysis, which are essentially the same as our results presented here. Also, Y. Qian et al. published a benzene thermal synthetic route to nanocrystalline GaN using salt metathesis between Li_3N and $GaCl_3$ (ref. [30], received February 15, 1996). The properties of the nanocrystalline GaN powder obtained are comparable to those of our material, although the average particle size (32 nm by TEM) seems somewhat larger.

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