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Precursor chemistry of Group III nitrides[☆] Part XVI. Synthesis and structure of monomeric penta-coordinated intramolecularly adduct-stabilized amidobisazides of aluminum, gallium and indium with an all-nitrogen coordination sphere: OMCVD of GaN using $(N_3)_2Ga\{N[CH_2CH_2(NEt_2)]_2\}$

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Abstract

New intramolecularly Lewis-base-stabilized halogeno alanes, gallanes and indanes of the general formula $(X)_2M\{N[(CH_2)_n(R')_2]_2\}$ (**1–6**) and $(X)_2M\{N(Et)[(CH_2)_2N(R')_2]\}$ (**7–9**) ($n = 2, 3$; $R' = Me, Et$; $X = Cl, Br$; $E = Al, Ga$ and In) as well as the azido derivatives $(N_3)_2Ga\{N[(CH_2)_2N(Et)_2]\}$ (**10**) and $(N_3)_2Ga\{N(Et)[(CH_2)_2N(Me)_2]\}$ (**11**) as representative examples of the homologous series were synthesised via standard salt metathesis routes and fully characterised by means of elemental analysis, NMR and IR spectroscopy. Compounds **1**, **2**, **3** and **10** were studied by X-ray crystallography revealing monomeric structures in the solid state. Compound **10** allowed the growth of crystalline GaN thin films on sapphire substrates at 750°C in the absence of ammonia using the technique of organometallic chemical vapour deposition at reduced pressure. The films were analysed by XRD and Raman spectroscopy showing a preferred orientation of the crystallites perpendicular to the *c*-plane of the sapphire substrate. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Aluminum; Gallium; Indium; Amide; Azide; Intramolecular adduct; OMCVD; Gallium nitride

1. Introduction

Compounds containing Group 13 metal nitrogen bonds, M–N (M = Al, Ga, In), have a long history [2,3]. Recent work in this area has greatly extended our knowledge of these systems. This includes the development of low coordinated Group 13 metal centres with bulky amido ligands [4], new clusters and cages [5] as well as the use of M–N compounds as so-called single molecule precursors to GaN [6–26]. Gallium nitride as well as the ternary alloys $Al_xGa_yIn_zN$ ($x + y + z = 1$) are wide-band gap semiconductors exhibiting an unique combination of properties to be useful for a number of advanced applications in optoelectronics and various other fields [27]. In particular, organometallic and inorganic azide compounds of the Group 13 metals, e.g. $[R_2Ga(N_3)]_3$ (R = Me, Et) [13,17], $[(\mu\text{-}NMe_2)Ga(N_3)(NMe_2)]_2$ [18] and $[HClGaN_3]_4$ [19] have been shown to serve as precursors for organometallic chemical vapour deposition of nitride layers. The azide unit appears as a very good choice to introduce the nitrogen component. The common precursors, e.g. MR_3 and ammonia or alkylamines, contain M–C, N–H and N–C bonds, the fragmentation of which leads to the incorporation of impurities into the nitride material. A drawback of the metal azide derivatives as precursors for the nitrides is their inherent tendency of exothermic decomposition. Nitrogen rich compounds such as $[H_2GaN_3]_3$ and $(N_3)_3Ga(L)$ (L = Me, Et) [20,21] may even detonate under certain circumstances. Also, unintentional hydrolysis of the $M–N_3$ bond may eventually take place

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[☆] For Part XV, see [1]

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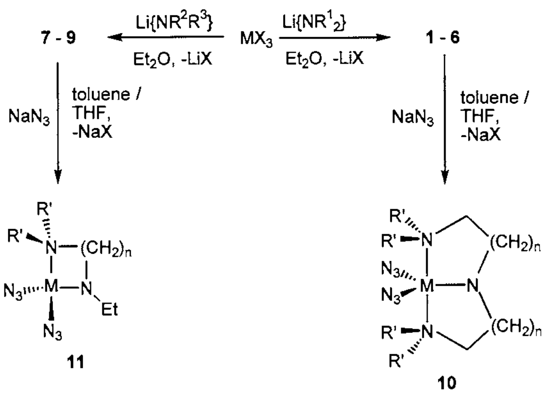
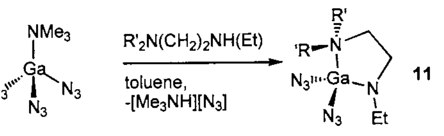


Scheme 1. Synthesis of the title compounds **1**–**11**. R^1: $[(CH_2)_n(R')_2]$; R^2: Et. R^3: $[(CH_2)_2N(R')_2]$; R′: Me, Et.



Scheme 2. Alternative synthesis of **11**.

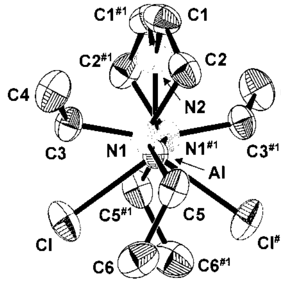


Fig. 1. The molecular structure of $Cl_2Al[N(CH_2CH_2NEt_2)_2]$ (**1**) in the solid state showing the C_2 symmetry of the molecule along the Al–N2 axis (ZORTEP [28] plot with 50% probability thermal ellipsoids). Selected bond lengths (pm) and angles (°): Al–N1, 220.90(18); Al–N2, 180.5(3); Al–Cl1, 217.57(10); N2–Al–Cl1, 125.16(3); N2–Al–N1, 81.20(5); N1–Al–N#1, 162.40(10); N1–Al–Cl1, 96.05(6); N1–Al–Cl1, 94.05(6); Cl1–Al–Cl1 #1, 109.69(6).

to produce traces of explosive hydrazoic acid which represent a significant danger in view of the technical use of azide-type precursors. Intramolecular adduct formation has been shown to stabilise even pyrophoric Group III alkyl compounds against the nucleophilic attack of water [22]. We followed this line and studied intramolecular adduct-stabilised azide compounds of the type $(N_3)_aM[(CH_2)_3NMe_2]_{3-a}$ (M = Al, Ga, In; $a = 1, 2$) [23–26] as precursors for the respective Group 13 nitride materials. In an extension of this work we present new results on the synthesis and characterisation of intramolecularly adduct-stabilised Group III metal azides using Lewis-donor-functionalised amido-ligands rather than donor-functionalised alkyl substituents, in order to achieve an all-nitrogen coordination sphere of the Group 13 metal centre and strictly monomeric structures in the solid state aimed at good volatility.

2. Synthesis and properties

According to Scheme 1 the Group III metal halides MX_3 (X = Cl, Br) were treated with the lithium amides of the general type $Li[NR^1R^2]$ to yield the mono amides $X_2M[NR^1R^2]$ (R^1 = Et; $R^2 = CH_2CH_2NR'_2$, R′ = Me, Et and $R^1 = R^2 = (CH_2)_nNR'_2$; $n = 2, 3$). The halide/azide exchange was accomplished by using excess sodium azide in refluxing toluene solution containing 5–10% of tetrahydrofuran to activate the sodium azide. The reaction was followed by IR spectroscopy using the $\nu(N_3)_{asym}$ bands at 2100–2000 cm^{-1}. The products were purified by crystallisation from concentrated toluene solutions. The compounds are moderately air stable, but prolonged exposure to moist air leads to hydrolysis and the formation of a viscous oil. The penta-coordinated bisazido complex **10** with two amino donors exhibit a surprisingly low volatility but can be sublimed at 10^{-5} mbar and 130°C. The bisazide **11** with only one amine donor shows much better volatility and readily sublimes at 10^{-2} mbar and 95°C. First, results on the OMCVD of the nitrides using intramolecularly adduct-stabilized amido/azides of the discussed type are given in Section 4. The new compounds were fully characterised by NMR, MS and IR spectroscopy as well as by elemental analysis and do not show unexpected spectroscopic features (see Section 5).

An alternative synthesis of the azidogallium compound **11** is shown in Scheme 2. Starting out with the adduct-stabilized triazidogallium complexes $(N_3)_3Ga(NMe_3)$ [19,21], ammonolysis with the respective amine ligand $HN(Et)[(CH_2)_2NMe_2]$ also gives **11**. But the yields of the isolated pure product **11** were low (10–20%). However, aiming at a one-pot large scale synthesis of precursor chemicals, this method would be attractive because the step of metallation of the amine is avoided; this clearly warrants further investigation.

3. Structure

The dihalides $X_2M[N(CH_2CH_2NEt_2)_2]$ (**1**–**3**) of Al, Ga and In are isostructural. The compounds crystallise as monomers from diethylether in the monoclinic space group *P*2/*c* with two molecules in the elementary cell. Figs. 1–3 show the molecular structures and Table 1 contains the crystallographic and data collection parameters. The cell volumes rise from the almost identical values for Al (**1**: 840.4 Å³) and Ga (**2**: 844.8 Å³) to the somewhat large value for In (**3**: 894.3 Å³) according to the larger ionic radius of In. The Group III metal is penta-coordinated in a trigonal-bipyramidal fashion with the NEt_2 amino donor groups in the apical positions (see Fig. 2). As expected, the bonding length of the covalent M–N bonds is shorter than the coordinative M–N analogues. Noticeably short intramolecular contacts are absent. Fig. 1 gives a projection of the Al compound **1** with the Al–N2 bond vector in the plane showing the C_2-symmetry along the Al–N2 axis.

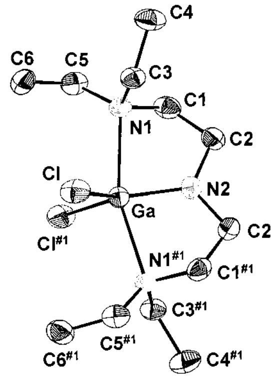


Fig. 2. The molecular structure of $Cl_2Ga[N(CH_2CH_2NEt_2)_2]$ (**2**) in the solid state axis (ZORTEP plot with 50% probability thermal ellipsoids). Selected bond lengths (pm) and angles (°): Ga–N1 228.7(4), Ga–N2 184.2(4), Ga–CH 221.1(1), N2–Ga–Cl1, 125.34(5), N2–Ga–N1 80.57(7), N1–Ga–N1$^{\#1}$ 161.13(13), N1–Ga–Cl1 96.51(10), N1–Ga–Cl$^{\#1}$ 94.37(10), Cl–Ga–Cl1$^{\#1}$ 109.33(10).

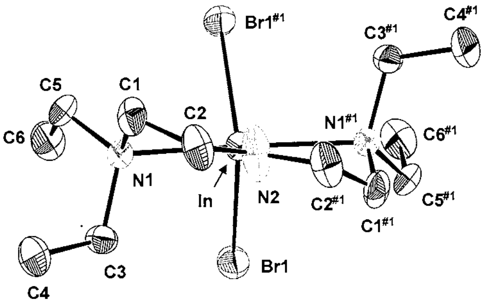


Fig. 3. The molecular structure of $Br_2In[N(CH_2CH_2NEt_2)_2]$ (**3**) in the solid state showing a projection of the molecule perpendicular to the In–N2 axis (ZORTEP plot with 50% probability thermal ellipsoids). Selected bond lengths (pm) and angles (°): In–N1 241.0(7), In–N2 201.9(10), In–Br1 252.20(13), N2–In–Br1 124.44(3), N2–In–N1 76.68(15), N1–In–N1$^{\#1}$ 153.4(3), N1–In–Br1 98.55(16), N1–In–Br$^{\#1}$ 96.43(16), Br1–In–Br1$^{\#1}$ 111.13(6).

Table 1

Numbering scheme of the new compounds $(X)_2M\{N[(CH_2)_nN(R')_2]_2\}$ (**1**–**10**) and $(X)_2M\{N(Et)[(CH_2)_2N(R')_2]\}$ (**7**–**9**, **11**)

Compound	M	X	n	R′
1, **4**	Al	Cl	2, 3	Et, Me
2, **5**	Ga	Cl	2, 3	Et, Me
3, **6**	In	Br	2, 3	Et, Me
10	Ga	N3	2	Et
7, **8**	Ga	Cl		Me
9	Al	Cl		Et
11	Ga	N_3		Me

The envelope conformation of the five-membered heterocycle M–N2–C1–C2–N1 can be seen in Fig. 3 which shows a projection of the indium compound **3** perpendicular to the In–N2 axis. The deviation of the angle N1–M–N1$^{\#1}$ from the value of 180° for an ideal trigonal bipyramidal coordination (Fig. 2) is a characteristic consequence of the steric demand of the five-membered heterocycles and the covalent radius of the central metal. The angle N1–M–N1$^{\#1}$ of the tripodal N-donor-substituted amido ligand decreases from about 162.4° for the Al and 161.1° for the Ga compound to about 153.4° for the In compound because of the longer In–N2 bond of 201.9(10) pm rather than Al–N2 of 180.5(3) pm and Ga–N2 of 184.2(4) pm. A longer alkyl chain between N1 and N2 would be needed to allow for a more linear N1–M–N1$^{\#1}$ arrangement. This is likely to be the case for the derivatives **4**–**6** which exhibit six-membered chelate rings. The donor acceptor bonds M–N1 with a tetra-coordinated N atom are expectedly longer than the polar covalent amido bonds M–N2 involving a tri-coordinated N atom. The M–N as well as the M–X (X = Cl, Br) distances are getting longer from Al to In within the usual range for such bonds.

The molecular structure of the gallium bisazide **10** in the solid state is shown in Fig. 4. Crystallographic and data collection parameters are compiled in Table 2. It was prepared in the same manner as the closely related arylgallium bisazide $(N_3)_2Ga[2,6\text{-}(Me_2NCH_2)_2C_6H_2]$ which was obtained by a metathetical reaction of the corresponding arylgallium dichloride with NaN_3 [29]. Both compounds are monomeric in the solid state due to an effective coordinative saturation of the gallium centre by intramolecular adduct formation. The few known other intramolecularly adduct-stabilized mono and bisazides of gallium and indium show a weak association in the solid state and form coordination polymers by head to tail azide bridges or dimers by head-bridging azide groups. Contrasting this, compound **10** is monomeric in the solid state without unusually short intermolecular contacts. The structural features of **10** with respect to the coordination of the amido-ligand are quite similar to the arylgallium diazide (Fig. 4). The geometry of both compounds around the penta-coordinated gallium centre is trigonal bipyramidal. The $NGa(N_3)_2$ moiety is planar within experimental error (sum of angles at Ga = 359.96°), the non-linear arrangement of N7–Ga–N9 163.92(15)° is a characteristic consequence of the steric requirements of the five-membered chelate rings. The Ga–N_{amide} bond, Ga–N8 of 183.8 pm and the Ga–N_{azide} bonds Ga–N1 of 194.5(4) pm and Ga–N4 of 192.3(4) pm, are expectedly shorter than the coordinative donor–acceptor bonds, Ga–N7 (225.0(5) pm) and Ga–N9 (224.4(4) pm). The two terminal azide groups N1–N2–N3 and N4–N5–N6 are quasi-linear and tilted away from the

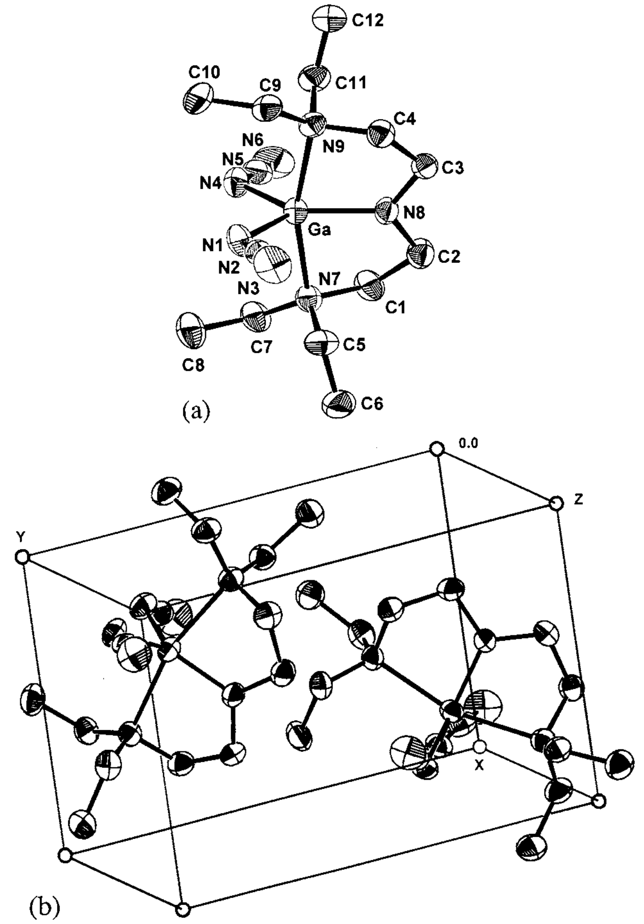


Fig. 4. (a) The molecular structure of $(N_3)_2Ga[N(CH_2CH_2NEt_2)_2]$ (**10**) in the solid state axis (ZORTEP plot with 50% probability thermal ellipsoids). Selected bond lengths (pm) and angles (°): Ga–N7 225.0(5), Ga–N9 224.4(4), Ga–N8(5), Ga–N4 192.3(4), Ga–N1 194.5(4), N1–N2 119.1(5), N2–N3 115.5(6), N4–N5 119.2(5), N5–N6 115.2(5), N8–Ga–N4 128.5(2), N8–Ga–N1 126.6(2), N8–Ga–N7 82.12(17), N8–Ga–N9 81.80(19), N7–Ga–N9 163.92(15), N7–Ga–N1 95.48(18), N7–Ga–N4 104.86(18), N8–Ga–N1 126.6(2), Ga–N1–N2 118.3(3), N1–N2–N3 175.5(5), Ga–N4–N5 124.2(3), N4–N5–N6 175.3(5). (b) The packing of two independent molecules $(N_3)_2Ga[N(CH_2CH_2NEt_2)_2]$ (**10**) in the elementary cell showing the absence of bridging azide groups.

plane defined by (N1)(N4)Ga–N8 with the N1–N2–N3 group pointing towards the 'C4 tip' of the Ga(–N8–C3–C4–N9–) envelope and with the N4–N5–N6 group towards the 'C1 tip' of the Ga(–N8–C2–C1–N7–) envelope.

The Ga–N–N angles (Ga–N1–N2, 118.3°; Ga–N4–N5, 124.2°) and the alternating N–N bond distances (N1–N2, 119.5 pm and N4–N5, 119.2 pm; N2–N3, 115.5 pm and N5–N6, 115.2 pm) are typical for covalent azides of Ga [30,31]. The C–C- and C–N bonds, respectively, of the ligand show nothing out of the ordinary.

The N7–Ga–N9 axes of the two molecules in the unit cell form a right angle.

Compound **10** represents the first example of a structurally characterized monomeric gallium bisazide with a nitrogen-only coordination sphere.

4. OMCVD of GaN using $(N_3)_2Ga\{N[CH_2CH_2(NEt_2)]_2\}$ (10)

Employing a simple isothermal horizontal hot-wall CVD reactor [32], crystalline GaN layers were grown in vacuo (10^{-3} mbar) at an oven temperature of 750°C using **10** as a single-source precursor in the absence of ammonia. The X-ray diffraction pattern and the Raman data of the films are shown in Figs. 5 and 6. Due to the unexpected low volatility of the precursor **10**, the growth rates of 10 nm h^{-1} were quite low. Nevertheless the data proves the possibility to grow GaN materials from intramolecularly adduct-stabilized amido/azide gallium compounds. Interestingly, the related compound $(N_3)_2Ga[2,6\text{-}(Me_2NCH_2)_2C_6H_2]$, as the only other known intramolecularly stabilized and pentacoordinated bisazide of gallium, was reported to be too stable to grow GaN films by OMCVD or MOMBE [29]. Compared to the GaN material grown on nitridated *c*-plane sapphire at 950°C and 1.5 mbar using $(N_3)_2Ga[(CH_2)_3NMe_2]$ [32,33] exhibiting a 90 arc sec FWHM of the rocking curve of the GaN(0002) reflection and a comparably strong room temperature (r.t.) band-edge photoluminescence of 365 nm (3.4 eV), the quality of the layers described here (Figs. 5 and 6) is still poor. However, the conditions of the OMCVD experiments have not been optimised. Further work will be undertaken to fully elucidate the potential of azide-type precursors for metal nitrides with an all-nitrogen coordination sphere.

5. Experimental

5.1. General procedures

All manipulations were performed utilizing carefully oven-dried reaction vessels (Schlenk techniques) under an inert atmosphere of purified argon as well as by using a glove box (argon, O_2 and $H_2O < 1$ ppm). Solvents were dried and distilled according to standard procedures and stored over 4 Å molecular sieves (residual water < 1 ppm, Karl-Fischer). The ^1H- and ^{13}C-NMR spectra were recorded with a Bruker AC200 instrument, calibrated against the residual protons of the deuterated solvents and corrected against TMS. All NMR solvents were carefully dried and stored over K/Na alloy before use. The IR spectra were obtained in solution (THF, toluene, pyridine) using 0.1 mm cells equipped with CaF_2 or NaCl windows or as KBr pellets on a Perkin–Elmer 1650 FT IR or a Bruker IFS 66

Table 2
Crystallographic data and collection parameters for compounds **1**, **2**, **3** and **10**

Compounds	**1**	**2**	**3**	**10**
Empirical formula	$C_{12}H_{28}AlCl_2N_3$	$C_{12}H_{28}Cl_2GaN_3$	$C_{12}H_{28}Br_2InN_3$	$C_{12}H_{28}GaN_9$
Formula weight (g mol^{-1})	312.26	355.00	489.01	368.15
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2/c$	$P2/c$	$P2/c$	$P2_1$
a (Å)	7.837(4)	7.893(9)	8.073(4)	7.683(4)
b (Å)	7.626(4)	7.582(9)	7.642(4)	10.307(10)
c (Å)	14.098(7)	14.144(16)	14.540(8)	11.639(9)
α (°)	90	90	90	90
β (°)	94.15(3)	93.54(9)	94.45(4)	106.93(6)
γ (°)	90	90	90	90
V (Å^3)	840.4(7)	844.8(17)	894.3(8)	881.7(13)
Z	2	2	2	2
D_{calc} (g cm^{-3})	1.234	1.396	1.816	1.387
Temperature (K)	203(2)	203(2)	203(2)	203(2)
μ (mm^{-1})	0.428	1.934	5.780	1.572
F(000)	336	372	480	388
λ (Å)	0.71073	0.71073	0.71073	0.71073
θ Range (°)	2.61–29.99	2.59–29.99	2.67–29.99	1.83–30.00
h, k, l ranges	11/10, 0/10, 0/19	−11/9, 0/10, 0/19	−11/6, 0/10, 0/20	−10/10, 0/14, 0/16
Crystal size (mm^3)	0.65 × 0.40 × 0.23	0.70 × 0.65 × 0.50	0.50 × 0.50 × 0.15	0.50 × 0.30 × 0.20
No. observed reflections ($I>2\sigma(I)$)	1749	1872	1570	2115
Transmission min/max	0.858/0.999	–	0.1602/0.4777	0.891/0.998
Refinement	Full-matrix least-squares refinements	Full-matrix least-squares refinements	Full-matrix least-squares refinements	Full-matrix least-squares refinements
Data/restraints/parameters	2453/0/139	2203/0/139	2221/0/88	2706/1/237
Final R indices ($I>\sigma(I)$) R_1/wR_2	0.0467/0.1255	0.0581/0.1325	0.0697/0.1936	0.0417/0.0852
Goodness-of-fit on F^2	1.045	1.040	1.026	1.061
Residual electron density (e Å^{-3})	0.382/−0.297	0.827/−1.494	2.439/−1.318	0.565/−0.320

instrument. Elemental analysis were provided by the Microanalytic Laboratory of the Chemical Institutes of the University of Heidelberg and the Ruhr-University Bochum. The metal content was determined by complexometric titration of EDTA (Titriplex, Merck KgA Darmstadt) solution. Melting points (uncorrected) were determined on a Gallenkamp hot-air melting point apparatus or using a Seiko TG/DTA 6300 SII thermobalance.

NOTE: Working with Group 13 azides generally requires special security precautions as face protection shield, special metal gloves and a leather body protection. The intramolecular adduct-stabilized azide compounds described here can be handled in solution under the exclusion of moisture without special precaution but care must be taken to avoid exposing the compounds to sudden heating and mechanical shock. At least in our hands there was no problem at all in subliming the azides in vacuo.

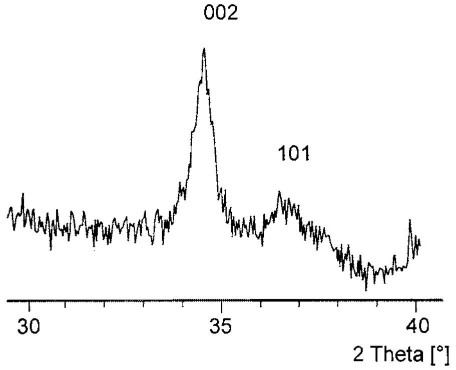


Fig. 5. Thin film X-ray diffraction pattern of a preferentially oriented crystalline GaN layer grown on c-plane sapphire using $(N_3)_2Ga[N(CH_2CH_2NEt_2)_2]$ in vacuo at 750°C.

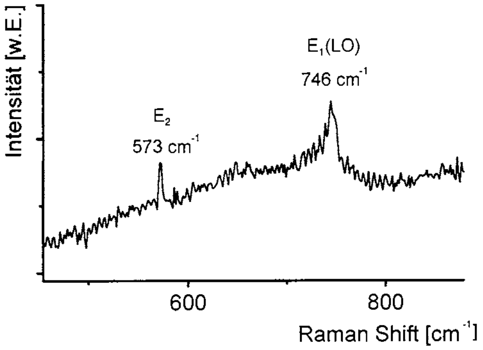


Fig. 6. Raman data of the GaN layer of Fig. 5. The characteristic absorption of bulk GaN, the E_2 and E_1 mode of the lattice vibration are clearly seen.

5.2. General procedure for the synthesis of the {[Bis(2-dialkylaminoethyl)]amido}dihalogenides and also for the synthesis of the {ethyl[(2-dialkylamino)ethyl]amido}-dihalogenides of aluminum, gallium and indium, $X_2E\{N[(CH_2)_nNR_2]_2\}$, (n = 2, R = Et; n = 3, R = Me); $X_2E\{N(C_2H_5)[(CH_2)_2\ NR_2]\}$, (R = Me, Et)

To a solution of [2,2′-aminobis(*N*,*N*-diethyl)ethyl]-amine (2 ml, 1.67 g, 7.77 mmol); [3,3′-aminobis(*N*,*N*-dimethyl)propyl]amine (5 ml, 4.20 g, 22.44 mmol); *N*,*N*-dimethyl-*N*′-ethylethylenediamine (5 ml, 3.69 g, 31.75 mmol); *N*,*N*,*N*′-triethylethylenediamine (5.9 ml, 4.8 g, 31.75 mmol)} in diethylether (80 ml), one equivalent of a 2.5 N hexane solution of *n*-butyllithium is dropwise added at − 78°C. After warming up to r.t. the reaction mixture is slowly added to a cooled (− 78°C) solution of one equivalent of the metal halogenide MX_3 (M = Al, Ga; X = Cl; E = In; X = Br) in diethylether (80 ml). After stirring for 24 h at r.t., filtration and removal of the solvent in vacuo, the products are collected as colourless needles that could be purified by recrystallization from toluene. Independently from our work, Beachley and Racette described the synthesis of {ethyl[(2-dimethylamino)ethyl]amido}-chloroaluminum [34].

*5.2.1. $Cl_2Al\{N[(CH_2)_2NEt_2]_2\}$ (**1**)*

Yield 2.23 g (7.16 mmol; 92.2%). M.p. 93.4°C. ^{1}H-NMR (C_6D_6, 293 K) *d* = 0.87 (t, 12H, $-CH_2-CH_3$), 2.43 (t, 4H, $>N-CH_2-CH_2-$), 2.65 (t, 4H, $>N-CH_2-CH_2-$), 3.16 (q, 8H, $-CH_2-CH_3$). ^{13}C-NMR (C_6D_6, 293 K) *d* = 7.97 ($-CH_2-CH_3$), 43.72 ($-CH_2-CH_3$), 45.19 ($>N-CH_2-CH_2-$), 51.99 ($>N-CH_2-CH_2-$). ^{27}Al-NMR (C_6D_6, 293 K) *d* = 110 ($h_{1/2}$ = 1650 Hz). Calc. for $C_{12}H_{28}N_3AlCl_2$ (312.26 g mol^{-1}): C, 46.16; H, 9.04; N, 13.46; Cl, 22.71; Al, 8.46. Anal. Found: C, 45.98; H, 8.88; N, 13.57; Cl, 22.42; Al, 8.28%.

*5.2.2. $Cl_2Ga\{N[(CH_2)_2NEt_2]_2\}$ (**2**)*

Yield 2.64 g (7.44 mmol, 95.8%). M.p. 86.8°C. ^{1}H-NMR (C_6D_6, 293 K) *d* = 0.82 (t, 12H, $-CH_2-CH_3$), 2.38 (t, 4H, $>N-CH_2-CH_2-$), 2.71 (t, 4H, $>N-CH_2-CH_2-$), 3.10 (q, 8H, $-CH_2-CH_3$). ^{13}C-NMR (C_6D_6, 293 K) *d* = 7.81 ($-CH_2-CH_3$), 43.02 ($-CH_2-CH_3$), 45.65 ($>N-CH_2-CH_2-$), 51.84 ($>N-CH_2-CH_2-$). Calc. for $C_{12}H_{28}N_3GaCl_2$ (355.00 g mol^{-1}): C, 40.60; H, 7.94; N, 11.83; Cl, 19.64; Ga, 19.64. Anal. Found: C, 39.89; H, 7.88; N, 11.46; Cl, 19.23; Ga, 20.28%.

*5.2.3. $Br_2In\{N[(CH_2)_2N(Et)_2]_2\}$ (**3**)*

Yield 3.25 g (6.65 mmol, 85.7%). M.p. 99.2°C. ^{1}H-NMR (C_6D_6, 293 K) *d* = 0.78 (t, 12H, $-CH_2-CH_3$), 2.31 (t, 4H, $>N-CH_2-CH_2-$), 2.85 (t, 4H, $>N-CH_2-CH_2-$), 3.03 (q, 8H, $-CH_2-CH_3$). ^{13}C-NMR (C_6D_6, 293 K) *d* = 8.11 ($-CH_2-CH_3$), 43.20 ($-CH_2-CH_3$), 46.95 ($>N-CH_2-CH_2-$), 53.72 ($>N-CH_2-CH_2-$). Calc. for $C_{12}H_{28}N_3InBr_2$ (489.00 g mol^{-1}): C, 28.31; H, 5.50; N, 8.15; Br, 32.68; In, 23.48. Anal. Found: C, 30.01; H, 6.21; N, 7.98; Br, 32.23; In, 24.59%.

*5.2.4. $Cl_2Al\{N[(CH_2)_3NMe_2]_2\}$ (**4**)*

Yield 5.44 g (19.94 mmol, 89.1%). M.p. 79.2°C. ^{1}H-NMR (C_6D_6, 293 K) *d* = 1.46 (m, 4H, $-CH_2-$), 2.29 (s, 12H, $-N(CH_3)_2$), 2.49 (t, 4H, $>N-CH_2-$), 3.00 (t, 4H, $-N-CH_2-CH_2-$). ^{13}C-NMR (C_6D_6, 293 K) *d* = 27.40 ($-CH_2-$), 47.97 ($-N(CH_3)_2$), 54.57 ($-N-CH_2-$), 60.85 ($>N-CH_2-$). Calc. for $C_{10}H_{12}N_3AlCl_2$ (272.11 g mol^{-1}): C, 44.13; H, 4.44; N, 15.44; Cl, 26.05; Al, 9.91. Anal. Found: C, 43.01; H, 5.21; N, 14.98; Cl, 25.23; Al, 10.59%.

*5.2.5. $Cl_2Ga\{N[(CH_2)_3NMe_2]_2\}$ (**5**)*

Yield 6.55 g (20.82 mmol, 92.8%). M.p. 82.5°C. ^{1}H-NMR (C_6D_6, 293 K) *d* = 1.49 (m, 4H, $-CH_2-$), 2.12 (s, 12H, $-N(CH_3)_2$), 2.27 (t, 4H, $>N-CH_2-$), 3.03 (t, 4H, $-N-CH_2-$). ^{13}C-NMR (C_6D_6, 293 K) *d* = 27.80 ($-CH_2-$), 45.98 ($-N(CH_3)_2$), 53.74 ($-N-CH_2-$), 59.75 ($>N-CH_2-$). Calc. for $C_{10}H_{12}N_3GaCl_2$ (314.85 g mol^{-1}): C, 38.14; H, 3.84; N, 13.35; Cl, 22.52; Ga, 22.14. Anal. Found: C, 43.01; H, 4.44; N, 14.01; Cl, 21.98; Ga, 23.23%.

*5.2.6. $Br_2In\{N[(CH_2)_3NMe_2]_2\}$ (**6**)*

Yield 7.16 g (16.96 mmol, 75.6%). M.p. 76.9°C. ^{1}H-NMR (C_6D_6, 293 K) *d* = 1.47 (m, 4H, $-CH_2-$), 2.20 (s, 12H, $-N(CH_3)_2$), 2.28 (t, 4H, $>N-CH_2-$), 3.15 (t, 4H, $-N-CH_2-CH_2-$). ^{13}C-NMR (C_6D_6, 293 K) *d* = 28.47 ($-CH_2-$), 46.78 ($-N(CH_3)_2$), 57.09 ($-N-CH_2-$), 60.34 ($>N-CH_2-$). Calc. for $C_{10}H_{12}N_3AlCl_2$ (448.85 g mol^{-1}): C, 26.75; H, 2.69; N, 9.36; Br, 53.60; In, 25.58. Anal. Found: C, 27.26; H, 3.37; N, 10.01; Br, 52.99; In, 25.54%.

*5.2.7. $Cl_2Ga\{N(Et)[(CH_2)_2NMe_2]\}$ (**7**)*

Yield 6.89 g (26.98 mmol, 85%). ^{1}H-NMR (C_6D_6, 293 K) *d* = 0.39 (t, 3H, $-N-CH_2-CH_3$), 1.05 (t, 2H, $-CH_2-CH_2-$), 2.09 (s, 6H, $-N(CH_3)_2$), 2.26 (t, 2H, $-CH_2-CH_2-$), 2.59 (t, 2H, $-CH_2-CH_2-$). ^{13}C-NMR

(C_6D_6, 293 K) $d=13.36$ ($-N(CH_2-CH_3)_2$), 43.04 ($-N(CH_2-CH_3)_2$), 43.96 ($-N(CH_3)_2$), 45.34 ($-CH_2-CH_2-$), 56.83 ($-CH_2-CH_2-$). Calc. for $C_6H_{15}N_2GaCl_2$ (255 g mol^{-1}): C, 28.16; H, 5.86; N, 10.95; Ga, 27.25. Anal. Found: C, 27.63; H, 5.92; N, 10.49; Ga, 28.10%.

5.2.8. $Cl_2Al\{N(Et)[(CH_2)_2NEt_2]\}$ (**8**)

Yield 6.27 g (26 mmol, 82%). ^{1}H-NMR (C_6D_6, 293 K) $d=0.39$ (t, 6H, $-N(CH_2-CH_3)_2$), 1.14 (t, 3H, $-N-CH_2-CH_3$), 2.09 (t, 2H, $-CH_2-CH_2-$), 2.27 (q, 4H, $-N(CH_2-CH_3)_2$), 2.36 (t, 4H, $-CH_2-CH_2-$), 2.69 (q, 2H, $-CH_2-CH_3$). ^{13}C-NMR (C_6D_6, 293 K) $d=7.60$ ($-N(CH_2-CH_3)_2$), 16.87 ($-N-CH_2-CH_3$), 43.83 ($-N(CH_2-CH_3)_2$), 45.06 ($-N-CH_2-CH_3$), 46.29 ($-CH_2-CH_2-$), 52.90 ($-CH_2-CH_2-$). Calc. for $C_8H_{19}N_2AlCl_2$ (241 g mol^{-1}): C, 39.85; H, 7.94; N, 11.62. Anal. Found: C, 40.13; H, 6.98; N, 11.62%.

5.2.9. $Cl_2Ga\{N(Et)[(CH_2)_2NEt_2]\}$ (**9**)

Yield 6.97 g (28.92 mmol, 78%). ^{1}H-NMR (C_6D_6, 293 K) $d=0.62$ (t, 6H, $-N(CH_2-CH_3)_2$), 1.37 (t, 3H, $-N-CH_2-CH_3$), 2.23 (t, 4H, $-CH_2-CH_2-$), 2.48 (q, 4H, $-N(CH_2-CH_3)_2$), 2.64 (t, 4H, $-CH_2-CH_2-$), 3.00 (q, 2H, $-N-CH_2-CH_3$).^{13}C-NMR (C_6D_6, 293 K) $d=$ 7.98 ($-N(CH_2-CH_3)_2$), 17.06 ($-N-CH_2-CH_3$), 44.43 ($-N(CH_2-CH_3)_2$), 48.15 ($-N-CH_2-CH_3$), 49.29 ($-CH_2-CH_2-$), 54.28 ($-CH_2-CH_2-$). Calc. for $C_8H_{19}N_2GaCl_2$ (284 g mol^{-1}): C, 34.09; H, 6.80; N, 9.95; Ga, 24.75. Anal. Found: C, 33.13; H, 6.79; N, 9.98; Ga, 22.50%

5.3. General procedure for the synthesis of the intramolecularly adduct-stabilised amidobisazides of aluminum, gallium and indium $(N_3)_2E\{N[(CH_2)nNR_2]_2\}$ ($n=2$, $R=Et$; $n=3$, $R=Me$); $(N_3)_2E\{N(Et)[(CH_2)_2NR_2]\}$ ($R=Me$, Et)

A sample of 3.5 equivalents (2.05 g, 31.45 mmol) of sodium azide in 20 ml of toluene was added to a solution of **2** and **7** (8.99 mmol) of 20 ml of toluene/5 ml of tetrahydrofuran. After refluxing for 24 h the solution was separated from the residue by filtration and removal of the solvent in vacuo. The products were obtained as colourless needles by recrystallisation from toluene.

5.3.1. $(N_3)_2Ga\{N[(CH_2)_2NEt_2]_2\}$ (**10**)

Yield 3.04 g (10.94 mmol, 75.6%). M.p. 86.8°C. ^{1}H-NMR (C_6D_6, 293 K) $d=0.84$ (t, 12H, $-CH_2-CH_3$), 2.36 (t, 4H, $(CH_3)_2N-CH_2-CH_2$), 2.69 (t, 4H, $>N-CH_2-CH_2-$), 3.12 (q, 8H, $-CH_2-CH_3$). ^{13}C-NMR (C_6D_6, 293 K) $d=7.81$ ($-CH_2-CH_3$), 43.02 ($-CH_2-CH_3$), 45.65 ($>N-CH_2-CH_2-$), 51.84 ($>N-CH_2-CH_2-$). Calc. for $C_{12}H_{28}N_9Ga$ (368.13 g mol^{-1}): C, 39.15; H, 7.66; N, 34.24; Ga, 18.93. Anal. Found: C, 40.21; H, 7.88; N, 34.22; Ga, 20.02%. IR ν [cm^{-1}] 2098 (s), $\nu(N_3)$.

5.3.2. $(N_3)_2Ga\{N(Et)[(CH_2)_2NMe_2]\}$ (**11**)

Yield 1.66 g (6.2 mmol, 69%). ^{1}H-NMR (C_6D_6, 293 K) $d=0.40$ (t, 3H, $-N-CH_2-CH_3$), 1.16 (t, 2H, $-CH_2-CH_2-$), 2.17 (s, 6H, $-N(CH_3)_2$), 2.41 (t, 2H, $-CH_2-CH_2-$), 2.53 (q, 2H, $-N-CH_2-CH_3$). ^{13}C-NMR (C_6D_6, 293 K) $d=16.10$ ($-N(CH_2-CH_3)_2$), 44.97 ($-CH_2-CH_2-$), 45.92 ($-N(CH_3)_2$), 48.18 ($-CH_2-CH_2-$), 60.07 ($-N-CH_2-CH_3$). Calc. for $C_6H_{15}N_8Ga$ (269 g mol^{-1}): C, 26.79; H, 5.58; N, 41.67; Ga, 25.94. Anal. Found: C, 28.51; H, 5.20; N, 41.74; Ga, 25.90%. IR ν [cm^{-1}] 2096 (s), $\nu(N_3)$.

5.4. Alternative procedure for the synthesis of the intramolecularly adduct-stabilized amidobisazide $(N_3)_2Ga\{N(Et)[(CH_2)_2NMe_2]\}$ (**11**)

A solution of 0.64 ml of *N*,*N*-dimethyl-*N*′-ethylethylenediamine (0.47 g, 4 mmol) in toluene (20 ml) was added to a solution of 1 g (4 mmol) of (trimethylamine)triazidogallium [21] in toluene (20 ml) at −78°C. The reaction was stirred for 12 h at r.t. Filtration and removal of the solvent in vacuo gave an viscous oil. The product is obtained in an analytically-pure form via flask to flask vacuum distillation (10^{-3} mbar, 98°C) as colourless crystals. Yield 0.15 g (0.4 mmol, 10%).

5.5. X-ray structure determination

Experimental details on the X-ray crystal structural analyses of **1**, **2**, **3** and **10** are listed in Table 1. Intensity data were collected on a Siemens-Stoe AED2 four-circle diffractometer with absorption corrections, using Mo–K_α radiation in ω-scans. φ-Scans were used for absorption corrections. The structures were solved by direct methods (SHELXS-86) [35] and refined by full-matrix least-squares methods based on F^2 using all measured reflections (SHELXL-93) [36] with anisotropic temperature factors for all non-hydrogen atoms.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 136835 for compound **1**, CCDC no. 136834 for compound **2**, CCDC no. 136836 for compound **3** and CCDC no. 136837 for compound **4**. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Rd., Cambridge CB2 1EX, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.com.ac.uk or www: http://www.ccdc.cam.ac.uk).

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