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Simple synthesis of organogallium azides: structural characterization of $[Mes_2GaN_3]_2$

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Salt elimination reactions between R_2GaCl [R = *n*-Bu, *s*-Bu, Mes ($C_6H_2Me_3$-2,4,6)] and NaN_3 leads to the bis-organogallium azides R_2GaN_3 (R = *n*-Bu **1**, *s*-Bu **2**, Mes **3**) in good yields. The compounds have been characterized by NMR, IR spectroscopy and mass spectrometry, elemental analyses and cryoscopic molecular weight determinations. While **1** and **2** are liquids at room temperature, **3** is a solid. Its solid state structure was determined by single crystal X-ray analysis.

Introduction

GaN is a semiconductor with a wide, direct band gap (3.45 eV). The development of blue-light emitting diodes based on GaN has forced researchers to intensify studies concerning the synthesis of potential precursors for this interesting material.[1] GaN has been grown by MOCVD using the reaction of $GaMe_3$ or $GaEt_3$ with NH_3 at temperatures above 1000 °C.[2] Alternatively, so called single source precursors have been used.[3] They often have lower deposition temperatures and are less pyrophoric. An attractive source are organogallium azides, which have been successfully used for the growth of GaN by metal organic chemical vapor deposition (MOCVD) at temperatures between 350 and 500 °C in excellent purity and crystallinity.[4] Recently, a novel "detonation chemistry" based on base-stabilized Ga-trisazides $R \longrightarrow Ga(N_3)_3$ was established to produce nanocrystalline GaN.[5]

Organogallium azides constitute a well documented class of compounds. The first example was synthesized by Müller and Dehnicke who prepared Et_2GaN_3 by reaction of $GaEt_3$ and ClN_3.[6] A more convenient route uses the reactions of sodium azide with organogallium chlorides under elimination of NaCl. Both mono- and di-substituted azides of the type $RR'GaN_3$ and $RGa(N_3)_2$ have been prepared by this reaction pathway.[4,5,7] In contrast to $[Ga(N_3)_3]_\infty$, which is extremely explosive, the monoazides are insensitive to shock and can be handled without decomposition. Recently, the very interesting compounds $[HClGaN_3]_4$ and H_2GaN_3 were prepared by a salt elimination reaction using LiN_3.[4f]

Herein, we describe the synthesis and structural characterization of bisorganogallium azides.

Results and discussion

Salt elimination reactions between NaN_3 and bisorganogallium chlorides R_2GaCl [R = *n*-Bu, *s*-Bu, Mes ($C_6H_2Me_3$-2,4,6)] yields the corresponding monoazides R_2GaN_3 (R = *n*-Bu **1**, *s*-Bu **2**, Mes **3**). Reactions in the presence of the phase-transfer catalyst dibenzo-18-crown-6 did not increase the yields. Compounds **1** and **2** are liquid at room temperature and can be distilled at 10^{-3} mbar between 125 and 140 °C. Compound **3** is a colorless solid which melts without decomposition at 182 °C. All of **1**–**3** have been characterized by elemental analyses, molecular weight determination, NMR, IR spectroscopy and mass spectrometry.

Each compound shows a set of bands in their infrared spectra corresponding to the symmetric and asymmetric modes of the azido groups. The spectra are almost identical, which is reasonable given the similarity of the compounds.

Table 1 Crystallographic data and data collection parameters for $[Mes_2GaN_3]_2$ **3**

Formula	$C_{36}H_{44}Ga_2N_6$
M_w	700.21
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	10.2385(4)
b/Å	13.6773(4)
c/Å	14.0356(5)
α/°	69.309(2)
β/°	74.268(2)
γ/°	75.279(2)
U/Å^3	1742.3(1)
Z	2
Radiation (λ/Å)	Mo-Kα (0.71073)
μ/mm^{-1}	1.579
T/K	123(2)
D_c/g cm^{-3}	1.34
Crystal dimensions/mm	0.40 × 0.30 × 0.20
$2\theta_{max}$/°	56.5
No. of reflections recorded	27441
No. of non-equivalent reflections recorded (N_o)	6472
R_{merg}	0.025
No. of parameters refined (N_p)	410
$R1$;[a] wR[b]	0.027, 0.072
Goodness of fit[c]	1.095
Max. shift/e.s.d. in final least-squares cycle	0.000
Final max., min. $\Delta\rho$/e Å^{-3}	0.316, −0.500

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ [for $I > 2\sigma(I)$]. [b] $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$. [c] Goodness of fit $= \{\Sigma[w(|F_o^2| - |F_c^2|)^2]/(N_o - N_p)\}^{\frac{1}{2}}$.

^1H and ^{13}C NMR spectra show the expected resonances for the organic ligands. In the mass spectra of **1** and **2**, the peaks with the highest mass indicate the compounds to be dimeric containing four-membered Ga_2N_2 ring systems. For compound **3** only the monomeric unit is observable. Cryoscopic molecular weight determinations in benzene proved **1**–**3** to be dimeric in solution.

The solid state structure of **3** was investigated by single crystal X-ray analysis and crystal data and data collection parameters are given in Table 1. Suitable crystals were grown in hexane at −30 °C and **3** crystallizes in the triclinic space group $P\bar{1}$. Fig. 1 clearly shows the central four-membered ring. Compound **3** is the first structurally characterized example of a dimeric bisorgano-group 13 azide containing μ-bridging azide ligands. $[(Me_2N)_2GaN_3]_2$ was shown to be dimeric in the solid

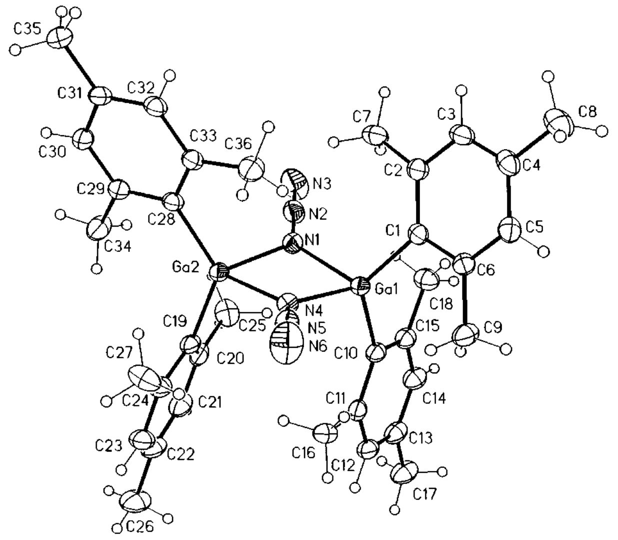

Fig. 1 ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **3**.

Table 2 Selected bond lengths (pm) and angles (°) for **3**

N1–Ga1	204.4(2)	N4–N5	121.9(3)
N4–Ga1	204.8(1)	N5–N6	113.6(3)
N1–Ga2	204.2(2)	Ga1–C1	197.4(2)
N4–Ga2	204.8(2)	Ga1–C10	197.9(2)
N1–N2	122.6(3)	Ga2–C19	197.3(2)
N2–N3	113.3(3)	Ga2–C28	196.7(2)
Ga1–N1–Ga2	102.6(1)	N1–Ga2–N4	76.8(1)
Ga1–N4–Ga2	102.2(1)	C19–Ga2–C28	129.2(1)
N1–Ga1–N4	76.7(1)	C19–Ga2–N1	110.7(1)
C1–Ga1–C10	129.2(9)	C19–Ga2–N4	103.0(1)
C1–Ga1–N1	115.4(1)	C28–Ga2–N1	108.7(1)
C1–Ga1–N4	107.8(1)	C28–Ga2–N4	116.2(1)
C10–Ga1–N1	104.3(1)	N2–N1–Ga2	127.3(2)
C10–Ga1–N4	111.2(1)	N5–N4–Ga2	129.5(2)
N2–N1–Ga1	130.1(2)	N1–N2–N3	179.6(2)
N5–N4–Ga1	127.8(2)	N4–N5–N6	179.6(2)

state, but the ring is formed by two bridging amino groups and the azide ligands are terminally bound to the Ga centers, showing weak interactions with a Ga center of a second molecule, resulting in a polymeric chain structure. While $[Me_2GaN_3]_3$ and $[Et_2GaN_3]_3$ appear to be trimeric in solution, X-ray analysis of $[Me_2GaN_3]_3$ established this compound to be polymeric in the solid state, forming a spiral chain by bridging μ-N_3 units.[8] Other structurally characterized gallium azides are $[ClHGaN_3]_4$,[4f] containing an azide bridged, eight-membered Ga_4N_4-ring system, and $Na[GaN_3]_4$, showing a four membered ring system with two bridging azide groups and one Ga and Na atom $[NaGa(\mu\text{-}N_3)_2]$.[4g] In addition, the structures of two Ga bis-azides[4d,7b] and base stabilized Ga tris-azides[5a,9] have been investigated. $[(N_3)_2Ga\{(CH_2)_3NMe_2\}]$ was described as dimeric in the solid state,[9a] but the two Ga–N distances within the four-membered ring system differ significantly (195 and 245 pm), indicating one Ga–N σ-bond and a second weak donor interaction between the azide unit and Ga. By contrast, the Ga–N bond distances (Table 2) within the non-planar four-membered ring (torsion angle Ga1–N1–Ga2–N4 10.1°) in **3** are 204.4 and 204.8 pm. This agrees well with values found in $[ClHGa(N_3)]_4$ (191.8–206.3 pm) and $(Me_2GaN_3)_\infty$ (205.1 pm) with bridging azide groups, but is longer than in Ga azides with terminal bound N_3-units. The average Ga–C bond length (197.3 pm) and C–Ga–C bond angle (129.2°) are almost the same as in the starting compound $(Mes_2GaCl)_2$ (197.2 pm and 126.6°).[10] The average Ga–N–Ga and N–Ga–N bond angles are 102.4 and 76.8°, respectively, while the average N–N–Ga angle is 128.7(2)°. As expected, two different distances were found in the azide unit (average 113.5 and 122.3 pm). The shorter distance corresponds to the terminal N_2 moiety, indicating a considerably activated azide towards N_2 elimination.

Currently, we are investigating the thermal behavior of the compounds with respect to their decomposition to GaN. In particular, **1** and **2**, which are liquid at room temperature and have a proton in the β-position to facilitate β-H elimination, promise to be interesting starting compounds for MOCVD reactions.

Experimental

General

All manipulations were performed in a glove-box under N_2-atmosphere or by standard Schlenk techniques. Solvents were carefully dried over sodium/potassium alloy and distilled under dry N_2. NaN_3 was purchased from Aldrich and dried at 80 °C (10^{-3} mbar, 12 h). *n*-Bu_2GaCl and *s*-Bu_2GaCl were prepared by standard ligand exchange reactions between R_3Ga (R = *n*-Bu, *s*-Bu) and $GaCl_3$. Mes_2GaCl was prepared by a literature method.[11] Infrared spectra were recorded in Nujol between KBr plates with a Nicolet Magna 550 and are reported in cm^{-1}. A Bruker AMX 300 spectrometer was used for NMR spectroscopy. ^1H and $^{13}C\text{-}\{^1H\}$ spectra were referenced to internal C_6D_5H (δ_H 7.154, δ_C 128.0). Mass spectra were recorded on a VG Masslab 12-250 spectrometer in the electron ionisation mode at 20 eV. Melting points were observed in sealed capillaries and were not corrected. Elemental analyses were performed at the Mikroanalytisches Labor der Universität Bonn. Cryoscopic molecular weight determinations were performed in benzene.

Synthesis of compounds 1–3

Finely ground NaN_3 (0.39 g, 6 mmol) and the corresponding bisorganogallium chloride (5 mmol) were combined in toluene (60 mL) and stirred at room temperature for 18 h. The resulting suspension was filtered and the solvent removed leading to light yellow liquids (**1** and **2**), and a colorless solid (**3**). Compounds **1** and **2** were purified by distillation at 10^{-3} mbar, while **3** was dissolved in pentane, filtered and stored at −30 °C, resulting in the formation of colorless crystals.

Characterization data

***n*-Bu_2GaN_3 1.** Bp 125–130 °C (10^{-3} mbar) (Found: C, 42.11; H, 7.83; N, 18.02. $C_8H_{18}GaN_3$ requires C, 42.53; H, 7.98; N, 18.61%); molecular weight (benzene) 461 g mol^{-1}; ^1H NMR (300 MHz, C_6D_6, 25 °C) δ 0.85 (t, $^3J_{HH} = 7$, 2H, $GaCH_2$), 0.95 (t, $^3J_{HH} = 7$, 3H, CH_3), 1.40 (m, $^3J_{HH} = 7$, 2H, $CH_3CH_2CH_2$), 1.71 (m, $^3J_{HH} = 7$ Hz, 2H, CH_3CH_2); ^{13}C NMR (75 MHz, C_6D_6, 25 °C) δ 12.1 (β-CH_2), 14.3 (γ-CH_2), 28.3 (δ-CH_3); *m/z* 424 $[M(dimer) - N_2]^+$, 410 $(M - N_3)^+$, 395 $[M - (n\text{-}Bu)]^+$, 183 $(n\text{-}Bu_2Ga)$, 57 $(n\text{-}Bu)^+$; IR (Nujol, cm^{-1}): 2110 $[\nu_{as}(N_3)]$, 1258 $[\nu_s(N_3)]$.

***s*-Bu_2GaN_3 2.** Bp 132–140 °C (10^{-3} mbar) (Found: C, 41.93; H, 7.87; N, 18.13. $C_8H_{18}GaN_3$ requires C, 42.53; H, 7.98; N, 18.61%); molecular weight (benzene) 467 g mol^{-1}; ^1H NMR (300 MHz, C_6D_6, 25 °C) δ 0.99 (dt, $^3J_{HH} = 7$, $^5J_{HH} = 2$, 3H, CH_3CH_2), 1.24 (m, $^3J_{HH} = 7$, 1H, CH), 1.27 (d, $^3J_{HH} = 7$, 3H, CH_3CH), 1.61 (m, $^3J_{HH} = 7$ Hz, 2H, CH_2); ^{13}C NMR (75 MHz, C_6D_6, 25 °C) δ 14.3 (CH), 15.8 (CH_3CH_2), 17.7 (CH_3CH), 28.7 (CH_2); *m/z* 410 $[M(dimer) - N_3]^+$, 395 $[M - (s\text{-}Bu)]^+$, 225 $(M/2)^+$, 183 $(s\text{-}Bu_2Ga)$, 57 $(s\text{-}Bu)^+$; IR (Nujol, cm^{-1}): 2111 $[\nu_{as}(N_3)]$, 1284 $[\nu_s(N_3)]$.

$[Mes_2GaN_3]_2$ 3. Mp 182 °C (Found: C, 60.95; H, 6.12; N, 11.82; $C_{36}H_{44}Ga_2N_6$ requires C, 61.77; H, 6.29; N, 12.01%);

molecular weight (benzene) 681 g mol^{-1}; ^{1}H NMR (300 MHz, C_6D_6, 25 °C) δ 2.10 (s, 3H, *p*-CH_3), 2.38 (s, 6H, *o*-CH_3), 6.69 (s, 2H, *m*-H); ^{13}C NMR (75 MHz, C_6D_6, 25 °C) δ 21.5 (*p*-CH_3), 24.5 (*o*-CH_3), 120.6 (*ipso*-C), 139.4 (*m*-C), 140.9 (*p*-C), 143.8 (*o*-C); *m*/*z* 349 $[M/2]^+$, 321 $[(M/2) - N_2]^+$, 307 (Mes_2Ga). IR (Nujol, cm^{-1}): 2122 [$\nu_{as}(N_3)$], 1291 [$\nu_s(N_3)$].

Single-crystal X-ray diffraction analysis of 3

X-Ray quality crystals of **3** were grown in hexane at −30 °C. Crystallographic data are summarized in Table 1 with selected structural parameters in Table 2. Fig. 1 shows an ORTEP diagram of the solid state structure of **3**. Data were collected on a Nonius Kappa-CCD diffractometer. The structure of **3** was solved by direct methods (SHELXS-90/96)[12] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).[13] An extinction correction was applied.

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See http://www.rsc.org/suppdata/dt/1998/4127/ for crystallographic files in .cif format.

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