Tetraazido Complexes of Aluminium, Gallium, and Indium

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The new tetraazido complexes of aluminium, gallium, and indium $[thf_2Na][thf_2Al(N_3)_4]$ (**1**), $[py_2Na][py_2In(N_3)_4]$ (**2**), and $Na[Ga(N_3)_4]$ (**3**) have been synthesized from MCl_3 and NaN_3 by salt metatheses and characterized by X-ray diffraction analysis. In compounds **1** and **2**, the Group 13 metal atom and the sodium atom are each hexacoordinated by four azido groups and two additional solvent molecules. The azido groups act as μ(1,3)-bridging ligands between the Group 13 metal and sodium, thereby forming network structures. In contrast, complex **3** is solvent-free and exhibits a tetracoordinated gallium centre and a heptacoordinated sodium atom. The structure of **3** has also been investigated by means of X-ray powder data and the Rietveld method and the results are compared with the single-crystal data.

Introduction

Organometallic and inorganic azide derivatives of the Group 13 metals (M = Al, Ga, In), including the compounds $[X_2Ga(N_3)]_3$ (R = Et, H, Cl),[1] $[(\mu\text{-}NMe_2)\text{-}Ga(N_3)(NMe_2)]_2$,[2] $(N_3)_aM[(CH_2)_3NMe_2]_{3-a}$ (M = Al, Ga, In; a = 1, 2), and $Ga(N_3)_3(L)$ (L = NMe_3, NEt_3)[3] have been studied as precursors of the respective Group 13 nitride materials. Gallium nitride, as well as the ternary alloys $Al_xGa_yIn_zN$ ($x + y + z = 1$), are wide-band-gap semiconductors that exhibit a unique combination of properties making them useful for a number of advanced applications in optoelectronics and various other fields.[4] The azido unit would appear to be an interesting choice for the introduction of the nitrogen component in metal nitride synthesis. The commonly used precursors, e.g. MR_3 and ammonia or alkylamines, contain M−C, C−H, N−H, and N−C bonds, fragmentation of which leads to the incorporation of impurities into the nitride material. However, a drawback to the use of metal azide derivatives as precursors of nitrides is their inherent tendency to undergo exothermic decomposition. Nitrogen-rich compounds such as $[H_2Ga(N_3)]_3$ and $Ga(N_3)_3L_n$ may even detonate under certain circumstances.[1][5] Intramolecular adduct formation has, however, proved to be a reliable method for stabilizing Group 13 metal azides against explosive decomposition.[3] In the context of potential applications as electronic materials, the purity of nonexplosive azide precursors with regard to contamination by dangerous explosive species is a very important issue. We were thus interested in characterizing all the possible species involved when Group 13 metal halides are treated with alkali azides, e.g. NaN_3. We report herein on the synthesis and structural chemistry of the previously unknown tetraazido complexes of aluminium, gallium, and indium, **1−3**.

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Syntheses and Properties

During the course of our investigations of Group 13 metal azide complexes containing various donor ligands $M(N_3)_3L_n$ (L = NR_3, n = 1; L = py, n = 3), the three new complexes of aluminium, gallium, and indium **1−3** have been isolated (Scheme 1). When the Group 13 chlorides MX_3 are treated with precisely stoichiometric amounts of sodium azide in a toluene/pyridine mixture, the tripyridine compounds $M(N_3)_3py_3$ are formed, which can be isolated in high yields.[3b,3c,3d,6] However, only use of a significant excess of sodium azide (> 5 equiv.) and an appropriate combination of solvent and additional ligands selectively gives **1−3**. A large excess of sodium azide is generally required in order to avoid halide contamination of Group 13 azide derivatives due to incomplete Cl^-/N_3^- exchange.[6] The donor-stabilized triazidogallium complexes $Ga(N_3)_3(NR_3)$ (**4**) are thus typically synthesized from compound **3** as an (isolated) intermediate. This intermediate is also important in the synthesis of the donor-free parent compound $[Ga(N_3)_3]_\infty$ (**5**), which can be extracted with toluene as an unstable thf adduct $Ga(N_3)_3(thf)_x$, in a similar manner as in the synthesis of compound **4**.[6] However, the isolation of the pure tetraazides **1−3** requires special precautions since they are explosive compounds and will detonate spontaneously when heated above 200°C at rates greater than 2 K/min, or when exposed to mechanical shock. The enthalpy of detonation of compound **2** was measured as 2.3 $MJ\cdot kg^{-1}$ (607 $kJ\cdot mol^{-1}$) using a special sealed calorimeter.[7] This value compares well with that of 1.54 $MJ\cdot kg^{-1}$ (450 $kJ\cdot mol^{-1}$) found for $Pb(N_3)_2$.

Crystal Structures

Different representations of the structure of **1** in the solid state, showing the coordination at the metal centres as well as the packing in the crystal, are given in Figures 1a−b. Compound **1** crystallizes from saturated thf solutions in the triclinic space group $P\bar{1}$. Each metal cation is octahedrally coordinated by four azido groups in equatorial positions

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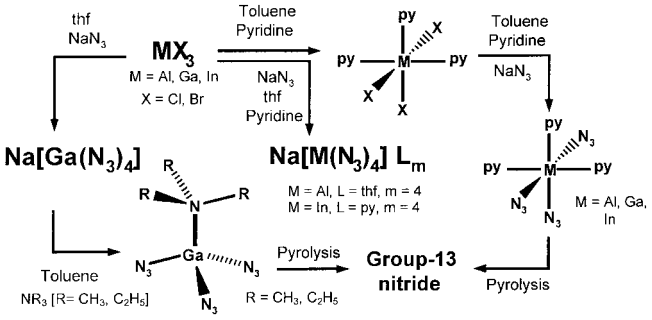

Scheme 1. Synthesis and chemistry of donor-stabilized triazido complexes and tetraazido complexes

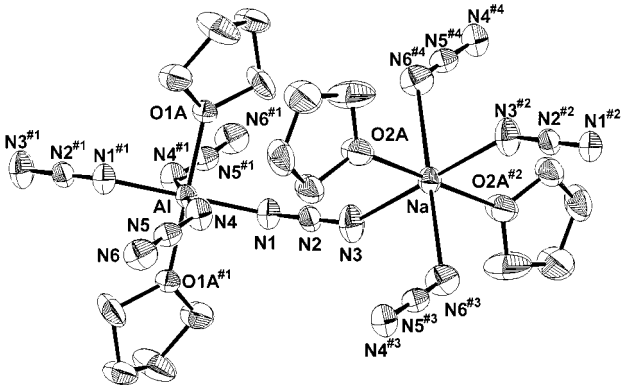

Figure 1a. Perspective view of the structure of **1** showing the coordination spheres of the aluminium and sodium atoms (ZORTEP[15] plot with 50% probability thermal ellipsoids); selected bond lengths [pm] and angles [°]: Al−N1 195.0(2), Al−N4 194.1(1), Al−O1A 201.3(9), Na−N3 249.9(2), Na−N6$^{\#3}$ 255.3(2), Na−O2A 235.9(1), N1−N2 119.7(2), N2−N3 114.2(2), N3−N4 119.2(2), N5−N6 114.7(2); Al−N1−N2 129.3(1), N1−N2−N3 175.3(2), Al−N4−N5 132.8(1), N4−N5−N6 176.0(2), Na−N3−N2 150.0(2), Na−N6$^{\#3}$−N5$^{\#3}$ 127.7(1)

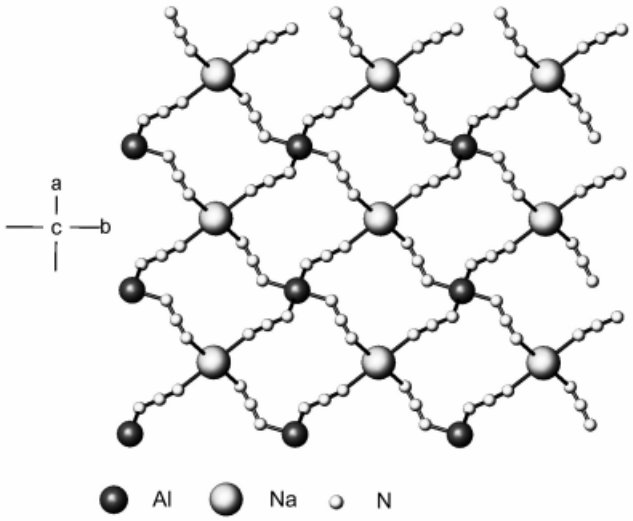

Figure 1b. Packing diagram of compound **1** in the solid state (projection along the *c* axis on the *ab* plane) showing an almost flat, two-dimensional network built-up of sodium and aluminium atoms interconnected by azido groups; the thf ligands, which are stacked between the metal azide layers, are omitted for the sake of clarity

and two apical thf molecules. The azido groups act as μ(1,3) bridging ligands between the aluminium and sodium octahedra, thereby forming a two-dimensional layer structure with the metal atoms and the azido groups in the *ab* plane of the unit cell. The thf molecules show a disordering, which could not be resolved. These positions were refined by assuming equivalent interatomic distances. The metal−O bond lengths were fixed at 201.3 pm for aluminium and at 235.9 pm for sodium. The Na−N bond lengths were found to be very similar to those in compound **3** and other related ionic sodium azides.[8][9] The Na−N_α−N_β angles were found to vary between 127.6(1)° (Na−N6−N5) and 150.0(2)° (Na−N3−N2). The corresponding values at the aluminium centre range from 129.3(1)° (Al−N1−N2) to 132.8(1)° (Al−N4−N5), which are similar to the angles found in other covalent metal azides and are thus indicative of sp^2 hybridization at the N_α atoms. An alternation of the N−N bond lengths, i.e. a longer N_α−N_β bond [119.7(2) pm and 119.2(2) pm] and a shorter N_β−N_γ bond [114.2(2) pm and 114.7(2) pm] is found, which is a typical feature of covalent azides.[10a,10b] These features indicate the presence of a more covalently bonded tetraazidoaluminium moiety and a more ionic interaction with the sodium cation. Compound **1** consists of layers made up of sodium and aluminium atoms interconnected by azido groups, which are oriented parallel to each other in the *ab* plane of the unit cell.

Representations of the structure of compound **2** in the solid state, showing the coordination at the two metal centres as well as the packing in the crystal, are given in Figures 2a−c. Compound **2** is obtained from pyridine solution in the form of needles, which are monoclinic with space group *C*2/*c*. As in the case of **1**, the structure in the crystal resembles that of a coordination polymer. The metal centres are surrounded by four azido groups and two pyridine ligands in an octahedral arrangement. Each indium atom is connected to four sodium atoms through the terminal nitrogen atoms (N_α or N_γ) of the azido (N_α−N_β−N_γ) groups and vice versa. At the indium centre, the azido groups occupy the *equatorial* positions and the pyridine ligands the *apical* positions. At the sodium centre, the pyridine ligands are *cis* orientated. The general features of the azide coordination and bonding properties compare well with the situation discussed for compound **2** and with the situations in other known covalent indium azides.[3b] The M−N_{py} distances measure 230.7(2) pm for M = In and 247.5(2) pm for M = Na. The In−N_{py} values are close to those in the related triazido compound $In(N_3)_3(py)_3$.[3b] The organic ligands do not show any unusually short intra- or intermolecular distances or any remarkable angles. Indeed, the structural parameters of compound **3** are rather similar to those of the isostructural compound $[(py)_2Na][(py)_2Cr(N_3)_4]$.[8] Because of the mutual *cis* orientation of the py ligands at the sodium atom, in contrast to the *trans* orientation of the thf ligands in the case of the related aluminium compound **1**, complex **2** forms a different type of coordination network. Whereas in **1** each metal atom in the layers parallel to the *ab* plane is interconnected through the

μ(1,3) azido groups (Figure 1b), in **2** the metal atoms in the layers parallel to the *ac* plane are only partly interconnected through μ(1,3) groups (Figure 2b). Every second sodium centre is connected through μ(1,3) azide bridges with the adjacent layers above and below (Figure 2c). Thus, a three-dimensional network is built-up. The py ligands occupy the holes in the packing in a similar fashion as the thf ligands of complex **1**.

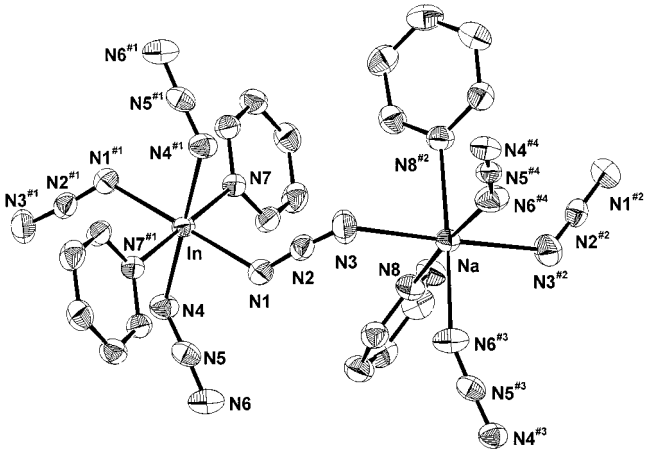

Figure 2a. A perspective view of the structure of **2** showing the coordination spheres of the indium and sodium atoms (ZORTEP plot with 50% probability thermal ellipsoids); selected bond lengths [pm] and angles [°]: In−N1 218.0(2), In−N4 222.6(2), In−N7 230.7(2), Na−N3 253.2(2), Na−N6 247.8(2), Na−N8 247.5(2), N1−N2 117.5(3), N2−N3 116.0(3), N3−N4 117.4(3), N5−N6 159.3(3); In−N1−N2 124.8(2), N1−N2−N3 176.2(2), Al−N4−N5 121.6(2), N4−N5−N6 176.5(2), Na−N3−N2 128.2(2), Na−N6−N5 151.6(2)

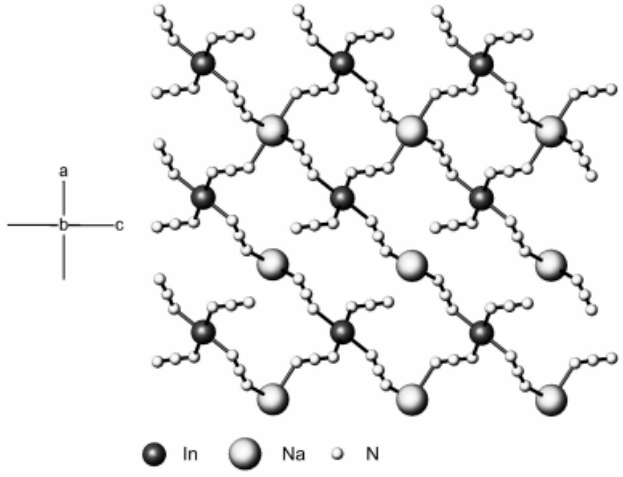

Figure 2b. Packing diagram of compound **2** in the solid state (projection along the *b* axis on the *ac* plane) showing a three-dimensional network with wave-like (in direction *b*) areas built-up of sodium and indium atoms interconnected by azido groups; the pyridine ligands, which are stacked between the metal azide layers, are omitted for the sake of clarity

Representations of the structure of **3** in the solid state, showing the coordination at the metal centres and the packing in the crystal, are given in Figures 3a−c. In contrast to **1** and **2**, compound **3** crystallizes from saturated THF solutions as a solvent-free complex in the orthorhombic

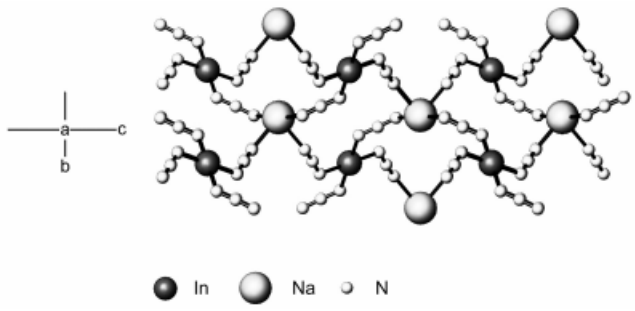

Figure 2c. Packing diagram of compound **2** in the solid state (projection along the *a* axis on the *bc* plane) showing the wave-like (in direction *b*) network built-up of sodium and indium atoms interconnected by azido groups; the pyridine ligands, which are stacked between the metal azide layers, are omitted for the sake of clarity

space group $P2_12_12_1$. The gallium atom is coordinated by azido groups in a tetrahedral fashion. Four of the six N−Ga−N angles are quite close to the ideal angle of 109°, while two show a stronger deviation [N10−Ga−N7: 93.7(1)°, N1−Ga−N7: 116.5(1)°]. The Ga−N bond lengths measure about 190(±2) pm, values that compare well with the bond lengths in other tetracoordinated gallium azides such as $(N_3)_2Ga[(CH_3)_3NMe_2]$ and $Ga(N_3)_3(NR_3)$.[5][6] The bending of the $Ga-N_\alpha-N_\beta$ units of 113.2(2)° (Ga−N1−N2) and 131.1(2)° (Ga−N7−N8) again indicates sp^2-hybridization at the N_α atom, which is typical for covalent metal azides. Three azido groups simultaneously bridge two different sodium atoms: one $Ga-N_\alpha-Na$ bridge and one head-to-tail $Ga-N_\alpha-N_\beta-N_\gamma-Na$ bridge. The azido group N10−N11−N12 is N_α-connected through N10 to the same sodium atom as N7. Interestingly, this azido group is *not* coordinated through the terminal atom N12, which is manifested in a higher temperature factor for this nitrogen. The sodium atoms are surrounded by seven azido groups, resulting in a rather asymmetric pentagonal bipyramid. Four azido groups bridge gallium and other sodium ions through their terminal nitrogen atom N_γ, while two azido groups are N_α-connected to gallium and N_γ-connected to other sodium ions. The N10−N11−N12 azide is only N_α bridged to gallium through N10. The $Na-N_{azide}$ bond lengths measure 250−260 pm, except for the Na−N7 bond, which is unusually long at 274.4(3) pm, probably as a result of steric requirements arising from the packing in the crystal. The series of $Na-N_\alpha-N_\beta$ angles are distinctly nonuniform and vary from 113.2(2)° (Na−N1−N2) to 170.5(3)° (Na−N6−N5), as expected for more ionic interactions. Each azido group exhibits the expected alternation in the N−N bond lengths, which is more pronounced than in the aluminium compound **1**, e.g. a short N2−N3 distance of 113.4(3) pm and a long N1−N2 distance of 122.9(3) pm. In this respect, the azide bonding to the gallium centre is rather similar to that in the covalent, neutral triazido congeners $Ga(N_3)_3(NR_3)$.[5][11] The packing of compound **3** (Figure 3c) can also be rationalized as a layer structure with cross-linking through μ(1,3) azido groups. The density of the packing is much higher than that in **1** and **2** due to the absence of the solvent ligands thf or py. As discussed above,

the N10−N11−N12 azide does not act as a μ(1,3) bridge. In the projection of Figure 3b, these groups point upwards and downwards along the *c* direction in an alternating fashion, into the empty space between the metal azide layers parallel to the *ab* plane.

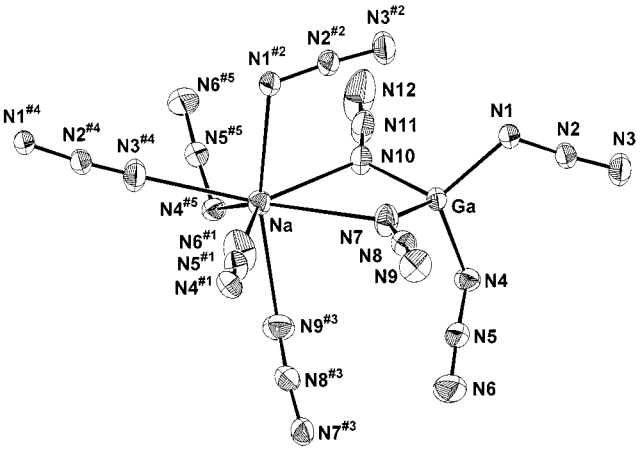

Figure 3a. A perspective view of the structure of **3** showing the coordination spheres of the gallium and sodium atoms (ZORTEP plot with 50% probability thermal ellipsoids); selected bond lengths [pm] and angles [°]: Ga−N1 189.6(2), Ga−N4 190.9(3), Ga−N7 190.9(2), Ga−N10 189.7(2); Ga−N1−N2 113.2(2), Ga−N4−N5 118.8(2), Ga−N7−N8 131.1(2), Ga−N10−N11 126.1(2); Na−$N1^{\#2}$ 251.8(3), Na−$N3^{\#4}$ 254.6(3), Na−$N4^{\#5}$ 258.5(3), Na−$N6^{\#1}$ 250.0(3), Na−$N9^{\#3}$ 252.3(3), Na−N7 274.4(3), Na−N10 258.9(3); N1−Ga−N4 110.1(1), N1−Ga−N7 116.5(1), N1−Ga−N10 112.6(1), N10−Ga−N4 111.6(1), N10−Ga−N7 93.7(1), N4−Ga−N7 111.5(1)

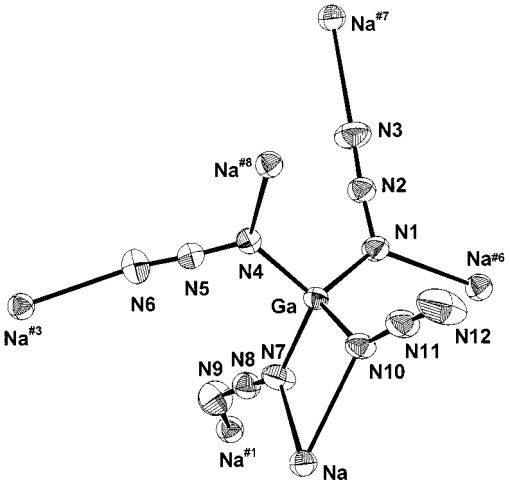

Figure 3b. A perspective view of the structure of **3** showing the interconnection between the sodium atoms and the azido groups (ZORTEP plot with 50% probability thermal ellipsoids); the azido group terminal atom N12 is not coordinated to any sodium atoms

X-ray Powder Diffraction and Rietveld Analysis of 3

As described above, compound **3** is a valuable intermediate in the synthesis of donor-stabilized gallium triazides $Ga(N_3)_3L_m$ (**4**) and other gallium azides, even for the parent

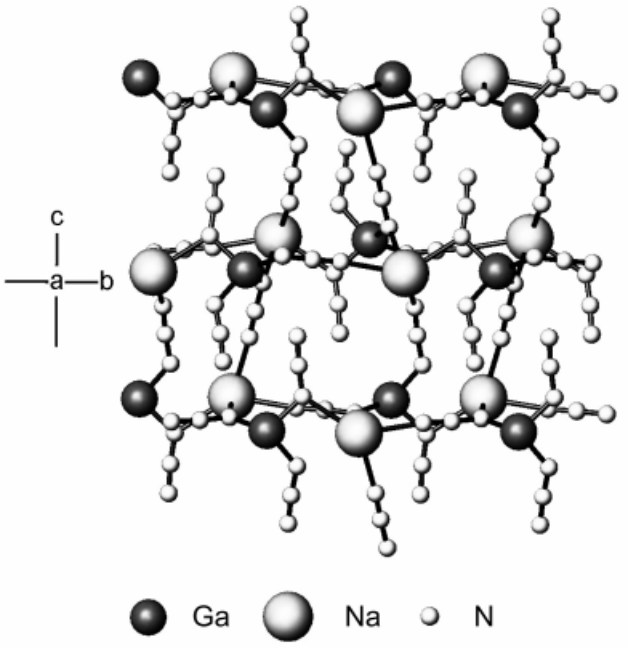

Figure 3c. Packing diagram of compound **3** in the solid state (projection along the *a* axis on the *bc* plane) showing a three-dimensional network built-up of sodium and gallium atoms interconnected by azido groups

compound $[Ga(N_3)_3]_\infty$ (**5**), which can all serve as percursors in the preparation of nanocrystalline GaN powders.[5] To verify the purity of the compounds **1−5**, it is necessary to check for the presence of sodium azide, gallium chloride, sodium chloride, and other possible inorganic impurities and side products. Reliable elemental analysis data are very difficult to obtain on a routine basis because of the explosive nature of the compounds. Consequently, we investigated X-ray powder diffraction patterns in detail using the Rietveld method so as to establish a routine tool to check the purities of **1−5** that could also be used for similar metal azide complexes and related problems. Compound **3** was selected for this study, because it is a likely and dangerous impurity in compounds of the type $Ga(N_3)_3L_m$ (**4**). Compound **3** is usually obtained as a microcrystalline powder. Figure 4 shows the measured and calculated XRD patterns. The difference curve exhibits only small deviations, thus indicating a very good agreement. The reflections induced by the beryllium window were fitted independently and have no influence on the overall structure refinement of the tetraazide. The general features of the structure of **3** are reproduced using the powder data, but details concerning bond lengths and angles differ to some extent. For example, the environment at the gallium centre shows a more marked deviation from tetrahedral in the case of the powder data and the obtained $Ga-N_{azide}$ bond lengths, which range from 201.4 pm to 216.2 pm, are longer. The $Ga-N_\alpha-N_\beta$ angles are close to the single-crystal data to within ±5°, with the exception of the Ga−N1−N2 angle where the powder data value of 130.5° is unusually large as compared with the single-crystal value of 113.2(2)°. Other deviations become apparent upon analyzing the bond lengths and angles in the

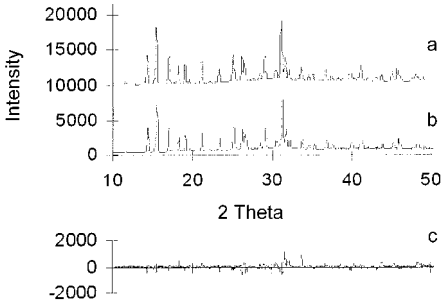

Figure 4. Detail of the X-ray patterns obtained for $NaGa(N_3)_4$ (**3**): (a) experimental data obtained with an aluminium sample holder and a beryllium window, (b) calculated data for the Rietveld structure refinement, (c) difference curve between observed and calculated data

plane containing the Na, Ga, N7, and N10 atoms. While the single-crystal data show the largest angle of 103.1(1)° located at N10 (Ga−N10−Na) and the smallest angle of 62.68(8)° at the Na atom (N7−Na−N10), the powder data show a largest angle of 106.3° for N7−Ga−N10 and a smallest angle of 81.3° at the Na centre (N7−Na−N10). Nevertheless, the constitution of the compound, the coordination features at the metal centres, and the packing mode in the crystal are reproduced quite well using X-ray powder diffraction analysis with Rietveld refinement. The deviations of the more specific structural parameters from the single-crystal reference (bond lengths and angles) are most likely attributable to the intrinsic limitations of the powder diffraction data. Moreover, the conditions of the two experiments were somewhat different. The powder data had to be collected at room temperature, while the single-crystal data were obtained at 203 K. Because of this difference in the conditions, a temperature-dependent phase transition also had to be taken into account. However, in view of the explosive nature of pure crystalline **3**, we decided not to pursue this matter further. Anyway, X-ray powder diffraction in combination with Rietveld analysis of the diffraction pattern constitutes a reliable method for establishing the identity and purity of compounds such as **3** and **4**, especially if single crystals are difficult to obtain. This is particularly true for $[Ga(N_3)_3]_\infty$ (**5**), the structure of which is still unknown due to the very poor X-ray powder diffraction data obtained to date. The work reported herein has shown that samples of **5** synthesized according to ref.[6] are essentially free of compound **3** and other likely by-products.

Experimental Section

General Procedures: All manipulations were performed using thoroughly oven-dried reaction vessels (Schlenk techniques) under an inert atmosphere of purified argon in a glove box (argon; O_2 and H_2O < 1 ppm). Solvents were dried and distilled according to standard procedures[12] and were stored over 4 Å molecular sieves (residual water < 1 ppm, Karl-Fischer). − The IR spectra were recorded in solution (thf, toluene, pyridine) using 0.1 mm CaF_2 or NaCl cells or freshly prepared KBr plates with a Perkin−Elmer 1650 FT-IR or a Bruker IFS-66 spectrometer. − Elemental analyses were provided by the Microanalytical Laboratory of the Chemical Institute at the University of Heidelberg. The metal content was determined by back-titration of excess EDTA solution (complexometric determination with Titriplex®, Merck KGaA, Darmstadt). − Melting points (uncorrected) were determined with a Gallenkamp hot-air melting point apparatus or a Seiko TG/DTA 6300

Table 1. Crystallographic data for the compounds **1**, **2**, and **3**

Compound	**1**	**2**	**3**
Empirical formula	$C_{16}H_{32}AlN_{12}NaO_4$	$C_{20}H_{20}InN_{16}Na$	$GaN_{12}Na$
Molecular mass [g mol^{-1}]	506.48	622.33	260.83
Crystal system	triclinic	monoclinic	orthorhombic
Space group (No.)	$P\bar{1}$ (2)	$C2/c$ (13)	$P2_12_12_1$(19)
a [Å]	7.728(4)	15.442(8)	7.011(4)
b [Å]	9.141(5)	10.432(5)	9.666(5)
c [Å]	9.169(5)	15.966(8)	12.320(6)
α [°]	75.34(5)	90	90
β [°]	88.90(5)	90.28(3)	90
γ [°]	89.16(5)	90	90
V [Å^3]	626.6(6)	2572.0(2)	834.9(8)
Z	2	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.343	1.607	2.075
Temperature [K]	203(2)	203(2)	203(2)
μ [mm^{-1}]	0.164	0.980	3.330
θ range for collection [°]	2.30−26.99	2.36−30.00	2.68−34.99
$h/k/l$ ranges	−9/9, −11/11, 0/1	−21/21, 0/14, 0/22	0/11, 0/15, 0/19
F(000)	268	1248	504
Crystal size [mm]	0.4 × 0.2 × 0.2	0.6 × 0.3 × 0.3	0.45 × 0.25 × 0.2
λ [Å]	0.71073	0.71073	0.71073
No. reflections collected	2748	3745	2107
No. independent reflections	2733 [R_{int} = 0.0408]	3745 [R_{int} = 0.0000]	2106 [R_{int} = 0.0000]
Transmission (min/max)	(0.766/0.998)	(0.881/1.000)	(0.862/0.999)
Refinement method	full-matrix least-squares on F^2		
Data/restraints/parameters	2732/42/247	3745/0/177	2106/0/128
Final R indices [$I > 2\sigma(I)$] $R1/wR2$	0.0390/0.01017	0.0275/0.0617	0.0275/0.0683
R indices [all data] $R1/wR2$	0.0496/0.1093	0.0426/0.0677	0.0368/0.0721
Goodness of fit on F^2	1.053	1.024	1.065
Residual electron density [eÅ^{-3}]	0.379/−0.204	0.348/−0.863	0.353/−0.794

SII thermobalance (DTA data). ***NOTE:*** Working with the described Group 13 azides requires strict adherence to special security precautions, i.e. the use of protective face shields, special gloves (metal net), and thick leather body protection. The compounds are shock-sensitive and detonate upon rapid heating (> 2 K/min) to temperatures above 200°C.

[Bis(tetrahydrofuran)sodium] [Tetraazidobis(tetrahydrofuran)aluminate], [thf_2Na][$thf_2Al(N_3)_4$] (1): A solution of anhydrous, freshly sublimed $AlCl_3$ (0.75 g, 5.63 mmol) in 25 mL of thf was slowly added to a suspension of sodium azide (1.45 g, 22.30 mmol) in 25 mL of THF at −78°C. After allowing the mixture to warm to room temperature, it was stirred for 15 h, then filtered, and the filtrate was concentrated to dryness in vacuo. The product was obtained in the form of colourless crystals. Yield: 2.43 g (4.8 mmol, 85.3% based on $AlCl_3$). − IR (KBr): $\tilde{\nu}(N_3)_{max}$ = 2122 cm^{-1} (vs), 2037 (vs), 1261 (w). − ***NOTE:*** The substance detonates vigorously on rapid heating (> 2 K/min) beyond 220°C! Decomposition at 200°C without melting. − $C_{16}H_{32}AlN_{12}NaO_4$ (506.48): calcd. Al 5.33; found Al 6.01. This large discrepancy may be attributed to evaporation of the coordinated thf and also to the very small amount of sample used for the analysis in view of the explosion risk.

[(Dipyridine)sodium] [Tetraazido(dipyridine)indate], [py_2Na][$py_2In(N_3)_4$] (2): A solution of anhydrous, freshly sublimed $InCl_3$ (1.0 g, 4.52 mmol) in 20 mL of pyridine was slowly added to a suspension of 1.3 g (20 mmol) of sodium azide in 10 mL of pyridine at −78°C. After allowing the mixture to warm to room temperature, it was stirred for 15 h, then filtered, and the filtrate was concentrated to dryness in vacuo. The product was obtained in the form of colourless crystals. Well-defined single crystals could be obtained by warming a saturated solution to 80°C and slowly cooling to room temperature. Yield: 2.43 g (3.93 mmol; 87% based on $InCl_3$). − IR (KBr): $\tilde{\nu}(N_3)_{max}$ = 2083 cm^{-1} (sh), 2067 (vs), 2037 (vs). − ***NOTE:*** The substance detonates vigorously on rapid heating (> 2 K/min) above 250°C! Decomposition at 200°C without melting. − $C_{20}H_{20}InN_{16}Na$ (622.33): calcd. C 38.60, H 3.24, N 36.01, In 18.45; found C 37.73, H 3.41, N 32.90, In 20.20.

Sodium Tetraazidogallate, Na[$Ga(N_3)_4$] (3): A solution of anhydrous, freshly sublimed $GaCl_3$ (1.05 g, 5.96 mmol) in 15 mL of thf was slowly added to a suspension of sodium azide (1.47 g, 22.61 mmol) in 25 mL of thf at −78°C. After allowing the mixture to warm to room temperature, 50 mL of toluene was added and the resulting solution was stirred for 15 h. It was then filtered and the filtrate was concentrated in vacuo. The product was obtained in the form of colourless crystals. Yield: 1.43 g (5.48 mmol; 92.0% based on $GaCl_3$). M.p. 122°C. − IR (KBr): $\tilde{\nu}(N_3)_{max}$ = 2094 cm^{-1} (sh), 2075 (s), 2064 (vs). − ***NOTE:*** The substance detonates vigorously on fast heating (> 2 K/min) above 150°C! − $GaN_{12}Na$ (260.83): calcd. Ga 26.73; found Ga 27.21.

X-ray Structure Determination: Experimental details relating to the X-ray crystal structure determinations of **1**, **2**, and **3** are listed in Table 1. Intensity data were collected with a Siemens−Stoe AED2 four-circle diffractometer using Mo-K_α radiation in ω-scan mode; an absorption correction was applied on the basis of φ scans. The structures were solved by direct methods (SHELXS-86)[13] and refined by full-matrix least-squares methods based on F^2 using all measured reflections (SHELXL-93)[13] with anisotropic temperature factors for all nonhydrogen atoms. X-ray powder diffraction data were collected with Cu-$K_{\alpha1/2}$ radiation employing a Siemens D500 instrument equipped with a secondary monochromator and a scintillation counter. In Table 2, the crystallographic data and parameters relating to the refinement are summarized. Data were collected in the Θ/2Θ mode with a step width of 0.02° and 15 s per step. The powder sample of **3** was carefully prepared in an aluminium sample holder for bulk measurements, which was covered by a beryllium window (0.25 mm) and sealed with epoxy resin to prevent decomposition by air or moisture. The measured data were refined using the program TOPAS.[14] The intensities were corrected for absorption by the beryllium window. The azido groups were defined as rigid bodies with five degrees of freedom (3 translation, 2 rotation). The isotropic temperature factors for sodium (0.5) and nitrogen (2.0) were fixed. The refined temperature factor for gallium was 0.3(1). The obtained R_{Bragg} factor of 3.2, which gives an indication of the refinement quality, is very good. Crystallographic data for the structures of **1**−**3** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-119351, -119352, and -119353. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystallographic data and refinement parameters from XRD powder diffraction analysis of compound **3**

Compound	**3**
Empirical formula	$NaGaN_{12}$
Molecular mass [g mol^{-1}]	260.83
Temperature [K]	293(2)
Crystal system	orthorhombic
Space group (No.)	$P2_12_12_1$ (19)
a [Å]	7.0483(4)
b [Å]	9.6941(4)
c [Å]	12.2983(7)
V [$Å^3$]	840.31(5)
Z	4
2Θ range for collection [°]	10−90
λ [Å] Cu-$K_{\alpha1,2}$	1.540596/1.544410
R_{wp} (all data)	6.9
R_{exp} (all data)	3.2
Goodness of fit	2.2
R_{Bragg}	3.2

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