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Binary Bismuth(III) Azides: $Bi(N_3)_3$, $[Bi(N_3)_4]^-$, and $[Bi(N_3)_6]^{3-}$**

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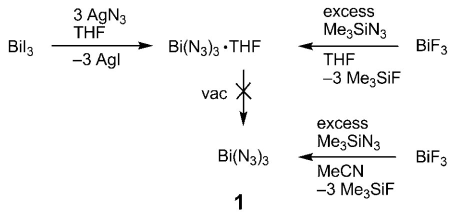
Binary azides of Group 15 elements form a class of highly endothermic compounds. Whereas numerous binary azides of the heavier Group 15 elements arsenic and antimony have been reported and characterized, such as $As(N_3)_3$,[1] $[As(N_3)_4]^+$,[2] $[As(N_3)_4]^-$,[2] $As(N_3)_5$,[3] $[As(N_3)_6]^-$,[2,4] $Sb(N_3)_3$,[1c,5] $[Sb(N_3)_4]^+$,[2] $[Sb(N_3)_4]^-$,[2] $Sb(N_3)_5$,[3] and $[Sb(N_3)_6]^-$,[2,3] no binary bismuth azides have been isolated to date. In the only report on binary bismuth triazide, the authors assumed the formation of $Bi(N_3)_3$ in the reaction of BiI_3 with AgN_3 in acetonitrile on the basis of IR data, but they were not able to isolate $Bi(N_3)_3$ from the reaction mixture.[6]

Crystal structures of binary Group 15 azides are only known for $As^{III}(N_3)_3$,[1c] $Sb^{III}(N_3)_3$,[1c] $[As^V(N_3)_6]^-$,[4] and $[Sb^V(N_3)_6]^-$,[3] but no experimentally observed structural data are available for binary bismuth azides and Group 15 azides of the type $[E^{(III)}(N_3)_4]^-$ (E = pnictogen).

The energetic azido moiety adds about 70 $kcal\,mol^{-1}$ to the energy content of a molecule.[7] Thus we started the search for high-nitrogen-content Bi–N compounds with the synthesis of bismuth triazide. In a second series of experiments, the synthesis of binary tetra-, penta-, and hexaazido bismuth compounds, which are highly endothermic polyazide compounds, was carried out in which the energy content increases with an increasing number of azido ligands. Following our interest in Group 15 element nitrogen compounds with a high nitrogen content,[8] we describe herein the synthesis, isolation, and full characterization of binary tri-, tetra-, and hexaazido bismuth compounds for the first time.

The synthesis of the binary compound $Bi(N_3)_3$ (**1**) was first achieved in the reaction of a solution of bismuth triiodide (BiI_3) in tetrahydrofuran (THF) and neat, carefully dried silver azide (AgN_3) at ambient temperature (Scheme 1). The resulting yellow suspension was stirred for two hours, resulting in an off-white suspension (mixture of AgI and **1**). Removal of solvent and drying in vacuo gives a pale brownish residue. The major problem is the isolation of **1** from this residue. The isolation procedure includes re-suspension and extraction of the residue in THF at 50 °C. Finally, removal of solvent from the filtrate in vacuo gives $Bi(N_3)_3{\cdot}THF$ as a colorless solid in low yields. The solvent molecule cannot be removed at elevated temperatures in vacuo.



Scheme 1. Synthesis of **1**.

An improved synthesis starts from bismuth trifluoride (BiF_3) and an excess trimethylsilylazide (Me_3SiN_3) in THF, and also yields $Bi(N_3)_3{\cdot}THF$ (yield > 98 %). Solvent-free **1** (Figure 1) can be isolated when this reaction is carried out in acetonitrile (Scheme 1). Both pure **1** and **1**·THF are obtained as colorless polycrystalline solids, which are not suitable for single-crystal structure elucidation, and were characterized by IR and Raman spectroscopy (Table 1). Although elemental analysis was successfully carried out for **1**·THF, an attempted elemental analysis for pure **1** resulted in a violent detonation within the apparatus. Both species **1** and **1**·THF are air-stable but hygroscopic and almost insoluble in common polar and unpolar solvents, such as SO_2, C_6H_6, THF, CH_2Cl_2, and CH_3CN. Azide **1**·THF is heat- but not shock-sensitive and is thermally stable up to over 248 °C, whilst shock-sensitive **1** can only be heated to 154 °C. At this temperature, a heavy detonation occurs, releasing a green cloud of smoke.

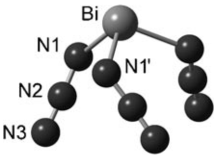


Figure 1. Calculated C_3-symmetric structure of the lowest-lying isomer of **1** in the gas phase. Selected bond lengths [Å] and angles [°]: Bi–N1 2.195, N1–N2 1.234, N2–N3 1.143; N1-Bi-N1′ 98.1, N2-N1-Bi 120.1, N3-N2-N1 175.5.

Two synthetic routes are feasible to isolate salts containing the binary $[Bi^{III}(N_3)_4]^-$ ion (Figures 2 and 3). 1) $(PPh_4)[Bi(N_3)_4]$ (**2**) is readily obtained in the reaction of **1**·THF with one equivalent of $(PPh_4)N_3$ in either THF, CH_2Cl_2, or CH_3CN, yielding yellow suspensions from which **2** was isolated as crystalline material (yield > 95 %) in THF or CH_3CN, whereas **2**·CH_2Cl_2 was isolated from the CH_2Cl_2 solution. The dichloromethane can be completely removed by prolonged drying in vacuo at 60 °C (yield > 95 %). The use

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Table 1: Selected IR/Raman data [cm^{-1}] and approximate assignment,[a] melting points/decomposition temperature [°C], and selected NPA partial charges q [*e*].[b]

	$Bi(N_3)_3$ (**1**)	$(PPh_4)[Bi(N_3)_4]$ (**2**)	$(PPh_4)_3[Bi(N_3)_6]$(**3**)
$\tilde{\nu}_{NN,as,ip}$	2118(m)/2115(4)	2055(m,br)/2086(6)	2055(m)/2063(2)
$\tilde{\nu}_{NN,as,op}$	2094(m),2051(s)/2084(1),2046(6)	2017(s,br)/2061(1),2035(8),2019(2)	1994(s,br)/2025(1),2007(1)
$\tilde{\nu}_{NN,s,ip}$	1325(m)/1334(6)	1312(s)/1325(3)	1312(s)/1325(3)
$\tilde{\nu}_{NN,s,op}$	1260(m)/1280(3)	1264(s)/1266(1)	1261(m)/1264(3)
δ_{NNN}	655(w),646(m),602(w),589(w), 578(w)/ 655(4),608(3)	650(s),641(s),614(m),599(m)/ 651(1),640(1),614(1)	635(m),615(m)/ 637(1),618(2)
$\tilde{\nu}_{Bi-N,ip}$	–/395(4)	–/337(4)	–/396(1)
$\tilde{\nu}_{Bi-N,op}$	–/341(10)	–/318(2),286(2),249(1)	–/322(3),293(2),258(2)
m.p./T_{dec}	–/154[c]	147/267	179/285
q(Bi)	+1.70	+1.71	+1.90
$q(N_\alpha)$	−0.71	−0.68	−0.61
$q(N_\beta)$	+0.22	+0.22	+0.22
$q(N_\gamma)$	−0.08	−0.23	−0.43

[a] as = asymmetric, ip = in-phase, op = out-of-phase. [b] NPA natural population analysis.[9] [c] **1**·THF: T_{dec} = 248 °C.

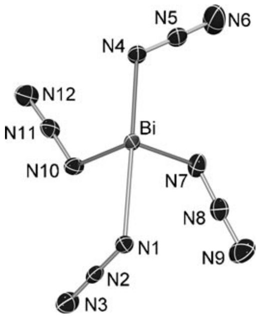


Figure 2. ORTEP representation of the anion of **2** in the crystal at 173 K (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles: N1–Bi 2.377(2), N4–Bi 2.449(2), N7–Bi 2.291(2), N10–Bi 2.273(2), N1–N2 1.216(3), N7–N8 1.207(3), N4–N5 1.198(3), N10–N11 1.209(3), N2–N3 1.144(3), N5–N6 1.144(4), N8–N9 1.148(4), N11–N12 1.149(3); N3-N2-N1 177.5(3), N6-N5-N4 178.5(3), N9-N8-N7 177.6(3), N12-N11-N10 176.7(3), N8-N7-Bi 114.7(2), N5-N4-Bi 122.9(2), N11-N10-Bi 115.4(2), N10-Bi-N7 86.95(9), N10-Bi-N1 80.46(8), N7-Bi-N1 86.64(9), N10-Bi-N4 83.06(8), N7-Bi-N4 80.30(8), N1-Bi-N4 159.45(8).

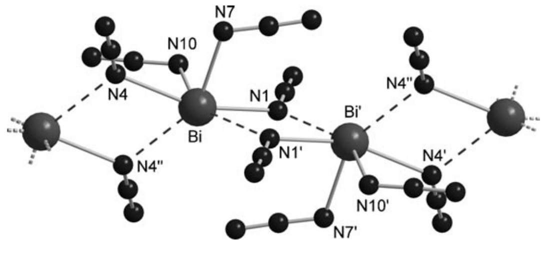
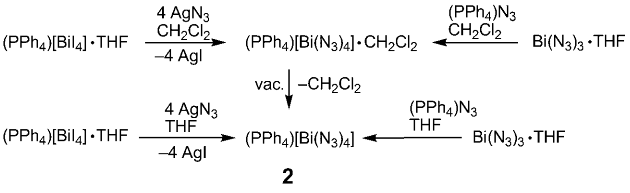


Figure 3. Section of the chain composed of $[Bi(N_3)_4]^-$ units in the crystal. Symmetry codes: (') −*x*+2, −*y*, −*z*+2; ('') −*x*+1, −*y*, −*z*+2. Three types of significantly different Bi–N bond lengths are observed: a) Bi–N10 2.273(2), Bi–N7 2.291(2); b) Bi-N1 2.377(2), Bi–N4 2.449(2); c) Bi–N1' 2.684(2), Bi–N4'' 2.717(2).

of **1**·THF instead of pure **1** for the synthesis of **2** has the advantage that it is less sensitive and thus minimizes the danger of explosion. 2) By adding four equivalents of AgN_3 to a solution of $(PPh_4)[BiI_4]$[10] in either THF or CH_2Cl_2, **2** and **2**·CH_2Cl_2 are also isolated as yellow crystals. $(PPh_4)[Bi(N_3)_4]$ is less sensitive than $Bi(N_3)_3$ and does not explode. Both azides were fully characterized by ^{14}N NMR, IR, and Raman spectroscopy, elemental analysis, and single-crystal structure elucidation. Yellow crystals of **2** melt at 147 °C and decompose at 254 °C without detonation. According to DSC measurements, **2**·CH_2Cl_2 releases CH_2Cl_2 at 107 °C (1 atm), forming pure **2** (Scheme 2).



Scheme 2. Synthesis of **2**.

By reaction of $(PPh_4)[Bi^{III}(N_3)_4]$ with two equivalents of $(PPh_4)N_3$, the $(PPh_4)_3[Bi^{III}(N_3)_6]$ salt (**3**) is formed in almost quantitative yield and was fully characterized (Table 1, Figure 4). The reaction of $[PPh_4]_3[Bi^{III}I_6]$ with AgN_3 also yields pure **3** (Scheme 3). Yellow crystalline **3** is neither heat- nor shock-sensitive and melts at 179 °C; decomposition starts at 285 °C. It is interesting to note that the attempted synthesis of a salt containing the pentaazide anion $[Bi^{III}(N_3)_5]^{2-}$ led to the formation of a mixture of $[Bi^{III}(N_3)_4]^-$ and $[Bi^{III}(N_3)_6]^{3-}$ in a 1:1 ratio (see the Supporting Information).

Table 1 summarizes the characterization of azides **1**–**3**. Two well-resolved ^{14}N NMR signals were found in the spectra run in different solvents (CH_2Cl_2, CH_3CN, DMSO)[10] at 300 K for **2** and **3**, while it was not possible to obtain NMR data for **1** owing to its low solubility. As expected, both ^{14}N spectra in DMSO solution show a sharp signal at $\delta = -136$ (**2**, $\Delta\upsilon = 43$ Hz) and −134 ppm (**3**, $\Delta\upsilon = 42$ Hz) for the N_β atoms and a medium-sharp signal at $\delta = -253$ (**2**, $\Delta\upsilon = 480$ Hz) and −260 ppm (**3**, $\Delta\upsilon = 390$ Hz) for the N_γ atoms in accord with known values for covalently bound azido groups.[1–7,11] The

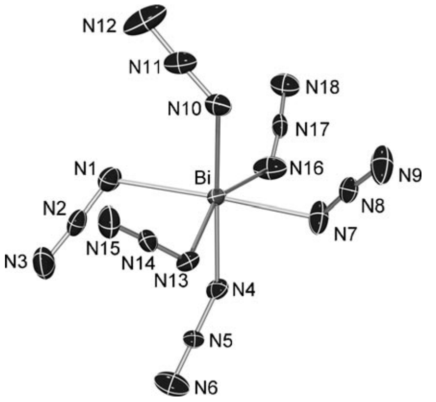
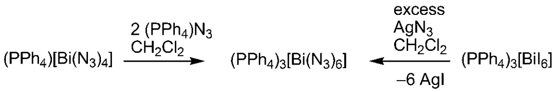


Figure 4. ORTEP representation of the anion of **3** in the crystal at 173 K (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Bi–N1 2.487(2), Bi–N4 2.32(2), Bi–N7 2.364(2), Bi–N10 2.478(2), Bi–N13 2.331(2), Bi–N16 2.719(5), N1–N2 1.188(3), N4–N5 1.27(3), N7–N8 1.194(3), N10–N11 1.188(3), N13–N14 1.203(3), N2–N3 1.149(3), N5–N6 1.10(2), N8–N9 1.140(3), N11–N12 1.158(3), N14–N15 1.150(3), N17–N18 1.19(2); N1-Bi-N4 94.4(5), N1-Bi-N10 89.03(7), N1-Bi-N13 85.59(7), N1-Bi-N16 108.8(2), N4-Bi-N7 86.8(5), N4-Bi-N13 84.3(4), N4-Bi-N16 78.2(4), N7-Bi-N10 88.53(7), N7-Bi-N13 88.47(7), N7-Bi-N16 77.4(2), N10-Bi-N13 84.10(7), N10-Bi-N16 111.9(1), N1-Bi1-N7 173.78(8), N4-Bi-N10 167.6(4), N13-Bi1-N16 158.8(2), N2-N1-Bi 119.5(2), N5-N4-Bi 124.5(1), N8-N7-Bi 123.2(2), N11-N10-Bi 120.7(2), N14-N13-Bi 119.1(2), N17-N16-Bi 133.4(9), N3-N2-N1 177.0(3), N6-N5-N4 177.5(2), N9-N8-N7 175.8(2), N12-N11-N10 177.6(3), N15-N14-N13 177.2(2).



$$(PPh_4)[Bi(N_3)_4] \xrightarrow[CH_2Cl_2]{2\,(PPh_4)N_3} (PPh_4)_3[Bi(N_3)_6] \xleftarrow[-6\,AgI]{\text{excess } AgN_3,\ CH_2Cl_2} (PPh_4)_3[BiI_6]$$

3

Scheme 3. Synthesis of **3**.

observation of only one set of azide signals and the absence of the N_α signal indicates strong quadrupole relaxation effects and a rapid ligand exchange on the NMR timescale.[12]

The vibrational spectra of all three azides feature the presence of covalently bonded azido ligands, as shown by the asymmetrical stretching mode in the range 2200–2000 cm^{-1}, the symmetrical stretching mode at 1400–1200 cm^{-1}, and the deformation mode at 700–600 cm^{-1}. The bismuth Bi–N stretching modes are found in the range 400–250 cm^{-1} (cf. 352 cm^{-1} in Me_2BiN_3).[13] The presence of more than one azido ligand results in in-phase and out-of-phase coupling.

The most prominent structural feature in all three bismuth(III) azides is the stereochemically active lone pair localized according to NBO analysis[9] in a mainly s-type atomic orbital. The s character of the lone pair (Table 1) increases in the order **1** (87.6 %) < **2** (88.5 %) < **3** (99.5 %). All of the Bi–N bonds are highly polarized and can be considered dominantly ionic. The degree of polarization increases in the order **1** < **2** < **3**. Although all three Bi–N bonds in **1** are localized to 19.7 % at the bismuth atom, in bisphenoidal **2** there is a considerable difference between the nitrogen atoms occupying the axial positions (8.5 %) compared to the equatorial nitrogen atoms (15.1 %) of the pseudo-trigonal bipyramid, indicating larger covalent character for the Bi–N bonds within the trigonal plane. In **3**, only 6–7 % of the electron density of the Bi–N bonds is found at the bismuth atom, indicating a predominantly ionic bonding situation for all six azido ligands attached to the bismuth atom.

The charge distribution for all three azides is characterized by alternating net charges along the $Bi^{(\delta+)}$–$N^{(\delta-)}$–$N^{(\delta+)}$–$N^{(\delta-)}$ units, with a large positive charge at the bismuth atom (**1** +1.70, **2** +1.71, **3** +1.90 *e*; Table 1). A closer look at the charges reveals that upon further N_3^- complexation, the charge at the Bi, N_α, and N_β atoms does not change much, whilst the terminal N_γ atoms feature a significantly larger negative charge (**1** −0.08, **2** −0.23, **3** −0.43 *e*).

As it was not possible to obtain experimental structural data, the structure of **1** was calculated for the gas phase at the B3LYP level of theory. For nitrogen, a standard 6-31G(d) basis set was used and a quasi-relativistic pseudopotential (ECP78MWB) and a (4s4p1d)/[2s2p1d] basis set for the bismuth atom. The lowest-lying C_3 symmetric isomer with the three azido ligands in an *anti* configuration with respect to the lone pair (Figure 1) was characterized as a minimum at the potential energy surface by a frequency analysis. It can be assumed that in the solid state owing to strong intermolecular interactions, such as in $E(N_3)_3$ (E = As, Sb), a three-dimensional network also exists.[1c] As shown on numerous occasions, the azido groups are almost linear, with N-N-N angles of 175.5°.[1–7,11] The tetrahedral angles at the bismuth atom decrease from an ideal value of 109.58 to 98.1°.

$(PPh_4)[Bi(N_3)_4]$ crystallizes in the monoclinic space group $P2_1/c$ with four formula units per cell, whereas $(PPh_4)[Bi(N_3)_4]\cdot CH_2Cl_2$ crystallizes in the triclinic space group $P\bar{1}$ with two formula units per cell. As the structural parameters for both compounds are very similar, we focus only on the data for $(PPh_4)[Bi(N_3)_4]$. The asymmetric unit consists of separated $(PPh_4)^+$ and $[Bi(N_3)_4]^-$ units with no significant cation–anion contacts. The $[Bi(N_3)_4]^-$ ion (Figure 2) adopts a distorted bisphenoidal geometry with two shorter (Bi–N10 2.273(2), Bi–N7 2.291(2) Å) and two longer Bi–N bonds (Bi–N1 2.377(2), Bi–N4 2.449(2) Å; $\Sigma r_{cov}(Bi–N) = 2.2$ Å),[14] in accord with the valence-shell electron-pair repulsion model. Both N7 and N10 are part of the trigonal plane with a N7-Bi-N10 angle of 86.95(9)°, whereas N1 and N4 sit on the axis with an N1-Bi-N4 angle of 159.45(8)°. For all four azido ligands, the typical *trans*-bent structure with N-N-N angles of about 176–179° is observed.[11] The N_α–N_β bonds are in the range 1.198(3)–1.216(3) Å (average 1.207 Å), and an average N_β–N_γ bond length of 1.146 Å is observed.[11]

A closer look at the interanionic interactions (Figure 3) reveals an expansion of the bismuth coordination number by the formation of nitrogen bridges involving the α-nitrogen atoms (N1, N4) of two of the azido ligands. This bridging mode results in the formation of four-membered rings composed of two hexacoordinated bismuth and two bridging N_α atoms. These rings are interconnected, with adjacent rings almost perpendicular to each other, thus forming infinite zigzag chains in the crystal. The $Bi–N_{bridge}$ bonds amount to Bi–N1′ 2.684(2) and Bi–N4″ 2.717(2) Å, which are considerably shorter than the sum of the van der Waals radii of 4.0 Å.[14]

$(PPh_4)_3[Bi(N_3)_6]$ crystallizes in the monoclinic space group $P2_1/n$ with four formula units per cell. The asymmetric unit consists of one $(PPh_4)_3[Bi(N_3)_6]$ unit without significant cation–anion contacts and two disordered azido ligands. Figure 4 shows the structure of the $[Bi(N_3)_6]^{3-}$ ion with a strongly distorted BiN_6 skeleton. It is well-known that bismuth atoms can accommodate at least six closely packed halide ligands, as in octahedral $[Bi^{III}X_6]^{3-}$ (X = F, Cl, Br, I), whilst for the $[Bi^{V}X_6]^{-}$ ion, only the fluorine species is known.[15] In contrast to the known pseudohalide complexes $[E^{V}(N_3)_6]^{-}$, with E = P, As, Sb, the analogous bismuth compound has not been reported, whilst for E = P, As, and Sb, the trivalent $[Bi(N_3)_6]^{3-}$ analogues remain unknown.

Interestingly, in **3** there is one significantly elongated Bi–N bond of 2.719(5) for Bi–N16, whilst the other five bonds are all in the range 2.32–2.49 Å, in accord with those found in **2**. The Bi–N16 bond compares well with the length of the Bi–N bridges in **2** (see above).

The electronic structure of $[Bi^{III}(N_3)_6]^{3-}$ is best compared to the $[Te^{IV}(N_3)_6]^{2-}$ ion, which also features a sterically active lone pair causing a strongly distorted octahedral symmetry of the EN_6 skeleton (E = Te, Bi).[16] Similar hexacoordinate azido species are neutral $W(N_3)_6$,[17] singly negatively charged $[As(N_3)_6]^{-}$,[2,4] $[Sb(N_3)_6]^{-}$,[3] $[Nb(N_3)_6]^{-}$,[18] and $[Ta(N_3)_6]^{-}$,[18] and doubly negatively charged $[Si(N_3)_6]^{2-}$,[19] $[Ge(N_3)_6]^{2-}$,[20] and $[Se(N_3)_6]^{2-}$.[21] However, for these species an almost perfect S_6 symmetry with an octahedral skeleton is observed.

In conclusion, we present herein the first synthesis and isolation of binary bismuth(III) azides and their full characterization. Although the structural elucidation of $[Bi^{III}(N_3)_4]^{-}$ and $[Bi^{III}(N_3)_6]^{3-}$ salts fills a gap in main group chemistry, $Bi(N_3)_3{\cdot}THF$ could qualify as a precursor for the generation of binary BiN in detonation experiments owing to its low shock and heat sensitivity.

Experimental Section

Caution! Covalent azides are potentially hazardous and can decompose explosively under various conditions! In particular, $Bi(N_3)_3$ described herein is extremely shock-sensitive and can explode violently upon the slightest provocation. Appropriate safety precautions (safety shields, face shields, leather gloves, protective clothing) should be taken, particularly when dealing with larger quantities. Experimental details are found in the Supporting Information.[10]

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