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ARTICLE TYPE

Syntheses and Structures of Triazides of Heavy Group 15 Elements

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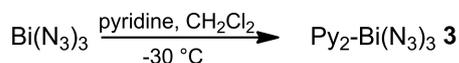
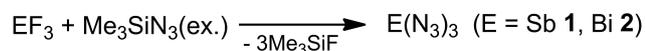
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5 **Synthesis of group 15-triazides E(N₃)₃ (E = Sb **1**, Bi **2**) and Py₂-Bi(N₃)₃ **3** (Py = pyridine). Single crystals of **1** were *in situ* grown by a IR-laser-assisted technique on the diffractometer. The structure of **3**, which represents the first structurally characterized neutral Bi-triazide, is influenced by crystal packing effects according to DFT calculations.**

Neutral binary group 15 azides of the types E(N₃)₃ and E(N₃)₅ have been intensely studied over the last decades. While phosphorous triazide could be neither isolated nor structurally characterized and phosphorous pentaazide is still unknown, to date,[1] the corresponding complexes of the heavier group 15 elements, As(N₃)₃,[2] As(N₃)₅,[3] Sb(N₃)₃[2b,4] and Sb(N₃)₅[3] have been synthesized within the last few years. Moreover, thermally more stable ionic complexes containing anions of the types E(N₃)₄⁻ (E = As, Sb)[5] and E(N₃)₆⁻ (E = P,[6] As,[5,7] Sb[5,3]) as well as cations E(N₃)₄⁺ (E = P,[8] As,[5] Sb[5]) have been synthesized and isolated. Very recently, Schulz *et al.* synthesized the first neutral and anionic bismuth azides Bi(N₃)₃, (thf)Bi(N₃)₃, Bi(N₃)₄⁻ and Bi(N₃)₆³⁻. [9] Even though these binary complexes, which are typically heat and shock-sensitive compounds, have been well characterized by means of IR and Raman spectroscopy, informations on their structures in the solid state are still rather scarce. To date, only As(N₃)₃,[2a] Sb(N₃)₃,[2a] P(N₃)₆,[10] As(N₃)₆,[7] Sb(N₃)₆,[3] Bi(N₃)₄,[9] and Bi(N₃)₆³⁻[9] have been structurally characterized.

30 Herein, we report on a slightly modified route for E(N₃)₃ (E = Sb **1**, Bi **2**) and the synthesis of Py₂-Bi(N₃)₃ **3**. **1** – **3** were characterized by NMR (¹⁴N), IR and Raman spectroscopy, **1** and **3** also by single crystal X-ray diffraction. **3** represents the first structurally characterized Lewis-base stabilized bismuth azide.



Scheme 1 Synthesis of **1** - **3**

1 and **2** were synthesized by reaction of SbF₃ and BiF₃, respectively, with an excess of Me₃SiN₃ in the absence of any additional organic solvents. **3** was obtained by re-crystallization from a solution of **2** in CH₂Cl₂ and pyridine at 0 °C. The ¹⁴N NMR spectrum (25 °C) of a solution of **1** in CH₂Cl₂ shows three well-resolved resonances due to the azido groups at -321 (Δν_{1/2} = 170 Hz (N_α), -134 (Δν_{1/2} = 26 Hz (N_β) and -169 ppm (Δν_{1/2} = 34

Hz (N_γ), respectively. These resonances are in accord with experimental values reported previously[2b,4] and correspond very well with typical values of covalently bound azido groups. The ¹⁴N NMR spectrum of a solution of **2** in CH₂Cl₂, which was not reported in the original contribution by Schulz *et al.* due to the low solubility of **2** in organic solvents,[9] shows comparable resonances for N_α (δ = -324, Δν_{1/2} = 140 Hz), N_β (δ = -135, Δν_{1/2} = 20 Hz) and N_γ (δ = -170, Δν_{1/2} = 32 Hz). Almost analogous values were observed for a solution of **3** in CH₂Cl₂, showing the expected resonances due to the azide groups (δ = -325, Δν_{1/2} = 580 Hz (N_α); -135, Δν_{1/2} = 25 Hz (N_β); -172, Δν_{1/2} = 480 Hz (N_γ)) and an additional resonance of the pyridine Lewis bases at -66 ppm (Δν_{1/2} = 120 Hz). IR and Raman spectra of **1** and **2** correspond very well with those previously reported[2b,4,9,11]. **3** shows strong adsorption bands due to the asymmetric (IR: ν = 2039, 2021 cm⁻¹; Raman: ν = 2095, 2044 cm⁻¹) and symmetric N-N-N stretching mode (IR: ν = 1316, 1253 cm⁻¹; Raman: ν = 1327, 1274 cm⁻¹) and the N-N-N deformation mode (IR: ν = 642, 593 cm⁻¹; Raman: ν = 650 cm⁻¹).

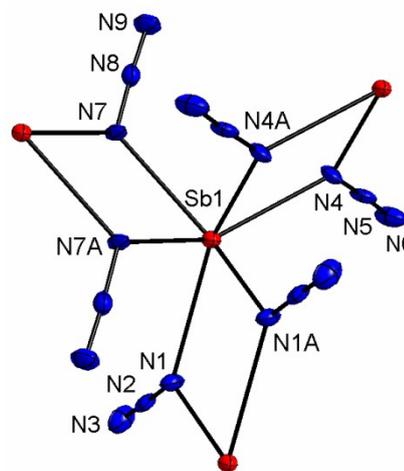


Fig. 1 Solid state structure of **1** showing the intermolecular coordination mode.

Single crystals of **1** were grown by a IR-laser-assisted technique in an open quartz glass capillary under an inert nitrogen atmosphere directly on the diffractometer. The IR-laser allowed a very controlled heating of the sample, hence allowing optimization of the growth conditions, in which the sample sublimizes without considerable decomposition. The successful growth of suitable crystals of **1** clearly demonstrates the promising potential of this method even for the structural

characterization of heat- and shock-sensitive complexes.

1 is the second polymorph of $\text{Sb}(\text{N}_3)_3$ as was verified by checking the elemental cell of **1** at 223 K and at ambient temperature. No signs of a phase transition was found in this temperature regime. The initially reported structure (**1'**), which was determined at 223 K,[2b] was found to crystallize as perfect C_3 symmetric molecule, whereas **1** crystallizes in the triclinic space group P-1 with one molecule in the asymmetric unit. The central Sb atom in **1** is sixfold coordinated by (asymmetrically) bridging azido groups as was previously observed. The azide units are almost linear with N-N-N bond angles between $177.4(6)$ and $178.5(6)^\circ$ and the Sb-N bond lengths range from 2.119(5) to 2.151(5) Å. These values differ only slightly from those reported for **1'** (N-N-N $178.3(5)^\circ$; Sb-N 2.119(4) Å) and $\text{SbCl}(\text{N}_3)_2$ ($177(1)$, $178.8(9)^\circ$).[12] The $\text{N}_\alpha\text{-N}_\beta$ bond lengths in **1** (N1-N2 1.231(7); N4-N5 1.248(7); N7-N8 1.235(7) Å) are longer than the $\text{N}_\beta\text{-N}_\gamma$ bond lengths (N2-N3 1.125(7); N5-N6 1.128(7); N8-N9 1.133(8) Å) as was observed for **1'** (1.233(6), 1.131(6) Å) and other Sb(III) azides ($\text{SbCl}(\text{N}_3)_2$ 1.22(1), 1.13(1) Å,[13] $[\text{N}_3\text{Sb}(\mu\text{-N}t\text{-Bu})_2]$ 1.222(5), 1.133(5) Å,[14] $[t\text{-BuC}(\text{N}i\text{-Pr})_2]\text{Sb}(\text{N}_3)_2$ av. values 1.216(2), 1.143(2) Å[15] and Sb(V) azides (Ph_4SbN_3 1.198(4), 1.150(4) Å,[16] $[\text{Ph}_4\text{P}][\text{Sb}(\text{N}_3)_6]$ av. values 1.22 and 1.12 Å[3]), respectively. The structures of **1** and **1'** are quite similar. The "Mitsubishi emblem-type"[2b] pattern of $\text{Sb}\cdots\text{N}_\alpha$ interactions in **1'** was also found in the structure of **1**. However, the secondary interactions in **1** range from 2.659(5) Å to 2.819(5) Å, whereas they are equidistant in **1'** (symmetry equivalence; 2.844 Å). Despite the shorter interactions as observed for **1**, the densities of **1** and **1'** are almost equal (**1**: 2.81; **1'**: 2.83 both at 223 K). The crystallographic data alone therefore do not allow a decision on which polymorph is the thermodynamically more stable one. The structures differ in the way the layers are related. In **1** they are equivalent via translation parallel to the b-axis, while in **1'** they are related via inversion.

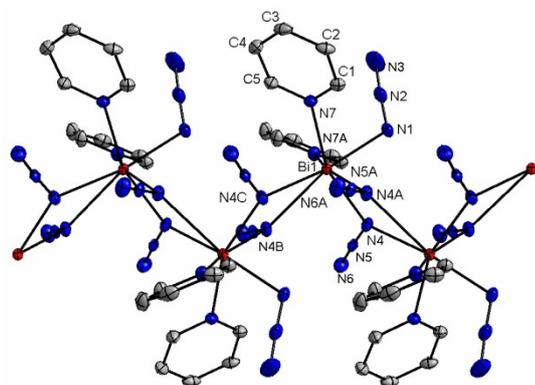


Fig. 2 Solid state structure of **3** showing the chain-like structure; H atoms are omitted for clarity.

Single crystals of **3** suitable for an X-ray structure determination were obtained from a solution of **3** in CH_2Cl_2 and pyridine after storage at 0 °C for 48 h. **3** crystallizes in the orthorhombic noncentrosymmetric space group $\text{Cmc}2_1$ with four independent molecules in the unit cell. The absolute structure was determined by refinement of the Flack parameter to -0.001, with a standard uncertainty of 0.006.[17] The asymmetric unit consists of one pyridine ligand, one azido ligand on a general position and

one placed in the mirror plane as well as a central Bi atom, which is also located in the mirror plane. As a consequence, the Bi atom in **3** is coordinated by two pyridine bases and three azido ligands with that on the special position adopting a terminal binding mode. The remaining two azido groups serve as (asymmetrically) bridging groups (through N_α), resulting in the formation of an endless chain structure constituted by 2_1 symmetry. Each Bi atom adopts a sevenfold coordination geometry.

To the best of our knowledge, $(\text{Py})_2\text{Sb}(\text{N}_3)\text{Cl}_2$ represents the only structurally characterized group 15 element azide complex that is coordinated by two additional Lewis bases.[18] However, this complex consists of isolated molecules as was observed recently for $[\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{Bi}(\text{N}_3)_2$.[19] In contrast, $[\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{Bi}(\text{N}_3)$ [19] forms a dimer in the solid state whereas Me_2BiN_3 adopts a polymeric N_α -bridged chain-like structure, in which each Bi atom is fourfold coordinated.[20] The azide groups in **3** differ only slightly from linearity (N1-N2-N3 $177.4(5)$, N4-N5-N6 $176.8(2)^\circ$ and the $\text{N}_\alpha\text{-N}_\beta$ bonds (N1-N2 1.214(4); N4-N5 1.213(3) Å) are longer than the $\text{N}_\beta\text{-N}_\gamma$ bonds (N2-N3 1.138(5); N5-N6 1.148(3) Å). The terminal bonded azide group shows the shortest Bi-N bond length (Bi1-N1 2.277(3) Å), whereas the Bi-N bond length to the pyridine bases (Bi1-N7 2.618(2) Å) is in between those observed for the bridging azide groups (Bi1-N4 2.304(2) Bi1-N4A 2.797(2) Å). These values are exactly within the range given by the sum of the single bond covalent radii (2.22 Å,[21] 2.16[22]) and the sum of the van-der-Waals radii (3.62 Å[22]). A Cambridge structure database search revealed that Bi-N bond lengths range from 2.10 to 2.90 Å with an average distance of 2.50 Å, respectively. These structural findings clearly indicate that the intermolecular Bi-N_α interaction is rather weak.

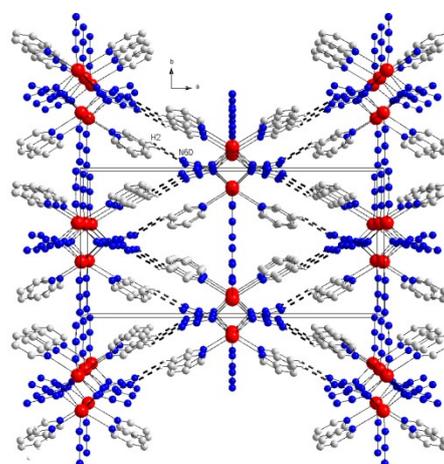


Fig. 3 Packing diagram of **3** showing the intermolecular hydrogen C-H \cdots N bridges.

As-formed chains show additional intermolecular $\text{CH}\cdots\text{N}$ hydrogen bridges to an adjacent chain (symmetry equivalent via C centring) through to interactions between N6 of bridging azides and H2 of the pyridine bases, resulting in the formation of a three dimensional network. C2-H2 \cdots N6D shows typical distances and angle of a non-classical hydrogen bond (H \cdots N 2.59 Å, CH \cdots N 128.6°), but the almost hexagonal arrangement (52.9° , 127.1° angles of the rhombus formed by adjacent chains) of the chains parallel to the c-axis suggests closest packing to be more

important for the composition of this structure.

Density functional theory (DFT) calculations employing different exchange-correlation functionals, i.e. BP86 and B3LYP, in conjunction with a basis set of triple-zeta valence quality and a relativistic pseudopotential for Bi were carried out starting from the crystal structure of $\text{Py}_2\text{-Bi}(\text{N}_3)_3$.^[11] A monomeric unit $\text{Py}_2\text{-Bi}(\text{N}_3)_3$ was considered using all azide ligands with a Bi-N distance below 2.62 Å. The resulting $\text{Py}_2\text{-Bi}(\text{N}_3)_3$ unit displays C_s symmetry, and geometry optimization followed by frequency analysis shows a C_s -symmetrical structure to be a minimum at the BP86 level of theory as well. On the other hand, at the B3LYP level of theory the C_s -symmetrical structure is found to be a first-order saddle point. The major difference between the calculated (BP86, B3LYP) and experimental structures is a rotation of those azide groups, which adopt bridging positions in the solid state structure of **3** (N4, N4A). The rotation brings the N_7 atoms of the azide groups closer to the pyridine ligands, in the case of B3LYP leading to a distance of about 2.98 Å, while with BP86 2.83 Å are found (in the following BP86 results are given in parentheses). The azide groups differ slightly from linearity as was observed in the crystal structure of **3**. The N1-N2-N3 bond angle of the terminal azide group of 175.4° (175.9°) is comparable to that of the N4-N5-N6 group of 176.1° (176.6°) and the N1-N2 (1.224 (1.215) Å) and N4-N5 bond lengths (1.219 (1.212) Å) agree very well. Both are longer than the N2-N3 (1.154 (1.136) Å) and N5-N6 bond lengths (1.155 (1.138) Å). Note that the B3LYP values are for the most part in excellent agreement with experimental values (vide supra). In contrast, the Bi-N distances (Bi-N1 2.235 (2.206), Bi-N4 2.247 (2.228), Bi-N7 2.822 (2.894) Å) differ more notably from experiment. Geometry optimization of the pyridine-free triazide $\text{Bi}(\text{N}_3)_3$ leads to a C_s -symmetrical structure in which position and orientation of the azide ligands remain qualitatively unaltered. Frequency analysis shows this structure to be a second-order saddle point at both levels of theory. Its energy is 3.8 (4.3) kJ/mol above that of the C_3 -symmetrical minimum as found by Schulz et al.^[9] and confirmed in calculations with our more extended basis set with both functionals, BP86 and B3LYP. A similar minimum structure was found for the $\text{Py}_2\text{-Bi}(\text{N}_3)_3$ units upon distortion of the C_s -symmetrical structure along the imaginary frequency mode found at the B3LYP level: after many geometry optimization steps one obtains a C_1 -symmetrical structure in which the two pyridine molecules coordinate to an essentially C_3 -symmetrical $\text{Bi}(\text{N}_3)_3$ group with Bi-N distances of 2.78 and 2.81 (2.86 and 2.84) Å, respectively, while the ortho H atoms form hydrogen bridges to the N_α atoms of the azide groups with lengths of 2.43 and 2.39 (2.46 and 2.48) Å. The energy difference from the C_s -symmetrical structure to this minimum structure is 15.0 (14.7) kJ/mol, roughly 11 kJ/mol larger than the corresponding energy difference in the free $\text{Bi}(\text{N}_3)_3$ complex. The additional stabilization of the minimum structure can be most likely explained by a gain in hydrogen bonding energy. However, this small energy difference may easily be overcome by the effect of the two additional bridging azide groups with long Bi-N bonds found in the crystal structure and by crystal packing effects.

Conclusions

A neutral Bi-triazide was structurally characterized for the first time. Moreover, the promising potential of a specific IR-laser-

assisted technique for the *in situ* growth of heat- and shock-sensitive compounds on the diffractometer is demonstrated.

Notes and references

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- † Electronic Supplementary Information (ESI) available: Full experimental details and characterization of **1** - **3** including single crystal structures (**1**, **3**) and computational details (**3**) are given in the supporting information file. See DOI: 10.1039/b000000x/
- ‡ S.S. and B.L. gratefully acknowledge the Fonds der Chemischen Industrie (FCI) for financial support and a doctoral fellowship (B.L.).
- Details of the crystal structure determination of **1** may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de,) on quoting the deposition number CSD-422405. CCDC-803386 contain the supplementary crystallographic data of complex **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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