

Synthesis and Structural Characterization of Antimony Polyazides**

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Dedication: In memory of Prof. Kurt Dehnicke

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Introduction

Binary group 15 azides of the types $E(N_3)_3$ and $E(N_3)_5$ ($E = P, As, Sb, Bi$) have been studied over the last decades. These highly endothermic polyazides are not only of pure academic interest but are also viable candidates for high energy-density materials (HEDM), as the azido group is known to add almost 70 kcal mol^{-1} to the energy content of a molecule.^[1] Even though these neutral binary polyazides are long known^[2] except for $P(N_3)_5$ and $Bi(N_3)_5$,^[3] only $As(N_3)_3$ ^[2b] and $Sb(N_3)_3$ ^[2b,4] have been structurally characterized, to date. Besides the neutral polyazides, both anionic ($E(N_3)_4^-$ (As, Sb, Bi); $E(N_3)_6^-$ (P, As, Sb); $Bi(N_3)_6^{3-}$) and cationic polyazides ($E(N_3)_4^+$ (P, As, Sb)) have also been synthesized.^[5] However, even though these ionic binary complexes are less heat and shock-sensitive compared to their neutral derivatives, only $P(N_3)_6^-$,^[5d] $As(N_3)_6^-$,^[5g] $Sb(N_3)_6^-$,^[2d] $Bi(N_3)_4^-$,^[2f] and $Bi(N_3)_6^{3-}$ ^[2f] were structurally characterized.

We became only recently interested in the synthesis of group 15 polyazides and reported on the X-ray crystal structures of several organoantimony diazides $RSb(N_3)_2$ ^[6] and the triazide $Sb(N_3)_3$.^[4] Moreover, the structure of $Pyr_2Bi(N_3)_3$, which represents the only structurally characterized base-stabilized, neutral binary polyazide of a group 15 element, was reported.^[4] Herein, we report on the synthesis and solid state structure of $[Ph_3PNPPh_3]_2[Sb(N_3)_5]$ **1** containing the pentaazido dianion $[Sb(N_3)_5]^{2-}$, which is without precedent in group 15 azide chemistry. Moreover, the synthesis and

structure of $[\text{Ph}_3\text{PNPPh}_3][\text{Sb}(\text{N}_3)_6]$ **2** is reported. **1** and **2** were fully characterized by elemental analyses, NMR (^1H , ^{13}C , ^{14}N , ^{31}P), IR and Raman spectroscopy and by single crystal X-ray diffraction.

((Scheme 1 here))

Results and Discussion

1 and **2** were synthesized by reaction of $[\text{Ph}_3\text{PNPPh}_3][\text{N}_3]$ with $\text{Sb}(\text{N}_3)_3$ and $\text{Sb}(\text{N}_3)_5$, respectively, in CH_2Cl_2 . Several attempts to synthesize $[\text{Ph}_3\text{PNPPh}_3][\text{Sb}(\text{N}_3)_4]$ and $[\text{Ph}_3\text{PNPPh}_3][\text{Sb}(\text{N}_3)_6]$ containing the $[\text{Sb}(\text{N}_3)_4]^-$ monoanion and the $[\text{Sb}(\text{N}_3)_6]^{3-}$ trianion failed. Even the reaction of $\text{Sb}(\text{N}_3)_3$ with less than one equivalent of $[\text{Ph}_3\text{PNPPh}_3][\text{N}_3]$ only gave **1** in high yield. ^1H , ^{13}C and ^{31}P NMR spectra of **1** and **2** only showed the expected resonances due to the $[\text{Ph}_3\text{PNPPh}_3]^+$ cation. ^{14}N NMR spectra (25 °C) of **1** and **2** each showed three well-resolved resonances due to the azido groups (**1**: -250, $\Delta\nu_{1/2} = 420$ Hz (N_α); -137, $\Delta\nu_{1/2} = 57$ Hz (N_β); -185 ppm, $\Delta\nu_{1/2} = 58$ Hz (N_γ); **2**: -283, $\Delta\nu_{1/2} = 686$ Hz (N_α); -140, $\Delta\nu_{1/2} = 47$ Hz (N_β); -184 ppm, $\Delta\nu_{1/2} = 83$ Hz (N_γ)), comparable to those observed for $\text{Sb}(\text{N}_3)_3$ (-321, $\Delta\nu_{1/2} = 170$ Hz (N_α); -134, $\Delta\nu_{1/2} = 26$ Hz (N_β); -169 ppm, $\Delta\nu_{1/2} = 34$ Hz (N_γ)) and covalent azides.^[2b,2e] In contrast, the ^{14}N resonance of the $[\text{Ph}_3\text{PNPPh}_3]^+$ cation was not observed.

((Fig 1 here))

((Fig 2 here))

IR (Fig. 1) and Raman spectra (Fig. 2) of **1** and **2** show strong adsorption bands due to the asymmetric (**1**: IR: $\nu = 2093, 2072, 2049, 2020$ cm^{-1} ; Raman: $\nu = 2097, 2076, 2053$ cm^{-1} ; **2**: IR: $\nu = 2085$ cm^{-1} ; Raman: $\nu = 2115, 2085$ cm^{-1}) and symmetric N-N-N stretching mode (**1**: IR: $\nu = 1297, 1160$ cm^{-1} ; Raman: $\nu = 1333, 1273$ cm^{-1} ; **2**: IR: $\nu = 1399, 1334$ cm^{-1} ; Raman: $\nu = 1336, 1262$ cm^{-1}). The absorption bands observed for the hexaazidoantimonate anion in **2** agree very well with those reported for $[\text{Et}_4\text{N}][\text{Sb}(\text{N}_3)_6]$ (IR: 1337, 1318, 1264 cm^{-1} ; Raman: 1319, 1275 cm^{-1}),^{5a} whereas those reported for $[\text{Ph}_4\text{P}][\text{Sb}(\text{N}_3)_6]$ (IR: 1256 cm^{-1} ; Raman: 1298 cm^{-1}) slightly differ.^{2d} The N-N-N deformation mode was only observed in the IR spectrum of **2** (IR: $\nu = 663, 581$ cm^{-1}), whereas this band is overlapped by strong absorption bands of the cation in the IR spectrum of **1** and the Raman spectra of **1** and **2**,

respectively. These experimental values also correspond well with calculated values (B3LYP and BP86 level of theory).^[14]

In order to investigate the stability of **1** in solution in respect to the possible formation of an equilibrium ($\text{Sb}(\text{N}_3)_5^{2-} // \text{Sb}(\text{N}_3)_4^- + \text{N}_3^-$), we monitored the IR spectrum of **1** upon dissolution in CH_2Cl_2 . Figure 3 clearly shows, that in solution no free azide monoanion is formed. After the solvent was removed, pure **1** again was obtained.

((Fig 3 here))

Single crystals of **1** were obtained from a solution in CH_2Cl_2 by slow evacuation of the solvent.^[7] **1** crystallizes in the orthorhombic space group $Pca2_1$ with one molecule in the asymmetric unit.

((Fig 4 here))

The $[\text{Sb}(\text{N}_3)_5]^{2-}$ dianion (Fig. 4) in **1** adopts a distorted square-pyramidal geometry as was observed for the $[\text{Te}(\text{N}_3)_5]^-$ monoanion,^[8] even though $[\text{Te}(\text{N}_3)_5]^-$ forms secondary $\text{Te}\cdots\text{N}$ interactions to neighboring $[\text{Te}(\text{N}_3)_5]^-$ anions. This results in an octacoordinated Te atom whereas the Sb atom in **1** is only fivefold coordinated. Moreover, $[\text{Fe}(\text{N}_3)_5]^-$, which to date is the only structurally characterized complex containing a pentaazido dianion $[\text{E}(\text{N}_3)_5]^{2-}$, adopts a trigonal-bipyramidal coordination sphere.^[9] To the best of our knowledge, dianionic $[\text{SbF}_5]^{2-}$ and $[\text{SbCl}_5]^{2-}$ are the only Sb(III)-complexes with a distorted square-pyramidal coordination sphere.^[10] In addition, this coordination geometry was observed for SbPh_5 ^[11] (and BiPh_5 as well^[12]). The equatorial Sb-N bonds (2.262(2) – 2.324(2) Å) in **1** are significantly elongated compared to the axial Sb(1)-N(7) bond (2.099(2) Å), which is very close to the sum of the covalent radii as reported by *Pyykko et al.* (2.11 Å).^[13] Analogous findings were reported for the pentaazidotellurate(IV).^[8] Compared to the Sb-N bond lengths in $\text{Sb}(\text{N}_3)_3$ (2.119(4) Å;^[2b] 2.119(5) – 2.151(5) Å^[4]), the Sb-N bonds of the equatorial bound N atoms in **1** are significantly elongated. The N-N bond lengths and N-N-N bond angles in **1** are in the typical range observed for covalent azides and also comparable to the values reported for $\text{Sb}(\text{N}_3)_3$.^[2b,4] The $[\text{Ph}_3\text{PNPPH}_3]^+$ cation shows no unusual structural parameters.

Density functional theory (DFT) calculations employing different exchange-correlation functionals, i.e. B3LYP and BP86, in conjunction with a basis set of triple-zeta valence quality and a relativistic

pseudopotential for Sb were carried out starting from the crystal structure of $[\text{Ph}_3\text{PNPPh}_3]_2[\text{Sb}(\text{N}_3)_5]$ **1**.^[14] Structure optimization followed by frequency analysis shows a C_1 -symmetrical structure to be a minimum at the B3LYP and BP86 levels of theory. The calculated structural parameters (Fig. 5) are mostly in excellent agreement with the experimental values (vide supra) except for the Sb-N distances of the equatorial N atoms (Sb-N 2.295 – 2.404 Å), which differ more notably from experimental values (Sb-N 2.262(2) – 2.324(2) Å). The Sb-N_{ax} bond length is shorter compared to the Sb-N_{eq} bonds and the azide groups differ slightly from linearity as was observed in the crystal structure of **1**.

((Fig 5 here))

The differing conformation of the $[\text{Sb}(\text{N}_3)_5]^{2-}$ dianion in the observed and calculated structure may be explained by an analysis of the packing of **1** which is dominated by C–H $\cdots\pi$ interactions between the $[\text{Ph}_3\text{PNPPh}_3]^+$ cations. These are connected via motif 3^[15] forming chains parallel to the b-axis, which are joined via a 6PE motif^[16] to form a layer parallel to (001) (Fig. 6). The neighboring chains are related by the c glide plane. The layers on their part are connected by isolated C–H $\cdots\pi$ interactions.

((Fig 6 here))

This 3-dimensional network of cations incorporates voids in which the anions were found. These adopt a sterically less demanding conformation due to the limited space available. In addition, N4, N5 and N6 as well as N13, N14, and N15 are involved in non-classical hydrogen bonds (Fig. 7) presumably capable of (over-)compensating the amount of energy necessary to change the conformation. Under the given circumstances it is not surprising, that E \cdots N interactions as observed in $[\text{Te}(\text{N}_3)_5]^-$, where no cation/cation interactions can be found, are missing. Moreover, in the tellurium complex the anion/anion repulsion is weaker due to the lower negative charge.

((Fig 7 here))

Single crystals of **2** (Fig. 8) were obtained from a solution of **2** in CH_2Cl_2 by slow evacuation of the solvent.^[7] **2** crystallizes in the trigonal space group $R\bar{3}$ with one sixth of each ion in the asymmetric unit and Sb1 and N4 occupying special positions ($\bar{3}$).

((Fig 8 here))

The $[\text{Sb}(\text{N}_3)_6]^-$ anion in **2** adopts an octahedral coordination sphere with $\bar{3}$ symmetry. While the $[\text{Sb}(\text{N}_3)_6]^-$ anion in $[\text{Ph}_4\text{P}][\text{Sb}(\text{N}_3)_6]$, to date the only structurally characterized complex containing this hexaazidoantimonate,^[2d] also shows octahedral coordination, its crystallographic symmetry is $\bar{1}$. The same structural findings were reported for two arsenate complexes containing hexaazidoarsenate $[\text{As}(\text{N}_3)_6]^-$ anions,^[5a,5g] and for the hexaazidophosphate anion in $[\text{Ph}_3\text{PNPPH}_3][\text{P}(\text{N}_3)_6]$.^[5d] The azide group in **2** only slightly deviates from linearity (N1-N2-N3 175.25(12)°) and shows typical N-N bond lengths of covalently bound azides (N1-N2 1.2235(13), N2-N3 1.1290(14) Å). The Sb-N bond length (2.0859(9) Å) is comparable to the axial bound azido group in **1** and in $[\text{Ph}_4\text{P}][\text{Sb}(\text{N}_3)_6]$ (2.065(2) – 2.085(3) Å). DFT structure optimization of the anion of **2** resulted in a S_6 -symmetrical structure ($\bar{3}$), which is a minimum according to frequency analysis. The Sb-N bond length was found to be 2.115 Å at the B3LYP level and 2.137 Å at the BP86 level of theory, respectively.

As mentioned earlier, any attempt to synthesize $[\text{Ph}_3\text{PNPPH}_3][\text{Sb}(\text{N}_3)_4]$ and $[\text{Ph}_3\text{PNPPH}_3]_3[\text{Sb}(\text{N}_3)_6]$, containing monoanionic tetraazidoantimonite and trianionic hexaazidoantimonite, respectively, failed. This is somewhat surprising since the synthesis of tetraphenylphosphonium tetraazidoantimonite $[\text{Ph}_4\text{P}][\text{Sb}(\text{N}_3)_4]$ was reported.^[5a] Unfortunately, its solid state structure couldn't be determined, but the structure of the anion was calculated at the B3LYP level of theory. In addition, $[\text{Ph}_4\text{P}]_3[\text{Bi}(\text{N}_3)_6]$ containing the trianionic hexaazidobismutite was recently structurally characterized by Schulz et al.^[2f] We therefore calculated possible structures of $[\text{Sb}(\text{N}_3)_4]^-$ and $[\text{Sb}(\text{N}_3)_6]^{3-}$ and compared their relative energies with that of pentaazidoantimonite $[\text{Sb}(\text{N}_3)_5]^{2-}$. We found that the structure of trianionic hexaazidoantimonite $[\text{Sb}(\text{N}_3)_6]^{3-}$ optimized in the S_6 -symmetry constraints is a third order saddle point and significantly higher in energy compared to monoanionic hexaazidoantimonate $[\text{Sb}(\text{N}_3)_6]^-$ (319 and 284 kJ/mol at the B3LYP and BP86 levels of theory). Dissociation of $[\text{Sb}(\text{N}_3)_6]^{3-}$ into $[\text{Sb}(\text{N}_3)_5]^{2-}$ and N_3^- is thermodynamically strongly favored (B3LYP: 412 kJ/mol; BP86: 399 kJ/mol), clearly proving that the trianion is rather unlikely to be obtained experimentally. According to the much smaller dissociation energy calculated for the dissociation of $[\text{Sb}(\text{N}_3)_5]^{2-}$ into $[\text{Sb}(\text{N}_3)_4]^-$ (C_s symmetry as also calculated by Klapötke et al.^[5a]) and N_3^- (B3LYP: 132 kJ/mol; BP86: 124 kJ/mol), pentaazidoantimonite

$[\text{Sb}(\text{N}_3)_5]^{2-}$ is more likely to be stable in the solid state by use of sterically demanding cations such as $[\text{Ph}_3\text{PNPPh}_3]^+$.

Conclusion. We synthesized complexes containing the pentaazidoantimonite dianion, to date an unforeseen group 15 element polyazide, and the hexaazidoantimonate monoanion. In contrast, the formation of the hexaazidoantimonite trianion, which lies much higher in energy compared to the dianion according to theoretical calculations, was not observed.

Experimental Section

Azidoantimonites and -antimonates are potentially toxic and can decompose explosively under various conditions! They should be handled only on a scale of less than 2 mmol with appropriate safety precautions (safety shields, safety glasses, face shields, leather gloves, protective clothing, such as leather suits, and ear plugs). Teflon containers should be used, whenever possible, to avoid hazardous fragmentation. Ignoring safety precautions can lead to serious injuries. Reactions were carried out in traps constructed from FEP tubes. Volatile materials were handled in a stainless steel-Teflon-FEP or Duran glass vacuum line, nonvolatile materials under Ar in a glove box. CH_2Cl_2 was dried over CaH_2 and degassed prior to use. $(\text{CH}_3)_3\text{SiN}_3$ was purified by fractional condensation prior to use. $[\text{Ph}_3\text{PNPPh}_3]\text{N}_3$ ^[17] and $\text{Sb}(\text{N}_3)_3$ ^[4] were prepared according to literature methods. NMR spectra were recorded on a Bruker Avance 300 spectrometer at 25 °C at 300.1 MHz (^1H), 75.5 MHz (^{13}C), 21.7 MHz (^{14}N) and 121.5 MHz (^{31}P). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to internal CDCl_3 (^1H : $\delta = 7.26$; ^{13}C : $\delta = 77.0$), $^{14}\text{N}\{^1\text{H}\}$ spectra to external CH_3NO ($\delta(^{14}\text{N}) = 0$) and $^{31}\text{P}\{^1\text{H}\}$ spectra to external 85 % H_3PO_4 ($\delta(^{31}\text{P}) = 0$). Raman spectra were recorded with a Bruker FT-Raman spectrometer RFS 100/S using the 1064 nm line of a Nd:YAG laser. The backscattered (180°) radiation was sampled and analysed (Stoke range: 0 to 3500 cm^{-1}). The powdered samples were measured in sealed capillaries (typical operation parameters: 8000 scans and a resolution of 4 cm^{-1}) using a laserpower of 100 mW. IR spectra were recorded on a Alpha-T FT-IR spectrometer with a single reflection ATR sampling module.

$[\text{Ph}_3\text{PNPPh}_3]_2[\text{Sb}(\text{N}_3)_5]$ (1**).** 0.22 g (0.87 mmol) $\text{Sb}(\text{N}_3)_3$ was loaded in the glovebox into a FEP reaction trap and suspended in 3 mL of CH_2Cl_2 . 0.33 g (0.57 mmol) neat $[\text{Ph}_3\text{PNPPh}_3]\text{N}_3$ was added at ambient

temperature and stirred for additional 2 hours. Thereafter, all volatile components were pumped off, yielding an off-white solid residue. Colorless single crystals of **1** were grown from a solution in CH₂Cl₂ by slow evaporation of the solvent in a dynamic vacuum.

Yield: 1.20 g (98 %). Melting point: 140 °C. Anal. Found (calcd) for C₇₂H₆₀N₁₇P₄Sb (1409.03 g mol⁻¹): C 61.37, H 4.29, N 16.90; found: C 61.49, H 4.68, N 16.11. IR (ATR, 32 scans): ν = 3321 (w), 3057 (w), 2093 (m), 2020 (s), 1587 (w), 1482 (w), 1435 (m), 1239 (s), 1181 (s), 1111 (s), 1026 (w), 996 (m), 983 (m), 861 (w), 796 (w), 746 (m), 720 (s), 688 (s), 525 (s), 494 (s), 391 cm⁻¹. Raman (100 mW, 25 °C, 8000 Scans): ν = 3174, 3145, 3061, 3010, 2993, 2959, 2907, 2097, 2076, 2053, 1589, 1575, 1439, 1333, 1273, 1184, 1164, 1111, 1028, 1000, 727, 664, 617, 414, 311, 267, 237, 198, 89 cm⁻¹. ¹H NMR (CDCl₃): δ = 7.43-7.50 (m, 24H), 7.65-7.69 (m, 6H). ¹³C{¹H} NMR (CDCl₃): δ = 126.9 (dd, ³J_{P,C} = 1.8 Hz, ¹J_{P,C} = 108.1 Hz, *C-*ipso**), 129.6 (m), 132.1 (m, 12C), 133.9 (s, *C-p*). ¹⁴N{¹H} (CDCl₃): δ = -137 (s, N_β, Δ_{v1/2} = 72 Hz), -184 (s, N_γ, Δ_{v1/2} = 56 Hz), -250 (s, N_α, Δ_{v1/2} = 450 Hz). ¹³P{¹H} (CDCl₃): δ = 21.1 (s).

[Ph₃PNPPh₃][Sb(N₃)₆] (2). 2 mL of (CH₃)₃SiN₃ was condensed to 0.22 g (1 mmol) SbF₅ in a FEP reaction trap at -196 °C. The trap was slowly warmed to -25 °C over a period of 6 h, during which the mixture was occasionally (be careful!) agitated. 0.58 g (1 mmol) [Ph₃PNPPh₃]₃ dissolved in 2 mL of CH₂Cl₂ was added at -25 °C. The reaction mixture was kept at -25 °C for 30 min and then slowly warmed to ambient temperature. Volatile components were pumped off, yielding a white solid residue. Colorless crystals of **2** were grown from a solution in CH₂Cl₂ by slow evaporation of the solvent in a dynamic vacuum.

Yield: 0.89 g (97 %). Melting point: 177 °C. Anal. Found (calcd) for C₃₆H₃₀N₁₉P₂Sb (912.46 g mol⁻¹): C 47.39, H 3.31, N 29.17; found: C 47.92, H 3.35, N 28.49. IR (ATR, 32 scans): ν = 2085 (s), 1588 (w), 1481 (w), 1436 (w), 1399 (s), 1334 (m), 1308 (w), 1262 (s), 1180 (m), 1160 (w), 1115 (s), 746 (m), 996 (w), 752 (w), 723 (s), 689 (s), 663 (m), 581 (w), 530 (s), 492 (s), 447 (w), 417 (s) cm⁻¹. Raman (100 mW, 25 °C, 8000 Scans): ν = 3176, 3150, 3065, 2957, 2903, 2115, 2085, 1589, 1576, 1438, 1336, 1262, 1182, 1160, 1114, 1028, 1000, 928, 847, 724, 658, 618, 411, 381, 266, 231, 182, 155, 91 cm⁻¹. ¹H NMR (CDCl₃): δ = 7.42-7.49 (m, 24H), 7.65-7.69 (m, 6H). ¹³C{¹H} NMR (CDCl₃): δ = 127.0 (dd, ³J_{PC} =

1.8 Hz, $^1J_{PC} = 108.0$ Hz, C-*ipso*), 129.5 (m), 132.1 (m), 133.9 (s, C-*p*). $^{14}\text{N}\{^1\text{H}\}$ (CDCl_3): $\delta = -140$ (s, N_β , $\Delta\nu_{1/2} = 58$ Hz), -184 (s, N_γ , $\Delta\nu_{1/2} = 820$ Hz), -282 (s, N_α , $\Delta\nu_{1/2} = 450$ Hz) ppm. $^{13}\text{P}\{^1\text{H}\}$ (CDCl_3): $\delta = 21.1$ (s).

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References

- [1] R. Haiges, J. A. Boatz, A. Vij, M. Gerken, S. Schneider, T. Schroer, K. O. Christe, *Angew. Chem.* **2003**, *115*, 6027; *Angew. Chem. Int. Ed.* **2003**, *42*, 5847.
- [2] a) T. M. Klapötke, P. Geissler, *J. Chem. Soc., Dalton Trans.* **1995**, 3365. b) R. Haiges, A. Vij, J. A. Boatz, S. Schneider, T. Schroer, M. Gerken, K. O. Christe, *Chem. Eur. J.* **2004**, *10*, 508. c) P. Geissler, T. M. Klapötke, H.-J. Kroth, *Spectrochim. Acta Part A* **1995**, *51*, 1075. d) R. Haiges, J. A. Boatz, A. Vij, V. Vij, M. Gerken, S. Schneider, T. Schroer, M. Yousufuddin, K. O. Christe, *Angew. Chem.* **2004**, *116*, 6844; *Angew. Chem. Int. Ed.* **2004**, *43*, 6676. e) T. M. Klapötke, A. Schulz, J. McNamara, *J. Chem. Soc. Dalton Trans.* **1996**, 2985. f) A. Villinger, A. Schulz, *Angew. Chem.* **2010**, *122*, 8190; *Angew. Chem. Int. Ed.* **2010**, *49*, 8017.
- [3] $\text{P}(\text{N}_3)_3$, initially reported by Buder, was neither isolated nor structurally characterized: a) W. Buder, A. Schmidt, *Z. Anorg. Allg. Chem.* **1975**, *415*, 263. b) K. B. Dillon, A. W. G. Platt, T. C. Waddington, *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 511. However, the photoelectron spectrum of $\text{P}(\text{N}_3)_3$ was recently reported: X. Zeng, W. Wang, F. Liu, M. Ge, Z. Sun, D. Wang, *Eur. J. Inorg. Chem.* **2006**, 416.
- [4] S. Schulz, B. Lyhs, G. Jansen, D. Bläser, C. Wölper, *J. Chem. Soc., Chem. Commun.* **2011**, *47*, 3401.
- [5] a) K. Karaghiosoff, T. M. Klapötke, B. Krumm, H. Nöth, T. Schmitt, M. Suter, *Inorg. Chem.* **2002**, *41*, 170. b) H. W. Roesky, *Angew. Chem.* **1967**, *79*, 651; *Angew. Chem. Int. Ed.* **1967**, *6*, 637. c) P. Volgnandt, A. Schmidt, *Z. Anorg. Allg. Chem.* **1976**, *425*, 189. d) P. Portius, P. W. Fowler, H. Adams, T. Z. Todorova, *Inorg. Chem.* **2008**, *47*, 12004. e) R. Haiges, S. Schneider, T. Schroer, K. O. Christe, *Angew. Chem.* **2004**, *116*, 5027; *Angew. Chem., Int. Ed.* **2004**, *43*, 4919. f) R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, *Angew. Chem.* **2004**, *118*, 3664; *Angew. Chem., Int. Ed.* **2006**, *45*, 3584. g) T. M. Klapötke, H. Nöth, T. Schütt, M. Warchhold, *Angew. Chem.* **2000**, *112*, 2197; *Angew. Chem. Int. Ed.* **2000**, *39*, 2108. h) A. Schmidt, *Chem. Ber.* **1970**, *103*, 3923. i) W. Buder, A. Schmidt, *Chem. Ber.* **1973**, *106*, 3812.
- [6] B. Lyhs, D. Bläser, C. Wölper, S. Schulz, *Chem. Eur. J.* **2011**, *17*, 4914.

[7] Bruker AXS D8 Kappa diffractometer with APEX2 detector (MoK α radiation, $\lambda = 0.71073 \text{ \AA}$; $T = 100(1) \text{ K}$). The structure was solved by Direct Methods (SHELXS-97, G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467) and refined by full-matrix least-squares on F^2 . Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick, Universität Göttingen, 1997. See also: Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2008**, *64*, 112.). **1:** $[\text{C}_{36}\text{H}_{30}\text{N}_2\text{P}_2]_2 \times \text{N}_{15}\text{Sb}$, $M = 1409.00$, colorless crystal (0.34 x 0.32 x 0.28 mm); orthorhombic, space group $Pca2_1$; $a = 19.8235(4)$, $b = 19.9339(4)$, $c = 16.5343(4) \text{ \AA}$; $\alpha = \beta = \gamma = 90^\circ$, $V = 6533.7(2) \text{ \AA}^3$; $Z = 4$; $\mu = 0.579 \text{ mm}^{-1}$; $\rho_{\text{ber.}} = 1.432 \text{ g cm}^{-3}$; 74037 reflexes ($2\theta_{\text{max}} = 57^\circ$), 15981 unique ($R_{\text{int}} = 0.0213$); 848 parameters; largest max./min. in the final difference Fourier synthesis 2.208 e\AA^{-3} [0.81 \AA from Sb(1)]/ -0.766 e\AA^{-3} ; max./min. transmission 0.75/0.65; $R_1 = 0.0293$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.0780. Refinement as racemic twin with Flack absolute structure parameter 0.155(8) in the final structure factor calculation (a) H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876. b) G. Bernadinelli, H. D. Flack, *Acta Crystallogr. Sect. A* **1985**, *41*, 500.). **2:** $[\text{C}_{36}\text{H}_{30}\text{N}_2\text{P}_2] \times \text{N}_{18}\text{Sb}$, $M = 912.48$, colorless crystal (0.42 x 0.35 x 0.28 mm); rhombohedral (hexagonal axes), space group $R\bar{3}$; $a = 14.3587(2)$, $b = 14.3587(2)$, $c = 16.6105(4) \text{ \AA}$; $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 2965.81(9) \text{ \AA}^3$; $Z = 3$; $\mu = 0.834 \text{ mm}^{-1}$; $\rho_{\text{ber.}} = 1.533 \text{ g cm}^{-3}$; 19369 reflexes ($2\theta_{\text{max}} = 61^\circ$), 2018 unique ($R_{\text{int}} = 0.0195$); 89 parameters; largest max./min. in the final difference Fourier synthesis 0.343 e\AA^{-3} / -0.292 e\AA^{-3} ; max./min. transmission 0.75/0.67; $R_1 = 0.0168$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.0450. The crystallographic data (without structure factors) were deposited as "supplementary publication no. CCDC-826702 and CCDC-826701" at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: (+44)1223/336033; E-mail: deposit@ccdc.cam-ak.uk).

[8] T. M. Klapötke, B. Krumm, P. Mayer, I. Schwab, *Angew. Chem.* **2003**, *115*, 6024; *Angew. Chem. Int. Ed.* **2003**, *42*, 5843.

[9] J. Drummond, J. S. Wood, *J. Chem. Soc., Chem. Commun.* **1969**, 1373.

[10] See for instance: a) P. Gravereau, C. Mirambet, L. Fournes, J. Grannec, L. Lozano, *Acta Crystallogr. Sect. C* **1990**, *46*, 2294. b) B. Kruss, M. L. Ziegler, *Z. Anorg. Allg. Chem.* **1972**, *388*, 158. c) L.Z. Chen, *Acta Crystallogr. Sect. E* **2009**, *65*, m689.

[11] a) P. J. Wheatley, *J. Chem. Soc.* **1964**, 3718. b) A. L. Beauchamp, M. J. Bennett, F. A. Cotton, *J. Am. Chem. Soc.* **1968**, *90*, 6675.

[12] A. Schmuck, J. Buschmann, J. Fuchs, K. Seppelt, *Angew. Chem.* **1987**, *99*, 1206; *Angew. Chem. Int. Ed.* **1987**, *26*, 1180.

[13] P. Pyykko, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186.

[14] Full details are given in the electronic supplement.

[15] C. Wölper, Dissertation TU Braunschweig, 2009, Papierflieger Verlag, Clausthal-Zellerfeld.

[16] G. R. Lewis, I. Dance, *J. Chem. Soc., Dalton Trans.* **2000**, 299.

[17] A. Martinsen, J. Songstad, *Acta Chem. Scand. A* **1977**, 31, 4247.

Schemes and Figures legends

Scheme 1. Synthesis of $[\text{Ph}_3\text{PNPPPh}_3]_2[\text{Sb}(\text{N}_3)_5]$ **1** and $[\text{Ph}_3\text{PNPPPh}_3][\text{Sb}(\text{N}_3)_6]$ **2**.

Figure 1. Comparison of IR spectra of $[\text{Ph}_3\text{PNPPPh}_3]\text{Cl}$ (top), **1** (middle) and **2** (bottom).

Figure 2. Comparison of Raman spectra of $[\text{Ph}_3\text{PNPPPh}_3]\text{Cl}$ (top), **1** (middle) and **2** (bottom).

Figure 3. Comparison of IR spectra of a dry (black) and CH_2Cl_2 -tempered (pink) single crystal of **1**, a diluted solution (green) and a concentrated solution (blue) of **1** in CH_2Cl_2 , and the crystalline residue obtained after removal of the solvent (red).

Figure 4. Representation of the pentaazido dianion of **1**. Selected bond lengths [Å] and angles [°]: Sb1-N1 2.262(2), Sb1-N4 2.2825(19), Sb1-N7 2.099(2), Sb1-N10 2.297(2), Sb1-N13 2.324(2), N1-N2 1.216(3), N2-N3 1.140(3), N7-N8 1.214(3), N8-N9 1.143(3); N1-Sb1-N4 84.32(9), N1-Sb1-N7 84.20(9), N1-Sb1-N10 93.20(9), N1-Sb1-N13 167.31(8), Sb1-N1-N2 116.47(17), Sb1-N10-N11 125.89(18), Sb1-N7-N8 117.83(18), N1-N2-N3 176.2(3).

Figure 5. Calculated (B3LYP) minimum structure of **1** in the gas phase. Selected bond lengths [Å] and angles [°]: Sb1-N_{ax} 2.113, Sb1-N_{eq} 2.295, 2.312, 2.382, 2.404, N1-N2 1.205, N2-N3 1.140, Sb1-N1-N2 123.08, N1-N2-N3 174.48.

Figure 6. Layer in the packing of **1** viewed parallel to *c*. 6PE motifs are shown in thin dashed lines, motif 3 in thick dashed lines. Bonds of the cations are represented by thin lines, those of the anion by thick ones. Hydrogen atoms not involved in interaction are omitted for clarity. Atoms displayed at arbitrary radii.

Figure 7. Environment of the anion. C–H···N related to the differing conformation between theory and experiment displayed in thick dashed bonds (others omitted). Phenyl rings not involved in interaction are reduced to the ipso C atoms and non-interacting H are removed for clarity. Atoms displayed at arbitrary radii.

Figure 8. Representation of the hexaazido monoanion of **2**. Selected bond lengths [Å] and angles [°]: Sb1-N1 2.0859(9), N1-N2 1.2235(13), N2-N3 1.1290(14); N1-Sb1-N1A 88.57(4), N1-Sb1-N1B 91.43(4), N1-Sb1-N1C 180.0, Sb1-N1-N2 115.21(7), N1-N2-N3 175.25(12). Symmetry operations: A: $-y, x-y, z$; B: $x-y, x, -z$; C: $-x, -y, -z$; D: $y, -x+y, -z$; E: $-x+y, -x, z$.

Entry for the Table of Contents

Layout 1

Benjamin Lyhs, Georg Jansen, Dieter Bläser and Christoph Wölper, Stephan Schulz*

Synthesis and Structural Characterization of Antimony Polyazides

Synthesis of antimony polyazides and structural characterization of the pentaazidoantimonite

$[\text{Sb}(\text{N}_3)_5]^{2-}$ dianion, that is without precedent in group 15 polyazide chemistry.

Catch Phrase: Polyazides

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