Supporting Information

Synthesis and Crystal Structures of the First Antimony(III) Aziridinides

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General: All reactions were performed under an inert atmosphere using standard Schlenk techniques or in an M. Braun N_2-filled glovebox with O_2 levels maintained at or below 1 ppm. Glassware was dried at 120 °C overnight. All solvents were dried by destillation from sodium/benzophenone under nitrogen atmosphere prior to use. $Sb(NMe_2)_3$ was synthesized after a previously published procedure [S1], other reagents were commercially available and used as received. NMR spectra were recorded THF-D_8 solution at 23(2)°C on a Bruker DPX 400 spectrometer (^{1}H: 400.1 MHz; ^{13}C: 100.6 MHz; ^{7}Li: 155.5 MHz). A saturated solution of LiCl in D_2O was used as reference for the ^{7}Li spectra (δ_{Li} = 0 ppm). IR spectra were recorded between 4000 cm^{-1} and 400 cm^{-1}, using a Bruker Vertex 70V spectrometer equipped with a diamond ATR unit and a "Golden Gate" unit. Electron impact mass spectra were measured on a MAT 95 spectrometer with an ionization energy of 70 eV, and elemental analyses (C, H and N) were performed using a VARIO EL cube apparatus.

Synthesis of $[\{Li_3Sb(\mu_3\text{-}Cl)_2(\mu\text{-}c\text{-}NC_2H_4)_4(THF)_2\}]_\infty$ (1): A solution of Aziridine (6.28 ml, 121 mmol) in 125 ml of THF at 0°C was treated slowly with a solution of *n*-Butyllithium in hexanes (75.6 ml, 1.6 mol/l, 121 mmol). The reaction mixture was stirred for 10 min at 0°C, then warmed to room temperature and stirred overnight. Subsequently, anhydrous $SbCl_3$ (9.20 g, 40.3 mmol) dissolved in 50 ml of THF was added dropwise at –20°C. The dark grey mixture was stirred for 1h at –20°C, then warmed to room temperature and stirred for another 5 d. After refluxing for 1 h, the reaction mixture was filtered and the yellow filtrate concentrated to a volume of 15 ml. Storing the solution at 4°C overnight afforded light yellow crystals of the solvate **1** · THF. These were filtered off and dried *in vacuo*, affording solvent-free **1**. Yield: 2.1 g (21%). Dec. 145 °C. **Elemental analysis**: calcd. for $C_{16}H_{32}Cl_2Li_3N_4O_2Sb$, *M* = 525.92 g/mol: C 36.54%, H 6.13%, N 10.65%; found: C 36.51%, H 6.19%, N 10.60%. **^{1}H-NMR**: δ = 1.72 (m, 8H; β-C*H*$_2$ THF), 1.86 (s, 16H; C*H*$_2$ Azn), 3.58 (m, 8H; α-C*H*$_2$ THF) ppm. **^{13}C-NMR**: δ = 21.1 (s; *C*H$_2$ Azn), 26.4 (s; β-*C*H$_2$ THF), 68.2 (s; α-*C*H$_2$ THF) ppm. ^{7}Li-NMR: δ = –1.41 (s) ppm. **IR**: ν = 2981m (ν_{as} CH$_2$), 2864m (ν_{sym} CH$_2$), 1467m (δ CH$_2$), 1235m (sym. ring breathing Azn), 1047m (ν C-O THF), 877s (δ ring Azn + ρ CH$_2$), 493m (ν_{as} Sb-N), 423m (ν_{sym} Sb-N) cm^{-1}. [S2, S3] **MS (EI)**: m/z (%) 249 (14) [^{123}Sb(Azn)$_3$]$^+$, 247 (19) [^{121}Sb(Azn)$_3$]$^+$, 207 (91) [^{123}Sb(Azn)$_2$]$^+$, 205 (100) [^{121}Sb(Azn)$_2$]$^+$, 165 (69) [^{123}Sb(Azn)]$^+$, 163 (74) [^{121}Sb(Azn)]$^+$, 123 (55) [^{123}Sb]$^+$, 121 (62) [^{121}Sb]$^+$.

Synthesis of $Sb_2(Azn)_6$ (2): A solution of $Sb(NMe_2)_3$ (8.45 g, 33 mmol) in 30 ml of THF at –20°C was treated slowly with Aziridine (5.18 ml, 100 mmol). The reaction mixture was stirred for 10 min at –20°C, then warmed to room temperature and stirred for 42 hours to give a light yellow solution. The solvent was removed *in vacuo* and the oily residue distilled at approx. 0.05 mbar and a bath temperature of 120°C, yielding colorless oil that gradually solidified to colorless crystals suitable for X-ray structure analysis. The crystals are a mixture of two modifications, which could not be separated and were only distinguished by X-ray determination of the unit cell parameters. Yield: 6.00 g (73%). Highly air-sensitive solid, M.p. 49–56°C. **Elemental analysis**: calcd. for $C_{12}H_{24}N_6Sb_2$, *M* = 495.89 g/mol: C 29.06%, H 4.88%, N

16.95%; found: C 29.05%, H 4.79%, N 16.99%. **^{1}H-NMR**: δ = 1.95 (s, 24H) ppm. **^{13}C-NMR**: δ = 21.1 (s) ppm. **IR**: ν = 2973m (ν_{as} CH_2), 2873m (ν_{sym} CH_2), 1464m (δ CH_2), 1223s (sym. ring breathing Azn), 860vs, 805s (δ ring Azn), 479m, 422m (ν Sb-N) cm^{-1}. [S2, S3] **MS (EI):** m/z (%) 249 (17) $[^{123}Sb(Azn)_3]^+$, 247 (22) $[^{121}Sb(Azn)_3]^+$, 207 (98) $[^{123}Sb(Azn)_2]^+$, 205 (100) $[^{121}Sb(Azn)_2]^+$, 165 (69) $[^{123}Sb(Azn)]^+$, 163 (72) $[^{121}Sb(Azn)]^+$, 123 (61) $[^{123}Sb]^+$, 121 (66) $[^{121}Sb]^+$.

Crystal Structure Analysis of $[\{Li_3Sb(\mu_3\text{-}Cl)_2(\mu\text{-}Azn)_4(THF)_2\} \cdot THF]_\infty$ (1 · THF)

CCDC depository number: 1532695

Crystallographer: P. Liebing
ID code: li0050 **Date:** 2016-06-01
Formula sum: $C_{20}H_{40}Cl_2Li_3N_4O_3Sb$
Formula moieties: $C_{16}H_{32}Cl_2Li_3N_4O_2Sb$, C_4H_8O

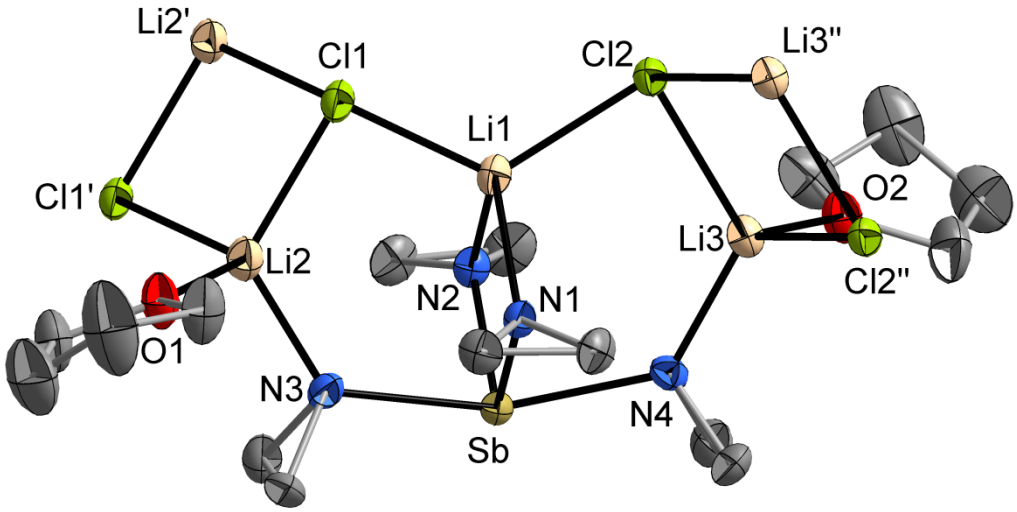

Figure S1. Molecular structure of compound **1** · THF in the crystal. Displacement ellipsoids with 50% probability, H atoms omitted for clarity. Symmetry codes: ' 1–x, 1–y, 1–z; '' 2–x, 2–y, 2–z.

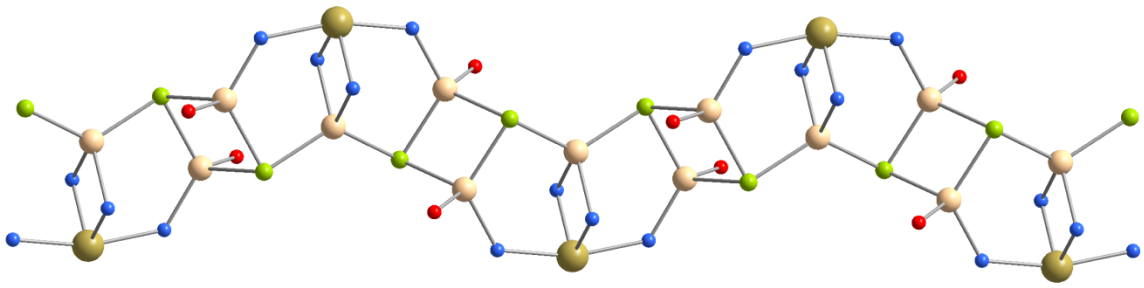

Figure S2. Representation of the polymeric structure of compound **1**. The polymeric ladder extends along the space-diagonal of the unit cell.

Crystallographic Data and Details on Structure Refinement for 1 · THF

formula sum	$C_{20}H_{40}Cl_2Li_3N_4O_3Sb$
formula weight	598.03
crystal color / shape / size (mm)	light yellow prisms, 0.32 × 0.25 × 0.13
crystal system	triclinic
space group	$P\bar{1}$
unit cell parameters	
a (Å)	11.5142(5)
b (Å)	12.0844(5)
c (Å)	12.4101(5)
α (deg)	102.187(3)
β (deg)	111.543(3)
γ (deg)	107.316(3)
unit cell volume V (Å^3)	1430.1(1)
molecules per cell z	2
crystallographic density ρ_{calcd} (g cm^{-3})	1.389
absorption coefficient μ (mm^{-1})	1.177
diffractometer	STOE IPDS 2T
radiation (λ [Å])	graphite-monochromated Mo-K_α (0.71073)
temperature (°C)	–120
scan type	ω scan (increment 1.5°, exposure 1 min)
completeness of dataset	99.7%
θ range of data collection (deg)	1.893 … 25.994
reflections collected	11919 (–13 ≤ h ≤ 14, –14 ≤ k ≤ 14, –15 ≤ l ≤ 15)
independent reflections	5603 (R_{int} = 0.0435)
independent reflections with $I>2\sigma(I)$	5054
structure solution method	patterson methods (SIR-97) [S4]
refinement method	full-matrix least-squares on F^2 (SHELXL 2016/4) [S5]
absorption correction method	numerical [S6]
range of transmission factors	0.7163 … 0.8878
data / parameters / restraints	5603 / 317 / 70[a]
goodness of fit (GooF) [all data]	1.181
final R values	
R_1 [all data, $I \geq 2\sigma(I)$]	0.0488, 0.0433
wR_2 [all data, $I \geq 2\sigma(I)$]]	0.1089, 0.1072
largest difference peak and hole	1.106 and –0.915 e Å^{-3}
Extinction coefficient	0.0040(6)

Refinement special details: THF C atoms C14 and C15 are disordered over two positions, where site occupancy factors were freely refined. [a] Restraints on anisotropic displacement parameters (SIMU with ESD of 0.01) of the C atoms of the THF ligand at Li3 (C13–C16), restraints on the non-coordinated THF molecule (SADI and SIMU).

Crystal Structure Analysis of the monoclinic modification of $Sb_2(Azn)_6$ (2)

CCDC depository number: 1532696

Crystallographer:	P. Liebing	
ID code:	li0201	**Date:** 2016-12-22
Formula sum:	$C_{12}H_{24}N_6Sb_2$	
Formula moieties:	$C_{12}H_{24}N_6Sb_2$	

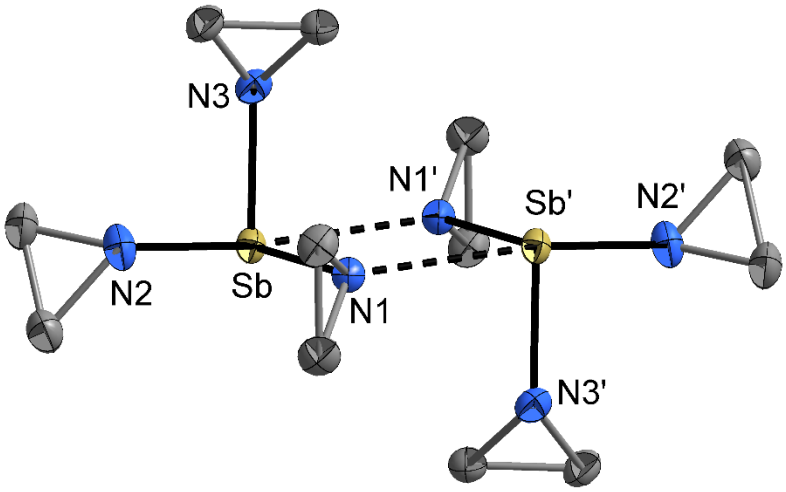

Figure S3. Molecular structure of compound **2** in the monoclinic crystal. Displacement ellipsoids drawn at the 50% probability level, H atoms omitted for clarity. Symmetry operator to generate equivalent atoms: ‘ 2–x, –y, 1–z.

Crystallographic Data and Details on Structure Refinement for 2 (monoclinic)

formula sum	$C_{12}H_{24}N_6Sb_2$
formula weight	495.87
crystal color / shape / size (mm)	colorless prisms / 0.30 × 0.17 × 0.10
crystal system	monoclinic
space group	$P2_1/c$
unit cell parameters	
a (Å)	7.6116(4)
b (Å)	17.4421(7)
c (Å)	6.8916(4)
α (deg)	90
β (deg)	113.505(4)
γ (deg)	90
unit cell volume V (Å^3)	839.03(8)
molecules per cell z	2
crystallographic density ρ_{calcd} (g cm^{-3})	1.963
absorption coefficient μ (mm^{-1})	3.221
diffractometer	STOE IPDS 2T
radiation (λ [Å])	graphite-monochromated Mo-K_α (0.71073)
temperature (°C)	–120
scan type	ω scan (increment 1.5°, exposure 1 min)
completeness of dataset	100%
θ range of data collection (deg)	2.335 … 26.999
reflections collected	6453 ($-9 \le h \le 9$, $-22 \le k \le 19$, $-8 \le l \le 8$)
independent reflections	1834 (R_{int} = 0.0337)
independent reflections with $I>2\sigma(I)$	1668
structure solution method	patterson methods (SIR-97) [S4]
refinement method	full-matrix least-squares on F^2 (SHELXL 2016/4) [S5]
absorption correction method	numerical [S6]
range of transmission factors	0.4895 … 0.7079
data / parameters / restraints	1834/ 92 / 0
goodness of fit (GooF) [all data]	1.042
final R values [a]	
R_1 [all data, $I \ge 2\sigma(I)$]	0.0174, 0.0136
wR_2 [all data, $I \ge 2\sigma(I)$]]	0.0316, 0.0308
largest difference peak and hole	0.320 and –0.444 e Å^{-3}
Extinction coefficient	0.0068(3)
Flack parameter	–
Refinement special details: –	

Crystal Structure Analysis of the triclinic modification of $Sb_2(Azn)_6$ (2)

Crystallographer: P. Liebing
ID code: li0201 **Date:** 2016-12-21
Formula sum: $C_{12}H_{24}N_6Sb_2$
Formula moieties: $C_{12}H_{24}N_6Sb_2$

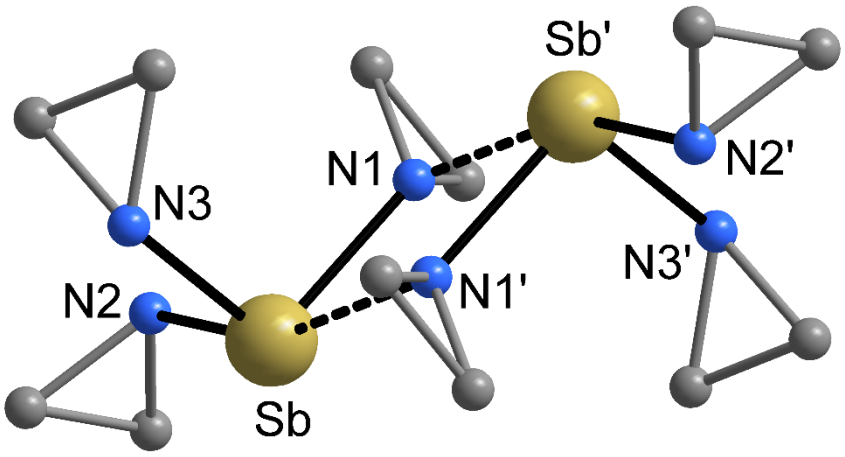

Figure S4. Molecular structure of compound **2** in the triclinic crystal. Symmetry operator to generate equivalent atoms: ' 1–x, 1–y, 1–z. Approx. Sb-N distances (pm) and angles (deg.): Sb-N1 210, Sb···N1' 253, Sb-N2 211, Sb-N3 204, N1-Sb-N1' 71, N1-Sb-N2 91, N1'-Sb-N2 159, N1-Sb-N3 101, N1'-Sb-N3 80, Sb-N1-Sb' 109.

Crystallographic Data and Details on Structure Refinement for 2 (triclinic)

formula sum	$C_{12}H_{24}N_6Sb_2$
formula weight	495.87
crystal color / shape / size (mm)	colorless prisms / 0.28 × 0.26 × 0.19
crystal system	triclinic
space group	$P\bar{1}$
unit cell parameters	
a (Å)	6.8918(6)
b (Å)	7.7053(7)
c (Å)	9.0566(7)
α (deg)	75.802(6)
β (deg)	88.088(6)
γ (deg)	65.913(6)
unit cell volume V (Å^3)	424.44(7)
molecules per cell z	1
crystallographic density ρ_{calcd} (g cm^{-3})	1.940
absorption coefficient μ (mm^{-1})	3.183
diffractometer	STOE IPDS 2T
radiation (λ [Å])	graphite-monochromated Mo-K_α (0.71073)
temperature (°C)	–120
scan type	ω scan (increment 1.5°, exposure 1 min)
completeness of dataset	99.7%
θ range of data collection (deg)	2.326 … 27.498
reflections collected	4144 (–8 ≤ h ≤ 6, –10 ≤ k ≤ 10, –11 ≤ l ≤ 11)
independent reflections	1935 (R_{int} = 0.0452)
independent reflections with $I>2\sigma(I)$	1935
structure solution method	patterson methods (SIR-97) [S4]
refinement method	full-matrix least-squares on F^2 (SHELXL 2016/4) [S5]
absorption correction method	none
range of transmission factors	–
data / parameters / restraints	1935 / 46 / 0
goodness of fit (GooF) [all data]	3.681
final R values [a]	
R_1 [all data, $I \geq 2\sigma(I)$]	0.0997, 0.0936
wR_2 [all data, $I \geq 2\sigma(I)$]]	0.3960, 0.3950
largest difference peak and hole	5.525 and –3.846 e Å^{-3}
Extinction coefficient	–
Flack parameter	–

Refinement special details: The crystals were not suitable for full structure refinement. Only the Sb atom was refined with anisotropic displacement parameters, H atoms were omitted.

References

[S1] Moedritzer, K. The Preparation of Trisdimethylaminostibine, *Inorg. Chem.* **1964**, *3*, 609–610.

[S2] Kiennemann, A.; Levy, G.; Schué, F.; Taniélian, C. Sur la Préparation de quelques Tris(dialcoylamino)stibines et sur quelques unes de leurs Propriétés. *J. Organomet. Chem.* **1972**, *35*, 143–148.

[S3] Spell, H. L. The Infrared Spectra of N-Substituted Aziridine Compounds. *Anal. Chem.* **1967**, *39*, 185–193.

[S4] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. SIR97: a new tool for crystal structure determination and refinement. *J. Appl. Cryst.* **1999**, *32*, 115–119.

[S5] Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8.

[S6] Stoe & Cie **2002**. *X-Area and X-Red*. Stoe & Cie, Darmstadt, Germany.