

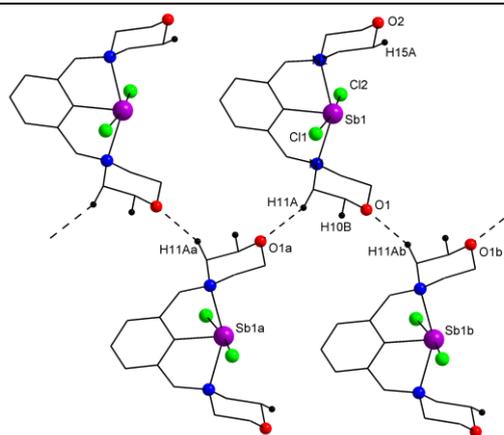
[2,6-{O(CH₂CH₂)₂NCH₂}₂C₆H₃]SbCl₂ – A NEW PINCER LIGAND-CONTAINING ORGANOANTIMONY(III) COMPOUND. MOLECULAR STRUCTURE AND SUPRAMOLECULAR ASPECTS

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The monoorganoantimony(III) dichloride [2,6-{O(CH₂CH₂)₂NCH₂}₂C₆H₃]SbCl₂ (**2**) was prepared by reacting [2,6-{O(CH₂CH₂)₂NCH₂}₂C₆H₃]Li, obtained *in situ* from 2,6-[O(CH₂CH₂)₂NCH₂}₂C₆H₃]Br (**1**) and ⁿBuLi in hexane, with SbCl₃ in Et₂O, in 1:1 molar ratio. The crystal and molecular structure of the **2**·CHCl₃ was established by single-crystal X-ray diffraction. A substitutional Cl/Br disorder was identified in the crystal of **2**, with average site occupancy factors of 87:13. In the molecule of **2** the organic group acts as an *NCN*-pincer ligand; both nitrogen atoms are strongly coordinated to the metal center [N–Sb 2.471(3), 2.480(3) Å] in *trans* to each other [N–Sb–N 151.07(9)°], thus leading to a distorted square pyramidal (*NCN*)SbX₂ geometry, with a T-shape arrangement of the primary bonds of the CSbX₂ core [Cl–Sb–Cl 171.65(12)°; Br–Sb–Br 170.1(4)°]. Intermolecular interactions, *i.e.* O···H and Cl···H (residual Br atoms are neglected), were found in the solid state resulting in a 3D supramolecular architecture.



INTRODUCTION

Over the last two decades, hypervalent organoantimony compounds were found to be very effective as reagents in transition-metal catalyzed cross-coupling reactions,¹ catalysts in organic chemistry,^{1f} *e.g.* one-pot three component Mannich-type reactions,² cross-condensation, cyclization–aromatization and epoxide aminolysis reactions,^{2b} Henry reaction,³ or as trapping agents for gaseous CO₂.⁴ Back in 1992, Atwood *et al.* used the *NCN*-pincer proligand 2,6-(Me₂NCH₂)₂C₆H₃Br to isolate the organoantimony(III) dichloride [2,6-(Me₂NCH₂)₂C₆H₃]SbCl₂, one of the first examples of hypercoordinated antimony(III) compound, by taking advantage of the two *sp*³ nitrogen atoms that can

coordinate to the metal centre.⁵ The aforementioned monoanionic ligand was proved to provide enough coordination protection at the metal center to allow isolation of stable monomeric antimony(III) chalcogenides, [2,6-(Me₂NCH₂)₂C₆H₃]Sb=E (E = Se, Te),⁶ and -carbonate, [2,6-(Me₂NCH₂)₂C₆H₃]SbCO₃,^{4a} as well as cyclic monoorganoantimony(III) chalcogenides, *cyclo*-[2,6-(Me₂NCH₂)₂C₆H₃Sb(μ-E)]₂ (E = O,^{4a,7} S,⁸ Se⁷). Later on, our group proposed a different *NCN* scaffold, *i.e.* R = 2,6-{MeN(CH₂CH₂)₂NCH₂}₂C₆H₃, that enabled the first structural characterization of 2-organo-1,3,2-dioxastibolane, RSb(OCR₂)₂ (R = H, Me) and -dioxastibole, RSb(O₂-1,2-C₆H₄).^{4c}

We report here on a new monoorganoantimony(III) dichloride, [2,6-{O(CH₂CH₂)₂NCH₂}₂

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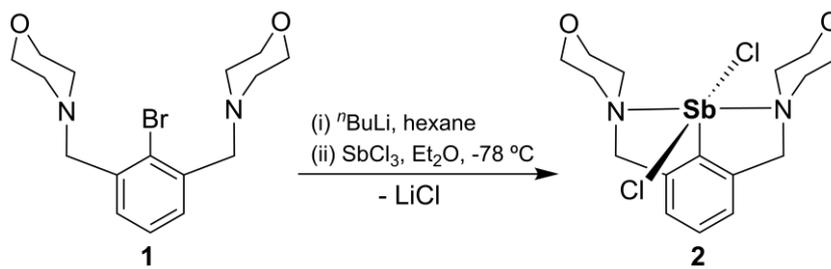
C_6H_3]SbCl₂ (**2**), which crystallized as a solvate with one molecule of CHCl₃ in the asymmetric unit and exhibits, in the solid state, substitutional Cl/Br disorder, *i.e.* [2,6-{O(CH₂CH₂)₂NCH₂}₂C₆H₃]SbBr_{0.27}Cl_{1.74}·CHCl₃, as proved by single-crystal X-ray diffraction.

RESULTS

The dichloride [2,6-{O(CH₂CH₂)₂NCH₂}₂C₆H₃]SbCl₂ (**2**) was prepared using a slightly modified method compared to that described in the literature.⁷ The lithiation of the proligand 2,6-[O(CH₂CH₂)₂NCH₂}₂C₆H₃Br (**1**) dissolved in *n*-hexane (instead of THF⁷) with a slight excess of ⁿBuLi in *n*-hexane was achieved at room temperature (instead of -78°C⁷), under argon

atmosphere. After removal of the solvent from the lithiation reaction mixture, diethyl ether was added, the resulting suspension was cooled to -78°C, and then added dropwise to a solution of SbCl₃ in diethyl ether (instead of THF⁷) (1:1 molar ratio), cooled to the same low temperature (Scheme 1).

After working up the reaction mixture in open atmosphere, compound **2** was isolated in about 43% yield (*cf.* 63%, using the procedure described in *ref.* 7) as a colorless, air and moisture stable crystalline solid. Details of the preparation is given in the Experimental section. The solution behavior of **2** was monitored by NMR spectroscopy and the spectra were found to exhibit only one set of ¹H and ¹³C{¹H} resonance signals with the same multiplicity and chemical shifts as previously reported.⁷



Scheme 1 – Synthesis of compound [2,6-{O(CH₂CH₂)₂NCH₂}₂C₆H₃]SbCl₂ (**2**).

Table 1

Selected interatomic distances (Å) and angles (deg) for [2,6-{O(CH₂CH₂)₂NCH₂}₂C₆H₃]SbBr_{0.27}Cl_{1.74}·CHCl₃ (**2**·CHCl₃)^a

Sb(1)–C(1)	2.104(3)		
Sb(1)–Cl(1)	2.700(7)	[Sb(1)–Br(1)]	[2.594(17)]
Sb(1)–Cl(2)	2.608(4)	[Sb(1)–Br(2)]	[2.674(15)]
Sb(1)–N(1)	2.471(3)		
Sb(1)–N(2)	2.480(3)		
N(1)–C(7)	1.478(5)	N(2)–C(12)	1.483(4)
N(1)–C(8)	1.493(5)	N(2)–C(13)	1.417(4)
N(1)–C(11)	1.482(4)	N(2)–C(16)	1.418(4)
O(1)–C(9)	1.402(5)	O(2)–C(14)	1.417(4)
O(1)–C(10)	1.423(6)	O(2)–C(15)	1.418(4)
Cl(1)–Sb(1)–Cl(2)	171.65(12)	[Br(1)–Sb(1)–Br(2)]	[170.1(4)]
C(1)–Sb(1)–Cl(1)	84.53(12)	[C(1)–Sb(1)–Br(1)]	[89.9(3)]
C(1)–Sb(1)–Cl(2)	87.17(10)	[C(1)–Sb(1)–Br(2)]	[80.3(3)]
N(1)–Sb(1)–N(2)	151.07(9)		
C(1)–Sb(1)–N(1)	75.65(10)		
C(1)–Sb(1)–N(2)	75.47(10)		
Cl(1)–Sb(1)–N(1)	93.61(15)	[Br(1)–Sb(1)–N(1)]	[96.2(4)]
N(1)–Sb(1)–Cl(2)	83.34(11)	[N(1)–Sb(1)–Br(2)]	[82.0(3)]
Cl(2)–Sb(1)–N(2)	93.68(11)	[Br(2)–Sb(1)–N(2)]	[91.6(3)]
N(2)–Sb(1)–Cl(1)	85.22(15)	[N(2)–Sb(1)–Br(1)]	[85.3(4)]

^a Molecular parameters involving the disordered bromine atoms are given in square brackets.

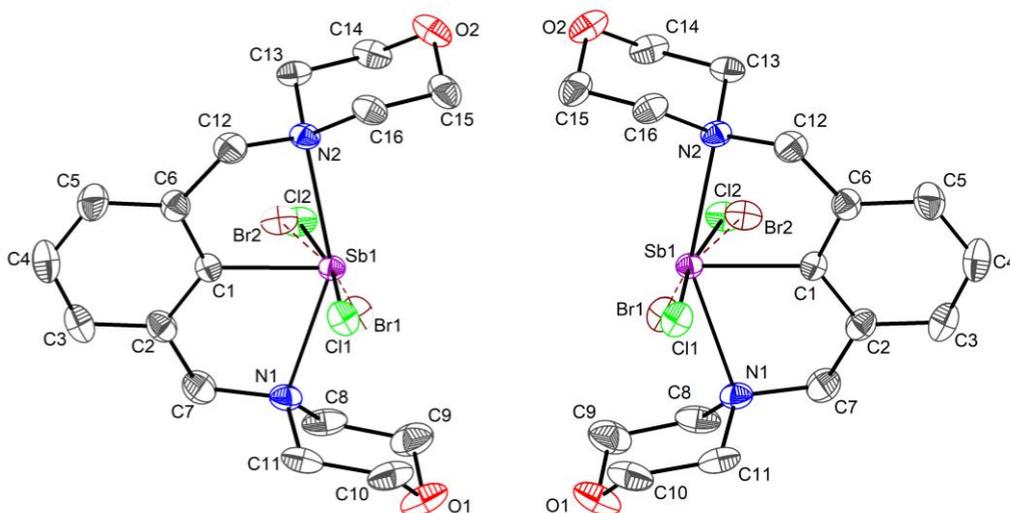


Fig. 1 – ORTEP representation at 30% probability and atom numbering scheme for the isomers $pS_{N(1)}-pS_{N(2)}$ (left) and $pR_{N(1)}-pR_{N(2)}$ (right) in the crystal of $[2,6-\{O(CH_2CH_2)_2NCH_2\}_2C_6H_3]SbBr_{0.27}Cl_{1.74} \cdot CHCl_3$ (**2**· $CHCl_3$). Hydrogen atoms are omitted for clarity.

Single crystals of quality appropriate for X-ray diffraction investigation were obtained by slow diffusion of *n*-hexane into a concentrated chloroform solution of **2**, in open atmosphere. The crystal and molecular structure was established by X-ray diffraction studies. Compound **2** crystallizes in the monoclinic space group $P2_1/n$ as a solvate with one molecule of $CHCl_3$ in the asymmetric unit. The solvent molecule is highly disordered and was refined as a two-part disorder with site occupancy factors of 85:15. Further substitutional Cl/Br disorder was identified in the crystal of **2**, with average site occupancy factors of 87:13. However, it should be noted that no fragments containing bromine were observed in the APCI(+) mass spectrum of **2**, when the spectrum was recorded for the colorless solid isolated from the reaction mixture.

The compound crystallizes in the monoclinic space group $P2_1/n$ as racemate, *i.e.* 1:1 mixtures of $pS_{N(1)}-pS_{N(2)}$ and $pR_{N(1)}-pR_{N(2)}$ with respect to the two non-planar chelate C_3NSb rings in a molecular unit. The ORTEP-like representation of the molecular structure of both isomers of **2**, with the atom numbering scheme, is depicted in Figure 1. Selected interatomic distances and bond angles are listed in Table 1.

DISCUSSION

Usually, for the lithiation of a bromide organic precursor, $ArBr$ (Ar = aryl group), an excess of nBuLi is used. Therefore, it is very likely that the resulted crude reaction mixture will contain a

certain amount of $LiBr$ formed following a side reaction between the butyl bromide (resulted in the lithiation reaction of the bromide precursor) and the excess of nBuLi . This was the case when the proligand $2,6-[O(CH_2CH_2)_2NCH_2]_2C_6H_3Br$ (**1**) was lithiated with an excess of nBuLi and the presence of $LiBr$ in the crude reaction mixture represents a main disadvantage of the synthetic method used to obtain $[2,6-\{O(CH_2CH_2)_2NCH_2\}_2C_6H_3]SbCl_2$ (**2**), due to potential halogen exchange reaction. This accounts for the residual bromine present in the analyzed crystal of **2**. The preparation of organopnicogen bromides following a halogen exchange reaction when the corresponding chlorides are treated with KBr is well documented in the literature;⁹ such methods were also successfully applied for the synthesis of other organometallic bromides, *e.g.* organotin(IV),¹⁰ -lead(IV),¹¹ -selenium(II),¹² -tellurium(IV),¹³ or -mercury(II)¹⁴ species.

The molecular structure of **2** exhibits a T-shaped $CSbX_2$ core ($X = Cl/Br$) (Figure 1). The presence of residual bromine atoms will be neglected in the following discussion of the molecular structure. The chlorine atoms are placed in *trans* positions [$Cl1-Sb1-Cl2$ $171.65(12)^\circ$] and the $Sb-Cl$ bond distances [$Sb1-Cl1$ $2.700(7)$ Å; $Sb1-Cl2$ $2.608(4)$ Å] are considerably longer than the sum of covalent radii of the corresponding atoms [$\Sigma r_{cov}(Sb,Cl)$ 2.41 Å],¹⁵ which is reminiscent of the $3c-4e$ theory of the hypervalent bond formation. The antimony center is strongly coordinated *trans* to each other by nitrogen atoms from both pendant arms of the NCN -pincer ligand [$N1-Sb1-N2$ $151.07(9)^\circ$], as demonstrated by the

corresponding Sb–N intramolecular distances [Sb1–N1 2.471(3) Å; Sb2–N2 2.480(3) Å] [*cf.* the sum of the covalent and van der Waals radii of the corresponding atoms: $\Sigma r_{\text{cov}}(\text{Sb},\text{N})$ 2.10 Å,¹⁵ and $\Sigma r_{\text{vdW}}(\text{Sb},\text{N})$ 4.13 Å,¹⁶ respectively]. The magnitude of the Sb–N bond distances compares well with the Sb–N bond distances reported in related arylantimony(III) dichlorides containing an *NCN*-pincer ligand: [2,6-(Me₂NCH₂)₂C₆H₃]SbCl₂ [Sb–N 2.491(9), 2.422(8) Å],⁵ or [2,6-{MeN(CH₂CH₂)₂NCH₂}₂C₆H₃]SbCl₂ [Sb–N range: 2.471(2) - 2.505(2) Å].^{4c}

As a result of the *NCN*-pincer behavior of the aryl ligand the overall coordination geometry at antimony in **2** is best described as distorted square pyramidal, with the carbon atom located in the apical position of the (*NCN*)SbCl₂ core (hypervalent *12-Sb-5* species).¹⁷ The intramolecular Sb–N interactions generate two non-planar five-membered SbC₃N chelate rings; thus planar chirality is induced, with the aromatic ring and the nitrogen atom as chiral plane and pilot atom, respectively.¹⁸ The two nitrogen atoms of the pincer ligand are placed on opposite sides of the planar system build by the metal atom, the aromatic ring and the methylene carbon atoms of the pendant arms attached to it [atom deviations from best *C*₆(*C*₂)*Sb* plane: N(1) 0.46 Å, N(2) –0.50 Å]. As result compound **2** crystallizes as racemate, *i.e.* 1:1 mixture of *pS*_{N(1)}-*pS*_{N(2)} and *pR*_{N(1)}-*pR*_{N(2)} isomers, with respect to the two chelate rings in a molecular unit (Figure 1).

In the crystal of **2** no intermolecular distances shorter than the sum of the van der Waals radii of the corresponding heavy atoms are present. However, *zig-zag* chain polymeric associations of *pS*_{N(1)}-*pS*_{N(2)} (Figure 2) and *pR*_{N(1)}-*pR*_{N(2)} isomers, respectively, are built along *b* axis through intermolecular C–H_{methylene}⋯O hydrogen bonds [O1⋯H11Ab 2.54 Å; *cf.* the sum of the van der Waals radii of the corresponding atoms, $\Sigma r_{\text{vdW}}(\text{O},\text{H})$ 2.70 Å¹⁶], which involves the oxygen atom of only one morpholinyl group of the molecular unit and a methylene hydrogen of the other morpholinyl group of a neighboring molecule.

Parallel chain polymers built of identical isomers, *i.e.* either *pS*_{N(1)}-*pS*_{N(2)} or *pR*_{N(1)}-*pR*_{N(2)} isomers, are doubly bridged into layers through inter-chain C–H_{methylene}⋯Cl interactions [Cl2⋯H10Bd 2.74 Å; symmetry equivalent atoms (*I*+*x*, *y*, *z*) are given by “d”; *cf.* the sum of the van der Waals radii of the corresponding atoms, $\Sigma r_{\text{vdW}}(\text{Cl},\text{H})$ 3.02 Å¹⁶] involving one chlorine atom per molecular unit (Figure 3). Further inter-layer C–H_{methylene}⋯Cl interactions [Cl1⋯H15Ae 2.90 Å; symmetry equivalent atoms (*I*–*x*, 2–*y*, *I*–*z*) are given by “e”], which involves the other chlorine atom of a molecular unit, connect parallel, alternating layers of *pS*_{N(1)}-*pS*_{N(2)} and *pR*_{N(1)}-*pR*_{N(2)} isomers, respectively, leading to a 3D supramolecular architecture in the crystal of **2** (Figure 4).

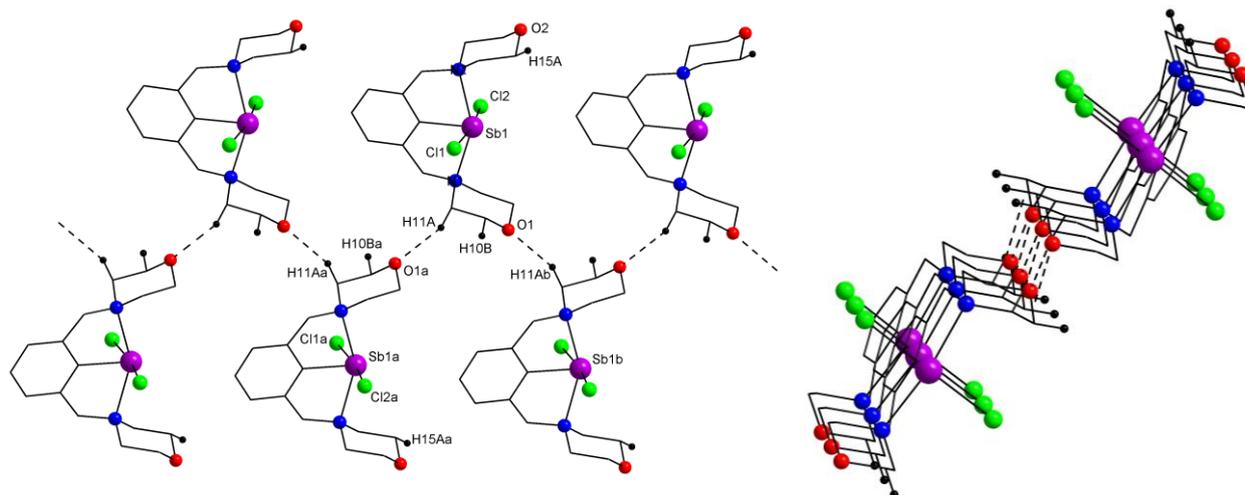


Fig. 2 – Fragment of 1D *zig-zag* chain association of *pS*_{N(1)}-*pS*_{N(2)} isomers in the crystal of **2**·CHCl₃, built through intermolecular O⋯H hydrogen bonds (*left*), and view along *b* axis of the same chain polymer (only hydrogens involved in intermolecular contacts are shown) [symmetry equivalent atoms (*0.5*–*x*, –*0.5*+*y*, *1.5*–*z*) and (*0.5*–*x*, *0.5*+*y*, *1.5*–*z*) are given by “a” and “b”].

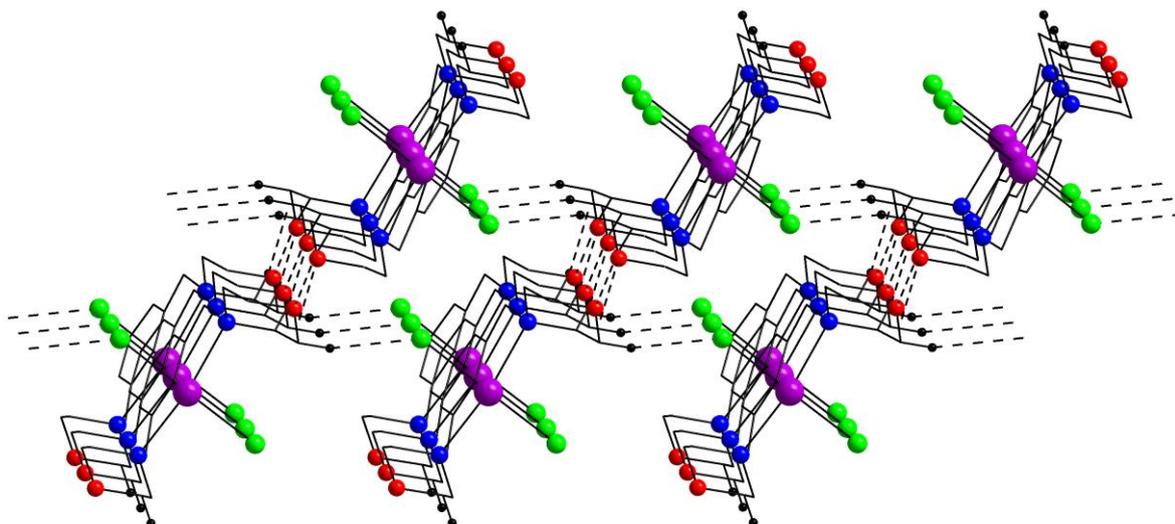


Fig. 3 – View along b axis of a fragment of 2D layer association of parallel $pS_{N(1)}-pS_{N(2)}$ chain polymers in the crystal of **2**·CHCl₃, built through inter-chain Cl···H interactions (only hydrogens involved in intermolecular contacts are shown).

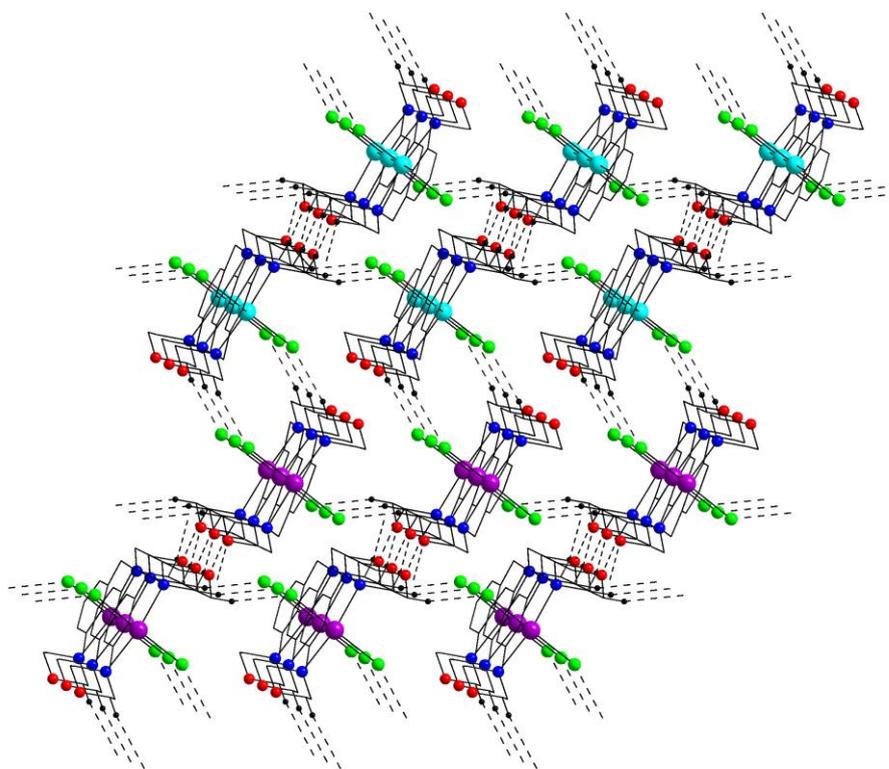


Fig. 4 – View along b axis of a fragment of the 3D supramolecular architecture in the crystal of **2**·CHCl₃, based on inter-layer Cl···H interactions between parallel, alternating layers of $pS_{N(1)}-pS_{N(2)}$ (bottom layer, metal atom depicted in *magenta* color) and $pR_{N(1)}-pR_{N(2)}$ (upper layer, metal atom depicted in *cyan* color) isomers.

EXPERIMENTAL

The reactions were performed under argon using a standard Schlenk line and the crude reaction mixture was worked-up in open atmosphere. All solvents were dried and freshly distilled under argon prior to use. The proligand 2,6-[O(CH₂CH₂)₂NCH₂]₂C₆H₃Br (**1**) was prepared according to a literature procedure.¹⁹ The ¹H and ¹³C{¹H} NMR spectra for

compound **2** were recorded at room temperature on a Bruker Avance III 400 MHz spectrometer, operating at 400.13 and 100.62 MHz, respectively, using solutions in CDCl₃. The ¹H chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (CHCl₃, 7.26 ppm). The ¹³C chemical shifts are reported in δ units (ppm) relative to the peak of the deuterated solvent (CDCl₃, 77.16 ppm).²⁰ The NMR spectra were processed using *MestReNova* software

package.²¹ APCI mass spectrum was recorded on a Thermo Scientific Orbitrap XL spectrometer equipped with standard APCI source. Data analysis and calculations of the theoretical isotopic patterns were carried out with the Xcalibur software package.²² The melting point was measured with an Electrothermal 9200 apparatus and is not corrected.

Synthesis of [2,6- $\{O(CH_2CH_2)_2NCH_2\}_2C_6H_3\}SbCl_2$ (**2**)

To a solution of 2,6- $\{O(CH_2CH_2)_2NCH_2\}_2C_6H_3Br$ (**1**) (5.23 g, 14.7 mmol) in 150 mL hexane, ⁿBuLi (9.2 mL, 1.6 M, in hexane solution) was added dropwise at room temperature, then the reaction mixture was left stirring overnight. The solvent was removed *via* a filtering cannula and the precipitate was dried *in vacuo*. Diethyl ether (150 mL) was added and the resulting suspension of the organolithium derivative thus obtained was cooled to -78°C , then added dropwise to a solution of $SbCl_3$ (2.51 g, 11 mmol) in 50 mL Et_2O , cooled to -78°C . The reaction mixture was slowly left to reach room temperature after which it was filtered through a glass frit. The resulted solid residue was extracted with a Soxhlet apparatus using 150 mL CH_2Cl_2 , the solvent was removed under reduced pressure yielding **2** as a colorless solid. Yield: 2.2 g (43%). M.p. = 223°C (dec). HRMS (APCI+, MeOH), m/z : $[M-Cl+2H]^+$ calcd. for $C_{16}H_{25}N_2O_2ClSb$ 433.06373. Found: 433.04347. For details regarding the NMR data, see reference 7.

Crystal structure determination

Crystals of **2**· $CHCl_3$, suitable for single-crystal X-ray diffraction, were grown by slow diffusion of *n*-hexane into a concentrated chloroform solution of **2**. One single crystal was mounted on a MiTeGen microMount cryoloop using Paratone oil and data was collected on a Bruker D8 VENTURE diffractometer using Mo-K α radiation (0.71073 Å) from a I μ S 3.0 micro focus source, at ambient temperature (295 K). Measurement at low temperature on two different single crystals were not successful and lead to incomplete data sets, due to fast change to a polycrystalline state. A slower transition of the crystal to a polycrystalline state was observed at room temperature, so a complete dataset was acquired in the shortest time possible. Data reduction was performed using SAINT²³ and was corrected for absorption effects using SADABS program.^{24,25} The structure was solved by dual methods (SHELXT-2018/2)²⁶ and refined by full matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-2019/1)²⁷ using the APEX4 software package.²⁸ The structure was refined with anisotropic thermal parameters for non-H atoms. Hydrogen atoms were placed in fixed, idealized positions and refined with a riding model and a mutual isotropic thermal parameter. Further details on the data collection and refinement methods can be found in Table 2. The drawings of the molecular structures were created with the Diamond program.²⁹

Table 2

Crystallographic data for [2,6- $\{O(CH_2CH_2)_2NCH_2\}_2C_6H_3\}SbBr_{0.27}Cl_{1.74}\cdot CHCl_3$ (2 · $CHCl_3$)	
Empirical formula	$C_{17}H_{24}Br_{0.27}Cl_{1.74}N_2O_2Sb$
Formula weight	599.17
Crystal size /mm	0.166 x 0.140 x 0.108
Crystal habit	colorless block
Wavelength (Å)	0.71073
Temperature (K)	295.(2)
Crystal system	monoclinic
Space group	P21/n
a (Å)	8.97070(10)
b (Å)	8.7905(2)
c (Å)	29.6387(5)
α (°)	90
β (°)	90.2770(10)
γ (°)	90
Volume (Å ³)	2337.19(7)
Z	4
Density (calculated) (g cm ⁻³)	1.703
Absorption coefficient (mm ⁻¹)	2.189
$F(000)$	1187
θ range for data collections (°)	2.37 – 25.00
T_{\max} / T_{\min}	0.80 / 0.72
Reflections collected	38131
Independent reflections, R_{int}	4119, 0.0270
Miller indices, h, k, l (min/max)	-10/10, -10/10, -35/35
Completeness to θ	100%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4119 / 141 / 265
Goodness-of-fit on F^2	1.035
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0272$ $wR_2 = 0.0729$
R indices (all data)	$R_1 = 0.0306$ $wR_2 = 0.0749$
Largest diff. peak and hole, eÅ ⁻³	1.386, -0.678
CCDC No.	2176717

Compound **2** crystallizes as a solvate with one molecule of CHCl_3 in the asymmetric unit. The solvent molecule is highly disordered and was refined as a two-part disorder with site occupancy factors of 85:15. Further substitutional Cl/Br disorders were identified in the main molecule of the asymmetric unit, with Cl to Br site occupancy factors of 84.8:15.2 for Cl1/Br1 and 88.7:11.3 for Cl2/Br2 respectively.

CONCLUSIONS

To avoid a random substitutional Cl/Br disorder during the preparation of organoantimony(III) chlorides from SbCl_3 and an aryllithium reagent obtained *in situ* from aryl bromide and $^n\text{BuLi}$, the excess of the later and the reaction temperature should be carefully controlled to prevent the formation of LiBr, a potential halogen exchange reagent. The crystal of $[\text{2,6-}\{\text{O}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}_2\text{C}_6\text{H}_3]\text{SbCl}_2$ (**2**) was investigated by single-crystal X-ray diffraction and a 3D supramolecular architecture was evidenced as result of intermolecular $\text{O}\cdots\text{H}$ and $\text{Cl}\cdots\text{H}$ interactions (residual Br atoms were neglected) established between parallel, alternating layers of $p\text{S}_{\text{N}(1)}-p\text{S}_{\text{N}(2)}$ and $p\text{R}_{\text{N}(1)}-p\text{R}_{\text{N}(2)}$ isomers.

Supplementary material

The CCDC reference number for **2**· CHCl_3 is 2176717. The supplementary crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>.

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