



*Dedicated to Professor Ion Grosu
on the occasion of his 65th anniversary*

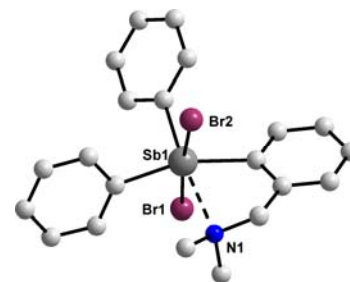
NEW HYPERCOORDINATED ORGANOANTIMONY(V) BROMIDES. SYNTHESIS AND STRUCTURAL CHARACTERIZATION

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The oxidative addition of bromine to [2-(Me₂NCH₂)C₆H₄]SbBr₂ and [2-(Me₂NCH₂)C₆H₄]Ph₂Sb resulted in the new hypercoordinated organoantimony(V) compounds [2-(Me₂NCH₂)C₆H₄]SbBr₄ (**1**) and [2-(Me₂NCH₂)C₆H₄]Ph₂SbBr₂ (**2**), respectively. The new species were isolated as colourless solids and their solution behaviour was investigated by ¹H and ¹³C{¹H} NMR spectroscopy. Single-crystal X-ray diffraction studies evidenced strong N→Sb intramolecular interactions in **1** and **2**. While **2** has a monomeric structure, in the crystal of **1** the molecules are associated in polymeric chains by weak Br⋯H contacts. The ionic derivative [{2-(Me₂NH⁺CH₂)C₆H₄}Ph₂SbBr₂]⁻Br⁻·CHCl₃ (**3**·CHCl₃) was isolated as a hydrolysis product during our attempts to grow single-crystals of **2** from a *n*-hexane/CHCl₃ mixture of solvents.



INTRODUCTION

Organoantimony halides were studied over years in connection with their structural aspects and their use as starting materials for various organoantimony compounds with potential in catalysis, biology and nanomaterials.¹ For compounds of type R_nSbX_{5-n} (n = 1 - 4) it was observed that the thermal stability decreases with the increase of the number of halogen atoms in the molecule. Similarly with the organoantimony(III) species, the aryl substituted organoantimony(V) derivatives are more stable than those containing alkyl groups.² The stability of organoantimony compounds can be significantly increased by using either bulky organic groups, *e.g.* [(Me₃Si)₂CH]₃SbBr₂,³ (2-C₄H₉S)₃SbBr₂,⁴

(C₆H₁₁)₃SbBr₂,⁵ (C₆F₅)₃SbBr₂,⁶ or organic groups bearing donor atoms capable to coordinate intramolecularly to metal.⁷ An increased coordination number at antimony and an increased stability was achieved either by dimerization through halogen bridging atoms, as in biphenyl-2,2'-diylphenylantimony dibromide (C₁₂H₈)PhSbBr₂,⁸ or by hypercoordination. By contrast with the large number of hypercoordinated antimony(III) compounds with *N,C*-chelating ligands reported during last years,^{1a} only few antimony(V) species were described till now, *e.g.* R(C₆H₄Me-4)₂SbCl₂ [R = 2-(Me₂NCH₂)C₆H₄, 8-(Me₂NCH₂)C₁₀H₆ or 8-(Me₂N)C₁₀H₆],⁹ (4-Me₂NC₆H₄)₃SbX₂ [X = F, Cl, PhC(O)O],¹⁰ {MeN(CH₂C₆H₄)₂}(C₆H₄Me-4)SbX₂ (X = F, Cl, Br),¹¹ RSbCl₄, R₂PhSbCl₂, RPh₂SbCl₂

[R = *o*-(CH=N-2,6-Prⁱ₂C₆H₃)C₆H₄],¹² as well as the ionic species [$\{\text{MeN}(\text{CH}_2\text{C}_6\text{H}_4)_2\}(\text{C}_6\text{H}_4\text{Me-4})\text{SbI}\}^+\text{I}^-$, [$\{\text{MeN}(\text{CH}_2\text{C}_6\text{H}_4)_2\}(\text{C}_6\text{H}_4\text{Me-4})\text{SbCl}\}[\text{SbCl}_6]$ and [$\{\text{MeN}(\text{CH}_2\text{C}_6\text{H}_4)_2\}(\text{C}_6\text{H}_4\text{Me-4})\text{SbBr}\}[\text{BF}_4]$].¹¹

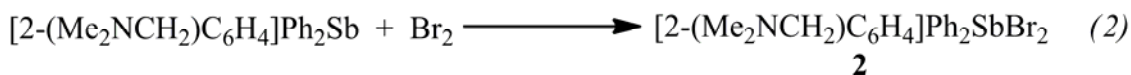
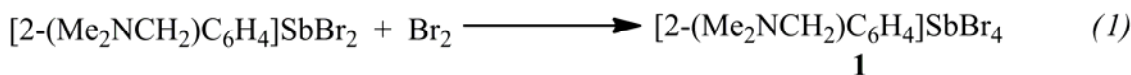
We have previously reported the synthesis and spectroscopic characterization of several organoantimony (III) halides and pseudohalides of type [2-(Me₂NCH₂)C₆H₄]_nSbX_{3-n} (n = 1, 2; X = Cl, Br, I,¹³ X = SCN, SeCN¹⁴), as well as about triorganoantimony(III) compounds of type [2-(Me₂NCH₂)C₆H₄]_nR_{3-n}Sb (n = 1, 2; R = Ph, Mes)¹⁵ and we observed in all cases that the nitrogen atom in the pendant arm of the 2-(Me₂NCH₂)C₆H₄ group is intramolecularly coordinated to antimony. As a continuation of our studies, we report here about the synthesis and structural characterization of two new organoantimony(V) compounds, namely [2-(Me₂NCH₂)C₆H₄]SbBr₄ (**1**) and [2-(Me₂NCH₂)C₆H₄]Ph₂SbBr₂ (**2**). In addition, the crystal structure of the ionic species

[{2-(Me₂NH⁺CH₂)C₆H₄}Ph₂SbBr₂]Br⁻·CHCl₃ (**3**·CHCl₃), serendipitously obtained, is also discussed.

RESULTS

Synthesis

The organoantimony(V) compounds [2-(Me₂NCH₂)C₆H₄]SbBr₄ (**1**) and [2-(Me₂NCH₂)C₆H₄]Ph₂SbBr₂ (**2**) were prepared by the oxidative addition of bromine to the corresponding organoantimony (III) starting materials, as depicted in *eq. 1* and *eq. 2*, respectively. The two compounds were isolated as microcrystalline colourless solids, soluble in common organic solvents.



Compounds **1** and **2** were investigated by ¹H and ¹³C{¹H} NMR spectroscopy in CDCl₃ solution. The crystal and molecular structures of **1**, **2** and of the ionic compound **3**·CHCl₃ were determined by single-crystal X-ray diffraction. The formation of **3** can be explained by the partial

hydrolysis of **2** in solution followed by the reaction of the resulting HBr with **2**. Selective interatomic distances and bond angles are given in Table 1, while the ellipsoids representations with atom numbering schemes for **1**, **2** and **3**·CHCl₃ are shown in Figures 1–3, respectively.

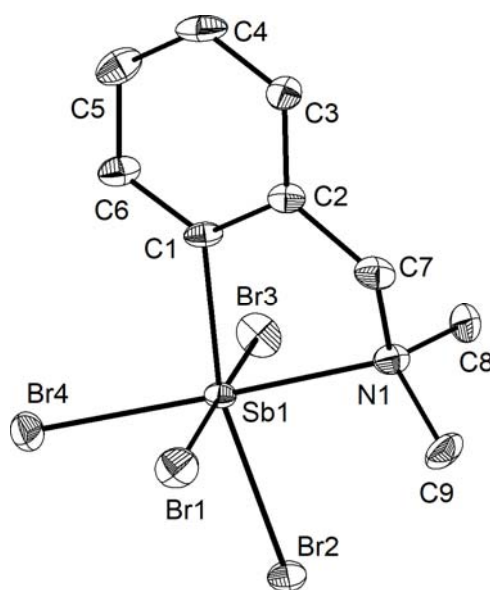


Fig. 1 – Thermal ellipsoids (30% probability) representation of *S*-1. Hydrogen atoms were omitted for clarity.

Table 1
Selected interatomic distances [Å] and bond angles [deg] in **1**, **2** and **3**·CHCl₃

1		2		3 ·CHCl ₃	
Sb(1)–C(1)	2.131(8)	Sb(1)–C(1)	2.127(4)	Sb(1)–C(1)	2.124(6)
Sb(1)–Br(1)	2.582(2)	Sb(1)–C(10)	2.143(5)	Sb(1)–C(10)	2.089(4)
Sb(1)–Br(2)	2.502(2)	Sb(1)–C(16)	2.143(5)	Sb(1)–C(16)	2.132(6)
Sb(1)–Br(3)	2.589(2)	Sb(1)···N(1)	2.623(4)	Sb(1)–Br(1)	2.6207(11)
Sb(1)–Br(4)	2.545(2)	Sb(1)–Br(1)	2.6339(6)	Sb(1)–Br(2)	2.6257(12)
Sb(1)···N(1)	2.347(7)	Sb(1)–Br(2)	2.6412(6)		
C(1)–Sb(1)···N(1)	78.7(3)	Br(1)–Sb(1)–Br(2)	174.41(2)	Br(1)–Sb(1)–Br(2)	172.89(3)
Br(1)–Sb(1)···N(1)	86.14(17)	C(1)–Sb(1)–C(10)	102.43(19)	C(1)–Sb(1)–C(10)	120.6(2)
Br(2)–Sb(1)···N(1)	87.77(18)	C(10)–Sb(1)–C(16)	98.62(18)	C(10)–Sb(1)–C(16)	115.1(2)
Br(3)–Sb(1)···N(1)	96.31(17)	C(1)–Sb(1)–C(16)	158.89(18)	C(1)–Sb(1)–C(16)	124.3(2)
Br(4)–Sb(1)···N(1)	174.65(18)	C(1)–Sb(1)···N(1)	72.25(15)	C(1)–Sb(1)–Br(1)	87.34(18)
C(1)–Sb(1)–Br(1)	93.0(2)	C(10)–Sb(1)···N(1)	173.71(16)	C(10)–Sb(1)–Br(1)	88.55(17)
C(1)–Sb(1)–Br(2)	166.1(2)	C(16)–Sb(1)···N(1)	86.64(15)	C(16)–Sb(1)–Br(1)	93.3(2)
C(1)–Sb(1)–Br(3)	90.6(2)	Br(1)–Sb(1)···N(1)	91.56(8)	C(1)–Sb(1)–Br(2)	87.57(18)
C(1)–Sb(1)–Br(4)	98.9(2)	Br(2)–Sb(1)···N(1)	83.98(8)	C(10)–Sb(1)–Br(2)	89.77(17)
Br(1)–Sb(1)–Br(2)	89.34(5)	C(1)–Sb(1)–Br(1)	88.64(12)	C(16)–Sb(1)–Br(2)	93.7(2)
Br(1)–Sb(1)–Br(3)	175.95(4)	C(10)–Sb(1)–Br(1)	91.67(14)		
Br(1)–Sb(1)–Br(4)	89.24(4)	C(16)–Sb(1)–Br(1)	92.30(13)		
Br(2)–Sb(1)–Br(3)	87.53(5)	C(1)–Sb(1)–Br(2)	86.78(12)		
Br(2)–Sb(1)–Br(4)	94.88(4)	C(10)–Sb(1)–Br(2)	92.45(14)		
Br(3)–Sb(1)–Br(4)	88.46(4)	C(16)–Sb(1)–Br(2)	90.82(13)		

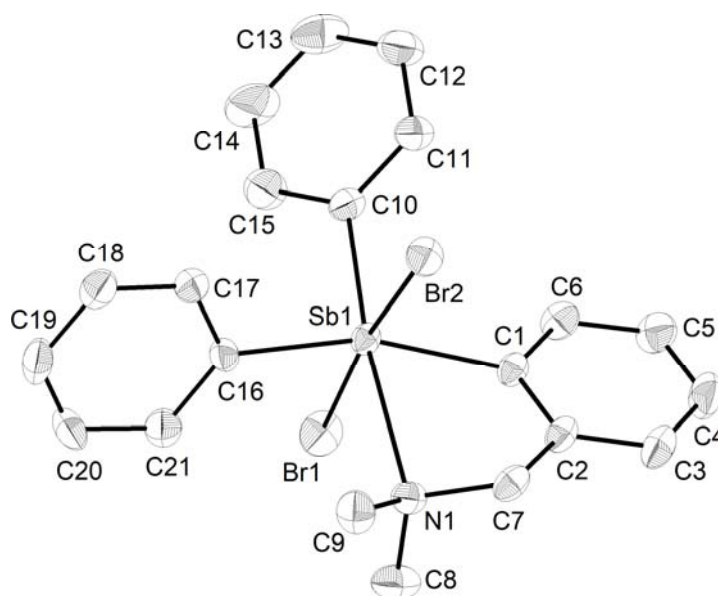


Fig. 2 – Thermal ellipsoids (30% probability) representation of $S_{N_2}A_{Sb-2}$. Hydrogen atoms were omitted for clarity.

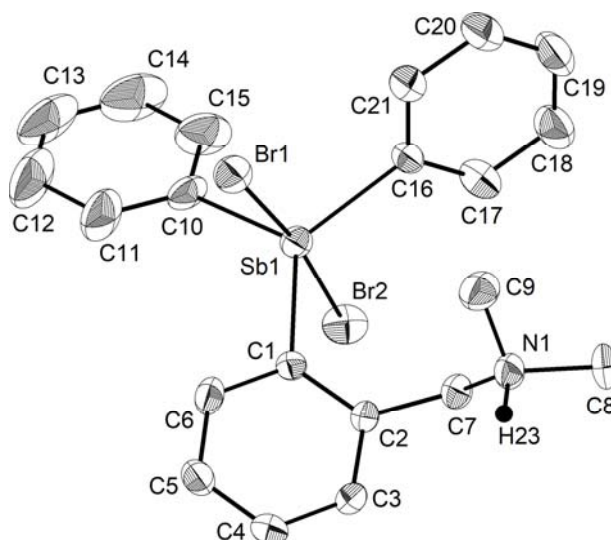


Fig. 3 – Thermal ellipsoids (30% probability) representation of the cation in $3 \cdot \text{CHCl}_3$. CHCl_3 and hydrogen atoms, except that attached to nitrogen, were omitted for clarity.

DISCUSSION

Spectroscopy

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** and **2** confirmed the purity of the two species. No evidence for the existence of an intramolecular $\text{N} \rightarrow \text{Sb}$ interaction in solution could be ruled out from the aliphatic region of the room temperature ^1H NMR spectra, which show, for both compounds, singlet resonances for the CH_2 and the CH_3 protons, respectively. For compound **2** the NMR spectra indicate clearly that the two phenyl groups attached to antimony are non-equivalent in solution. In the ^1H NMR spectrum two different multiplet resonances in a 1:1 molar ratio are present at δ 7.85–7.94 and 8.36–8.48 ppm, respectively, and they were assigned to the hydrogen atoms in *ortho* positions of the two phenyl groups, one of them in *trans* position to the intramolecularly coordinated nitrogen, and the other one in *cis* position. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum not all C_6H_5 carbons give separate resonances, but two different C_6H_5 -*ipso* resonances could be unambiguously identified at δ 141.74 and 146.27 ppm.

Crystal and molecular structure of
 $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{SbBr}_4$ (**1**),
 $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{Ph}_2\text{SbBr}_2$ (**2**) and $[2-$
 $(\text{Me}_2\text{NH}^+\text{CH}_2)\text{C}_6\text{H}_4]\text{Ph}_2\text{SbBr}_2[\text{Br}^- \cdot \text{CHCl}_3]$ (**3·CHCl₃**)

In compounds **1** and **2** the nitrogen atom in the pendant arm is intramolecularly coordinated to antimony, thus resulting in 12-*Sb*-6 hypercoordinated species,¹⁶ with a distorted

octahedral coordination geometry around antimony. In both compounds, the $\text{N} \rightarrow \text{Sb}$ intramolecular interactions ($\text{N1} \rightarrow \text{Sb1}$ 2.347(7) Å in **1** and 2.623(4) Å in **2**) are stronger than in $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{Ph}_2\text{Sb}$ (2.848(4) Å)^{15a} and much shorter than the sum of the van der Waals radii of the two elements ($\Sigma r_{\text{vdW}}(\text{N}, \text{Sb})$ 3.55 Å¹⁷). Moreover, the $\text{N} \rightarrow \text{Sb}$ intramolecular coordination induces planar chirality, thus resulting in a non-planar SbC_3N ring, folded about the $\text{Sb1} \cdots \text{C7}$ imaginary axis and, as a consequence, the two compounds crystallize as a mixture of *R* and *S* isomers. In addition, the two phenyl groups in **2** became non-equivalent as a result of the $\text{N} \rightarrow \text{Sb}$ intramolecular interaction, one of them placed in equatorial and the other one in axial position, *trans* to nitrogen, thus inducing chirality to antimony. In this way, compound **2** crystallizes as a racemic mixture of R_N, C_{Sb} and S_N, A_{Sb} isomers.¹⁸ While **2** has a monomeric structure, the molecules of **1** are associated by weak $\text{Br} \cdots \text{H}$ hydrogen bonding ($\text{Br4} \cdots \text{H7B}'$ 2.93 Å, vs. $\Sigma r_{\text{vdW}}(\text{Br}, \text{H})$ 3.15 Å¹⁷) in the crystal (Figure 4).

In the cation of **3·CHCl₃** (Figure 3) antimony has a distorted trigonal bipyramidal coordination geometry, with the bromine atoms in apices ($\text{Br}-\text{Sb}-\text{Br}$ 172.89(3)°). The nitrogen atom in the pendant arm is protonated and thus it is not coordinated to the metal centre. Besides the electrostatic interactions, in the crystal of **3·CHCl₃** each Br^- anion is involved in weak $\text{Br} \cdots \text{H}$ contacts with hydrogen atoms of two neighbouring molecules ($\text{Br3} \cdots \text{H23}$ 2.47 Å and $\text{Br3} \cdots \text{H20}$ 3.10 Å), which result in a chain-like polymeric association (Figure 5). The solvent molecule is not involved in any intermolecular interactions.

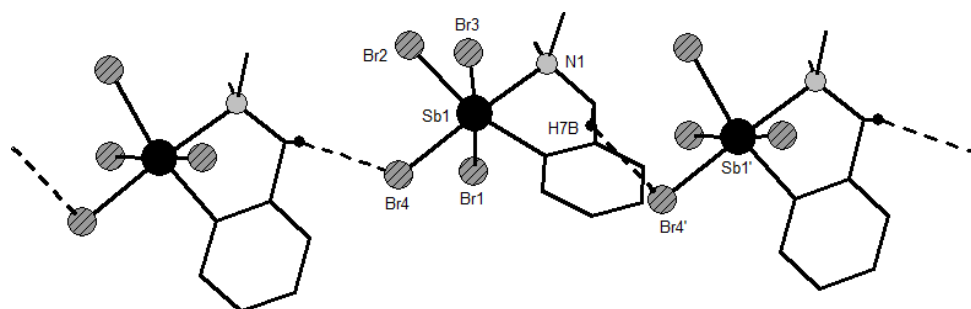


Fig. 4 – Polymeric association in 1. Hydrogen atoms not involved in H \cdots Br contacts were omitted for clarity. Symmetry equivalent positions $1/2+x$, $3/2-y$, $-1/2+z$ are given by “prime”.

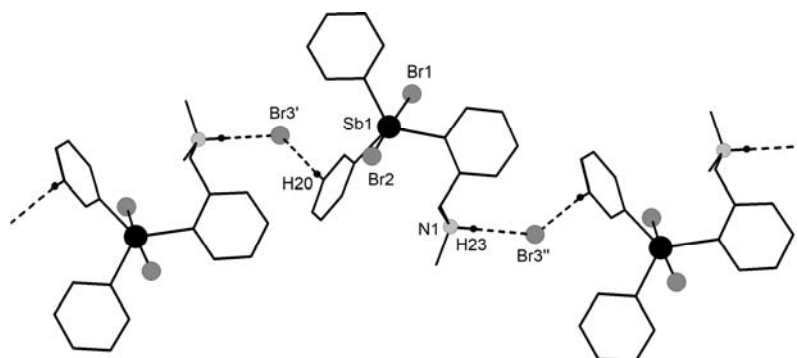
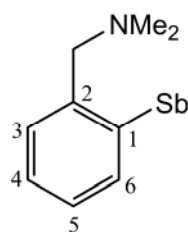


Fig. 5 – Cation-anion association in the crystal of 3·CHCl₃. Hydrogen atoms not involved in H \cdots Br cation – anion contacts, as well as CHCl₃, were omitted for clarity. Symmetry equivalent positions $3/2-x$, $-1/2+y$, $1/2-z$ and x , $-1+y$, z are given by “prime” and “second”, respectively.

EXPERIMENTAL

The starting organoantimony(III) materials were prepared according to literature procedures: [2-(Me₂NCH₂)C₆H₄]SbBr₂,¹³ and [2-(Me₂NCH₂)C₆H₄]Ph₂Sb.^{15a} Elemental analyses were performed on a Flash EA 1112 analyzer. Melting points were measured on an Electrothermal 9200 apparatus and are not corrected. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance DRX 300 or a Bruker Avance III 400 instruments. The chemical shifts are reported in δ units (ppm) relative to TMS (ref. CHCl₃: ¹H 7.26 ppm and ¹³C 77.16 ppm) and they were assigned based on 2D NMR experiments (COSY, HSQC and HMBC) and are given according to the numbering depicted in Scheme 1. The NMR spectra were processed using the MestReC and MestReNova software.¹⁹



Scheme 1

Synthesis of [2-(Me₂NCH₂)C₆H₄]SbBr₄ (1)

To a suspension of [2-(Me₂NCH₂)C₆H₄]SbBr₂ (0.72 g, 1.73 mmol) in toluene (10 mL) was added a solution of bromine (0.28 g, 1.73 mmol) in toluene (20 mL) at -20 °C and the reaction mixture was left under stirring for two hours. From the red solution toluene was removed under reduced

pressure. The remained yellow solid was washed with hexane (2 x 10 mL) and dried under reduced pressure. Yield: 0.88 g (88%). M.p. 173–175 °C (dec.). Elemental analysis calcd. for C₉H₁₂Br₄NSb (MW = 575.58): C, 18.78; H, 2.10; N, 2.43%. Found C, 18.92; H, 2.12; N, 2.48%. ¹H NMR (CDCl₃, 400.13 MHz): δ 3.01 (s, 6H, N(CH₃)₂), 4.23 (s, 2H, CH₂N), 7.07 (d, 1H, H-3, ³J_{HH} 7.4 Hz), 7.42 (t, 1H, H-4, ³J_{HH} 7.4 Hz), 7.53 (t, 1H, H-5, ³J_{HH} 7.3 Hz), 7.78 (d, 1H, H-6, ³J_{HH} 8.1 Hz). ¹³C{¹H} NMR (CDCl₃, 100.61 MHz): δ 47.89 N(CH₃)₂, 59.37 (CH₂N), 124.97 (C₆H₄, C-6), 126.98 (C₆H₄, C-3), 127.48 (C₆H₄, C-2), 130.20 (C₆H₄, C-5), 132.32 (C₆H₄, C-4), 154.49 (C₆H₄, C-1).

Synthesis of [2-(Me₂NCH₂)C₆H₄]Ph₂SbBr₂ (2)

To a solution of [2-(Me₂NCH₂)C₆H₄]Ph₂Sb (4.27 g, 10 mmol) in petroleum ether (330 mL) was added dropwise a solution of bromine (1.66 g, 10 mmol) in petroleum ether (20 mL) at 0 °C and the reaction mixture was left under stirring for 72 hours after reaching the room temperature. The solvent was removed at reduced pressure when the title compound resulted as a colourless solid. M.p. 216–218 °C. Yield 4.63 g (78%). Elemental analysis calcd. for C₂₁H₂₂Br₂NSb (MW = 569.98): C, 44.25; H, 3.89; N, 2.46%. Found C, 44.48; H, 4.02; N, 2.51%. ¹H NMR (300 MHz, CDCl₃): δ 2.29 (s, 6H, N(CH₃)₂), 3.94 (s, 2H, CH₂N), 7.23 (d, 1H, C₆H₄, ³J_{HH} 6.38 Hz), 7.33–7.53 (m, 2H, C₆H₄ + 6H, C₆H₅-meta+para), 7.60 (d, 1H, C₆H₄, ³J_{HH} 6.38 Hz), 7.85–7.94 (m, 2H, C₆H₅-ortho), 8.36–8.48 (m, 2H, C₆H₅-ortho). ¹³C{¹H} NMR (75.47 MHz, CDCl₃): δ 45.93 (s, N(CH₃)₂), 61.39 (s, CH₂N), 128.44 (C₆H₅), 128.72 (C₆H₅), 128.86 (C₆H₄), 129.42 (C₆H₄, C-3), 129.99 (C₆H₄), 130.36 (C₆H₅), 130.70 (C₆H₄, C-6), 133.18 (C₆H₅-ortho), 134.77 (C₆H₄, C-2), 135.44 (C₆H₅-ortho), 141.74 (C₆H₅-ipso), 146.27 (C₆H₅-ipso), 148.68 (C₆H₄, C-1).

Table 2

Crystal and structure refinement data for compounds **1**, **2** and **3**·CHCl₃

	1	2	3 ·CHCl ₃
Empirical formula	C ₉ H ₁₂ Br ₄ NSb	C ₂₁ H ₂₂ Br ₂ NSb	C ₂₂ H ₂₄ Br ₃ Cl ₃ NSb
Formula weight, g/mol	575.59	569.97	770.25
Temperature, K	294(2)	297(2)	297(2)
Wavelength, Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	9.486(7)	9.2459(14)	9.717(3)
<i>b</i> [Å]	15.964(11)	13.933(2)	19.049(6)
<i>c</i> [Å]	9.662(7)	16.247(2)	14.910(5)
α [°]	90	90	90
β [°]	97.113(15)	92.948(3)	98.320(6)
γ [°]	90	90	90
Volume, Å ³	1451.9(18)	2090.2(5)	2730.7(16)
Z	4	4	4
Density (calculated), g/cm ³	2.633	1.811	1.874
Absorption coefficient, mm ⁻¹	12.879	5.147	5.704
<i>F</i> (000)	1056	1104	1480
Crystal size, mm	0.29 × 0.23 × 0.21	0.42 × 0.34 × 0.14	0.36 × 0.22 × 0.14
θ range for data collection, °	2.478 to 24.992	1.93 to 25.00	1.75 to 25.00
Reflections collected	13109	19772	19648
Independent reflections	2553 [<i>R</i> (int) = 0.1045]	3671 [<i>R</i> (int) = 0.0600]	4811 [<i>R</i> (int) = 0.0581]
Completeness to $\theta = 25^\circ$, %	99.8	100	99.9
Refinement method		Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	2553 / 0 / 136	3671 / 0 / 228	4811 / 48 / 275
Goodness-of-fit on <i>F</i> ²	0.974	1.074	1.098
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0455, <i>wR</i> 2 = 0.0948	<i>R</i> 1 = 0.0391, <i>wR</i> 2 = 0.0863	<i>R</i> 1 = 0.0534, <i>wR</i> 2 = 0.1036
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0657, <i>wR</i> 2 = 0.1018	<i>R</i> 1 = 0.0471, <i>wR</i> 2 = 0.0893	<i>R</i> 1 = 0.0745, <i>wR</i> 2 = 0.1103
Largest diff. peak and hole, e·Å ⁻³	1.002 and -1.218	0.809 and -0.575	0.815 and -0.668

Single-crystal X-ray diffraction studies

Single crystals of **1** and **2** were grown by slow diffusion from a mixture of dry solvents, CH₂Cl₂ and *n*-hexane (1:4, v/v). The attempts to grow single crystals of **2** from a mixture of CHCl₃ and *n*-hexane (1:4, v/v) in open atmosphere resulted in the hydrolysis product [$\{2-(\text{Me}_2\text{NH}^+\text{CH}_2)\text{C}_6\text{H}_4\}$ Ph₂SbBr₂]Br⁻·CHCl₃ (**3**·CHCl₃). The data were collected at room temperature on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The details of the crystal structure determination and refinement are given in Table 2.

The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. One chlorine atom in **3**·CHCl₃ is disordered over two positions with 44 and 56% occupancies, respectively. The structures were solved and refined using the software package SHELX-97²⁰ and the drawings of the molecular structures were created with the Diamond program.²¹ Short Br \cdots H intermolecular contacts were found with PLATON.²²

CONCLUSIONS

The new antimony(V) compounds [$2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$]SbBr₄ (**1**) and [$2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$]Ph₂SbBr₂ (**2**) were prepared and structurally characterized both in solution and in solid state. An octahedral environment around antimony was evidenced by single-crystal X-ray diffraction studies in both compounds, as a result of a strong N \rightarrow Sb interaction. For compound **2** the NMR spectra suggested that the intramolecular coordination is preserved in solution as well. Single-crystals of the ionic species [$\{2-(\text{Me}_2\text{NH}^+\text{CH}_2)\text{C}_6\text{H}_4\}$ Ph₂SbBr₂]Br⁻·CHCl₃ (**3**·CHCl₃) resulted from the reactions of **2** with traces of HBr formed *in situ*. While the crystal of **2** contains independent molecules separated by normal van der Waals distances, the crystals of **1** and **3**·CHCl₃ contain polymeric chains formed by weak Br \cdots H contacts.

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Supplementary material

CCDC 1960753, 1960754 and 1960755 contain the supplementary crystallographic data for compounds **1**, **2**, and **3**·CHCl₃, respectively. 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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