



Structural study on the organoantimony(III) NCN – Chelated compounds [2,6-(Me₂NCH₂)₂C₆H₃]SbX₂ – Influence of the polar group X

Libor Dostál^{a,*}, Roman Jambor^a, Robert Jirásko^b, Zdeňka Padělková^a, Aleš Růžička^a, Jaroslav Holeček^a

^a Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ – 532 10, Pardubice, Czech Republic

^b Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ – 532 10, Pardubice, Czech Republic

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ABSTRACT

The reactions of organoantimony chloride LSbCl₂ (**1**) (L = [2,6-(Me₂NCH₂)₂C₆H₃][−]) with the silver salts of selected carboxylic acids (1:2 molar ratio) resulted to the corresponding organoantimony carboxylates LSbX₂, where X = CH₃COO for (**2**); CF₃COO for (**3**). Similar reactions of **1** with the silver salt of the low nucleophilic CB₁₁H₁₂[−] anion (1:0.5 and 1:1 molar ratio) gave the ionic compounds [LSb(Cl)–Cl–Sb(Cl)L]⁺[CB₁₁H₁₂][−] (**4**), and [LSbCl]⁺[CB₁₁H₁₂][−] (**5**). All compounds were characterized by the help of the elemental analysis, ESI-MS, ¹H, ¹¹B, ¹³C NMR spectroscopy and IR spectroscopy. The solid state structure investigation using single crystal X-ray diffraction technique (**3–5**) revealed the presence of the strong Sb–N intramolecular dative connections in all cases and also significant differences in the shapes of the coordination polyhedra around the central antimony atoms was observed, i.e. a tetragonal pyramidal environment in **3** (CF₃COO groups are placed mutually in *trans* positions), an unusual chlorine bridged dinuclear cation consisting of one apex (Cl atom) sharing square pyramids in **4**, and finally a vacant ψ-trigonal bipyramid around the central antimony atom in **5**. Even more, crystallization of **5** from THF provided the single crystals of a THF adduct of **5** [LSbCl(THF)]⁺[CB₁₁H₁₂][−] **5a**, where the central antimony atom is located in a tetragonal pyramidal environment. The solid state structures of **3–5** are retained in solution. Solution structure of the compound **2** was determined by the help of VT-¹H NMR spectroscopy and IR spectroscopy showing, that both carboxylates (CH₃COO) are unidentate and are placed mutually in *cis* positions in the coordination polyhedron around the central antimony atom. The whole coordination polyhedron in **2** might be best described as a biccapped – trigonal pyramid, due to the additional Sb–N intramolecular interactions.

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1. Introduction

The chemistry of YCY chelating, so called pincer type, ligands attracted considerable attention of many groups during the last decades [1]. Nevertheless, it seems that the investigation in this field will be extensively developed also in the future since many novel types of these ligands continue to emerge [2]. The unrivalled position of these ligands among others in the organometallic chemistry stems in part from their high flexibility allowing them to coordinate the central metal in an uni-, bi- or tridentate fashion and the fact that the strength of the dative Y–M connection can be quite easily driven by the Lewis acidic properties of both donor group Y and the central metal M. Possibility of quite simple modification of the ligands backbones, which allows to anchor them on larger systems such as dendrimers, etc. [3], to tune their electronic properties [4], or to introduce chiral centres [5], are other reasons for their widespread utilization. Although majority of these studies

are devoted to the transition metals [1], there are several exciting examples of their applications in the chemistry of the main group elements as well [6].

Recently, we have demonstrated that using of two types of these pincer ligands, (i.e. OCO and NCN type ([2,6-(YCH₂)₂C₆H₃][−], Y = OR, NMe₂, Fig. 1), in the group 14 and 15 chemistry led to the isolation of several interesting and in some cases unique compounds, that would be only hardly prepared without significant stabilizing effect of the pincer ligands [7–11].

It was shown, that the NCN ligand can be with success used as an alternative for sterically encumbered terphenyl ligands in the stabilization of low-valent metal centers in the heavier acetylene analogue LSnSnL [7], in the unique organoantimony Sb₅ cluster compound, that possesses a propylene-like structure, or in the stabilization of the terminal Sb–Se(Te) bonds [8]. The organostannylenes supported by the NCN or OCO ligands were used as promising ligands to the transition metals such as Pd, Pt, Rh, W, etc. [9]. The OCO ligands were used for controlled hydrolysis of the organotin halides yielding unique cationic organostannoxanes that exhibited high catalytic activity in the esterification reactions [10]. Both li-

* Corresponding author. Fax: +420 466037068.

E-mail address: libor.dostal@upce.cz (L. Dostál).

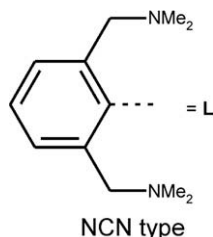


Fig. 1. Pincer ligand used in this study.

gands were shown to be excellent ancillary groups for the stabilization of the main group organometallic cations as interesting strong Lewis acids [11].

With the regard to our continual interest in the chemistry of the pincer compounds and in order to further develop the chemistry of their main group metal derivatives, we report here on the synthesis, solution and solid state structure of four novel organoantimony compounds, derivatives of the NCN chelating ligand $[(2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3)]^-$, denoted as L hereafter), LSbX_2 , where $\text{X} = \text{CH}_3\text{COO}$ for **2**; $\text{X} = \text{CF}_3\text{COO}$ for **3** and the ionic compounds $[\text{LSb}(\text{Cl})-\text{Cl}-\text{Sb}(\text{Cl})\text{L}]^+[\text{CB}_{11}\text{H}_{12}]^-$ **4**, and $[\text{LSbCl}]^+[\text{CB}_{11}\text{H}_{12}]^-$ **5**. All compounds were characterized by the combination of elemental analysis, ESI-MS, ^1H , ^{11}B , ^{13}C NMR spectroscopy and IR spectroscopy. We observed a strong influence of the polar group used (CH_3COO , CF_3COO , Cl , $\text{CB}_{11}\text{H}_{12}$) on the coordination polyhedron around the central antimony atom both in the solid state (X-ray) and in solution (IR, VT- ^1H NMR) along this set of compounds.

2. Experimental

2.1. General consideration

All manipulations were carried out under argon atmosphere using standard Schlenk technique. All solvents were dried by standard procedures and distilled prior to use. ^1H , ^{11}B and ^{13}C NMR spectra were recorded on Bruker500 Avance spectrometer. Appropriate chemical shifts in ^1H and ^{13}C NMR spectra were related to the residual signals of the solvent (CDCl_3 : $\delta(^1\text{H}) = 7.27$ ppm and $\delta(^{13}\text{C}) = 77.23$ ppm, $\text{THF}-d_8$: $\delta(^1\text{H}) = 1.73$ and 3.58 ppm and $\delta(^{13}\text{C}) = 25.4$ and 67.6 ppm). ^{11}B NMR spectra are related to the external standard $\text{BF}_3\cdot\text{OEt}_2$ (0.00 ppm). The positive-ion and negative-ion full scan mass spectra measured on an Esquire 3000 ion trap (Bruker Daltonics, Bremen, Germany). The samples were dissolved in acetonitrile and analyzed by the direct infusion at the flow rate of $5 \mu\text{l}/\text{min}$. Mass spectra were recorded in the range of 50–1500 m/z both in positive- and negative-ion modes. The ion source temperature was 300°C , the flow rate and the pressure of nitrogen were $4 \text{ l}/\text{min}$ and 10 psi, respectively.

Infrared spectra were recorded in the range $5000\text{--}400 \text{ cm}^{-1}$ as KBr pellets or as solutions in CHCl_3 on the FT-IR spectrometer Bruker IFS 55.

2.1.1. X-ray structure determination

The single crystals of compounds of **3–5(a)** were mounted on glass fibre with an inert oil and measured on four-circle diffractometer KappaCCD with CCD area detector by monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at $150(1)\text{K}$. The crystallographic details are summarized in Table 1, empirical absorption corrections [12] were applied (multiscan from symmetry-related measurements). The structures were solved by the direct method (SIR97 [13]) and refined by a full matrix least squares procedure based on F^2 (SHELXL97 [14]). Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors H_{iso}

($\text{H}) = 1.2 U_{\text{eq}}$ (pivot atom) or of $1.5U_{\text{eq}}$ for the methyl moiety with $\text{C-H} = 0.96, 0.97,$ and 0.93 \AA for methyl, methylene, and hydrogen atoms in aromatic ring, respectively, the C-H and B-H distances in carborane cages were defined to be 1.1 \AA . The final difference maps displayed no peaks of chemical significance as the highest peaks and holes are in close vicinity ($\sim 1 \text{ \AA}$) of antimony atoms. For **5a**, the disordered solvents (THF and water) were found and attempts were made to model these disorders or split it into two or three positions, but were unsuccessful. PLATON/SQUEZZE [15] was used to correct the data for the presence of disordered solvent. A potential solvent volume of 602 \AA^3 was found, 175.4 electrons per unit cell worth of scattering were located in the void. The stoichiometry of solvent was calculated to be four 'squeezed' molecules of THF and 1.5 molecules of water per unit cell which results in 175 electrons per unit cell. The carbon atoms in molecule of THF coordinated by the oxygen atom to the antimony atom in **5a** are modeled in two rather equivalent positions.

2.2. Synthesis

The starting chemicals CH_3COOAg (99.9%), CF_3COOAg (98%), $[\text{Me}_3\text{NH}]^+[\text{CB}_{11}\text{H}_{12}]^-$ were obtained from commercial suppliers and used as delivered. The compounds $\text{Ag}^+[\text{CB}_{11}\text{H}_{12}]^-$ [16], 2,6- $(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{SbCl}_2$ [17] were prepared according to the literature procedures. All reaction flasks were light protected by an aluminum foil.

2.2.1. Preparation of 2,6- $(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{Sb}(\text{OOCCH}_3)_2$ (**2**)

Silver acetate (130 mg, 0.78 mmol) was added to a solution of **1** (150 mg, 0.39 mmol) in CH_2Cl_2 (15 ml) and resulting suspension was stirred overnight. Then the insoluble material was filtered off and the solvent was evaporated *in vacuo*. Compound **2** was obtained after washing with hexane (5 ml) as colourless solid (121 mg, 72%), mp $130\text{--}132^\circ\text{C}$. Anal. Calc. for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O}_4\text{Sb}$: C, 44.6%; H, 5.8. Found: C, 44.3%; H, 5.6%. ^1H NMR (CDCl_3 , 240 K) δ (ppm): 2.04 (s, 6H, COCH_3); 2.09 (s, 6H, NCH_3); 2.50 (s, 6H, NCH_3); 3.18 and 4.42 (AX pattern, 4H, NCH_2); 7.12 (d, 2H, Ar-H3,5); 7.29 (t, 1H, Ar-H4). ^{13}C NMR (CDCl_3 , 300 K): 23.1 (s, CH_3), 45.4 (s, $(\text{CH}_3)_2\text{N}$), 64.4 (s, NCH_2), 126.0 (s, Ar-C3,5), 129.9 (s, Ar-C4), 147.2 (s, Ar-C2,6), 176.2 (s, C=O), (Ar-C1) not detected. IR (CHCl_3): 1664 [$\nu_{\text{as}}(\text{CO}_2)$], 1307 [$\nu_{\text{s}}(\text{CO}_2)$]. IR (KBr): 1666 [$\nu_{\text{as}}(\text{CO}_2)$], 1300 [$\nu_{\text{s}}(\text{CO}_2)$]. ESI/MS – positive mode: m/z 699 [$2^+ \text{M} - 3^+ \text{CH}_3\text{COOH} + \text{H}_2\text{O} + \text{H}$] $^+$; m/z 371 [$\text{M} - \text{CH}_3\text{COOH} + \text{H}$] $^+$, 100%.

2.2.2. Preparation of 2,6- $(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{Sb}(\text{OOCF}_3)_2$ (**3**)

Similarly to the procedure as for **2**: **1** (188 mg, 0.49 mmol), silver trifluoroacetate (217 mg, 0.98 mmol) yielded white crystals of (**3**; 198 mg, 75%), mp $183\text{--}185^\circ\text{C}$. Anal. Calc. for $\text{C}_{16}\text{H}_{19}\text{F}_6\text{N}_2\text{O}_4\text{Sb}$: C, 35.7%; H, 3.6. Found: C, 35.5%; H, 3.5%. ^1H NMR (CDCl_3 , 300 K) δ (ppm): 2.72 (s, 12H, $\text{N}(\text{CH}_3)_2$); 4.05 (s, 4H, NCH_2); 7.27 (d, 2H, Ar-H3,5); 7.42 (t, 1H, Ar-H4). ^{13}C NMR (CDCl_3 , 300 K) δ (ppm): 46.1 ($\text{N}(\text{CH}_3)_2$); 65.0 (NCH_2); 115.9 (q, CF_3 , $^1J(^{19}\text{F}, ^{13}\text{C}) = 291 \text{ Hz}$); 125.6 (Ar-C3,5); 131.3 (Ar-C4); 144.8 (Ar-C2,6); 151.8 (Ar-C1), 162.1 (q, C=O , $^2J(^{19}\text{F}, ^{13}\text{C}) = 37 \text{ Hz}$). IR (KBr, cm^{-1}): 1682 [$\nu_{\text{as}}(\text{CO}_2)$]; 1460 [$\nu_{\text{s}}(\text{CO}_2)$]. IR (CHCl_3 , cm^{-1}): 1679 [$\nu_{\text{as}}(\text{CO}_2)$]; 1470 [$\nu_{\text{s}}(\text{CO}_2)$]. ESI/MS positive mode: m/z 425 [$\text{M} - \text{CF}_3\text{COOH} + \text{H}$] $^+$; m/z 329 [$\text{M} - 2^+ \text{CF}_3\text{COOH} + \text{H}_2\text{O} + \text{H}$] $^+$, 100%.

2.2.3. Preparation of $[\text{2,6-}(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{SbCl}-\text{Cl}-\text{2,6-}(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{SbCl}]^+[\text{CB}_{11}\text{H}_{12}]^-$ (**4**)

Similarly to the procedure as for **2**: **1** (76 mg, 0.20 mmol), $\text{CB}_{11}\text{H}_{12}\text{Ag}$ (25 mg, 0.10 mmol) yielded white crystals (**4**; 154 mg, 70%), mp $208\text{--}211^\circ\text{C}$. Anal. Calc. for $\text{C}_{25}\text{H}_{50}\text{B}_{11}\text{Cl}_3\text{N}_4\text{Sb}_2$: C, 34.3%; H, 5.8. Found: C 34.6%; H 6.0%. ^1H NMR (CDCl_3 , 300 K) δ (ppm): 2.77 (s, 12H, $\text{N}(\text{CH}_3)_2$); 4.11 (s, 4H, NCH_2); 7.26 (d, 2H, Ar-H3,5); 7.42 (t, 1H, Ar-H4). ^{13}C NMR (CDCl_3 , 300 K) δ (ppm): 47.4

Table 1
Crystal data and structure refinement of **3–5** and **5a**.

	3	4	5	5a
Empirical formula	C ₁₆ H ₁₉ F ₆ N ₂ O ₄ Sb	C ₂₅ H ₅₀ B ₁₁ Cl ₂ N ₂ Sb	C ₁₄ H ₃₂ B ₁₁ Cl ₄ N ₂ Sb	C ₂₅ H ₅₅ B ₁₁ Cl ₁ N ₂ O ₃ Sb
Colour	Colourless	Colourless	Colourless	Colourless
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P2 ₁ /c	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
<i>a</i> (Å)	10.2812(5)	8.2032(8)	9.4273(6)	10.5293(10)
<i>b</i> (Å)	23.9243(7)	12.5731(8)	9.8622(9)	10.8182(10)
<i>c</i> (Å)	8.3097(7)	19.3258(16)	15.7555(16)	17.2577(14)
α (°)	90	106.697(6)	106.974(7)	103.413(5)
β (°)	93.424(6)	90.020(7)	93.878(8)	101.554(5)
γ (°)	90	89.940(8)	104.891(7)	93.041(8)
<i>Z</i>	4	2	2	2
μ (mm ⁻¹)	1.430	0.881	1.439	0.840
<i>D_x</i> (Mg m ⁻³)	1.755	1.201	1.517	1.262
Crystal size (mm)	0.3 × 0.17 × 0.11	0.46 × 0.34 × 0.18	0.31 × 0.23 × 0.12	0.60 × 0.49 × 0.23
Crystal shape	Needle	Plate	Plate	Block
θ Range, deg	1–27.5	1–27.5	1–27.5	1–27.5
<i>T_{min}</i> , <i>T_{max}</i>	0.753, 0.856 ^a	0.695, 0.921 ^a	0.731, 0.911 ^a	0.702, 0.849 ^a
No. of reflections measured	14966	15783	27872	33331
No. of unique reflections; <i>R_{int}</i>	4636, 0.049	7384, 0.068	6136, 0.099	8359, 0.108
No. of observed ref. [<i>I</i> > 2(<i>I</i>)]	3789	6440	5122	6090
No. of parameters	262	406	289	321
<i>S</i> ^b all data	1.153	1.100	1.171	1.063
Final <i>R</i> ^a indices [<i>I</i> > 2(<i>I</i>)]	0.054	0.051	0.050	0.064
<i>wR</i> ^{2a} indices (all data)	0.11	0.141	0.122	0.149
$\Delta\rho$, max., min. (e Å ⁻³)	1.441, -0.769	1.889, -3.974	1.346, -1.755	0.772, -0.780

^a Correction by SORTAV program.

^b Definitions: $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR^2 = [\sum (w(F_o^2 - F_c^2))^2 / \sum (w(F_o^2))^2]^{1/2}$, $S = [\sum (w(F_o^2 - F_c^2))^2 / (N_{\text{reflins}} - N_{\text{params}})]^{1/2}$.

(N(CH₃)₂); 52.0 (CB-cage); 64.7 (NCH₂); 125.9 (Ar-C3,5); 131.4 (Ar-C4); 144.1 (Ar-C2,6); 152.7 (Ar-C1). ¹¹B NMR (CDCl₃, 300 K) δ (ppm): -10.5 (bs), -16.6 (bs), -19.3 (bs). IR (KBr, cm⁻¹): [ν(BH)] 2542. ESI/MS – positive mode: *m/z* 347 [M-CB₁₁H₁₂]⁺; *m/z* 329 [M-CB₁₁H₁₂-HCl + H₂O]⁺, 100%. ESI/MS – negative mode: *m/z* 145 [CB₁₁H₁₂]⁻, 100%.

2.2.4. Preparation of [2,6-(Me₂NCH₂)₂C₆H₃SbCl]⁺ CB₁₁H₁₂⁻ (**5**)

Similarly to the procedure as for **2**: **1** (90 mg, 0.23 mmol), CB₁₁H₁₂Ag (70 mg, 0.28 mmol) yielded white crystals (**5**; 154 mg, 70%), mp 216–219 °C. Anal. Calc. for C₁₃H₃₁B₁₁ClN₂Sb: C, 31.8%; H, 6.4. Found: C, 32.1%; H, 6.2%. ¹H NMR (CDCl₃, 300 K) δ (ppm): 2.76 (s, 6H, NCH₃); 2.88 (s, 6H, NCH₃); 4.05 and 4.24 (AX pattern, 4H, NCH₂); 7.38 (d, 2H, Ar-H3,5); 7.56 (t, 1H, Ar-H4). ¹H NMR (THF, 300 K) δ (ppm): 2.79 (s, 12H, N(CH₃)₂); 4.18 (s, 4H, NCH₂); 7.42 (d, 2H, Ar-H3,5); 7.58 (t, 1H, Ar-H4). ¹³C NMR (THF, 300 K) δ (ppm): 47.0 (N(CH₃)₂); 51.7 (CB-cage), 65.3 (NCH₂); 127.0 (Ar-C3,5); 133.6 (Ar-C4); 146.3 (Ar-C2,6); 149.3 (Ar-C1). ¹¹B NMR (THF, 300 K) δ (ppm): -4.7 (bs), -11.1 (bs), -14.26 (bs). IR (KBr, cm⁻¹): [ν(BH)] 2547. ESI/MS – positive mode: *m/z* 347 [M-CB₁₁H₁₂]⁺; *m/z* 329 [M-CB₁₁H₁₂-HCl + H₂O]⁺, 100%. ESI/MS – negative mode: *m/z* 145 [CB₁₁H₁₂]⁻, 100%.

3. Results and discussion

3.1. Synthesis of studied compounds

The compounds **2** and **3** were obtained as colourless crystalline solids *via* the reaction of the starting organoantimony dichloride **1** [17] with two equivalents of the silver salt of the appropriate carboxylic acid in CH₂Cl₂ (Scheme 1). The reaction of **1** with 1 eq. of AgCB₁₁H₁₂ gave firstly besides the target compound **5** a tiny amount of single crystals identified as an unexpected chlorine-bridged-dinuclear ionic compound **4**. This compound was then selectively prepared by the reaction of **1** with only 0.5 eq. of AgCB₁₁H₁₂ in a high yield as the only isolable product. On the other hand, a slight excess of AgCB₁₁H₁₂ (~15%) was used in the reaction

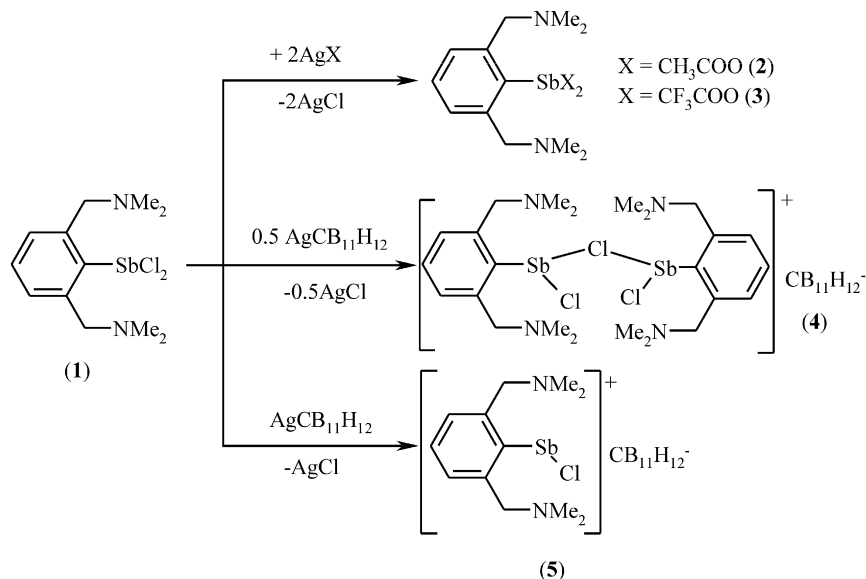
with **1** to guarantee full conversion to the ionic compound **5** (Scheme 1). All compounds are nearly insoluble in aliphatic hydrocarbons and readily soluble in chlorinated solvents (**2–4**) or in THF (**5**). The purity of all compounds was established with the help of the satisfactory elemental analysis, ESI-MS, ¹H, ¹¹B and ¹³C NMR spectroscopy (see Section 2).

3.2. Solid state structures

The molecular structures of **3–5** and **5a** (for formation of **5a** see further discussion) were determined by the single crystal X-ray diffraction and are depicted together with the relevant geometric parameters in Figs. 2–5. Crystallographic details are given in Table 1.

Both trifluoroacetic groups are coordinated to the central anti-mony atom Sb(1) in an unidentate fashion in **3** as demonstrated by fairly different Sb–O distances within each carboxylic group (Sb(1)–O(1) 2.322(4) and Sb(1)–O(2) 3.272(4); Sb(1)–O(3) 2.218(4) and Sb(1)–O(4) 3.208(5) Å), the C–O bond distances within carboxylic moieties also support this statement (C(13)–O(1) 1.267(6) and C(13)–O(2) 1.204(6); C(15)–O(3) 1.275(6) and C(15)–O(4) 1.194(7) Å). In contrast to these findings, in the case of the OCO chelated analogue one of the trifluoroacetates was coordinated in the bidentate fashion [18]. Both nitrogen donor atoms of the ligand L in **3** are coordinated to the central atom through intramolecular interaction (Sb(1)–N(1) 2.440(4) and Sb(1)–N(2) 2.373(4) Å) mutually in pseudo *trans* positions with the angle N(1)–Sb(1)–N(2) 149.54(14)°. The overall geometry around the antimony atom can be, thus, described as a tetragonal pyramid with C(1) in the apical position and with the Sb(1) atom and two oxygen atoms (O(1), O(2)) and two nitrogen atoms (N(1), N(2)) forming the basal plane.

The molecular structure of the compound **4** is built up as a well separated ion pair [LSb(Cl)–Cl–Sb(Cl)L]⁺ and [CB₁₁H₁₂]⁻. The structure of the cationic part of **4**, which is of particular interest (Fig. 3), consists of two distorted tetragonal pyramids around two central antimony atoms Sb(1) and Sb(2a) sharing one apex (Cl(3)). Both



Scheme 1. Preparation of the studied compounds 2–5.

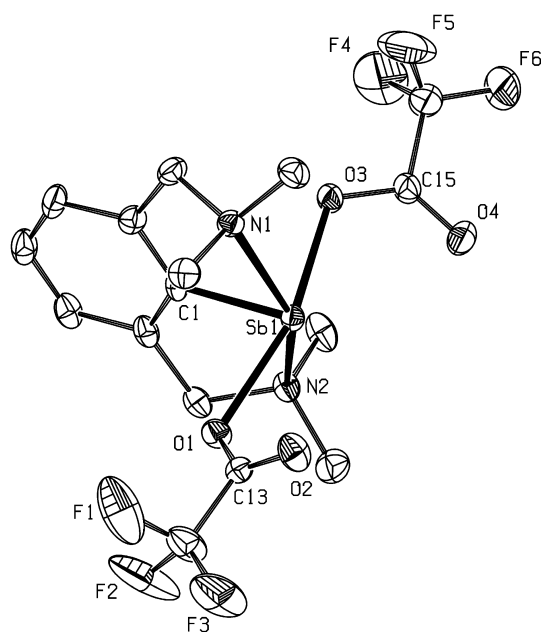


Fig. 2. ORTEP drawing (30% probability atomic displacement ellipsoids) of **3**. Hydrogen atoms have been omitted for clarity. Selected bond distance [Å]: C(1)–Sb(1) 2.103(5), N(1)–Sb(1) 2.440(4), N(2)–Sb(1) 2.373(4), O(1)–Sb(1) 2.322(4), O(2)–Sb(1) 3.272(4), O(3)–Sb(1) 2.218(4), O(4)–Sb(1) 3.208(5), C(13)–O(1) 1.267(6), C(13)–O(2) 1.204(6), C(15)–O(3) 1.275(6), C(15)–O(4) 1.194(7). Selected bonding angles [°]: N(1)–Sb(1)–N(2) 149.54(14), O(1)–Sb(1)–O(3) 162.93(13), C(1)–Sb(1)–N(1) 74.49(17), C(1)–Sb(1)–N(2) 75.12(17), C(1)–Sb(1)–O(1) 80.52(17), C(1)–Sb(1)–O(3) 82.46(17).

ligands L are coordinated in a tridentate fashion to the central antimony atoms Sb(1) and Sb(2a). The value of the bonding angle Sb(1)–Cl(3)–Sb(2a) describing the bridge 165.34(5) deviates slightly from the linearity and causes inclination of both ligands (aromatic rings) too each other. In both tetragonal pyramids around both central atoms, the *ipso* carbon atoms of the ligands occupy the apical positions. The basal planes are formed via two chlorine atoms Cl(1) and Cl(3) (or Cl(3) and Cl(2a)) mutually placed in the *trans* positions and two nitrogen atoms N(1) and N(2) (or N(3a) and N(4a)), the range of the present Sb–N intramolecular interac-

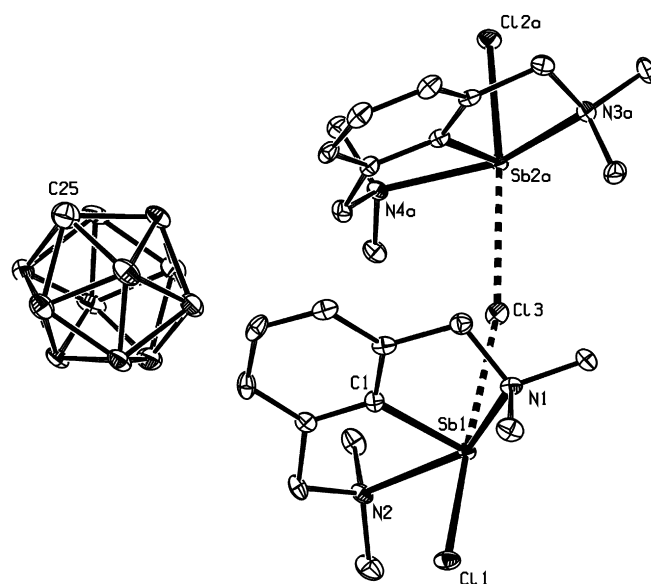


Fig. 3. ORTEP drawing (30% probability atomic displacement ellipsoids) of **4**. Hydrogen atoms have been omitted for clarity. Selected bond distance [Å]: C(1)–Sb(1) 2.103(5), N(1)–Sb(1) 2.394(5), N(2)–Sb(1) 2.492(5), Cl(1)–Sb(1) 2.4362(14), Cl(3)–Sb(1) 2.9459(14), Cl(3)–Sb(2a) 2.9459(14), N(3a)–Sb(2a) 2.499(5), N(4a)–Sb(2a) 2.394(5), Cl(2a)–Sb(2a) 2.4333(14). Selected bonding angles [°]: N(1)–Sb(1)–N(2) 149.18(14), N(3a)–Sb(2a)–N(4a) 149.06(15), Cl(1)–Sb(1)–Cl(3) 174.23(5), Sb(1)–Cl(3)–Sb(2a) 165.34(5), Cl(3)–Sb(2a)–Cl(2a) 174.23(5).

tions is 2.394(5)–2.499(5) Å). The bond distances between terminal chlorine atoms and the antimony atoms Sb(1)–Cl(1) 2.4362(14) and Sb(2a)–Cl(2a) 2.4333(14) Å approach the sum of the covalent radii for the single covalent bond (2.45 Å), but the position of the bridging chlorine atom Cl(3) is more interesting. The bond lengths Cl(3)–Sb(1) and Cl(3)–Sb(2a) 2.9454(14) Å are significantly longer than the sum of the covalent radii indicating that these bonds might be understood as medium strong interactions rather than normal covalent bonds, which offers an alternative view on the structure of this cationic part of **4**. From this viewpoint, the chloride anion (Cl(3)) is caught between two organoantimony cations [LSbCl]⁺ through electronic interactions. Formation of similar ionic organobismuth compound containing another type of

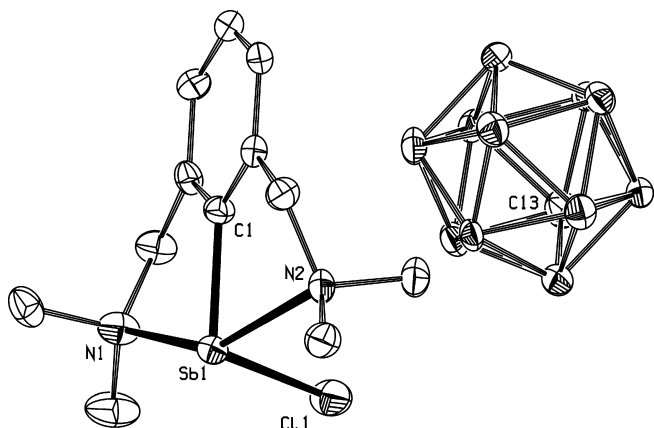


Fig. 4. ORTEP drawing (30% probability atomic displacement ellipsoids) of **5**. Hydrogen atoms have been omitted for clarity. Selected bond distance [Å]: C(1)–Sb(1) 2.090(5), N(1)–Sb(1) 2.379(5), N(2)–Sb(1) 2.422(4), Cl(1)–Sb(1) 2.3546(16). Selected bonding angles [°]: N(1)–Sb(1)–N(2) 148.60(16), C(1)–Sb(1)–N(1) 75.00(17), C(1)–Sb(1)–N(2) 73.88(17), C(1)–Sb(1)–Cl(1) 97.96(14).

CNC chelating ligand has been recently reported by Shimada and coworkers [19].

The $\text{CB}_{11}\text{H}_{12}^-$ anion is again well separated from the organoantimony cation $[\text{LSbCl}]^+$ in the case of the compound **5**, similarly to **4** (Fig. 4). The pincer ligand is strongly coordinated to the central antimony atom Sb(1) in a tridentate fashion in the structure of the cationic part of **4** (the Sb–N bond lengths are 2.379(5) and 2.422(4) Å, respectively). The overall geometry around the Sb(1) atom can be described as a distorted ψ -trigonal bipyramid with both nitrogen donor atoms placed in the axial positions (the bonding angle N(1)–Sb(1)–N(2) 148.60(16)°), similarly to the organoantimony cation containing two NC-chelating ligands $[\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{Sb}^+$ [20]. The significant deviation from the ideal environment is the value of the angle formed by the nitrogen donor atoms in the axial positions (the angle N(1)–Sb(1)–N(2) 148.60(16)°), which can be ascribed to the ligand's rigidity. The chlorine atom and the *ipso* carbon atom form the equatorial plane.

Interestingly, when the compound **5** was crystallized from a donor solvent such as THF, the adduct $[\text{LSbCl}(\text{THF})]^+[\text{CB}_{11}\text{H}_{12}]^-$ **5a** was obtained and its structure was determined by X-ray diffraction technique. The molecular structure of **5a** closely resembles this of **5** in regard to the coordination of the ligand L. However, in

contrast to the molecular structure of **5**, the coordination polyhedron of the central antimony atom is completed with a THF molecule, which is coordinated to the central metal through an intermolecular interaction as demonstrated by the bond length Sb(1)–O(1) 2.768(3). The overall geometry in **5a** is a distorted tetragonal pyramid, where the THF molecule and the chlorine atom are located mutually in *trans* positions and the *ipso* carbon atom occupies the axial position.

3.3. Solution structures

Although all attempts to grow single crystals of the acetate **2** failed to this moment, its structure was described in solution. IR spectra of **2** in CHCl_3 solution revealed only one band for antisymmetric and symmetric CO_2 stretching proving equivalently bonded carboxylic groups. The $\Delta\nu$ between the antisymmetric and symmetric CO_2 stretching (357 cm^{-1}) proves unidentate coordination of both acetates [18,21] (similar situation was observed in the solid sample, proving similar coordination of the carboxylates in both phases). The ^1H NMR spectra revealed broader set of signals at 300 K, that is resolved to an AX pattern for the NCH_2 and two signals in 1:1 integral ratio for the $\text{N}(\text{CH}_3)_2$ groups at 230 K. These findings correspond to a fluxional behaviour of the coordination of the ligand at 300 K, which is slowed down upon cooling resulting to the *cis* coordination of both $\text{CH}_2\text{N}(\text{CH}_3)_2$ pendant arms of the ligand (*trans* position of these donor groups gives rise to only singlet resonances for both NCH_2 and $\text{N}(\text{CH}_3)_2$ groups in the case of the compound **3** *vide infra*). The structure of **2** in solution can be, thus, described as a trigonal pyramid formed by the antimony atom *ipso* carbon atom and two oxygen atoms (from acetates), which is *cis* coordinated (bi-capped) by two nitrogen donor atoms coming from the ligand [22]. Very similar situation has been recently observed in the case of the OCO chelated analogue, whose molecular structure was determined by the X-ray diffraction technique [18].

The molecular structure of **3** as described in the solid state is retained in solution, which was proven by analogous IR spectra in KBr and CHCl_3 solution (see Section 2) as well as by the ^1H NMR spectra, where only one set of sharp signals (singlets) were obtained for the NCH_2 and the $\text{N}(\text{CH}_3)_2$ moieties proving their symmetrical (*trans*) arrangement in the antimony coordination sphere (similarly to the solid state structure *vide supra*).

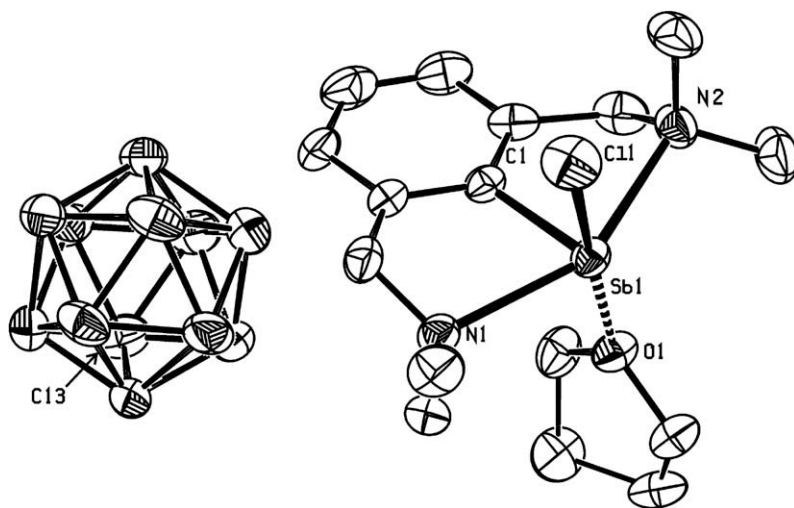


Fig. 5. ORTEP drawing (30% probability atomic displacement ellipsoids) of **5a**. Hydrogen atoms have been omitted for clarity. Selected bond distance [Å]: C(1)–Sb(1) 2.098(5), N(1)–Sb(1) 2.425(5), N(2)–Sb(1) 2.418(5), Cl(1)–Sb(1) 2.3730(19), O(1)–Sb(1) 2.768(3). Selected bonding angles [°]: N(1)–Sb(1)–N(2) 149.04(16), Cl(1)–Sb(1)–O(1) 174.77(10), C(1)–Sb(1)–O(1) 80.94(16), C(1)–Sb(1)–Cl(1) 95.77(15).

The ionic nature of both **4** and **5** in solution, similarly to the solid state, was corroborated by the ^{11}B NMR spectra, where three well resolved resonances in the 1:5:5 ratio (at -10.5 , -16.6 , -19.3 ppm for **4** and -4.7 , -11.1 , -14.26 ppm for **5**) were observed, the typical pattern for the free $\text{CB}_{11}\text{H}_{12}^-$ anion [11a]. The ^1H NMR spectrum in CDCl_3 of **4** revealed only one set of signals for the NCH_2 and the $\text{N}(\text{CH}_3)_2$ groups, on the other hand the unsymmetrical coordination sphere of the cationic part of **5** was reflected in the observation of an AX pattern for the NCH_2 and two signals in the 1:1 integral ratio for the $\text{N}(\text{CH}_3)_2$ groups. However, the ^1H NMR spectra of **5** recorded in THF showed only one set of signal, which is most probably the consequence of a fast coordination/decoordination of the solvent THF molecules. The ability of **5** to accommodate a THF molecule in its coordination sphere was clearly demonstrated in the solid state by the isolation of the adduct **5a** (*vide supra*). Similar coordination of THF molecules was observed also in the case of the organoantimony and organobismuth OCO chelated compounds [11a].

4. Conclusions

We have shown that the behaviour of the polar group X in the compounds of the type $[\text{2,6-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{SbX}_2$ has a significant effect on the geometry around the central antimony atom. The coordination environment around the central atoms range from a biccapped – trigonal pyramid ($\text{X} = \text{CH}_3\text{COO}$, **2**), through a distorted tetragonal pyramid ($\text{X} = \text{CF}_3\text{COO}$, **3**) to a ψ -trigonal bipyramid ($\text{X} = \text{Cl}$, $\text{CB}_{11}\text{H}_{12}$, **5**). Even more, an unusual dinuclear ionic complex **4** was prepared and characterized and in this case the structure of the organometallic cation in **4** can be described as one apex sharing distorted tetragonal pyramids. The cationic part of the compound **5** is able to form the THF adduct **5a** reflecting high Lewis acidity of the central atom. The geometries around the central antimony atom are stabilized due to the strong tridentate coordination of the NCN pincer type ligand in all cases. The studies dealing with further reactivity of the compounds **2–5** are currently underway.

5. Supplementary material

CCDC 742903, 742904, 742905 and 742906 contain the supplementary crystallographic data for **3–5** and **5a**. 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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