Intramolecularly coordinated organoantimony(III) carboxylates

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Abstract

The reactions of organoantimony chlorides $L^{1,2}SbCl_2$ **1** and **2** ([2,6-$(ROCH_2)_2C_6H_3$]$^-$, R = Me; L^1 and R = *t*-Bu; L^2) with silver salts of selected carboxylic acids resulted to corresponding organoantimony carboxylates $L^{1,2}Sb(OOCR')_2$, **1a–c** (for L^1) and **2a–c** (for L^2), where $R' = CH_3$ for **1a**, **2a**; $R' = CH{=}CH_2$ for **1b**, **2b** and $R' = CF_3$ for **1c**, **2c**. All compounds were characterized by the help of elemental analysis, ESI–MS, ^1H and ^{13}C NMR spectroscopy. The solid state structure investigation using single crystal X-ray diffraction techniques (**2a**, **c**) and IR spectroscopy revealed significant differences in coordination mode of both O,C,O chelating ligand and carboxylic groups in this set of compounds. The structure of all compounds in solution of non-coordinating solvent ($CDCl_3$) was determined by means of variable temperature ^1H, ^{13}C, ^{19}F NMR spectroscopy and IR spectroscopy.
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1. Introduction

The synthesis and structures of organoantimony(V) carboxylates were extensively studied during the last two decades [1]. Carboxylates as versatile ligands were shown to act as unidentate [2], bidentate [3] or bridging ligands [3a,4] in organoantimony(V) compounds by X-ray diffraction techniques (XRD). The carboxylates need not bridge only two antimony centres, but also the heterobimetallic compounds containing this unit as a spacer between Sb and ferrocene moiety, or Sb and Ge atoms emerged [5]. The latter compounds were investigated in reference to their potential antitumor activity. The utilization of dicarboxylic acids has been studied recently as well [6].

In contrast to organoantimony(V) carboxylates the investigation of carboxylates containing Sb(III) atom is rare. Organoantimony(III) carboxylates characterized in the solid state by the XRD method include $Sb(OOCCH_3)_3$ [7], $Sb(OOCCH_2CH_3)_3$ [8], $Sb(OOCCF_3)_3$ [9] and $SbPh_2(OOCCH_3)$, that forms polymeric chains in the solid state through acetate bridges [10]. The phthalic acid was used as a bridging ligand between two antimony centres as well [11]. Compounds of the type $Sb(OOCNR_2)_3$ have been recently investigated as precursors for deposition of antimony oxides [12].

In order to further develop the chemistry of organoantimony(III) carboxylates, we report here on synthesis, solution and solid state structure of six novel antimony dicarboxylates, derivatives of O,C,O chelating ligands ([2,6-$(ROCH_2)_2C_6H_3$]$^-$, R = Me; L^1 and R = *t*-Bu; L^2), $L^{1,2}Sb(OOCR')_2$, where $R' = CH_3$ for **1a**, **2a**; $R' = CH{=}CH_2$ for **1b**, **2b** and R = CF_3 for **1c**, **2c**. This set of compounds enables us to follow the influence of both

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ligand (steric factors) and carboxylate (increasing electron withdrawing ability of the polar groups $OOCCF_3 > OOCCH_3 \approx OOCCH=CH_2$) on the coordination polyhedron of the central atom and on their behaviour in solution.

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, ^{13}C and ^{19}F NMR spectra were recorded on Bruker500 Avance spectrometer. Appropriate chemical shifts in ^1H and ^{13}C NMR spectra were calibrated on the residual signals of the solvent ($CDCl_3$: $\delta(^1H) = 7.27$ ppm and $\delta(^{13}C) = 77.23$ ppm). ^{19}F NMR chemical shifts were related according to the external standard $KF\delta(^{19}F) = -130$ ppm. Positive-ion and negative-ion electrospray ionization (ESI) mass spectra were measured on an ion trap analyzer Esquire 3000 (Bruker Daltonics, Bremen, Germany) in the range m/z 50–1000. The samples were dissolved in acetonitrile and analyzed by direct infusion at the flow rate 5 μl/min. The ion source temperature was 300 °C, the tuning parameter compound stability was 100% for measuring of positive ions and 20% for measuring of negative, the flow rate and the pressure of nitrogen were 4 l/min and 10 psi, respectively.

IR spectra were recorded in chloroform solution, nujol or KBr suspension on Perkin Elmer 684 equipment (cm^{-1}).

2.1.1. X-ray structure determination

Colourless single crystals of **2a** and **2c** were obtained by crystallization from toluene/n-hexane (1:2) solution at −30 °C. The crystal of compounds of **2a**, **c** were mounted on glass fibre with epoxy cement and measured on four-circle diffractometer KappaCCD with CCD area detector by monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K. The crystallographic details are summarized in Table 1, empirical absorption corrections [13] were applied (multiscan from symmetry-related measurements). The structures were solved by the direct method (SIR97 [14]) and refined by a full matrix least squares procedure based on F^2 (SHELXL97 [15]). Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom), for the methyl moiety multiple of 1.5 was chosen. The final difference maps displayed no peaks of chemical significance. In the both crystals the solvent molecules are disordered over two positions and were constrained into idealized geometry and refined with rigid body approximation.

2.2. Synthesis

The starting chemicals CH_3COOAg (99.9%), CF_3COOAg (98%), $CH_2CHCOONa$ (98% – converted to

Table 1
Crystal data and structure refinement of **2a** and **2c**

	2a	**2c**
Empirical formula	$C_{20}H_{31}O_6Sb$ $0.5(C_7H_8)$	$C_{20}H_{25}F_6O_6Sb$ $0.5(C_7H_8)$
Colour	Colourless	Colourless
Crystal system	Orthorhombic	Triclinic
Space group	$Pbca$ (No. 61)	$P\bar{1}$ (No. 2)
a (Å)	16.0970(1)	9.6550(2)
b (Å)	13.6920(3)	12.4070(4)
C (Å)	22.9430(4)	12.4700(2)
α (°)		89.0970(16)
β (°)		70.5330(15)
γ (°)		67.7280(12)
Z	8	2
μ (mm^{-1})	1.124	1.147
D_x ($mg\ m^{-3}$)	1.406	1.652
Crystal size (mm)	$0.4 \times 0.25 \times 0.1$	$0.22 \times 0.2 \times 0.15$
Crystal shape	Plate	Prism
θ Range (°)	1–27.5	1–27.5
$T_{minimum}$, $T_{maximum}$	0.785, 0.885[a]	0.791, 0.847[a]
No. of reflections measured	68916	23763
No. of unique reflections; R_{int}	5815, 0.056	5945, 0.036
No. of observed reflections $[I > 2\sigma(I)]$	4399	5358
No. of parameters	256	309
S[b] All data	1.058	1.054
Final R[a] indices $[I > 2\sigma(I)]$	0.041	0.029
$wR2$[a] indices (all data)	0.109	0.072
w_1/w_2[c]	0.0469/11.464	0.0354/1.0657
$\Delta\rho_{maximum,\ minimum}$ (e $Å^{-3}$)	1.916, −1.058	0.923, −0.660

[a] Correction by SORTAV program.
[b] Definitions: $R(F) = \Sigma ||F_o| - || F_c||/\Sigma |F_o|$, $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$, $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{reflns} - N_{params})]^{1/2}$.
[c] Weighting scheme $w = [\sigma^2(F_o^2) + (w_1P) + w_2P]^{-1}$. $P = [\max(F_o^2, 0) + 2F_c^2]/3$. $R_{int} = \Sigma |F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$ (summation is carried out only where more than one symmetry equivalent is averaged).

silver salt by reaction with $AgNO_3$ in minimum amount of water) were obtained from commercial suppliers and used as delivered. The compounds **1** and **2** were prepared according to literature procedures [16]. All reaction flaks were light protected by aluminum foil.

2.2.1. Preparation 2,6-(MeOCH₂)₂C₆H₃Sb(OOCCH₃)₂ (1a)

Silver acetate 126 mg (0.74 mmol) was added to a solution of **1** 134 mg (0.37 mmol) in CH_2Cl_2 (15 ml) and resulting suspension was stirred overnight. Then insoluble material was filtered off and solvent was evaporated *in vacuo*. Compound **1a** was obtained after washing with hexane (5 ml) as colourless highly viscous oil (104 mg, 69%). Anal. Calc. for $C_{14}H_{19}O_6Sb$: C, 41.51; H, 4.73. Found: C, 41.62; H, 4.62%. ^1H NMR ($CDCl_3$) δ (ppm): 2.09 (s, 6H, $COCH_3$); 3.52 (s, 6H, OCH_3); 4.74 (s, 4H, OCH_2); 7.17 (d, 2H, Ar–$H3,5$); 7.30 (t, 1H, Ar–$H4$). ^{13}C NMR ($CDCl_3$) δ (ppm): 21.7 (CH_3CO); 59.1 (OCH_3); 76.1 (OCH_2); 125.2 (Ar–$C3,5$); 129.4 (Ar–$C4$); 146.3 (Ar–$C2,6$); 149.5 (Ar–$C1$); 175.4 ($C=O$). IR (neat, cm^{-1}): 1675 [$\nu_{as}(CO_2)$]; 1367 [$\nu_s(CO_2)$]. IR ($CHCl_3$, cm^{-1}): 1675

$[\nu_{as}(CO_2)]$;1372 $[\nu_s(CO_2)]$. ESI/MS – positive mode: m/z 345 $[M-CH_3COO]^+$, 100%.

2.2.2. Preparation of 2,6-(MeOCH$_2$)$_2$C$_6$H$_3$Sb-(OOCCHCH$_2$)$_2$ (1b)

Similarly to procedure as for **1a**:**1** 73 mg (0.2 mmol), silver acrylate 146 mg (0.4 mmol) yielded colourless highly viscous oil (**1b**; 101 mg, 75%). Anal. Calc. for C$_{16}$H$_{19}$O$_6$Sb: C, 44.79; H, 4.46. Found: C, 44.59; H, 4.65%. ^{1}H NMR (CDCl$_3$) δ (ppm): 3.50 (s, 6H, OCH_3); 4.74 (s, 4H, OCH_2); 5.75 (d, 2H, *trans* CH_2=, $^3J(^1H_{trans}$, $^1H_{gem}) = 10.2$ Hz); 6.15 (dd, 2H, –CH=, $^3J(^1H_{trans}$, $^1H_{gem}) = 10.2$ Hz, $^3J(^1H_{cis}$, $^1H_{gem}) = 17.1$ Hz); 6.34 (d, 2H, *cis* CH_2=, $^3J(^1H_{cis}$,$^1H_{gem}) = 17.1$ Hz); 7.19 (d, 2H, Ar–H3,5); 7.32 (t, 1H, Ar–H4). ^{13}C NMR (CDCl$_3$) δ (ppm): 59.2 (OCH$_3$); 76.1 (OCH$_2$); 125.1 (Ar–C3,5); 127.2 (CH$_2$=) 129.4 (Ar–C4); 130.2 (–CH=); 146.4 (Ar–C2,6); 149.8 (Ar–C1); 170.0 (C=O). IR (neat, cm^{-1}): 1670 $[\nu_{as}(CO_2)]$; 1608 $[\nu(C=C)]$; 1310 $[\nu_s(CO_2)]$. IR (CHCl$_3$, cm^{-1}): 1670 $[\nu_{as}(CO_2)]$; 1608 $[\nu(C=C)]$; 1318 $[\nu_s(CO_2)]$. ESI/MS – positive mode: m/z 357 $[M-CH_2CHCOO]^+$, 100%.

2.2.3. Preparation of 2,6-(MeOCH$_2$)$_2$C$_6$H$_3$Sb(OOCCF$_3$)$_2$ (1c)

Similarly to procedure as for **1a**:**1** 120 mg (0.34 mmol), silver trifluoroacetate 148 mg (0.68 mmol) yielded white crystals of (**1c**; 101 mg, 59%), m.p. 148–150 °C (decomposition). Anal. Calc. for C$_{14}$H$_{13}$F$_6$O$_6$Sb: C, 37.78; H, 2.55. Found: C, 37.62; H, 2.61%. ^{1}H NMR (CDCl$_3$) δ (ppm): 3.61 (s, 6H, OCH_3); 4.86 (s, 4H, OCH_2); 7.22 (d, 2H, Ar–H3,5); 7.34 (t, 1H, Ar–H4). ^{13}C NMR (CDCl$_3$) δ (ppm): 59.3 (OCH$_3$); 75.6 (OCH$_2$); 115.1 (q, CF$_3$, $^1J(^{19}$F, ^{13}C) = 286.2 Hz); 125.2 (Ar–C3,5); 130.0 (Ar–C4); 145.8 (Ar–C2,6); 160.4 (q, C=O, $^2J(^{19}$F, ^{13}C) = 40.2 Hz); (Ar–C1) not detected. ^{19}F NMR (CDCl$_3$) δ (ppm): −74.4. IR (KBr, cm^{-1}): 1738, 1690 $[\nu_{as}(CO_2)]$; 1458, 1402 $[\nu_s(CO_2)]$. IR (CHCl$_3$, cm^{-1}): 1721 $[\nu_{as}(CO_2)]$; 1400 $[\nu_s(CO_2)]$. ESI/MS positive mode: m/z 623 $[LSbOSbLOH+H_2O]^+$, 100%; m/z 605 $[LSbOSbLOH]^+$; m/z 399 $[M+H-CF_3COOH]^+$; m/z 321 $[LSbOH+H_2O]^+$; m/z 303 $[LSbOH]^+$. ESI/MS – negative mode: m/z 625 $[M+CF_3COO]^-$, 100%.

2.2.4. Preparation 2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$Sb(OOCCH$_3$)$_2$ (2a)

Similarly to procedure as for **1a**:**2** 200 mg (0.45 mmol), silver acetate 151 mg (0.9 mmol) yielded white crystals (**2a**; 154 mg, 70%), m.p. 105–108 °C. Anal. Calc. for C$_{20}$H$_{31}$O$_6$Sb: C, 49.10; H, 6.39. Found: C, 49.24; H, 6.27%. ^{1}H NMR (CDCl$_3$) δ (ppm): 1.32 (s, 18H, C(CH_3)$_3$); 2.02 (s, 6H, COCH_3); 4.72 (s, 4H, OCH_2); 7.14 (d, 2H, Ar–H3,5); 7.23 (t, 1H, Ar–H4). ^{13}C NMR (CDCl$_3$) δ (ppm): 22.0 (CH$_3$CO); 27.7 (C(CH$_3$)$_3$); 65.3 (OCH$_2$); 77.7 (OC(CH$_3$)$_3$); 124.5 (Ar–C3,5); 128.7 (Ar–C4); 147.7 (Ar–C2,6); 148.6 (Ar–C1); 174.8 (C=O). IR (nujol, cm^{-1}): 1680 $[\nu_{as}(CO_2)]$; 1365 $[\nu_s(CO_2)]$. IR (CHCl$_3$, cm^{-1}): 1676 $[\nu_{as}(CO_2)]$; 1370 $[\nu_s(CO_2)]$. ESI/MS – positive mode: m/z 815 $[LSbOSbLOH-butene-H_2O+CH_3COOC(CH_3)_3]^+$ m/z 773 $[LSbOSbLOH]^+$, 100%; m/z 699 $[LSbOSbLOH-butene-H_2O]^+$; m/z 643 $[LSbOSbLOH-2^*butene-H_2O]^+$; m/z 429 $[M+H-CH_3COOH]^+$; m/z 387 $[LSbOH]^+$; m/z 331 $[LSbOH-butane]^+$; m/z 313 $[LSbOH-butane-H_2O]^+$; m/z 257 $[LSbOH-2^*butane-H_2O]^+$.

2.2.5. Preparation 2,6-(^{t}BuOCH$_2$)$_2$-C$_6$H$_3$Sb(OOCCHCH$_2$)$_2$ (2b)

Similarly to procedure as for **1a**:**2** 147 mg (0.33 mmol), silver acrylate 119 mg (0.66 mmol) yielded white crystals (**2b**; 144 mg, 84%), m.p. 132–134 °C. Anal. Calc. for C$_{22}$H$_{31}$O$_6$Sb: C, 51.49; H, 6.09. Found: C, 51.24; H, 6.27%. ^{1}H NMR (CDCl$_3$) δ (ppm): 1.32 (s, 18H, C(CH_3)$_3$); 4.74 (s, 4H, OCH_2); 5.68 (d, 2H, *trans* CH_2=, $^3J(^1H_{trans}$, $^1H_{gem}) = 10.2$ Hz); 6.13 (dd, 2H, –CH=, $^3J(^1H_{trans}$, $^1H_{gem}) = 10.2$ Hz, $^3J(^1H_{cis}$, $^1H_{gem}) = 17.3$ Hz); 6.27 (d, 2H, *cis* CH_2=, $^3J(^1H_{cis}$, $^1H_{gem}) = 17.3$ Hz); 7.18 (d, 2H, Ar–H3,5); 7.26 (t, 1H, Ar–H4). ^{13}C NMR (CDCl$_3$) δ (ppm): 28.0 (C(CH$_3$)$_3$); 65.6 (OCH$_2$); 77.8 (OC(CH$_3$)$_3$); 124.8 (Ar–C3,5); 128.9 (Ar–C4); 129.7 (–CH=); 130.8 (CH$_2$=); 148.0 (Ar–C2,6); 149.4 (Ar–C1); 169.7 (C=O). IR (nujol, cm^{-1}): 1669 $[\nu_{as}(CO_2)]$; 1610 $[\nu(C=C)]$; 1319 $[\nu_s(CO_2)]$. IR (CHCl$_3$, cm^{-1}): 1673 $[\nu_{as}(CO_2)]$; 1610 $[\nu(C=C)]$; 1318 $[\nu_s(CO_2)]$. ESI/MS – positive mode: m/z 827 $[LSbOSbLOH-butene-H_2O+CH_2=CHCOOC(CH_3)_3]^+$ m/z 773 $[LSbOSbLOH]^+$, 100%; m/z 699 $[LSbOSbLOH-butene-H2O]^+$; m/z 643 $[LSbOSbLOH-2^*butene-H_2O]^+$; m/z 441 $[M+H-CH_2=CHCOOH]^+$; m/z 387 $[LSbOH]^+$; m/z 331 $[LSbOH-butane]^+$; m/z 313 $[LSbOH-butane-H_2O]^+$; m/z 257 $[LSbOH-2^*butane-H_2O]^+$.

2.2.6. Preparation 2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$Sb(OOCCF$_3$)$_2$ (2c)

Similarly to procedure as for **1a**:**2** 200 mg (0.45 mmol), silver trifluoroacetate 200 mg (0.9 mmol) yielded white crystals (**2c**; 175 mg, 65%), m.p. 108–110 °C. Anal. Calc. for C$_{20}$H$_{25}$F$_6$O$_6$Sb: C, 40.23; H, 4.22. Found: C, 40.14; H, 4.36%. ^{1}H NMR (CDCl$_3$) δ (ppm): 1.41 (s, 18H, C(CH_3)$_3$); 4.79 (s, 4H, OCH_2); 7.26 (d, 2H, Ar–H3,5); 7.38 (t, 1H, Ar–H4). ^{13}C NMR (CDCl$_3$) δ (ppm): 28.2 (C(CH$_3$)$_3$); 66.0 (OCH$_2$); 80.3 (OC(CH$_3$)$_3$); 115.0 (q, CF$_3$, $^1J(^{19}$F, ^{13}C) = 287.5 Hz); 124.4 (Ar–C3,5); 130.1 (Ar–C4); 147.0 (Ar–C2,6); 147.4 (Ar–C1); 160.2 (q, C=O, $^2J(^{19}$F, ^{13}C) = 40 Hz). ^{19}F NMR (CDCl$_3$) δ (ppm): −74.5. IR (KBr, cm^{-1}): 1723, 1693 $[\nu_{as}(CO_2)]$; 1411, 1386 $[\nu_s(CO_2)]$. IR (CHCl$_3$, cm^{-1}): 1738 $[\nu_{as}(CO_2)]$; 1400 $[\nu_s(CO_2)]$. ESI/MS – positive mode: m/z 869 $[LSbOSbLOH-butene-H_2O+CF_3COOC(CH_3)_3]^+$ m/z 773 $[LSbOSbLOH]^+$, 100%; m/z 699 $[LSbOSbLOH-butene-H_2O]^+$; m/z 643 $[LSbOSbLOH-2^*butene-H_2O]^+$; m/z 483 $[M+H-CF_3-COOH]^+$; m/z 387 $[LSbOH]^+$; m/z 331 $[LSbOH-butane]^+$; m/z 313 $[LSbOH-butane-H_2O]^+$; m/z 257 $[LSbOH-2^*butane-H_2O]^+$. ESI/MS – negative mode: m/z 709 $[M+CF_3COO]^-$, 100%.

3. Results and discussion

3.1. Synthesis of studied compounds 1a–c and 2a–c

All compounds **1a–c** and **2a–c** were prepared *via* reaction of starting organoantimony dichlorides **1** and **2** [16] with two equivalents of silver salt of appropriate carboxylic acid in CH_2Cl_2 (Scheme 1) as colourless highly viscous oils (**1a**, **1b**) or white crystalline solids. All derivatives are sparingly soluble in aliphatic hydrocarbons and readily soluble in chlorinated solvents as well as in THF. The purity of all compounds was established with the help of satisfactory elemental analyses, ESI-MS spectrometry and ^1H and ^{13}C NMR spectroscopy (see Section 2).

3.2. Solid state structures

The molecular structures of **2a** and **2c** were determined by single crystal X-ray diffraction and are depicted in Figs. 1 and 2, selected bond lengths and bonding angles are given in Table 2.

Both acetate groups are coordinated to the central antimony atom Sb(1) in unidenate fashion in **2a** as demonstrated by fairly different Sb–O bond lengths within each carboxylic group (Sb(1)–O(3) 2.080(3) and Sb(1)–O(4) 2.890(3); Sb(1)–O(5) 2.059(3) and Sb(1)–O(6) 3.078(2) Å), the distances of C–O bonds in carboxylic moieties also support this statement (C(17)–O(3) 1.311(4) and C(17)–O(4)

1.206(5); C(19)–O(5) 1.322(4) and C(19)–O(6) 1.245(6) Å). The coordination polyhedron of Sb(1) can be best described as a trigonal pyramid formed by Sb(1), C(1), O(3) and O(5), sum of angles around the $SbCO_2$ girdle being 259.6°. The resulting trigonal pyramid is further attacked by medium-strength Sb–O intramolecular interactions of both donor atoms of the ligand L^2 (Sb(1)–O(1) 2.692(3) and Sb(1)–O(2) 2.596(2) Å; Σ_{cov}(Sb, O) 2.14 Å and Σ_{vdW}(Sb, O) 3.78 Å [17]). If these interaction are taken into account the overall geometry can be described as a strongly distorted square pyramid, with donor oxygen atoms located mutually in *cis* fashion (angle O(1)–Sb(1)–O(2) 119.92(7)°) similarly to the starting compound **2** [16].

An entirely different coordination mode of both ligand L^2 and carboxylic groups was detected for compound **2c** (Fig. 2). While one of the trifluoracetate groups acts as unidentate ligand in **2c** as demonstrated by bond lengths Sb(1)–O(3) 2.215(5) and Sb(1)–O(4) 3.063(3) Å the second one represents bidentate carboxylate with bond distances Sb(1)–O(5) 2.575(2) and Sb(1)–O(6) 2.580(2) Å and nearly identical C(19)–O(5) 1.239(4) and C(19)–O(6) 1.243(3) Å distances within carboxylic moiety. Such a symmetric bidentate carboxylic group in organoantimony compounds was found only in $PhSb(OOCCH_3)_4$ [3b]. Both donor atoms of ligand L^2 in **2c** are coordinated to the central atom through strong intramolecular interaction (Sb(1)–O(1) 2.312(2) and Sb(1)–O(2) 2.334(2) Å) mutually in pseudo *trans* position with angle O(1)–Sb(1)–O(2) 146.11(6)°,
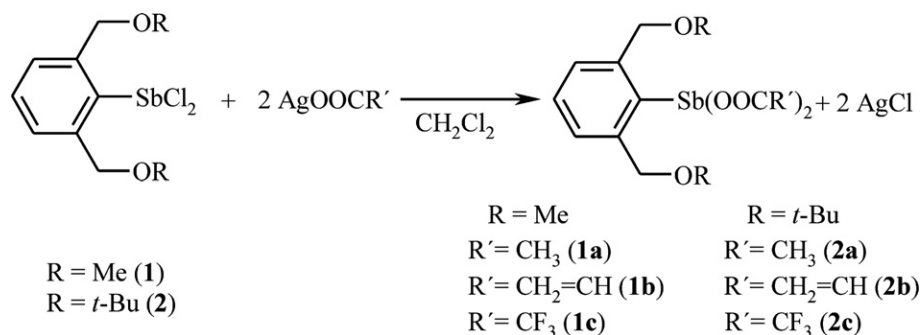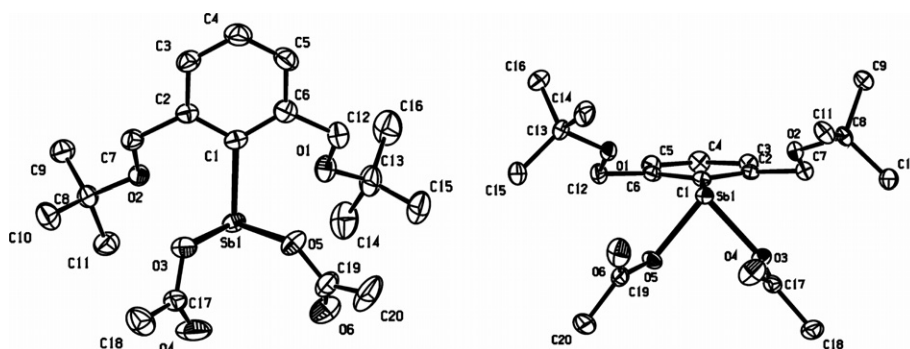

Scheme 1. Synthesis of studied compounds.

Fig. 1. ORTEP drawing (50% probability atomic displacement ellipsoids) of 2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$Sb(OOCCH$_3$)$_2$ (**2a**). Hydrogen atoms and solvent (toluene) molecule have been omitted for clarity.
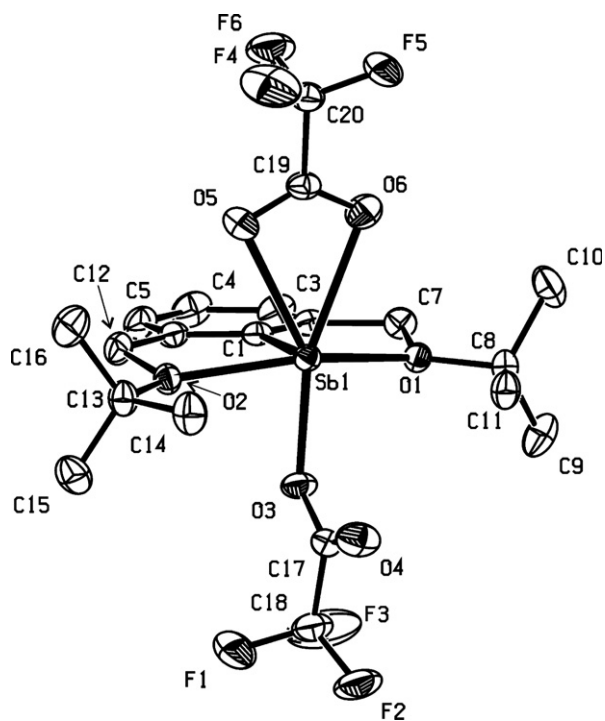
Fig. 2. ORTEP drawing (50% probability atomic displacement ellipsoids) of 2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$Sb(OOCCF$_3$)$_2$ (**2c**). Hydrogen atoms and solvent (toluene) molecule have been omitted for clarity.

Table 2
Selected bond distances (Å) and bonding angles (°) of **2a** and **2c**

Compound **2a**		Compound **2c**	
Sb1–O1	2.692(3)	Sb1–O1	2.312(2)
Sb1–O2	2.596(2)	Sb1–O2	2.334(2)
Sb1–O3	2.080(3)	Sb1–O3	2.215(2)
Sb1–O4	2.890(3)	Sb1–O4	3.063(3)
Sb1–O5	2.059(3)	Sb1–O5	2.575(2)
Sb1–O6	3.078(2)	Sb1–O6	2.580(2)
Sb1–C1	2.147(3)	Sb1–C1	2.091(2)
C17–O3	1.311(4)	C17–O3	1.278(3)
C17–O4	1.206(5)	C17–O4	1.212(3)
C19–O5	1.322(4)	C19–O5	1.239(3)
C19–O6	1.245(6)	C19–O6	1.243(3)
O1–Sb1–O2	119.92(7)	O1–Sb1–O2	146.11(6)
O3–Sb1–O5	80.63(10)	O1–Sb1–O3	81.65(7)
C1–Sb1–O3	90.77(11)	O2–Sb1–O3	80.15(7)
C1–Sb1–O5	88.22(11)	O5–Sb1–O6	50.99(6)
		C1–Sb1–O1	75.08(8)
		C1–Sb1–O2	74.47(8)
		C1–Sb1–O3	82.84(9)
		C1–Sb1–O5	86.39(9)
		C1–Sb1–O6	84.94(8)

which is in contrast to the *cis* position of both oxygen donor atoms in **2a**. The overall geometry around the antimony atom can be best described as a pentagonal pyramid with C(1) in apical position and with Sb(1) and all oxygen atoms (O(1), O(2), O(3), O(5) and O(6)) forming the basal plane (the sum of angles around this girdle 355.75°). An interesting aspect of the structure of **2c** can be seen in the

fact, that both donor atoms of the ligand L^2 are bound to the central atom more tightly than the chelating trifluoroacetate.

All these results are in good agreement with data obtained by IR spectroscopy in the solid state (Table 3). Compounds **1a**, **1b**, **2a** and **2b** revealed only one band for antisymmetric and symmetric CO$_2$ stretching proving equivalently bonded carboxylic groups. The Δv between the antisymmetric and symmetric CO$_2$ stretching ranging from 308 to 360 cm^{-1} proves unidentate coordination of both carboxylates in **1a**, **1b**, **2a** and **2b** as well [2g]. On the other hand IR spectra of **1c** and **2c** contained in both cases two signals for antisymmetric and symmetric CO$_2$ stretching indicating non-equivalence of both triflouroacetates. The Δv between the antisymmetric and symmetric CO$_2$ stretching for **1c** (336 and 232 cm^{-1}) and for **2c** (337 and 282 cm^{-1}) points to [2g] one trifluoroacetate is coordinated as chelating ligand while the second one remains unidenate (as was shown for **2c** by X-ray diffraction).

3.3. Solution structure

Compounds **1a, b** and **2a–c** displayed analogous structure in solution. ^{1}H and ^{13}C NMR spectra of these derivatives contained one set of signals corresponding to the proposed structures at ambient temperature (see Section 2). Upon cooling the samples the signals appropriate to benzylic OCH$_2$ groups in ^{1}H NMR spectra were split to an AX pattern indicating *cis* coordination of both ligands donor groups at low temperatures [16]. IR spectra (CHCl$_3$) of these compounds revealed one antisymmetric and symmetric CO$_2$ stretching with Δv (range from 303 to 355 cm^{-1}) indicating unidentate coordination mode of both carboxylates [2g]. This means **1a, b** and **2a–c** have a similar structure in solution as detected for **2a** in the solid state (*vide supra*).

The solution structure of **1c** seems to be more complex. One set of broad signals detected for both OCH$_2$ and CH$_3$ groups in ^{1}H NMR spectrum at 300 K (indicating fast

Table 3
IR data of studied compounds (cm^{-1})

Compound	Conditions	v_{as}(CO$_2$)	v_s(CO$_2$)	Δv
1a	Neat	1675	1367	308
	CH$_3$Cl	1675	1372	303
1b	Neat	1670	1310	360
	CH$_3$Cl	1670	1318	352
1c	KBr	1738/1690[a]	1458/1402[a]	336/232[a]
	CH$_3$Cl	1721	1400	321
2a	Nujol	1680	1365	315
	CH$_3$Cl	1676	1370	306
2b	Nujol	1669	1319	350
	CH$_3$Cl	1673	1318	355
2c	KBr	1723/1693[a]	1411/1386[a]	337/282[a]
	CH$_3$Cl	1738	1400	338

[a] Two signals.

fluxional behaviour of **1c** at this temperature) has changed to one AX and two AB patterns for OCH_2 groups and three signals for CH_3 group (two of them in 1:1 integral ratio) at 220 K (Fig. 3). The possible explanation for these findings is the presence of two isomers of **1c** in solution at low temperature. The first one (AX for OCH_2 and one signal for CH_3, marked with ∗ in Fig. 3) represents an analogous structure detected for other compounds (i.e. *cis* coordination of both ligands arms and trifluoroacetates remain unidentate). The second isomer is most probably a structure with *cis* coordinated oxygen donor atoms of L^1, where one of the trifluoroacetates is unidentate and the second one bidentate, in turn it leads to non-equivalence of both OCH_2 and CH_3 (two AB patterns for OCH_2 groups and two signals for CH_3 groups in 1:1 integral ratio marked with ○ in Fig. 3).

This hypothesis is further supported by ^{19}F NMR spectra, where one sharp signal at -74.4 ppm observed at 300 K is split into three signals at 220 K (-73.4, -73.7 and -75.1 ppm, see Fig. 4). One of these signals can be assigned to the isomer (∗) with both unidentate carboxylic groups and the remaining two signals prove non-equivalence of trifluoroacetates in the second isomer (○) of **1c**. For instance only one signal was detected for compound **2c** in ^{19}F NMR spectra (300–220 K), where both trifluoroacetates are believed to be identically bound.

Fig. 3. Temperature dependence of ^1H NMR spectra of compound **2c** (CDCl$_3$).

Fig. 4. ^{19}F NMR spectrum of **2c** at 220 K (CDCl$_3$).

4. Conclusions

In summary we have prepared six novel organoantimony carboxylates containing O,C,O chelating ligand. It turns out, that structures of the studied compounds depend both on the ligand used as well as on the polar group: (i) using of a more electron-withdrawing trifluoroacetate group in **2c** leads to increase of intramolecular Sb–O interactions in comparison to **2a**, (ii) trifluoroacetate groups were shown to act as bidentate ligand both in the solid state (**1c** and **2c**) and in solution (**1c**), and (iii) on the other hand carboxylates (acetates and acrylates) in other compounds remain unidentate.

5. Supplementary material

CCDC 639795 and 639796 contain the supplementary crystallographic data for **2a** and **c**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] (a) W. Levason, G. ReidComprehensive Coordination Chemistry II, vol. 3, Elsevier, 2003, 465 and references cited therein;
(b) K.Y. Akiba, Y. Yamamoto, in: S. Patai (Ed.), The Chemistry of Organic Arsenic Antimony Bismuth Compounds, John Wiley and Sons, 1994, p. 761 (Chapter 20).
[2] (a) For example see: V.V. Sharutin, O.K. Sharutina, A.P. Pakusina, T.P. Platonova, G.K. Fukin, L.N. Zakharov, Coord. Chem. 27 (2001) 396;
(b) H. Barucki, S.J. Coles, J.F. Costello, T. Gelbrich, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (2000) 2319;
(c) T. Westhoff, F. Huber, H. Preut, J. Organomet. Chem. 348 (1988) 185;
(d) V.V. Sharutin, O.K. Sharutina, E.A. Bonsae, A.P. Pakusina, Yu.V. Gatilov, N.Yu. Adonin, V.F. Starichenko, Coord. Chem. 28 (2002) 356;
(e) S.P. Bone, D.B. Sowerby, Phosphorus, Sulfur, Silicon, Relat. Elem. 45 (1989) 23;
(f) G. Ferguson, B. Kaitner, C. Glidewell, S. Smith, J. Organomet. Chem. 419 (1991) 283;
(g) M.N. Gibbons, D.B. Sowerby, J. Organomet. Chem. 555 (1998) 271;
(h) H. Barucki, S.J. Coles, J.F. Costello, M.B. Hursthouse, Chem. Eur. J. 9 (2003) 2877;
(i) C. Silvestru, I. Haiduc, E.R.T. Tiekink, D. de Vos, M. Biesemans, R. Willem, M. Gielen, Appl. Organomet. Chem. 9 (1995) 597.
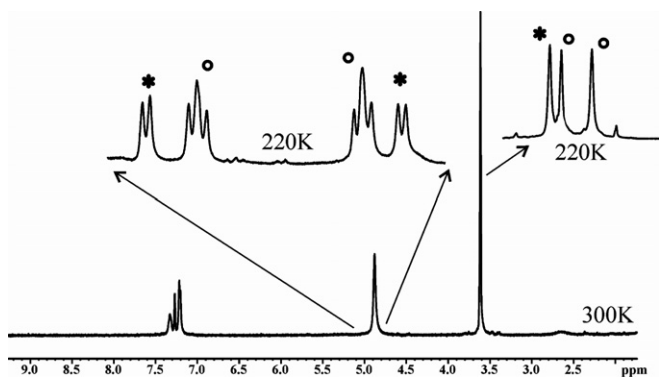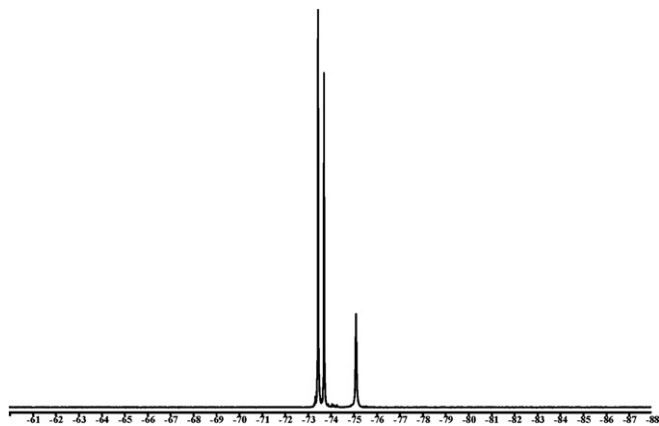
[3] (a) D.B. Sowerby, M.J. Begley, P.L. Millington, Chem. Commun. (1984) 896;
(b) M. Wieber, I. Fetzer-Kremling, H. Reith, C. Burschka, Z. Naturforsch. B: Chem. Sci. 42 (1987) 815.

[4] G. Lang, K.W. Klinkhammer, C. Recker, A. Schmidt, Z. Anorg. Allg. Chem. 624 (1998) 689.

[5] (a) L. Yu, Y.Q. Ma, R.C. Liu, G.C. Wang, J.S. Li, G.H. Du, J.J. Hu, Polyhedron 23 (2004) 823;
(b) Y. Ma, J. Li, Z. Xuan, R. Liu, J. Organomet. Chem. 620 (2001) 235.

[6] (a) V.V. Sharutin, O.K. Sharutina, A.P. Pakusina, V.K. Belsky, J. Organomet. Chem. 536 (1997) 87;
(b) V.V. Sharutin, O.K. Sharutina, I.G. Mel'nikova, G.K. Fukin, L.N. Zakharov, A.I. Yanovsky, Yu.T. Struchkov, Russ. Chem. Bull. (1996) 2082;
(c) V.V. Sharutin, O.K. Sharutina, E.A. Bondar, V.S. Senchurin, A.P. Pakusina, Yu.V. Gatilov, N.Yu. Adonin, V.F. Starichenko, Russ. J. Gen. Chem. 72 (2002) 2029.

[7] M. Hall, D.B. Sowerby, J. Chem. Soc., Dalton Trans. (1980) 1292.

[8] D. Rosmann, K.W. Klinkhammer, A. Schmidt, Monatsh. Chem. 127 (1996) 461.

[9] D.P. Bullivant, M.F.A. Dove, M.J. Haley, J. Chem. Soc., Dalton Trans. (1980) 105.

[10] S.P. Bone, D.B. Sowerby, J. Organomet. Chem. 184 (1980) 181.

[11] M. Wieber, D. Wirth, Ch. Burschka, Z. Naturforsch. B: Chem. Sci. 39 (1984) 600.

[12] G.A. Horley, M.F. Mahon, K.C. Molloy, P.W. Haycock, C.P. Myers, Inorg. Chem. 41 (2002) 5052.

[13] (a) SORTAV: R.H. Blessing, J. Appl. Cryst. 30 (1997) 421;
(b) PLATON:A.L. Spek, J. Appl. Cryst. 36 (2003) 7.

[14] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Cryst. 27 (1994) 435.

[15] G.M. Sheldrick, SHELXL97, University of Göttingen, Germany, 1997.

[16] L. Dostál, I. Císařová, R. Jambor, A. Růžička, R. Jirásko, J. Holeček, Organometallics 25 (2006) 4366.

[17] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2005. http://www.cryst.chem.uu.nl/platon/.