Note

Unexpected product formed by the reaction of [2,6-(MeOCH₂)₂C₆H₃]Li with SbCl₃: Structure of Sb–O intramolecularly coordinated organoantimony cation

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Abstract

Reaction of [2,6-(MeOCH₂)₂C₆H₃]Li (**1**) with SbCl₃ in 1:1 molar ratio yielded except the intended product [2,6-(MeOCH₂)₂-C₆H₃]SbCl₂ (**2**) unexpected complex **3** consisting of antimony anion [Sb₆Cl₂₂]⁴⁻ compensated by four intramolecularly coordinated organoantimony cations [2,6-(MeOCH₂)₂C₆H₃]Sb⁺. Compound **3** is labile in CH₂Cl₂(CHCl₃) solution and decomposes to compound **2** and SbCl₃. Both compounds were characterized by the help of ¹H and ¹³C NMR spectroscopy, ESI-mass spectrometry and in the case of **3** by single crystal X-ray diffraction techniques.
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1. Introduction

Recently, we have prepared and structurally characterized a set of organoantimony(III) and organobismuth(III) dihalides containing O,C,O chelating ligands [2,6-(ROCH₂)₂-C₆H₃]⁻ [1]. Nowadays, we notice and discover formation of an unexpected product during preparation of the previously reported intramolecularly coordinated antimony compound [2,6-(MeOCH₂)₂C₆H₃]SbCl₂ (**2**). This new product was shown to be an ionic complex (**3**) consisting of four organoantimony cations [2,6-(MeOCH₂)₂C₆H₃]₂Sb⁺ compensated by unusual [Sb₆Cl₂₂]⁴⁻ anion. A similar antimony

cluster anion was found only in the copper complex (C₄₆H₅₄Cl₂Cu₂N₆O₄²⁺)₂(Sb₆Cl₂₂)⁴⁻ [2].

The reaction of [2,6-(MeOCH₂)₂C₆H₃]Li (**1**) with SbCl₃ in 1:1 molar ratio led to the formation of mixture of two products (before re-crystallization of the product vide infra), that were shown to be the intended one [2,6-(MeOCH₂)₂C₆H₃]SbCl₂ (**2**) (minor product less than 10% based on ¹H NMR) and an unexpected complex (**3**) consisting of antimony anion [Sb₆Cl₂₂]⁴⁻ stabilized by four intramolecularly coordinated organoantimony cations [2,6-(MeOCH₂)₂C₆H₃]₂Sb⁺ (Scheme 1).

In this mixture, compound **2** was characterized by the help of ¹H and ¹³C NMR spectra that were consistent with those found for this compound recently [1]. Interestingly, the second set of signals in addition to this of **2** was observed directly after reaction (without re-crystallization

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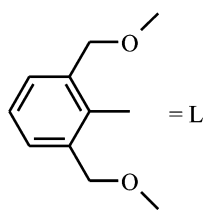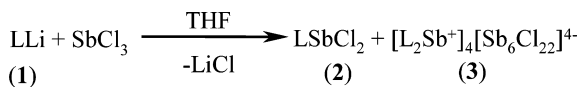
Scheme 1.

of products) both in ^{1}H and ^{13}C NMR spectra (Fig. 1(A)). The ESI mass spectra revealed the signals of values m/z 451 in positive ion ESI mass spectrum indicating presence of L_2Sb^+ cation and m/z 261 in negative ion ESI mass spectrum corresponding to $SbCl_4^-$ anion (as fragment of cluster anion) proving the presence and identity of **3**.

The single crystals of **3** were obtained during evaporation of the reaction mixture and were studied by X-ray diffraction techniques (Figs. 2 and 3). The molecular structure of **3** is formed by four intramolecularly coordinated organoantimony cations compensated by an unusual $[Sb_6$-$Cl_{22}]^{4-}$ cluster anion.

The coordination polyhedron around the antimony atom in organoantimony cations is best described as a distorted ψ-trigonal bipyramid (Fig. 2). Two oxygen donor atoms of one of the ligands are coordinated to the central metal through strong intramolecular interactions $Sb\cdots O$ (range of Sb–O bond lengths 2.272(3)–2.330(4) Å, $\Sigma_{cov}(Sb,O)$ 2.14 Å [3]) in axial positions (range of O–Sb–O bond angles 145.82(12)–147.53(12)°). The significant deviation from the ideal value 180° is a consequence of ligands' rigidity hence both coordinated oxygen atoms originate from one ligand. The remaining two donor atoms from the second ligand are coordinated to the central atom very weakly or are placed out of the antimony coordination sphere (range of Sb–O distances 2.972(4)–3.848(4) Å,
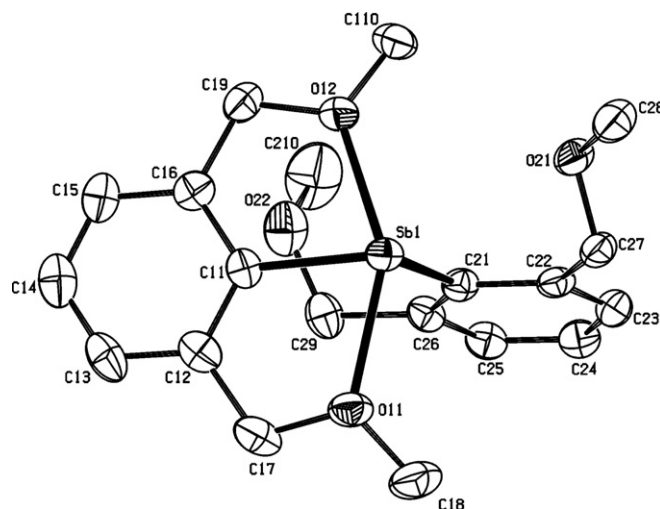

Fig. 2. ORTEP drawing (50% probability atomic displacement ellipsoids) showing one of the four organoantimony cations incorporated in **3**. Hydrogen atoms have been omitted for clarity.
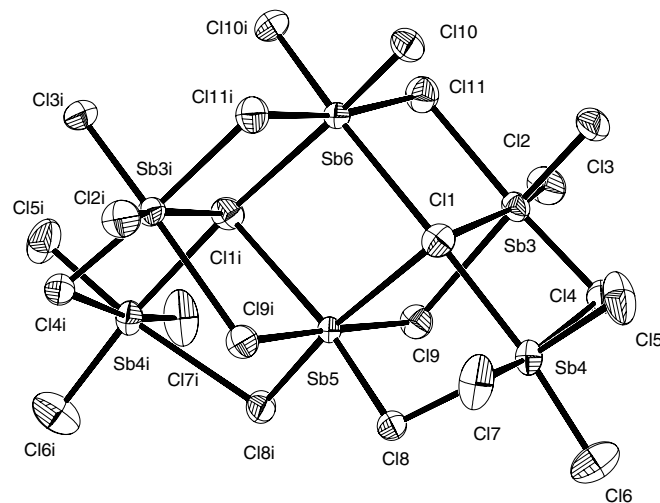

Fig. 3. View on the anionic part $(Sb_6Cl_{22}^{4-})$ of compound **3**. Displacement ellipsoids are drawn on 50% probability level. Symmetry code (i): $-x$, y, $0.5 - z$. Selected bond distances (Å): Sb(3)–Cl(2) 2.3908(13), Sb(3)–Cl(3) 2.4016(12), Sb(3)–Cl(4) 2.4637(12), Sb(3)–Cl(11) 2.9026(13), Sb(4)–Cl(5) 2.3618(14), Sb(4)–Cl(6) 2.4395(15), Sb(4)–Cl(7) 2.3773(15), Sb(4)–Cl(1) 2.9188(12), Sb(5)–Cl(8) 2.4070(11), Sb(5)–Cl(9) 2.6144(11), Sb(6)–Cl(10) 2.3592(11), Sb(6)–Cl(11) 2.6103(12); Cl(1)–Sb(3) 3.2213(12), Cl(1)–Sb(4) 2.9188(12), Cl(1)–Sb(5) 3.2752(12), Cl(1)–Sb(6) 3.3874(12).
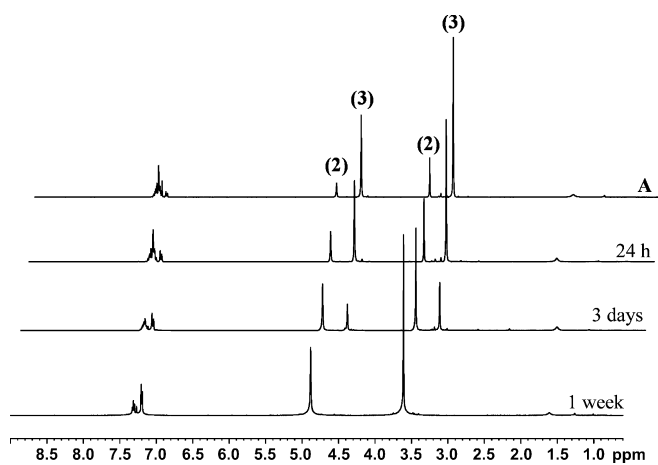
$\Sigma_{vdW}(Sb,O)$ 3.78 Å [3]). The equatorial plane is formed by two *ipso* carbon atoms of both ligands and the vacant place is most probably occupied by the lone pair of electrons. Although similar geometry was found in the organonatimony cation containing N,C-chelating ligand $[2,6-(Me_2NCH_2)_2C_6H_4]_2Sb^+PF_6^-$ [4], this cation represents the first example of organoantimony(III) cation stabilized by O,C-chelating ligand.

The anionic part of **3** $[Sb_6Cl_{22}]^{4-}$ cluster anion is a member of large family of halogenoantimonates [5], in which Sb^{III} is supposed to be coordinated with distorted octahedral geometry. An anion $[Sb_3Cl_{11}]_n^{2n-}$ stoichiometrically

Fig. 1. ^{1}H NMR spectra demonstrating gradual decomposition of **3** in $CDCl_3$.

identical to the title compound was found only in three structures in Cambridge Structural Database [2,6], whereas the dimeric $[Sb_6X_{22}]^{4-}$ species is more typical for iodoantimonates [7].

With regards to the structure, the anion represents a new arrangement, manifesting large variety in the condensation of SbX_6 subunits. It consists of six $SbCl_6$ octahedra sharing edges to form unsymmetrical Sb–Cl–Sb bridges (Fig. 3). In the crystal the anion follows the symmetry of twofold rotation axis passing through the atoms Sb(5) and Sb(6). Consequently the octahedrons around Sb(3) and Sb(4) have symmetrically identical equivalents in the cluster.

There are three types of octahedrons with regard to the number of linked edges. Two octahedrons (Sb(4), Sb(4)^i) share two edges, three chlorine atoms being terminal. Three octahedra (Sb(3), Sb(3)^i and Sb(6); symmetry code: (i) $-x$, y, $0.5 - z$) are incorporated via their three edges, (i.e. two remaining Cl atoms are terminal). Finally, the octahedron around Sb(5) is connected via five edges, without any terminal Cl.

All polyhedra appear to be strongly deformed in bond lengths as well as in angles. Each Sb atom forms short Sb–Cl bonds [Sb(3) and Sb(4) three; Sb(5) and Sb(6) four] which fall into the interval 2.3592–2.6144 Å. The other cluster distances are somewhat longer, but all of them fall well below the sum of van der Walls radii for Sb(III) and Cl (4.0 Å [3]) and hence should be regarded as bonding contacts [6b]. Among them, two are significantly shorter (Sb(4)–Cl(1) 2.9188(12) Å; Sb(3)–Cl(11) 2.9026(13) Å), than the rest falling within interval 3.1400(12)–3.3834 (12) Å. The Cl–Sb–Cl angles involving Cl atoms mutually in *cis* position vary from 78.11(3)° (Cl(1)–Sb(4)–Cl(8)) to 103.92(3)° (Cl(4)–Sb(4)–Cl(8)) while angles for *trans* contacts lie between 166.07(4)° (Cl(1)–Sb(3)–Cl(2)) and 178.29 (5)° (Cl(9)–Sb(5)–Cl(9)^i).

For a more detailed analysis of the bond network, the bond valence model [3] was applied on the $[Sb_6Cl_{22}]^{4-}$ anion. Only Sb–Cl distances shorter than 3.0 Å make significant contribution to the sum of bond valence, ranging from 2.693 to 2.940 for antimony and from 0.785 to 0.975 for the terminal chlorine atoms. The bridging chlorine atoms show lower values, extraordinarily low 0.215 bond valence sum was observed for Cl(1), which is not accompanied by large displacement parameters of Cl(1), as could be expected for weakly bonded atom in distorted environment. By contrast, the position of the Cl(1) anion appears to be very well defined (see Fig. 3). Even if the interactions of Cl(1) could be affected by lone electron pairs of surrounding antimony atoms, the nature of bonds within the cluster still need to be elucidated.

Compound **3** is unstable in $CHCl_3$ or CH_2Cl_2 solution and slowly (Fig. 1) decomposes to **2** along with the precipitation of an insoluble white material. Compound **2** was after filtration from insoluble material characterized by ^1H, ^{13}C NMR spectroscopy, ESI mass spectrometry and observed data are consistent with those reported for **2** before [1].

The whole process can be most probably described as conversion of **3** to compound **2** and $SbCl_3$ (Scheme 2). This conclusion is further supported because the insoluble material was shown to be a hydrolytic product of $SbCl_3$ in particular $Sb_4O_5Cl_2/Sb_2O_3 \cdot 2SbOCl$ (PDF No. 30-0091 [8]) by X-ray powder diffraction technique (the hydrolysis of incipient $SbCl_3$ is not surprising, hence this reaction was performed on air and in a wet solvent) [9].
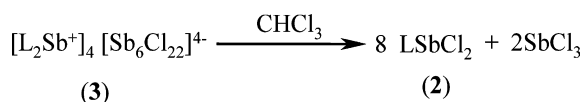
To summarize, the formation of **3** can be explained as intermediate in the reaction between organolithium compound **1** and $SbCl_3$ in THF (1:1 ratio), when the low excess of $SbCl_3$ and incomplete formation of LiCl leads after exposure to air to stabilization of **3**. The possibility to precipitate the excessive antimony chloride by careful re-crystallization of **3** from chlorinated solvents ($CHCl_3$ or CH_2Cl_2) shifts the reaction to intended product **2** in good yield as was shown before [1].

2. Experimental

All air and moisture sensitive manipulations were carried out under an argon atmosphere using standard Schlenk tube techniques. ^1H and ^{13}C NMR spectra were recorded on Bruker AMX360 and Bruker500 Avance spectrometers respectively. Electrospray ionization (ESI) mass spectra were measured on an ion trap analyzer Esquire 3000 (Bruker Daltonics, Bremen, Germany).

2.1. Synthesis of [2,6-(MeOCH₂)₂C₆H₃]SbCl₂ (2) and {[2,6-(MeOCH₂)₂C₆H₃]₂Sb⁺}₄[Sb₆Cl₂₂]⁴⁻ (3)

*2.1. Synthesis of $[2,6\text{-}(MeOCH_2)_2C_6H_3]SbCl_2$ (**2**) and $\{[2,6\text{-}(MeOCH_2)_2C_6H_3]_2Sb^+\}_4[Sb_6Cl_{22}]^{4-}$ (**3**)*

^{n}BuLi (4.1 ml, 1.6 M hexane solution, 6.53 mmol) was added to a solution of $2,6\text{-}(MeOCH_2)_2C_6H_3Br$ (1.6 g, 6.53 mmol) in THF 40 ml at -80 °C. Resulting yellow solution was stirred for 2 h and then added dropwise to a solution of $SbCl_3$ (1.49 g, 6.53 mmol) in THF 100 ml at -80 °C. The reaction mixture was allowed to reach room temperature, stirred for additional 2 h and evaporated in vacuo. The residue was extracted with 2×50 ml of CH_2Cl_2 and evaporated. The resulting solid was characterized as mixture of **2** (10%) and **3** (90% – based on ^1H NMR). Single crystals of **3** were obtained during evaporation of this mixture. Data found for **2** (after complete decomposition of **3** vide supra – analogous to previously reported [1]): M.p. 186–188 °C. Anal. Calc. for $C_{10}H_{13}Cl_2O_2Sb$ (357.87): C, 33.56; H, 3.66; Found: C, 33.49; H, 3.64%. ESI mass spectra: m/z 605 $[L^1SbOSbL^1OH]^+$; m/z 303 $[L^1SbOH]^+$, 100%; m/z 271 $[L^1SbOH–CH_3OH]^+$; m/z 241 $[L^1SbOH–HCOH–CH_3OH]^+$. Negative-ions ESI mass spectra: m/z 391 $[M+Cl]^-$, 100%. ^1H NMR (500 MHz, CDCl₃): 3.61 (6H, s, CH_3O), 4.88 (4H, s,

$$[L_2Sb^+]_4 \, [Sb_6Cl_{22}]^{4-} \xrightarrow{\;\;CHCl_3\;\;} 8 \; LSbCl_2 \; + \; 2SbCl_3$$

$$(\mathbf{3}) \qquad\qquad\qquad\qquad\qquad (\mathbf{2})$$

Scheme 2.

OCH_2), 7.20 (2H, d, Ar–H3,5), 7.30 (1H, t, Ar–H4). ^{13}C NMR (125.76 MHz, CDCl$_3$): 58.60 (s, CH_3O), 75.33 (s, OCH_2), 125.30 (s, Ar–C3,5), 129.70 (s, Ar–C4), 145.86 (s, Ar–C2,6), 151.36 (s, Ar–C1). Data found for **3** (analysis of collected single crystals): Mp >140 °C decomposition. Anal. Calc. for C$_{40}$H$_{52}$Cl$_{11}$O$_8$Sb$_5$ (1659.5): C, 28.95; H, 3.16; Found: C, 29.49; H, 3.36%. ESI mass spectra: m/z 451 [L$_2$Sb]$^+$, 100%. Negative-ions ESI mass spectra: m/z 433 [Cl$_2$SbOSbCl$_3$]$^-$; m/z 261 [SbCl$_4$]$^-$ 100%; m/z 207 [OSbCl$_2$]$^-$. ^{1}H NMR (500 MHz, CDCl$_3$): 3.28 (6H, s, CH_3O), 4.57 (4H, s, OCH_2), 7.20–7.37 (m, Ar–H). ^{13}C NMR (125.76 MHz, CDCl$_3$): 58.50 (s, CH_3O), 76.13 (s, OCH_2), 128.09 (s, Ar–C3,5), 129.38 (s, Ar–C4), 144.80 (s, Ar–C2,6), 146.98 (s, Ar–C1).

2.2. X-ray structure determination

C$_{40}$H$_{52}$Cl$_{11}$O$_8$Sb$_5$, $M = 1659.52$, monoclinic, $C2/c$, $a = 36.3170(3)$ Å, $b = 13.8660(1)$ Å, $c = 28.3610(3)$ Å, $\beta = 127.8521(5)°$, $V = 11276.86(17)$ Å^3, $Z = 8$, $D_x = 1.955$ Mg m^{-3}. A colourless crystal of dimensions $0.3 \times 0.15 \times 0.12$ mm was measured at Nonius KappaCCD diffractometer by monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K. The analytical correction on absorption was applied ($\mu = 2.931$ mm^{-1}, $T_{min} = 0.499$, $T_{max} = 0.726$; a total of 102435 diffractions were measured in the range $h = -37$ to 47, $k = -17$ to 18, $l = -36$ to 36 ($\theta_{max} = 27.49°$), from which 12926 were unique ($R_{int} = 0.0498$) and 10529 observed according to the $I > 2\sigma(I)$ criterion. Cell parameters from 75629 reflections ($\theta = 1$–27.49°). The structure was solved by direct methods (SIR92, Altomare, 1994) and refined by full-matrix least squares based on F^2 (SHELXL 97). The hydrogen atoms were fixed into idealised positions (riding model) and assigned temperature factors either $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or $H_{iso}(H) = 1.5\ U_{eq}$ (pivot atom) for methyl moiety. The final difference map displayed no peaks of chemical significance as the highest maxima are in close vicinity of antimony ($\Delta\rho_{max} = 2.426$, $\Delta\rho_{min} -2.050$ e Å^{-3}).

2.3. X-ray powder diffraction

Powder X-ray diffraction data were obtained with a D8-Advance diffractometer (Bruker AXE, Germany) using Cu Kα radiation with a secondary graphite monochromator. Diffraction angles were measured from 10° to 65° (2Θ) in 0.02° steps with a counting time of 10 s per step.

3. Supplementary material

CCDC 624442 contains the supplementary crystallographic data for **3**. 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.

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[8] Joint Committee on Powder Diffraction Standards, International Centre of Diffraction Data, Swarthmore, PA.
[9] The decomposition of **3** to **2** was performed under argon atmosphere to avoid the hydrolysis of incipient SbCl$_3$ for several times, unfortunately in all cases the observed insoluble material was of amorphous nature thus unsuitable for X-ray powder diffraction method.