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Note

Unexpected product formed by the reaction of [2,6-$(MeOCH_2)_2C_6H_3$]Li with $SbCl_3$: Structure of Sb–O intramolecularly coordinated organoantimony cation

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Abstract

Reaction of [2,6-$(MeOCH_2)_2C_6H_3$]Li (**1**) with $SbCl_3$ in 1:1 molar ratio yielded except the intended product [2,6-$(MeOCH_2)_2$-C_6H_3]$SbCl_2$ (**2**) unexpected complex **3** consisting of antimony anion $[Sb_6Cl_{22}]^{4-}$ compensated by four intramolecularly coordinated organoantimony cations [2,6-$(MeOCH_2)_2C_6H_3$]$_2Sb^+$. Compound **3** is labile in CH_2Cl_2($CHCl_3$) solution and decomposes to compound **2** and $SbCl_3$. Both compounds were characterized by the help of ^{1}H and ^{13}C NMR spectroscopy, ESI-mass spectrometry and in the case of **3** by single crystal X-ray diffraction techniques.

Keywords: Antimony; Pincer ligand; Hypervalent compounds; Chloroantimonates

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-$(ROCH_2)_2$-C_6H_3]$^-$ [1]. Nowadays, we notice and discover formation of an unexpected product during preparation of the previously reported intramolecularly coordinated antimony compound [2,6-$(MeOCH_2)_2C_6H_3$]$SbCl_2$ (**2**). This new product was shown to be an ionic complex (**3**) consisting of four organoantimony cations [2,6-$(MeOCH_2)_2C_6H_3$]$_2Sb^+$ compensated by unusual $[Sb_6Cl_{22}]^{4-}$ anion. A similar antimony cluster anion was found only in the copper complex $(C_{46}H_{54}Cl_2Cu_2N_6O_4^{2+})_2(Sb_6Cl_{22})^{4-}$ [2].

The reaction of [2,6-$(MeOCH_2)_2C_6H_3$]Li (**1**) with $SbCl_3$ 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-$(MeOCH_2)_2C_6H_3$]$SbCl_2$ (**2**) (minor product less than 10% based on ^{1}H NMR) and an unexpected complex (**3**) consisting of antimony anion $[Sb_6Cl_{22}]^{4-}$ stabilized by four intramolecularly coordinated organoantimony cations [2,6-$(MeOCH_2)_2C_6H_3$]$_2Sb^+$ (Scheme 1).

In this mixture, compound **2** was characterized by the help of ^{1}H and ^{13}C 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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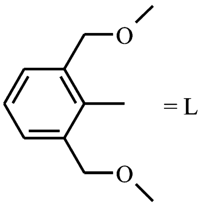
$$\underset{(\mathbf{1})}{\mathrm{LLi}} + \mathrm{SbCl_3} \xrightarrow[\text{-LiCl}]{\text{THF}} \underset{(\mathbf{2})}{\mathrm{LSbCl_2}} + \underset{(\mathbf{3})}{[\mathrm{L_2Sb^+}]_4[\mathrm{Sb_6Cl_{22}}]^{4-}}$$



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 $[Sb_6Cl_{22}]^{4-}$ 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···O (range of Sb–O bond lengths 2.272(3)–2.330(4) Å, Σ_{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, Σ_{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 $[2,6\text{-}(Me_2NCH_2)_2C_6H_4]_2Sb^+PF_6^-$ [4], this cation represents the first example of organoantimony(III) cation stabilized by O,C-chelating ligand.

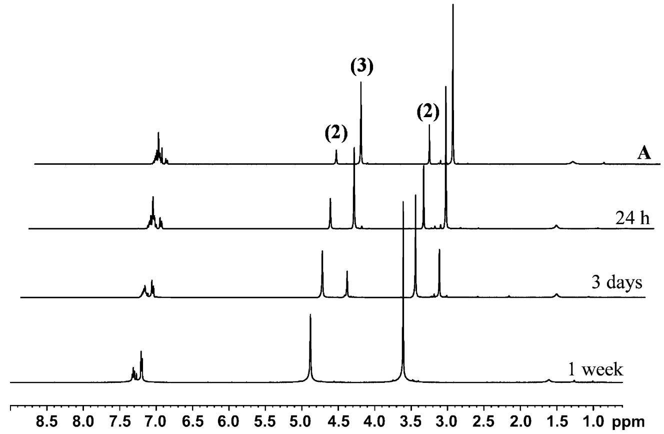


Fig. 1. ^{1}H NMR spectra demonstrating gradual decomposition of **3** in $CDCl_3$.

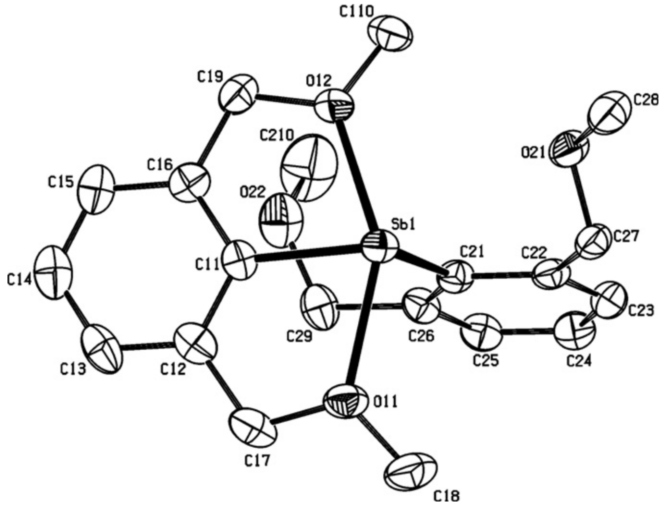


Fig. 2. ORTEP drawing (50% probability atomic displacement ellipsoids) showing one of the four organoantimony cations incorporated in **3**. Hydrogen atoms have been omitted for clarity.

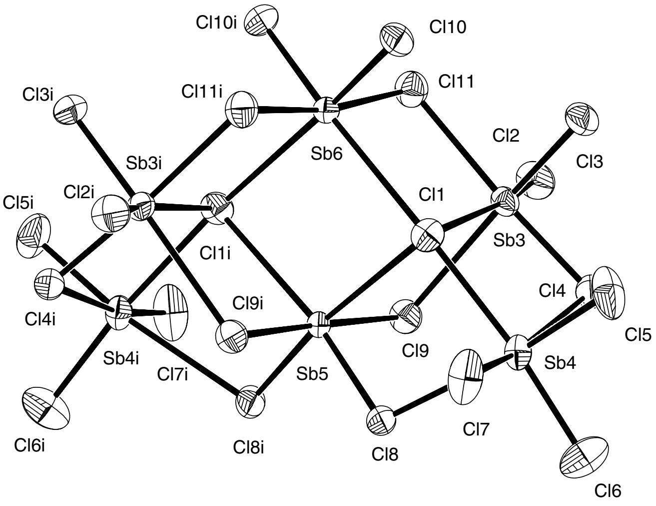


Fig. 3. View on the anionic part ($Sb_6Cl_{22}^{4-}$) of compound **3**. Displacement ellipsoids are drawn on 50% probability level. Symmetry code (i): −*x*, *y*, 0.5 − *z*. Selected bond distances (Å): Sb(3)–Cl(2) 2.3908(13), Sb(3)–Cl(3) 2.4016(12), Sb(3)–Cl(4) 2.4637(12), Sb(3)–Cl(11) 2.9026(13), Sb(4)–Cl(5) 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).

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