

SYNTHESIS AND STRUCTURE OF AROXY-TETRA-*P*-TOLYLANTIMONY (4-MeC₆H₄)₄SbOC₆H₂Br₂-2,6-(*t*-Bu)-4

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Penta-*p*-tolylantimony interaction with 2,6-dibromo(4-*tert*-butyl)phenol has led to synthesis of the complex tetra-*p*-tolylantimony 2,6-dibromo(4-*tert*-butyl)phenoxide, whose structure has been established by X-ray diffraction. The antimony atom in the molecule (4-MeC₆H₄)₄SbOC₆H₂Br₂-2,6-(*t*-Bu)-4 has distorted trigonal-bipyramidal coordination with the aroxy group in axial position. The bond Sb–O is 2.229(2) Å, the axial angle CSbO is 176.82(10)°.

Keywords: tetra-*p*-tolylantimony 2,6-dibromo(4-*tert*-butyl)phenoxide, synthesis, molecular structure, X-ray analysis.

Introduction

It is well known that in antimony derivatives of the general formula R₄SbX the coordination polyhedron of the central atom and the character of its bonding with the electronegative ligand X is determined by the nature of this ligand and the organic radicals R. In the vast majority of R₄SbX compounds the antimony atoms have trigonal-bipyramidal coordination in various degrees of distortion. Such compounds are of indisputable interest, as they make it possible to reveal the factors that determine the transition of SbC₄ fragment into the tetrahedral structure. The analysis of the published structural data for aroxy-tetra-phenylantimony Ph₄SbOAr has shown that the distortion of the central atom coordination polyhedron in them increases if in aroxy group there are electron-donating substituents [1–5].

In continuation of the study how the nature of phenol and aryl radicals at the antimony atom influences the geometric characteristics of aroxy-tetra-arylantimony molecules we have synthesized and established the structure of new aroxy-tetra-*p*-tolylantimony: (4-MeC₆H₄)₄SbOC₆H₂Br₂-2,6-(*t*-Bu)-4 (**1**).

Experimental

Synthesis of tetra-*p*-tolylantimony 2,6-dibromo(4-*tert*-butyl)phenoxide (1**).** The mixture of 0.29 g (0.5 mmol) penta-*p*-tolylantimony, 0.15 g (0.5 mmol) 2,6-dibromo(4-*tert*-butyl)phenol and 5 mL toluene was allowed to stand for 24 h at room temperature, then it was reduced to 1 mL and cooled. The yield was 0.35 g (87 %) of colorless crystals **1** with m.p. 209 °C. IR spectrum (ν , cm⁻¹): 1592, 1299, 1251, 1212, 1189, 1061, 1015, 866, 830, 797, 729, 575, 553, 486. Found, %: C 57.38; H 5.07; Br 20.05. Calculated for C₃₈H₃₉OBr₂Sb, %: C 57.50; H 4.92; Br 20.18.

IR spectrum was recorded with the use of the IR spectrometer Bruker Tensor 27 in KBr pellet in the range 4000–400 cm⁻¹.

X-ray diffraction analysis of the complex **1** crystal was performed on the Bruker D8 QUEST automatic four-circle diffractometer (Mo K α -emission, λ = 0.71073 Å, graphite monochromator). The data were collected and analyzed, the unit cell parameters were refined, and the absorption correction was applied using the SMART and SAINT-Plus programs [6]. All calculations for structure determination and refinement were performed using the SHELXL/PC programs [7,8]. The structure **1** was determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The position of hydrogen atoms was refined according to riding model ($U_{iso}(H) = 1.2U_{eq}(C)$). The main crystallographic data and refinement results for structure **1** are listed in Table 1, the geometric characteristics of the antimony atom coordination tetrahedron are given in Table 2.

Table 1

Crystallographic data and the experimental and structure refinement parameters for compound 1

Parameter	Value
Empirical formula	C ₃₈ H ₃₉ Br ₂ OSb
Formula weight	793.26
<i>T</i> , K	273(2)
Crystal system	Triclinic
Space group	<i>P</i> 1
<i>a</i> , Å	10.7287(17)
<i>b</i> , Å	13.0075(18)
<i>c</i> , Å	14.446(2)
α, deg	74.905(7)
β, deg	75.639(8)
γ, deg	66.692(7)
<i>V</i> , Å ³	1763.5(5)
<i>Z</i>	2
ρ(calcd.), g/cm ³	1.494
μ, mm ⁻¹	3.075
<i>F</i> (000)	792
Crystal size, mm	0.690 x 0.590 x 0.240
Range of refraction indices	-13 ≤ <i>h</i> ≤ 13, -14 ≤ <i>k</i> ≤ 16, -18 ≤ <i>l</i> ≤ 18
Measured reflections	19747
Independent reflections	5586 (<i>R</i> _{int} = 0.0345)
Refinement variables	402
<i>GOOF</i>	1.031
<i>R</i> factors for <i>F</i> ² > 2σ(<i>F</i> ²)	<i>R</i> ₁ =0.0337, <i>wR</i> ₁ =0.0808
<i>R</i> factors for all reflections	<i>R</i> ₁ =0.0498, <i>wR</i> ₁ =0.0870
Residual electron density (min/max), e/Å ³	0.882/-0.658

Table 2

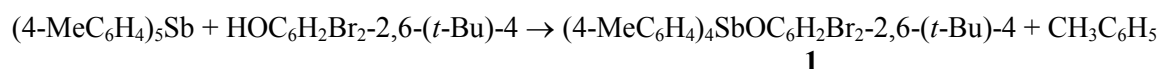
Selected bond lengths (*d*) and bond angles (ω) in the structure of compound 1

Bond	<i>d</i> , Å	Angle	ω, deg
Sb(1)–C(1)	2.114(3)	C(1)Sb(1)O(31)	176.82(10)
Sb(1)–C(11)	2.112(3)	C(11)Sb(1)C(1)	108.58(12)
Sb(1)–C(21)	2.111(3)	C(21)Sb(1)C(1)	126.19(12)
Sb(1)–C(31)	2.174(3)	C(1)Sb(1)C(31)	94.38(12)
Sb(1)–O(1)	2.229(2)	C(21)Sb(1)C(11)	123.25(12)
O(1)–C(41)	1.320(4)	C(1)Sb(1)O(1)	84.75(10)
		C(41)O(1)Sb(1)	126.96(19)

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 1048264; deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk>).

Results and Discussion

Aroxy-tetra-*p*-tolylantimony **1** has been produced *via* dearylation of penta-*p*-tolylantimony by 2,6-dibromo(4-*tert*-butyl)phenol at mild conditions with 87 % yield:



Compound **1** was crystallized from the toluene solution directly in the process of concentration.

According to X-ray diffraction analysis, in **1** the antimony atom has a distorted trigonal-bipyramidal coordination, trigonality degree τ=0.84 [9], with the oxygen atom of the aroxy group in axial position (Fig. 1).

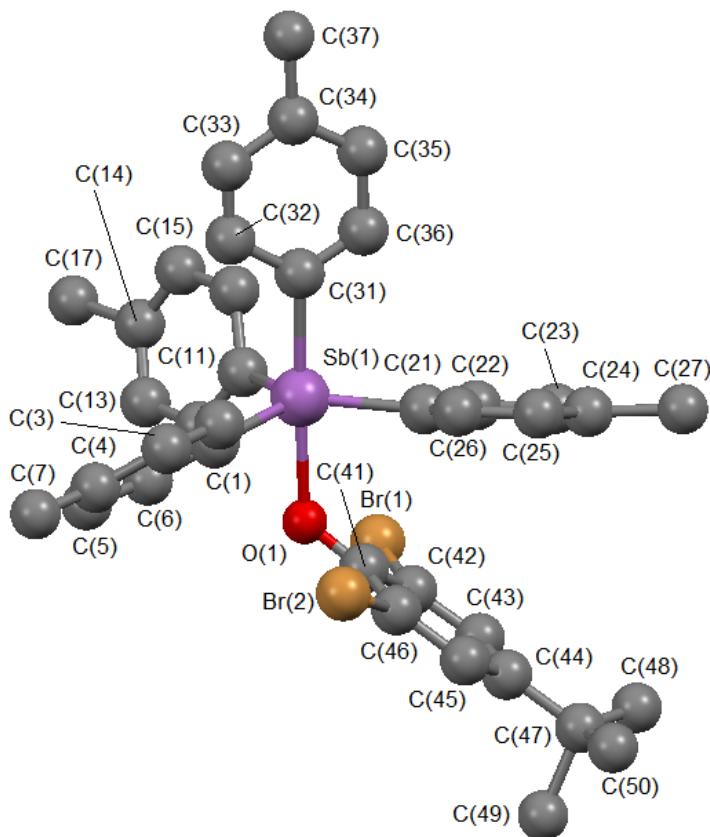


Fig. 1. The structure of compound 1

The atoms of the *tert*-butyl group C(48)–C(50) are disordered, they displace two positions with the ratio 0.62/0.38. The angle between the positions of the disordered fragment is equal to approximately 62° in relation to the bond C(44)–C(47). The axial angle OSbC equals 176.82(10)°, the sum of the angles CSbC in equatorial plane is equal to 358.0(3)°. The antimony atom deviates from the equatorial plane [C₃] towards the axial carbon atom for 0.172 Å, which causes departure of the angle values between axial and equatorial bonds from the theoretical value 90°. The angles OSbC_{eq} and C_{ax}SbC_{eq} change within the range 84.62(10)°–86.83(10)° and 93.46(12)°–96.35(12)°, respectively, the bonds Sb–C_{eq} coincide within the measurement accuracy and equal 2.111(3)–2.114(3) Å. The lengths Sb–C_{ax} [2.174(3) Å] are longer than equatorial ones, which is typical for trigonal-bipyramidal structures. The length Sb–O equals 2.229(2) Å, much higher than the sum of covalent radii of antimony and oxygen atoms (2.07 Å [10]).

All observed geometrical parameters for the molecule of compound 1 (decrease of the sum of equatorial angles, significant deviation of the antimony atom from the equatorial plane, approximation of the values for axial and equatorial bonds) point at the tendency of the antimony trigonal-bipyramidal coordination to transform into tetrahedral one [11].

It should be noted that unlike compound 1, tetraphenylantimony picrate (2) is an ionic compound.

Changing of the antimony atom coordination polyhedron in the series of tetraarylantimony aroxides can be explained by consideration of the Sb–O bond nature in respect to the phenolate anion basicity, which is determined by electron density redistribution in the aroxy group, depending on the substituent nature in it. The lower is the phenolate anion basicity, the less strong is the coordination bond Sb–O, and the structure of the compound Ar₄SbOAr' approaches ionic character to a greater extent. Three nitro groups in 2, with their negative inductive effect, contribute to stabilization of phenolate anion and decrease in its basicity, at that the group Ph₄Sb transforms into the stable tetrahedral cation.

Conclusions

To summarize, the distortion of trigonal-bipyramidal configuration of aroxy-tetraarylantimony compounds and the lengthening of the Sb–O bond are both determined by electron acceptor properties of the aroxy group, which strengthen with increasing number of electron acceptor substituents in the aromatic ring.

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СИНТЕЗ И СТРОЕНИЕ АРОКСИДА ТЕТРА-ПАРА-ТОЛИЛСУРЬМЫ (4-MeC₆H₄)₄SbOC₆H₂Br₂-2,6-(t-Bu)-4

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Взаимодействием пента-пара-толилсурьмы с 2,6-дибром(4-трет-бутил)фенолом в толуоле синтезирован 2,6-дибром(4-трет-бутил)феноксид тетра-пара-толилсурьмы, строение которого установлено методом РСА. Атом Sb в молекуле (4-MeC₆H₄)₄SbOC₆H₂Br₂-2,6-(t-Bu)-4 имеет искаженную тригонально-бипирамидальную

координацию с ароксигруппой в аксиальном положении. Связь Sb–O равна 2.229(2) Å, аксиальный угол CSbO составляет 176.82(10)°.

Ключевые слова: 2,6-дибром(4-трет-бутил)феноксид тетра-пара-толилсурьмы, синтез, молекулярная структура, рентгеноструктурный анализ.

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