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# $\mu_2$-Oxo-Bis[(2,5-Dinitrophenoxo)triarylantimony]: Syntheses, Structures, and Reactions with Pentaarylantimony

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**Abstract**—Antimony aroxides $[Ph_3SbOC_6H_3(NO_2)_2\text{-}2,5]_2O$ (**I**) and $[(4\text{-}MeC_6H_4)_3SbOC_6H_3(NO_2)_2\text{-}2,5]_2O$ (**II**) were synthesized by the oxidation of triarylantimony with *tert*-butyl hydroperoxide in the presence of 2,5-dinitrophenol. The SbOSb fragments in compounds **I** and **II** are bent (the corresponding angles are 139.70(10)° and 142.32(12)°). The $Sb-O_{br}$ bonds (1.973(3), 1.980(3) Å in **I**; 1.975(2), 1.977(2) Å in **II**) are substantially shorter than $Sb-O_t$ (2.211(3), 2.213(3) and 2.191(2), 2.191(2) Å in **I** and **II**, respectively). Aroxides $Ar_4SbOC_6H_3(NO_2)_2\text{-}2,5$ (Ar = Ph (**III**) and 4-$MeC_6H_4$ (**IV**)) and carbonates $(Ar_4Sb)_2CO_3$ (Ar = Ph (**V**) and 4-$MeC_6H_4$ (**VI**)) are formed from $Ar_5Sb$ and compounds **I** and **II** in the presence of oxygen and carbon dioxide, respectively. In the trigonal bipyramidal molecules of compounds **III** and **IV**, the CSbO axial angles are 175.80(7)° and 176.86(10)° (Sb–O 2.290(2) and 2.342(2) Å, respectively). One of the antimony atoms in compound **V** and in crystallographically independent molecules of two types of compound **VI** is pentacoordinated (the $Sb-O_{ax}$ bond is 2.245(6) Å in **V** and is 2.263(3) and 2.263(3) Å in **VIa** and **VIb**, respectively), whereas the second antimony atom is hexacoordinated (Sb–O 2.249(6) and 2.273(5) Å in **V**; 2.216(2), 2.251(2) Å and 2.217(2), 2.251(2) Å in **VIa** and **VIb**). The crystallographic data are deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1890704 (**I**), 1890706 (**II**), 1890713 (**III**), 1890714 (**IV**), 994519 (**V**), and 994177 (**VI**)).

*Keywords:* tri- and tetraarylantimony 2,5-dinitrophenoxides, synthesis, diffraction studies

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## INTRODUCTION

At the present time, the arylantimony compounds evoke interest of researchers due to their biological [1, 2] and photocatalytic activity [3] and a possibility of efficient using in fine organic synthesis [4]. The most known organoantimony compounds are the antimony derivatives $Ar_3SbX_2$ and $(Ar_3SbX)_2O$ synthesized mainly by the oxidation of triarylantimony. It is known that compounds $Ar_3Sb(OAr)_2$ or $(Ar_3SbOAr)_2O$ are formed upon the addition of peroxide to a mixture of triarylantimony, acid HX, and diethyl ether [5, 6], but only bridged compounds are formed in some cases. For example, triphenylantimony reacts with picric acid and hydrogen peroxide to give the antimony compound with the SbOSb fragment [7]. It is most likely that $Ph_3Sb(OAr)_2$ cannot be synthesized because of steric hindrances caused by the presence of two bulky aroxyl substituents at the central atom. Therefore, the study of the synthesis of the antimony derivatives containing the Sb–O–Sb group seems to be very urgent.

## EXPERIMENTAL

$\mu_2$-Oxo-bis[(2,5-dinitrophenoxo)triphenylantimony] (**I**) was synthesized using a described procedure [5]. The yield of the red-brown crystals was 92%, mp = 172°C. IR (ν, $cm^{-1}$): 3072, 3055 (Ar), 1533, 1346 ($NO_2$), 1280 (C–O), 734, 690 (Ph), 463 (Sb–C).

| For $C_{48}H_{36}N_4O_{11}Sb_2$ | | |
|---|---|---|
| Anal. calcd., % | C, 52.94 | H, 3.31 |
| Found, % | C, 52.67 | H, 3.54 |

$\mu_2$-Oxo-bis[(2,5-dinitrophenoxo)tri-*para*-tolylantimony] (**II**) was synthesized similarly. The yield of the red-brown crystals was 89%, $T_{decomp}$ = 217°C. IR (ν, $cm^{-1}$): 3107, 3018(Ar), 2922 (Me), 1533, 1346 ($NO_2$), 1298 (C–O), 734, 698 (Ph), 486 (Sb–C).

| For $C_{54}H_{48}N_4O_{11}Sb_2$ | | |
|---|---|---|
| Anal. calcd., % | C, 55.29 | H, 4.09 |
| Found, % | C, 55.02 | H, 4.13 |

**Syntheses of $Ar_4SbOC_6H_3(NO_2)_2$-2,5 (III) and $(Ar_4Sb)_2CO_3$ (V)** were carried out from a reaction mixture containing pentaphenylantimony (101 mg, 0.2 mmol), compound **I** (109 mg, 0.2 mmol), and benzene (10 mL) using fractional crystallization from a benzene–octane (2 : 1 vol/vol) solution. The yield of the red-brown crystals was 88 mg (72%), mp = 199°C. IR (ν, $cm^{-1}$): 3078, 3066 (Ar), 1530, 1346($NO_2$), 1288 (C–O), 733, 690 (Ph), 457 (Sb–C).

| For $C_{54}H_{48}N_4O_{11}Sb_2$ | | |
|---|---|---|
| Anal. calcd., % | C, 58.73 | H, 3.75 |
| Found, % | C, 58.66 | H, 3.82 |

The second reaction product represented colorless crystals of compound **V** (60 mg, 65%), mp = 227°C. IR (ν, $cm^{-1}$): 3433, 3138, 3062, 3049, 2987, 2951, 2902, 2837, 2640, 2596, 2519, 1953, 1886, 1815, 1631, 1577, 1479, 1471, 1433, 1429, 1382, 1332, 1305, 1263, 1186, 1157, 1099, 1066, 1022, 997, 972, 918, 850, 831, 729, 692, 663, 653, 464, 457, 449.

| For $C_{49}H_{40}O_3Sb_2$ | | |
|---|---|---|
| Anal. calcd., % | C, 63.91 | H, 4.35 |
| Found, % | C, 63.85 | H, 4.46 |

Compounds **IV** and **VI** were obtained similarly. The yield of compound **IV** as red-brown crystals was 68%, mp = 185°C. IR (ν, $cm^{-1}$): 3078, 3066 (Ar), 1530, 1346 ($NO_2$), 1302 (C–O), 733, 691 (Ph), 486 (Sb–C).

| For $C_{34}H_{31}N_2O_5Sb$ | | |
|---|---|---|
| Anal. calcd., % | C, 60.99 | H, 4.63 |
| Found, % | C, 60.81 | H, 4.74 |

The yield of compound **VI** was 65%, mp = 236°C. IR (ν, $cm^{-1}$): 3431, 3064, 3028, 3008, 2962, 2918, 2864, 2729, 2605, 2524, 2077, 1909, 1809, 1743, 1641, 1593, 1562, 1492, 1473, 1394, 1311, 1261, 1211, 1188, 1143, 1114, 1099, 1058, 1039, 1016, 989, 966, 947, 831, 796, 750, 702, 684, 636, 582, 572, 487, 408.

| For $C_{57}H_{56}O_3Sb_2$ | | |
|---|---|---|
| Anal. calcd., % | C, 66.28 | H, 5.43 |
| Found, % | C, 66.13 | H, 5.52 |

The IR spectra of complexes **I–VI** were recorded on a Shimadzu IR Affinity-1S FT-IR spectrometer in KBr pellets in a range of 4000–400 $cm^{-1}$.

**X-ray diffraction analyses** of the crystals of compounds **I–VI** were carried out on a D8 Quest diffractometer (Bruker) (Mo$K_\alpha$ radiation, λ = 0.71073 Å, graphite monochromator) at 293 K. The data were collected and edited, the unit cell parameters were refined, and an absorption correction was applied using the SMART and SAINT-Plus programs [8]. All calculations on structure determination and refinement were performed using the SHELXL/PC [9] and OLEX2 [10] programs. The structures were solved by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and structure refinement results for compounds **I–VI** are presented in Table 1. Selected bond lengths and bond angles are given in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1890704 (**I**), 1890706 (**II**), 1890713 (**III**), 1890714 (**IV**), 994519 (**V**), and 994177 (**VI**); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

A number of the antimony compounds bearing the Sb–O–Sb group in which the terminal ligands are organosulfonate [11–14], dimethylphosphinate [15], nitro [16], carboxylate [17, 18], and other organic moieties [19–21] was described.

In this work, we continue to study the oxidation synthesis of triarylantimony oxoaroxides. The binuclear antimony compounds $[Ar_3SbOC_6H_3(NO_2)_2$-$2,5]_2O$ (Ar = Ph (**I**) and 4-$MeC_6H_4$ (**II**)) were found to be the products of the reactions of triphenyl- and tri(*para*-tolyl)antimony with 2,5-dinitrophenol in the presence of *tert*-butyl hydroperoxide in diethyl ether regardless of the ratio of the initial reagents.

$$2Ar_3Sb + 2HOC_6H_3(NO_2)_2\text{-}2,5 + 2tert\text{-}BuOOH \rightarrow [Ar_3SbOC_6H_3(NO_2)_2\text{-}2,5]_2O,$$
$$Ar = Ph\,(\mathbf{I}),\ 4\text{-}MeC_6H_4\,(\mathbf{II})$$

Red-brown crystals stable in air were obtained after the recrystallization of the reaction products from a benzene–octane mixture.

The pentacoordinated antimony atoms in compounds **I** and **II** are bound to each other via the oxygen atoms (Fig. 1). The $O_{ax}SbO_{ax}$ angles (175.31(8)°, 176.80(8)° in **I**

**Table 1.** Crystallographic data and experimental and structure refinement parameters for compounds **I**–**VI**

| Parameter | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| *FW* | 1088.31 | 1172.46 | 613.25 | 669.36 | 920.31 | 1032.54 |
| Crystal system | Triclinic | Monoclinic | Monoclinic | Monoclinic | Orthorhombic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ | *Pbca* | $P2_1/n$ |
| *a*, Å | 12.675(10) | 15.005(8) | 10.858(4) | 10.090(8) | 20.5819(16) | 11.2249(4) |
| *b*, Å | 13.436(16) | 14.320(6) | 14.490(6) | 18.101(11) | 11.4595(8) | 16.5244(7) |
| *c*, Å | 15.462(12) | 25.684(13) | 17.086(8) | 18.204(12) | 34.417(3) | 27.6426(11) |
| α, deg | 105.92(4) | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| β, deg | 98.65(4) | 102.66(3) | 95.78(2) | 103.90(3) | 90.00 | 96.1559(13) |
| γ, deg | 112.57(4) | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| *V*, Å$^3$ | 2239(4) | 5385(5) | 2674.5(19) | 3228(4) | 8117.6(11) | 5097.7(3) |
| *Z* | 2 | 4 | 4 | 4 | 8 | 4 |
| $\rho_{calc}$, g/cm$^3$ | 1.614 | 1.446 | 1.523 | 1.378 | 1.506 | 1.345 |
| $\mu_{Mo}$, mm$^{-1}$ | 1.273 | 1.064 | 1.074 | 0.896 | 1.372 | 1.101 |
| *F*(000) | 1084.0 | 2360.0 | 1232.0 | 1360.0 | 3680.0 | 2096.0 |
| Crystal size, mm | 0.22 × 0.19 × 0.07 | 0.52 × 0.51 × 0.31 | 0.44 × 0.2 × 0.12 | 1 × 0.51 × 0.32 | 0.47 × 0.26 × 0.11 | 0.59 × 0.29 × 0.16 |
| 2θ, deg | 6.28–65.34 | 5.8–65.22 | 6.4–56.68 | 5.68–71.38 | 3.12–26.4 | 2.99–26.07 |
| Ranges of reflection indices | $-19 \le h \le 19$, $-20 \le k \le 20$, $-23 \le l \le 23$ | $-22 \le h \le 22$, $-21 \le k \le 21$, $-38 \le l \le 38$ | $-14 \le h \le 14$, $-19 \le k \le 19$, $-22 \le l \le 22$ | $-16 \le h \le 16$, $-29 \le k \le 29$, $-29 \le l \le 29$ | $-25 \le h \le 25$, $-14 \le k \le 11$, $-43 \le l \le 42$ | $-13 \le h \le 13$, $-20 \le k \le 20$, $-34 \le l \le 34$ |
| Total number of reflections | 112727 | 247088 | 43963 | 133239 | 86607 | 148451 |
| Independent reflections ($R_{int}$) | 16320 (0.0540) | 19466 (0.0459) | 6642 (0.0250) | 14847 (0.0491) | 8258 (0.0834) | 20073 (0.0267) |
| Number of reflections with $F^2 > 2\sigma(F^2)$ | 16320 | 19466 | 6642 | 14847 | 5198 | 16608 |
| Number of refined parameters | 586 | 646 | 343 | 383 | 487 | 1133 |
| GOOF | 1.018 | 1.163 | 1.108 | 1.114 | 1.087 | 1.184 |
| *R* Factors for $F^2 > 2\sigma(F^2)$ | $R_1 = 0.0387$, $wR_2 = 0.0855$ | $R_1 = 0.0494$, $wR_2 = 0.0848$ | $R_1 = 0.0256$, $wR_2 = 0.0604$ | $R_1 = 0.0649$, $wR_2 = 0.1325$ | $R_1 = 0.0642$, $wR_2 = 0.1557$ | $R_1 = 0.0373$, $wR_2 = 0.0782$ |
| *R* Factors for all reflections | $R_1 = 0.0732$, $wR_2 = 0.1016$ | $R_1 = 0.0886$, $wR_2 = 0.1036$ | $R_1 = 0.0338$, $wR_2 = 0.0655$ | $R_1 = 0.1222$, $wR_2 = 0.1587$ | $R_1 = 0.1147$, $wR_2 = 0.1803$ | $R_1 = 0.0494$, $wR_2 = 0.0883$ |
| Residual electron density (max/min), e/Å$^3$ | 1.84/−1.41 | 2.01/−1.10 | 0.42/−0.85 | 0.83/−0.87 | 1.80/−0.67 | 1.04/−0.54 |

**Table 2.** Selected interatomic distances and bond angles in the structures of compounds **I**–**VI**

| Bond | *d*, Å | Angle | ω, deg |
|---|---|---|---|
| | | **I** | |
| Sb(1)–O(1) | 1.973(3) | O(1)Sb(1)O(2) | 175.31(8) |
| Sb(1)–O(2) | 2.211(3) | O(1)Sb(1)C(1) | 93.67(11) |
| Sb(1)–C(1) | 2.109(3) | O(1)Sb(1)C(11) | 94.58(12) |
| Sb(1)–C(11) | 2.093(3) | O(1)Sb(1)C(21) | 92.90(12) |
| Sb(1)–C(21) | 2.097(3) | C(1)Sb(1)O(2) | 90.36(11) |
| Sb(2)–O(1) | 1.980(2) | C(11)Sb(1)O(2) | 81.63(12) |
| Sb(2)–O(7) | 2.213(3) | C(11)Sb(1)C(1) | 112.87(11) |
| Sb(2)–C(51) | 2.107(3) | C(11)Sb(1)C(21) | 129.87(12) |
| Sb(2)–C(61) | 2.102(3) | C(21)Sb(1)O(2) | 87.48(12) |
| Sb(2)–C(41) | 2.101(3) | C(21)Sb(1)C(1) | 115.99(12) |
| O(7)–C(71) | 1.312(4) | O(1)Sb(2)O(7) | 176.80(8) |
| O(2)–C(31) | 1.307(3) | O(1)Sb(2)C(51) | 92.54(12) |
| C(75)–N(4) | 1.475(5) | O(1)Sb(2)C(61) | 92.52(11) |
| C(72)–N(3) | 1.453(4) | O(1)Sb(2)C(41) | 97.31(12) |
| C(35)–N(2) | 1.475(5) | C(51)Sb(2)O(7) | 90.59(12) |
| C(32)–N(1) | 1.459(4) | C(61)Sb(2)O(7) | 85.61(11) |
| N(3)–O(8) | 1.219(5) | C(61)Sb(2)C(51) | 113.59(12) |
| O(9)–N(3) | 1.205(4) | C(41)Sb(2)O(7) | 82.04(12) |
| O(10)–N(4) | 1.206(5) | C(41)Sb(2)C(51) | 113.47(13) |
| O(6)–N(2) | 1.205(4) | C(41)Sb(2)C(61) | 131.28(12) |
| O(3)–N(1) | 1.215(4) | Sb(1)O(1)Sb(2) | 139.70(10) |
| | | **II** | |
| Sb(1)–O(2) | 2.191(2) | O(1)Sb(1)O(2) | 178.17(9) |
| Sb(1)–O(1) | 1.975(2) | O(1)Sb(1)C(1) | 96.15(11) |
| Sb(1)–C(1) | 2.112(3) | O(1)Sb(1)C(21) | 96.46(11) |
| Sb(1)–C(21) | 2.105(3) | O(1)Sb(1)C(11) | 90.97(11) |
| Sb(1)–C(11) | 2.113(3) | C(1)Sb(1)O(2) | 85.68(11) |
| Sb(2)–O(1) | 1.977(2) | C(1)Sb(1)C(11) | 118.10(12) |
| Sb(2)–O(7) | 2.191(2) | C(21)Sb(1)O(2) | 82.41(10) |
| Sb(2)–C(61) | 2.111(3) | C(21)Sb(1)C(1) | 126.00(13) |
| Sb(2)–C(41) | 2.104(3) | C(21)Sb(1)C(11) | 113.92(12) |
| Sb(2)–C(51) | 2.115(4) | C(11)Sb(1)O(2) | 88.17(10) |
| O(2)–C(31) | 1.303(4) | O(1)Sb(2)O(7) | 177.51(10) |
| O(7)–C(71) | 1.317(4) | O(1)Sb(2)C(61) | 92.94(11) |
| C(75)–N(4) | 1.495(5) | O(1)Sb(2)C(41) | 98.93(11) |
| C(72)–N(3) | 1.477(5) | O(1)Sb(2)C(51) | 92.34(12) |
| C(32)–N(1) | 1.460(5) | C(61)Sb(2)O(7) | 88.46(11) |
| C(35)–N(2) | 1.481(5) | C(61)Sb(2)C(51) | 116.60(14) |
| O(3)–N(2) | 1.204(4) | C(41)Sb(2)O(7) | 82.27(10) |
| O(5)–N(1) | 1.236(4) | C(41)Sb(2)C(61) | 116.09(13) |
| O(10)–N(4) | 1.206(5) | C(41)Sb(2)C(51) | 125.23(14) |
| O(8)–N(3) | 1.231(5) | C(51)Sb(2)O(7) | 85.19(12) |
| O(4)–N(2) | 1.220(4) | Sb(1)O(1)Sb(2) | 142.32(12) |

**Table 2.** (Contd.)

| Bond | *d*, Å | Angle | ω, deg |
|---|---|---|---|
| | | **III** | |
| Sb(1)–O(1) | 2.2902(16) | C(21)Sb(1)O(1) | 81.62(6) |
| Sb(1)–C(21) | 2.118(2) | C(21)Sb(1)C(31) | 98.21(8) |
| Sb(1)–C(11) | 2.111(2) | C(11)Sb(1)O(1) | 80.16(7) |
| Sb(1)–C(1) | 2.109(2) | C(11)Sb(1)C(21) | 123.56(8) |
| Sb(1)–C(31) | 2.157(2) | C(11)Sb(1)C(31) | 96.54(8) |
| O(1)–C(41) | 1.300(2) | C(1)Sb(1)O(1) | 85.16(7) |
| C(45)–N(2) | 1.475(3) | C(1)Sb(1)C(21) | 111.91(9) |
| C(42)–N(1) | 1.467(3) | C(1)Sb(1)C(11) | 119.07(8) |
| O(3)–N(1) | 1.223(3) | C(1)Sb(1)C(31) | 98.76(8) |
| O(2)–N(1) | 1.212(3) | C(31)Sb(1)O(1) | 175.80(7) |
| | | **IV** | |
| Sb(1)–O(1) | 2.342(2) | C(1)Sb(1)O(1) | 83.67(12) |
| Sb(1)–C(1) | 2.120(3) | C(1)Sb(1)C(31) | 99.37(14) |
| Sb(1)–C(11) | 2.115(3) | C(11)Sb(1)O(1) | 79.33(11) |
| Sb(1)–C(21) | 2.106(3) | C(11)Sb(1)C(1) | 113.03(13) |
| Sb(1)–C(31) | 2.159(3) | C(11)Sb(1)C(31) | 98.68(12) |
| O(1)–C(41) | 1.299(4) | C(21)Sb(1)O(1) | 81.38(9) |
| C(45)–N(2) | 1.476(6) | C(21)Sb(1)C(1) | 114.71(11) |
| C(42)–N(1) | 1.460(5) | C(21)Sb(1)C(11) | 125.55(12) |
| O(4)–N(2) | 1.187(6) | C(21)Sb(1)C(31) | 97.96(11) |
| N(2)–O(5) | 1.213(5) | C(31)Sb(1)O(1) | 176.86(10) |
| | | **V** | |
| Sb(1)–O(1) | 2.245(6) | C(21)Sb(1)C(1) | 118.4(3) |
| Sb(1)–C(1) | 2.126(8) | C(31)Sb(1)C(1) | 113.6(3) |
| Sb(1)–C(21) | 2.112(10) | C(31)Sb(1)C(21) | 124.7(4) |
| Sb(1)–C(11) | 2.181(9) | C(51)Sb(2)O(2) | 163.1(3) |
| Sb(1)–C(31) | 2.103(9) | C(51)Sb(2)O(3) | 105.2(3) |
| Sb(2)–O(2) | 2.273(5) | C(51)Sb(2)C(8) | 133.9(3) |
| Sb(2)–O(3) | 2.249(6) | C(61)Sb(2)C(8) | 79.2(3) |
| Sb(2)–C(8) | 2.656(9) | C(61)Sb(2)C(41) | 161.6(3) |
| Sb(2)–C(41) | 2.179(9) | C(71)Sb(2)O(3) | 152.8(3) |
| Sb(2)–C(51) | 2.177(9) | C(71)Sb(2)C(8) | 124.2(3) |
| Sb(2)–C(61) | 2.169(9) | C(71)Sb(2)C(51) | 101.9(4) |
| Sb(2)–C(71) | 2.152(9) | C(71)Sb(2)C(61) | 95.6(3) |
| O(1)–C(8) | 1.260(10) | C(8)O(1)Sb(1) | 124.1(6) |
| O(2)–C(8) | 1.302(10) | C(8)O(2)Sb(2) | 91.9(5) |
| O(3)–C(8) | 1.278(10) | C(8)O(3)Sb(2) | 93.6(5) |
| | | **VI** | |
| Sb(1)–C(21) | 2.159(4) | C(21)Sb(1)C(1) | 96.17(15) |
| Sb(1)–C(1) | 2.166(4) | C(21)Sb(1)C(11) | 95.32(15) |
| Sb(1)–C(11) | 2.165(4) | C(21)Sb(1)O(2) | 151.82(11) |
| Sb(1)–O(2) | 2.216(2) | C(21)Sb(1)O(3) | 92.88(11) |
| Sb(1)–O(3) | 2.251(2) | C(21)Sb(1)C(8) | 122.16(12) |
| Sb(1)–C(8) | 2.611(3) | C(21)Sb(1)C(31) | 104.22(14) |

**Table 2.** (Contd.)

| Bond | *d*, Å | Angle | ω, deg |
|---|---|---|---|
| Sb(1)–C(31) | 2.178(3) | C(1)Sb(1)O(2) | 82.35(13) |
| Sb(4)–O(4) | 2.263(2) | C(1)Sb(1)O(3) | 85.63(12) |
| Sb(4)–C(121) | 2.119(4) | C(1)Sb(1)C(8) | 83.64(13) |
| Sb(4)–C(151) | 2.170(3) | C(1)Sb(1)C(31) | 93.15(15) |
| Sb(4)–C(141) | 2.117(4) | C(11)Sb(1)C(1) | 165.55(15) |
| Sb(4)–C(131) | 2.127(3) | C(11)Sb(1)O(2) | 83.39(14) |
| Sb(3)–O(5) | 2.217(2) | C(11)Sb(1)O(3) | 85.08(12) |
| Sb(3)–C(101) | 2.157(4) | C(11)Sb(1)C(8) | 82.84(13) |
| Sb(3)–C(8) | 2.166(4) | C(11)Sb(1)C(31) | 92.48(15) |
| Sb(3)–O(6) | 2.251(2) | O(2)Sb(1)O(3) | 58.94(8) |
| Sb(3)–C(9) | 2.609(3) | O(2)Sb(1)C(8) | 29.67(9) |
| Sb(3)–C(111) | 2.177(3) | O(3)Sb(1)C(8) | 29.28(9) |
| Sb(3)–C(91) | 2.165(4) | C(31)Sb(1)O(2) | 103.97(12) |
| Sb(2)–C(41) | 2.120(4) | C(31)Sb(1)O(3) | 162.89(12) |
| Sb(2)–C(71) | 2.172(3) | C(31)Sb(1)C(8) | 133.61(13) |
| Sb(2)–O(1) | 2.263(2) | C(121)Sb(4)O(4) | 86.32(11) |
| Sb(2)–C(51) | 2.114(4) | C(121)Sb(4)C(151) | 97.00(14) |
| Sb(2)–C(61) | 2.125(3) | C(121)Sb(4)C(131) | 116.86(14) |

and 178.17(9)°, 177.51(10)° in **II**) differ slightly. The shift of the antimony atoms from the [$C_3$] planes to the central oxygen atoms are 0.136, 0.155 Å in compound **I** and 0.171, 0.176 Å in compound **II**. The Sb–O–Sb fragments of the molecules of compounds **I** and **II** are bent, and the SbOSb angles are 139.70(10)° and 142.32(12)°, which are close to a similar angle in μ2-oxo-bis[(2,4,6-trinitrophenolato)triphenylantimony] (142.5(8)°) [7]. The Sb–C distances vary in the ranges 2.093(3)–2.109(3) and 2.104(3)–2.115(4) Å in compounds **I** and **II**, respectively; and their average values in the phenyl derivatives are lower than those in the tolyl derivatives. The Sb–$O_{br}$ (1.973(3), 1.980(2) Å in **I** and 1.975(2), 1.977(2) Å in **II**) are shorter than Sb–$O_t$ (2.211(3), 2.213(3) Å in **I** and 2.191(2), 2.191(2) Å in **II**). Note that the Sb–$O_{br}$ distances almost coincide, whereas the Sb–$O_t$ distances in compound **I** are longer than those in compound **II**. The C–O bonds in the phenolate ligands (1.307(3), 1.312(4) Å in **I** and 1.303(4), 1.317(4) Å in **II**) are comparable in length but are longer than those in the isolated 2,5-dinitrophenolate anions (1.268(6) Å [22]). In the crystal of compound **I**, the intermolecular hydrogen bonds O(3)···H(64) (2.42 Å) link the structural units into the single whole. In the crystal of complex **II**, structure formation occurs due to the hydrogen bonds between the oxygen atom of the *ortho*-nitro group of the phenolate ligand of one molecule and the *meta*-H atom of the phenolate group of another molecule.

We showed that the products of the reactions of pentaarylantimony with compounds **I** and **II** were tetraarylantimony aroxides $Ar_4SbOC_6H_3(NO_2)_2$-2,5 (Ar = Ph (**III**) and 4-$MeC_6H_4$ (**IV**)) and tetraarylantimony carbonates formed on contact of the reaction mixture with carbon dioxide of air [23].

$$2Ar_5Sb + \left[Ar_3SbOC_6H_3(NO_2)_2\text{-}2,5\right]_2O \rightarrow 2\,Ar_4SbOC_6H_3(NO_2)_2\text{-}2,5 + (Ar_4Sb)_2O,$$
$$Ar = Ph\,(\mathbf{III}),\ \ 4\text{-}MeC_6H_4\,(\mathbf{IV}).$$
$$(Ar_4Sb)_2O + CO_2 \rightarrow (Ar_4Sb)_2CO_3,$$
$$Ar = Ph\,(\mathbf{V}),\ \ 4\text{-}MeC_6H_4\,(\mathbf{VI}).$$

Compounds **III** and **IV** were also synthesized from pentaarylantimony and 2,5-dinitrophenol.

According to the X-ray diffraction data, the oxygen atoms occupy axial positions in the trigonal bipyramidal molecules of compounds **III** and **IV** (Fig. 2). The axial angles in compounds **III** (175.80(7)°) and **IV** (176.86(10)°) are close to the ideal value, as well as the sums of the angles in the equatorial plane (354.54(9)° in **III** and 353.29(12)° in **IV**). The OSb$C_{eq}$ angles are smaller than 90° (80.16(7)°–85.16(7)°, 79.33(11)°–83.67(12)°), because the deviations of the antimony atoms from the equatorial planes to the axial carbon atoms (0.286 and 0.317 Å) are fairly substantial. The Sb–$C_{eq}$ bonds (2.109(2)–2.118(2) Å in **III** and 2.106(3)–2.120(3) Å in **IV**) are longer than the sum of covalent radii of the Sb and C ($sp^2$) atoms (2.07 Å [24]). The axial Sb–C bonds (2.157(2), 2.159(3) Å) are significantly longer and are also equal within the experimental inaccuracy. The Sb–O bond in compound **IV** (2.342(2) Å) is appreciably longer than that in compound **III** (2.290(2) Å) and significantly longer

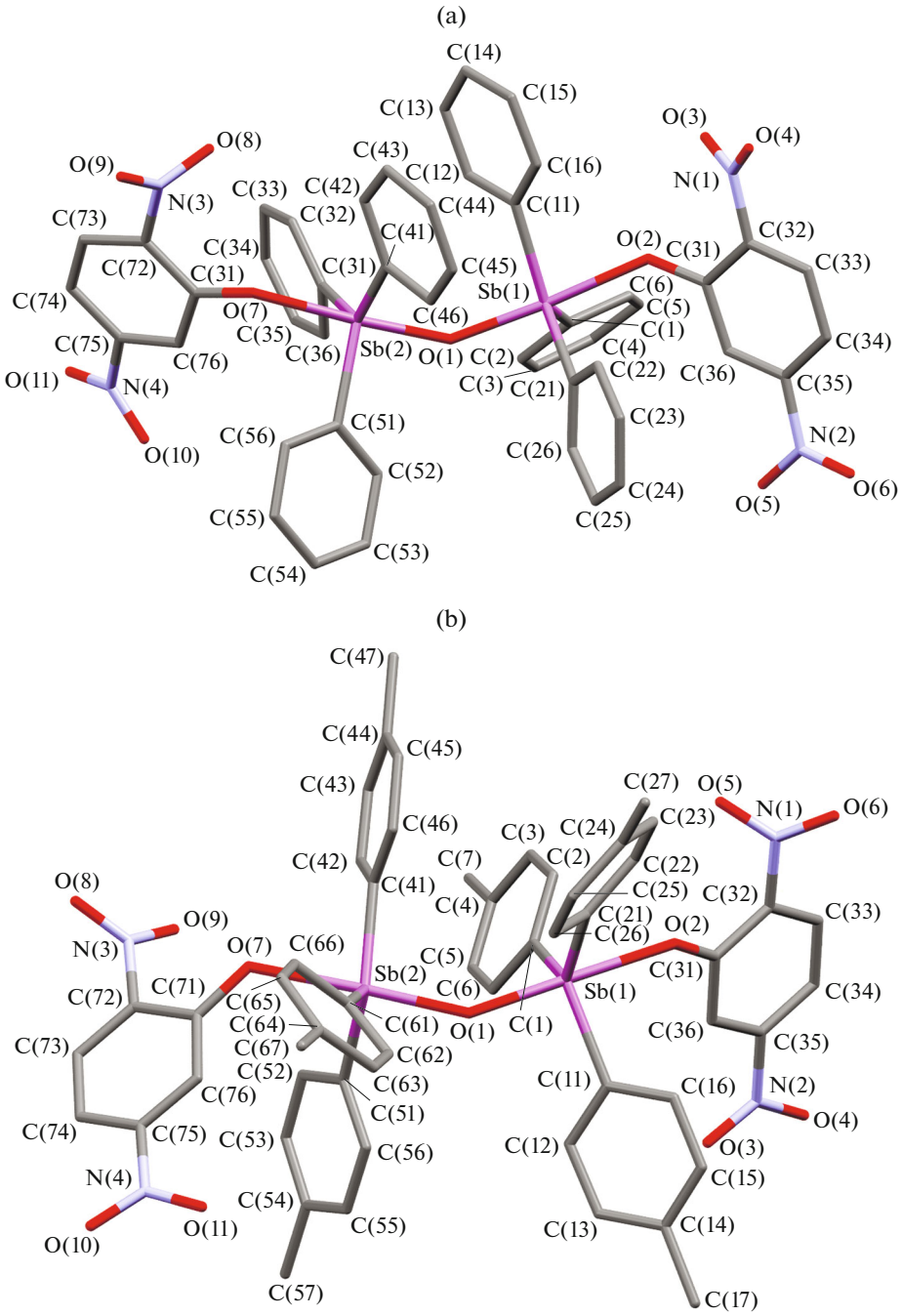


**Fig. 1.** Molecular structures of compounds (a) **I** and (b) **II**.

than similar distances in compounds **I** and **II**. The elongation of the Sb–O bond in a molecule of compound **IV** correlates with a higher distortion of the trigonal bipyramidal polyhedron of the antimony atom in this molecule, which follows from a comparison of the bond angles between the axial and equatorial planes in compounds **III** and **IV**. Weak hydrogen bonds O···H–C (O···H 2.52–2.98 Å) join the structural units in the crystal of compound **III** unlike compound **IV**.

The structures of isolated tetraarylantimony carbonates **V** and **VI** were proved by X-ray diffraction analysis. The triclinic [25] and monoclinic [26] modifications are known for compound **V**. We pioneered in decoding the orthorhombic modification. We structurally characterized compound **VI** for the first time

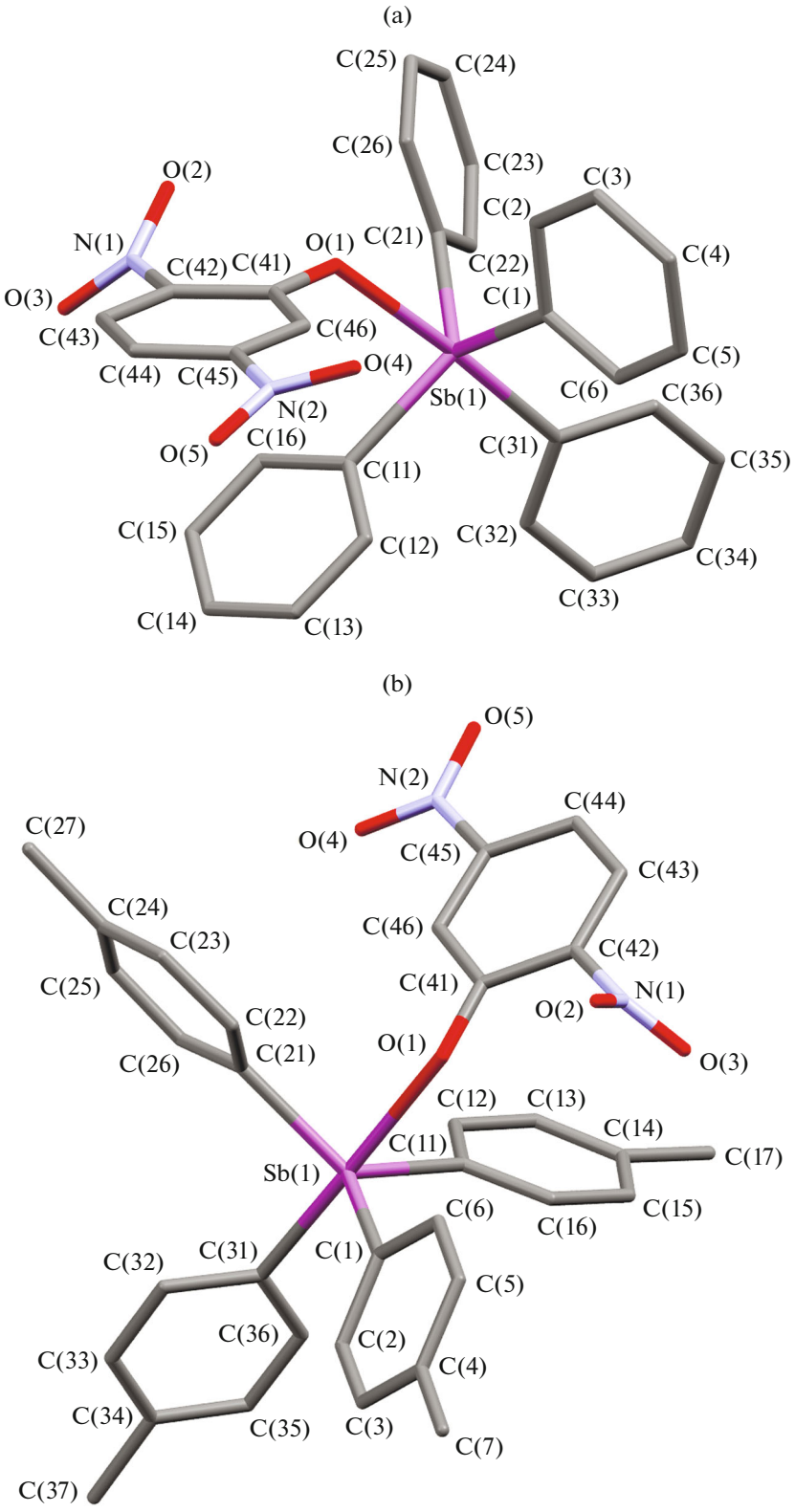


**Fig. 2.** Molecular structures of compounds (a) **III** and (b) **IV**.

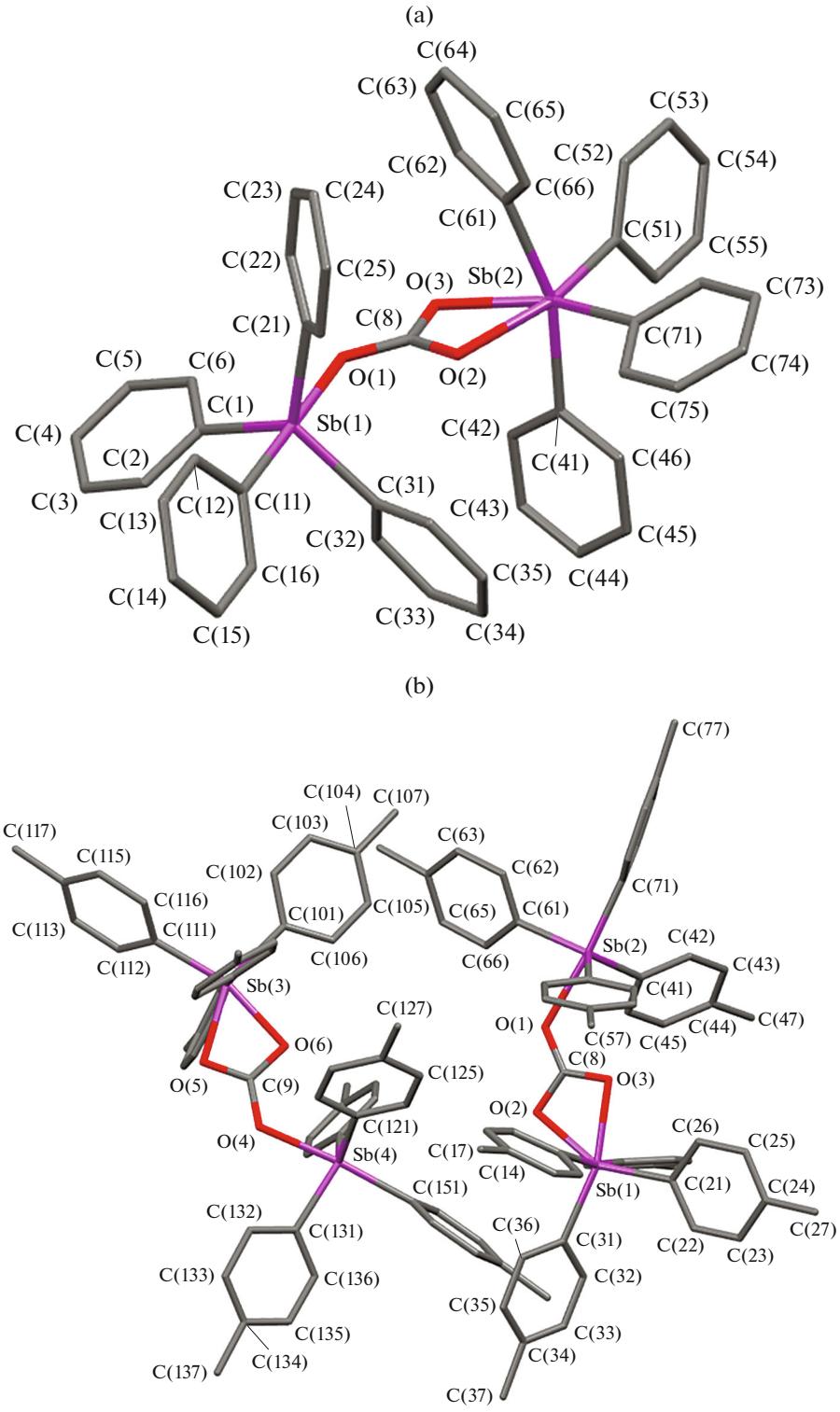


**Fig. 3.** Molecular structures of compounds (a) **V** and (b) **VI**.

(monoclinic modification, two types of crystallographically independent molecules **a** and **b**). In the molecules of compounds **V** and **VI**, the antimony atoms are characterized by different coordination numbers of 5 and 6 (Fig. 3). The trigonal bipyramidal coordination mode of the antimony atoms is not almost distorted, and the axial OSbC angles are 178.7(3)° in compound **V** and 175.2(1)°, 175.1(1)° in

modifications **VIa**, **VIb**. The sums of angles in the equatorial plane are 356.7(3)° and 356.9(1)°, 356.9(1)°. The Sb–$C_{eq}$ bonds (2.114(9) and 2.120(4), 2.121(4) Å) are shorter, on the average, than Sb–$C_{ax}$ (2.181(9) and 2.170(3), 2.172(3) Å). The Sb–O bonds (2.245(6) and 2.263(3), 2.263(3) Å) in compounds **V** and **VI** are shorter than those in compounds **III** and **IV**.

The sums of the bond angles between the bonds in the equatorial plane [$O_2C_2$] at the octahedral antimony atoms are 359.9(4)° in **V** and 360° in **VIa** and **VIb**. However, the individual values of angles differ strongly: OSbO do not exceed 60° and CSbC are ~105°. The *trans* angles in the equatorial plane CSbO are 163.1(3)°, 152.8(3)° and 162.9(1)°, 151.8(1)°; 163.0(1)°, 151.8(1)°. The angles between the axial bonds CSbC are also smaller than the theoretical value (161.6(3)° and 165.6(2)°, 165.8(2)°). The Sb–C distances vary in the ranges 2.152(9)–2.179(9) and 2.159(4)–2.178(3), 2.157(4)–2.177(3) Å. The carbonate ligand coordinates to the antimony atom via the nonsymmetric mode: the Sb–O distances are 2.249(6), 2.273(5) and 2.216(2), 2.251(2); 2.217(2), 2.251(2) Å; and the tolyl ligands are bound to the central atom more strongly than the phenyl ligands. The C–O bond lengths in the carbonate group differ: 1.260(10), 1.302(10), and 1.278(10) Å in **V**; 1.284(4), 1.293(4), and 1.277(4) Å in **VIa**; and 1.285(4), 1.293(4), and 1.274(4) Å in **VIb**. The following regularity is observed: the longer C–O bond corresponds to the shorter Sb–O bond. Note that the bond angles in the triclinic, monoclinic, and orthorhombic modifications of compound **V** are close in values. Some differences are observed for the Sb–O bond lengths. For example, these distances are 2.258, 2.185, and 2.325 Å in the molecules of the triclinic modification [25], whereas they are 2.273, 2.239, and 2.262 Å in the monoclinic molecules [26].

Thus, new phenyl and *para*-tolyl derivatives of antimony(V) were synthesized and structurally characterized. It is found that the strength of binding of the antimony atom with the ligands depends on both the nature of the aryl substituents and the type of the organoantimony compound.

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## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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