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# Synthesis and Structure of Triphenylantimony Bis(Acetophenoneoximate)

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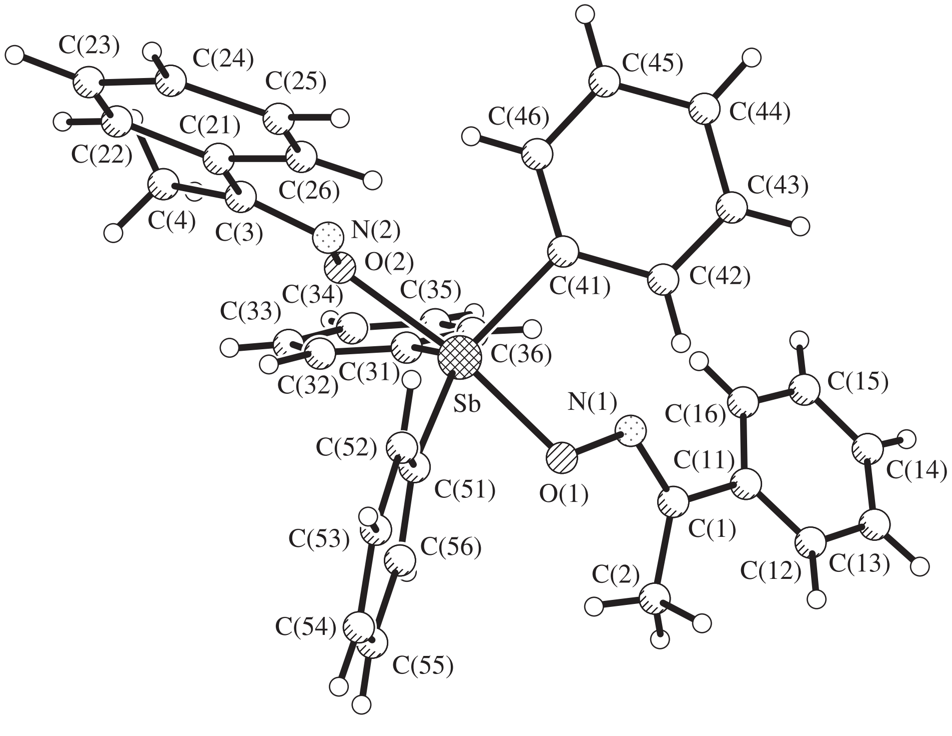
**Abstract**—Triphenylantimony bis(acetophenoneoximate) was synthesized by the reaction of triphenylantimony with hydrogen peroxide in the presence of acetophenone oxime (taken in the molar ratio of 1 : 1 : 2) in ether. The structure of the obtained compound was determined by X-ray diffraction. The Sb atom has a distorted trigonal-bipyramidal coordination with the oxime groups in the axial positions. The Sb–C(Ph)$_{eq}$ bond lengths are 2.110(1)–2.113(1) Å, and the Sb–O distances are 2.058(1) and 2.067(1) Å. The intramolecular Sb(1)···N(1, 2) contacts and O(1)SbO(2) axial angle are 2.990(1), 2.916(1) Å and 172.49(4)°, respectively.

It is known that reactions of triarylantimony with carboxylic or arenesulfonic acids in the presence of hydrogen peroxide yield triarylantimony diacylates [1, 2] or bis(arenesulfonates) [3, 4]. Similar reactions with oximes are unknown.

In continuation of studies into the synthesis and structure of antimony compounds with the general formula $Ar_3SbX_2$ (X is an electronegative ligand), we synthesized triphenylantimony bis(acetophenoneoximate) (**I**) and investigated its molecular and crystal structure.

## EXPERIMENTAL

**Synthesis** of **I** was carried out by the following procedure. 0.32 ml of a 30% aqueous solution (2.82 mmol) of $H_2O_2$ was added to a solution of 1.00 g (2.83 mmol)



Molecular structure of complex **I**.

**Table 1.** Crystallographic data and details of the experiment and refinement of structure **I**

| Parameter | Value |
|---|---|
| Empirical formula | $C_{34}H_{31}N_2O_2Sb$ |
| $M$ | 621.36 |
| Temperature, K | 293(2) |
| Wave length | Mo$K_\alpha$ (0.71073 Å) |
| Space group | $P\bar{1}$ |
| $a$, Å | 9.565(1) |
| $b$, Å | 10.000(1) |
| $c$, Å | 15.754(2) |
| α, deg | 81.666(2) |
| β, deg | 79.836(2) |
| γ, deg | 85.492 |
| $V$, Å$^3$ | 1465.5(3) |
| $Z$ | 2 |
| ρ(calcd.), g/cm$^3$ | 1.408 |
| μ, mm$^{-1}$ | 0.974 |
| $F$(000) | 632 |
| Crystal shape | Prism<br>(0.30 × 0.20 × 0.15 mm) |
| Region of data collection (θ), deg | 2.06–30.03 |
| Ranges of reflection indexes | $-13 \le h \le 13$, $-13 \le k \le 14$,<br>$-22 \le l \le 22$ |
| Measured reflections | 16030 |
| Independent reflections | 8400 ($R_{int}$ = 0.0306) |
| Reflections with $I > 2\sigma(I)$ | 6773 |
| Refinement method | Full-matrix least-squares method for $F^2$ |
| Refined parameters | 354 |
| GOOF | 0.937 |
| $R$ factors for $F^2 > 2\sigma(F^2)$ | $R_1 = 0.0287$, $wR_2 = 0.0619$ |
| $R$ factors for all reflections | $R_1 = 0.0388$, $wR_2 = 0.0643$ |
| Residual electronic density (min/max), $e$/Å$^3$ | –0.310/0.465<br>(near Sb atom) |

of triphenylantimony $Ph_3Sb$ and 0.76 g (5.63 mmol) of acetophenone oxime HON=C($CH_3$)Ph in 20 ml of ether. The mixture was kept for 12 h at 20°C. Colorless crystals formed as a result of the oxidative addition reaction

$$Ph_3Sb + H_2O_2 + 2HON{=}C(CH_3)Ph \longrightarrow Ph_3Sb[ON{=}C(CH_3)Ph]_2 + 2H_2O$$

(**I**)

These crystals were filtered off and dried. The yield was 1.60 g (91%), mp 163°C. The IR spectrum (ν, cm$^{-1}$): 1305, 1160, 1078, 1022, 990, 920.

**Table 2.** Atomic coordinates and isotropic equivalent thermal parameters ($U_{eq}$) in structure **I**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$, Å$^2$ |
|---|---|---|---|---|
| Sb | 0.612438(9) | 0.873994(9) | 0.743809(5) | 0.03778(2) |
| O(1) | 0.7697(1) | 1.0023(1) | 0.68482(6) | 0.0492(3) |
| O(2) | 0.4759(1) | 0.7258(1) | 0.80377(6) | 0.0460(2) |
| N(1) | 0.7526(1) | 1.0828(1) | 0.60650(7) | 0.0459(3) |
| N(2) | 0.4145(1) | 0.7447(1) | 0.88931(7) | 0.0420(3) |
| C(1) | 0.8681(1) | 1.1361(1) | 0.56828(8) | 0.0413(3) |
| C(2) | 1.0055(2) | 1.1114(2) | 0.6012(1) | 0.0650(5) |
| C(3) | 0.3530(2) | 0.6415(1) | 0.9323(1) | 0.0422(3) |
| C(4) | 0.3467(2) | 0.5127(2) | 0.8958(1) | 0.0887(7) |
| C(11) | 0.8605(1) | 1.2273(1) | 0.4853(1) | 0.0407(3) |
| C(12) | 0.9607(2) | 1.3225(2) | 0.4540(1) | 0.0565(4) |
| C(13) | 0.9536(2) | 1.4078(2) | 0.3769(1) | 0.0679(5) |
| C(14) | 0.8493(2) | 1.3973(2) | 0.3298(1) | 0.0627(5) |
| C(15) | 0.7489(2) | 1.3030(2) | 0.3599(1) | 0.0607(5) |
| C(16) | 0.7540(2) | 1.2199(2) | 0.4369(1) | 0.0534(4) |
| C(21) | 0.2845(1) | 0.6555(1) | 1.0227(1) | 0.0400(3) |
| C(22) | 0.2307(2) | 0.5458(2) | 1.0794(1) | 0.0617(5) |
| C(23) | 0.1695(2) | 0.5591(2) | 1.1639(1) | 0.0748(6) |
| C(24) | 0.1604(2) | 0.6800(2) | 1.1940(1) | 0.0691(5) |
| C(25) | 0.2110(2) | 0.7908(2) | 1.1395(1) | 0.0611(5) |
| C(26) | 0.2725(2) | 0.7794(2) | 1.0540(1) | 0.0522(4) |
| C(31) | 0.6347(1) | 0.7615(2) | 0.6381(1) | 0.0440(3) |
| C(32) | 0.6471(2) | 0.6213(2) | 0.6525(1) | 0.0605(5) |
| C(33) | 0.6559(2) | 0.5479(2) | 0.5833(1) | 0.0809(6) |
| C(34) | 0.6487(2) | 0.6141(2) | 0.5013(1) | 0.0869(6) |
| C(35) | 0.6358(2) | 0.7517(2) | 0.4875(1) | 0.0773(6) |
| C(36) | 0.6298(2) | 0.8267(2) | 0.5551(1) | 0.0574(4) |
| C(41) | 0.4506(2) | 1.0301(1) | 0.7533(1) | 0.0415(3) |
| C(42) | 0.4849(2) | 1.1644(2) | 0.7428(1) | 0.0524(4) |
| C(43) | 0.3788(2) | 1.2649(2) | 0.7497(1) | 0.0640(5) |
| C(44) | 0.2377(2) | 1.2327(2) | 0.7682(1) | 0.0677(5) |
| C(45) | 0.2035(2) | 1.1008(2) | 0.7783(1) | 0.0612(5) |
| C(46) | 0.3093(2) | 0.9994(2) | 0.7705(1) | 0.0518(4) |
| C(51) | 0.7416(1) | 0.8382(1) | 0.8413(1) | 0.0407(3) |
| C(52) | 0.6852(2) | 0.8542(2) | 0.9269(1) | 0.0508(4) |
| C(53) | 0.7722(2) | 0.8383(2) | 0.9890(1) | 0.0699(5) |
| C(54) | 0.9133(2) | 0.8047(2) | 0.9683(1) | 0.0811(6) |
| C(55) | 0.9699(2) | 0.7881(2) | 0.8835(1) | 0.0782(6) |
| C(56) | 0.8856(2) | 0.8056(2) | 0.8196(1) | 0.0563(4) |

**IR spectra** were recorded on a Hitachi-215 spectrometer with mineral oil mulls between sodium chloride plates.

**Table 3.** Selected bond lengths and angles in structure **I**

| Bond | *d*, Å | Angle | ω, deg |
|---|---|---|---|
| Sb–O(1) | 2.058(1) | O(1)SbO(2) | 172.49(4) |
| Sb–O(2) | 2.067(1) | O(1)SbC(51) | 82.15(4) |
| Sb–C(51) | 2.110(1) | O(2)SbC(51) | 93.52(4) |
| Sb–C(41) | 2.112(1) | O(1)SbC(41) | 94.29(5) |
| Sb–C(31) | 2.113(1) | O(2)SbC(41) | 93.17(5) |
| O(1)–N(1) | 1.400(1) | C(51)SbC(41) | 118.04(5) |
| O(2)–N(2) | 1.405(1) | O(1)SbC(31) | 94.24(5) |
| N(1)–C(1) | 1.277(2) | O(2)SbC(31) | 83.03(4) |
| N(2)–C(3) | 1.273(2) | C(51)SbC(31) | 123.74(5) |
| C(1)–C(2) | 1.487(2) | C(41)SbC(31) | 118.22(5) |
| C(1)–C(11) | 1.491(2) | C(1)N(1)O(1) | 111.9(1) |
| C(3)–C(21) | 1.480(2) | C(3)N(2)O(2) | 113.4(1) |
| C(3)–C(4) | 1.494(2) | N(1)C(1)C(2) | 124.1(1) |
| C(11)–C(12) | 1.382(2) | N(1)C(1)C(11) | 116.2(1) |
| C(11)–C(16) | 1.387(2) | C(2)C(1)C(11) | 119.7(1) |
| C(12)–C(13) | 1.389(2) | N(2)C(3)C(21) | 116.0(1) |
| C(13)–C(14) | 1.362(3) | N(2)C(3)C(4) | 123.6(1) |
| C(14)–C(15) | 1.374(2) | C(21)C(3)C(4) | 120.4(1) |
| C(15)–C(16) | 1.374(2) | C(12)C(11)C(16) | 117.8(1) |
| C(21)–C(22) | 1.382(2) | C(12)C(11)C(1) | 120.5(1) |
| C(21)–C(26) | 1.388(2) | C(16)C(11)C(1) | 121.7(1) |
| C(22)–C(23) | 1.376(2) | C(11)C(12)C(13) | 120.6(2) |
| C(23)–C(24) | 1.353(3) | C(14)C(13)C(12) | 120.6(2) |
| C(24)–C(25) | 1.364(2) | C(13)C(14)C(15) | 119.6(2) |
| C(25)–C(26) | 1.389(2) | C(14)C(15)C(16) | 120.1(2) |
| C(31)–C(36) | 1.380(2) | C(15)C(16)C(11) | 121.4(1) |
| C(31)–C(32) | 1.387(2) | C(22)C(21)C(26) | 117.4(1) |
| C(32)–C(33) | 1.386(3) | C(22)C(21)C(3) | 121.4(1) |
| C(33)–C(34) | 1.375(3) | C(26)C(21)C(3) | 121.2(1) |
| C(34)–C(35) | 1.360(3) | C(23)C(22)C(21) | 121.0(2) |
| C(35)–C(36) | 1.380(2) | C(24)C(23)C(22) | 121.1(2) |
| C(41)–C(46) | 1.380(2) | C(23)C(24)C(25) | 119.5(2) |
| C(41)–C(42) | 1.387(2) | C(24)C(25)C(26) | 120.3(2) |
| C(42)–C(43) | 1.372(2) | C(21)C(26)C(25) | 120.8(1) |
| C(43)–C(44) | 1.382(3) | C(36)C(31)C(32) | 119.6(2) |
| C(44)–C(45) | 1.364(2) | C(33)C(32)C(31) | 119.8(2) |
| C(45)–C(46) | 1.378(2) | C(34)C(33)C(32) | 119.9(2) |
| C(51)–C(56) | 1.384(2) | C(35)C(34)C(33) | 120.1(2) |
| C(51)–C(52) | 1.389(2) | C(34)C(35)C(36) | 120.9(2) |
| C(52)–C(53) | 1.377(2) | C(35)C(36)C(31) | 119.7(2) |
| C(53)–C(54) | 1.359(3) | C(46)C(41)C(42) | 119.2(1) |
| C(54)–C(55) | 1.379(3) | C(43)C(42)C(41) | 112.0(2) |
| C(55)–C(56) | 1.380(3) | C(42)C(43)C(44) | 120.3(2) |
|  |  | C(45)C(44)C(43) | 120.0(2) |
|  |  | C(44)C(45)C(46) | 120.1(2) |
|  |  | C(45)C(46)C(41) | 120.4(2) |
|  |  | C(56)C(51)C(52) | 119.1(1) |
|  |  | C(53)C(52)C(51) | 120.1(2) |
|  |  | C(54)C(53)C(52) | 121.0(2) |
|  |  | C(53)C(54)C(55) | 119.2(2) |
|  |  | C(54)C(55)C(56) | 121.0(2) |
|  |  | C(55)C(56)C(51) | 119.6(2) |

**X-ray diffraction analysis** of crystals **I** was carried out using a SMART-1000 CCD (Bruker) spectrometer. The data were collected in sets of 606 frames at $\varphi = 0°$, 120°, and 240° (ω scan mode with a 0.3° step and 10 s exposure per frame; the distance between the crystal and detector was 45 mm).

The structure was solved by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were placed in the geometrically calculated positions and refined in the rider model (the C–H distances are 0.93 Å for phenyl and 0.96 Å for methyl groups).

Collection and editing of the data and refinement of the unit cell parameters were carried out with the SMART and SAINT Plus programs [5]. All calculations for solution and refinement of the structure were performed with the SHELXTL/PC programs [6].

Selected crystallographic data and results of the structure refinement are given in Table 1. Atomic coordinates are listed in Table 2. Bond lengths and angles are given in Table 3.

## RESULTS AND DISCUSSION

The X-ray diffraction analysis of **I** shows that the Sb atom has a distorted trigonal-bipyramidal coordination (figure) with the O atoms of the oxime ligands in the axial positions. The phenyl rings C(31)–C(36), C(41)–C(46), and C(51)–C(56) are rotated about the equatorial plane through 45.8°, 112.3°, and 36.8°, respectively; the Sb atom extends from the C(31)C(41)C(51) equatorial plane by 0.0058 Å. The sum of the C(Ph)SbC(Ph) angles in the equatorial plane is 360°, and the O(1)SbO(2) axial angle is 172.49(4)°. The C(Ph)SbC(Ph) angles between the equatorial phenyl ligands are unequal: 118.04(5)°, 123.74(5)°, and 118.22(5)°. The Sb–O(1) and Sb–O(2) distances, 2.058(1) and 2.067(1) Å, respectively, are essentially shorter than the analogous distances in triphenylantimony diacylates [2, 7] and disulfonates [3, 4, 8].

The plane of the phenyl ring C(21)–C(26) of one of the oxime ligands is almost coplanar to the plane of the oxime group O(2)N(2)C(3)C(4) (the dihedral angle between them is 8.5°); the value of the analogous angle in the other acetophenoneoximate ligand is 22.1°.

The Sb(1)··N(1) and Sb(1)··N(2) distances, 2.990(1) and 2.916(1) Å, respectively, are less than the sums of the van der Waals radii of the Sb and N atoms (3.8 Å [9]). The C(51)Sb(1)C(31) angle (123.74(5)°) at the Sb(1)··N(1) and Sb(1)··N(2) intramolecular contacts only slightly exceeds the standard value of 120°. Therefore, the coordination number of the Sb atom in **I** is 7 (5 + 2). Note that the Sb··O=C intramolecular contacts are found in triphenylantimony diacylates; the equatorial angle at the contacts differs significantly from the other two and achieves a value of 151.7(2)° [2].

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