REACTIONS OF TRI(*ORTHO*-TOLYL)- AND TRI(*META*-TOLYL)ANTIMONY WITH OXIMES IN THE PRESENCE OF AN OXIDANT. THE STRUCTURES OF TRI(*ORTHO*-TOLYL)- AND TRI(*META*-TOLYL)ANTIMONY DIOXIMATES

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The triarylantimony dioximates: $(o\text{-}CH_3C_6H_4)_3Sb(ON{=}CHC_6H_4N(CH_3)_2\text{-}4)_2$ (1), $(o\text{-}CH_3C_6H_4)_3Sb(ON{=}CMePh)_2$ (2), $(m\text{-}CH_3C_6H_4)_3Sb(ON{=}CHC_4H_3O)_2$ (3) were obtained from the reactions of tri(*ortho*-tolyl)antimony and tri(*meta*-tolyl)antimony with appropriate oximes in the presence of hydrogen peroxide and *tert*-butyl hydroperoxide. According to the X-ray analysis data, antimony atoms are bound to oxygen atoms of axial oximate ligands in the trigonal bipyramidal coordination in molecules 1–3. The peculiarities of molecular structures are short intramolecular contact Sb···N, which is 1 Å less than the sum of Van der Waals radiuses.

Keywords: tri(ortho-tolyl)antimony, tri(meta-tolyl)antimony, oximes, tert-butyl hydroperoxide, hydrogen peroxide, oxidizing reactions, bis[4-N,N(dimethylamino)-benzaldoximato]tri(ortho-tolyl)antimony, bis(acetophenonoximato)_tri(ortho-tolyl)antimony, bis(furfuradloximato)tri(meta-tolyl) antimony, molecular structures, X-ray analysis.

Introduction

Triarylantimony oxidative addition reaction (reagent is an acid with the general formula HA, the oxidizing agent is peroxide) is of interest as an effective single-stage reaction to synthetize antimony (V) aryl derivatives Ar_3SbX_2. However, using oxime in such reaction, even with 1:2:1 mole ratio of the reactants, led to the formation of two different product: $Ar_3Sb(ONCRR')_2$ and $(Ar_3SbONCRR')_2O$ [1, 2]. This resulted in a necessity for product separation. It was found that the interaction of triphenylantimony with oxime in the presence of hydrogen peroxide (1:1:1 molar ratio of the reactants) led to the formation of oxo-derivatives of triarylantimony $(Ph_3SbONCRR')_2O$ [3]. One further peculiarity of oxidative addition reaction between triarylantimony and oximes is the dependence of the product molecular structure on the nature of aryl ligands, situated at antimony atom. Thus, furfuraloxime ligands are bidentate bridging ligands in the molecule of *bis*(μ_2-furfuraloximato)-(μ_2-oxo)-*bis*[triphenylantimony]. These ligands are coordinated by the oxygen atom to the first antimony atom and by the nitrogen atom to the second antimony atom. This fact increases antimony coordination number to six [3]. However, the molecule of μ_2-oxo-*bis*[(furfuraldoximato)tri*(o*-tolyl)antimony] is of the regular molecular structure type which includes monodentate ligands [4]. 2-Hydroxybenzaldoxim reacts with triphenylantimony and tri(*o*-tolyl)antimony in the presence of an oxidizing agent to form triarylantimony dioximates [5, 6], whereas its reaction with tri(*m*-tolyl)antimony and *tris*(5-bromo-2-methoxyphenyl)antimony leads to the formation of binuclear complex with Sb–O–Sb bond in which every ligand is tridentate chelating-bridging one [6, 7].

To improve oxidative synthesis method of organoantimony compounds with oxime ligands the present paper continuates investigating reactions of tri(*o*-tolyl)antimony and tri(*m*-tolyl)antimony with oximes in the presence of hydrogen peroxide or *tert*-butyl hydroperoxide (1:2:1 and 1:1:1 mole ratio of the reactants) in various solvents.

Experimental

Synthesis of *bis*[4-N,N(dimethylamino)benzaldoximato]tri(*o*-tolyl)antimony (1).

a) Tri(*o*-tolyl)antimony (100 mg, 0.25 mmol) was dissolved in diethyl ether (30 mL). Then 4-N,N-(dimethylamino)benzaldoxime (82 mg, 0.50 mmol) and hydrogen peroxide (28 mg, 30 % aqueous, 0.25 mmol) were added. The solution was left to stand for 24 hours at temperature 20 °C. When the solvent evaporated, the product was a light green crystalline substance; yield 156 mg (85 %), MP: 154 °C.

b) Tri(*o*-tolyl)antimony (150 mg, 0.40 mmol) was dissolved in diethyl ether (30 mL). Then 4-N,N(dimethylamino)benzaldoxime (125 mg, 0.80 mmol) and *tert*-butyl hydroperoxide (49 mg, 70 % aqueous, 0.40 mmol) were added. The solution was left to stand for 24 hours at temperature 20 °C. The fine-cristalline substance were obtained; the product yield 267 mg (97 %), MP: 155 °C.

c) Tri(*o*-tolyl)antimony (100 mg, 0.25 mmol) was dissolved in diethyl ether (30 mL). Then 4-N,N(dimethylamino)benzaldoxime (41 mg, 0.25 mmol) and hydrogen peroxide (32 mg, 30 % aqueous, 0.25 mmol) were added. The solution was left to stand for 24 hours. The solid precipitate was washed with small portions of heated toluene. The fine white toluene insoluble precipitate powder with decomposition heat more than 300 °C weighted 17 mg (16 %). Substance **1** (yield 79 mg (87 %), MP: 154 °C) was isolated from toluene solution.

IR spectrum (ν, cm^{-1}): 3045, 3006, 2949, 2922, 2801, 1608, 1525, 1479, 1444, 1412, 1366, 1329, 1232, 1178, 1122, 1066, 1032, 1006, 945, 878, 817, 797, 744, 703, 609, 524, 485, 438, 412.

For $C_{39}H_{43}N_4O_2Sb$ anal. calcd. (%): C 64.86, H 5.96. Found, %: C 64.80, H 6.07.

Synthesis of bis(acetophenonoximato)tri(o-tolyl)antimony (2).

a) Tri(o-tolyl)antimony (150 mg, 0.40 mmol) was dissolved in diethyl ether (30 mL). Then acetophenonoxime (103 mg, 0.80 mmol) and hydrogen peroxide (43 mg, 30 % aqueous, 0.4 mmol) were added. The solution was left to stand for 24 hours at temperature 20 °C. When the solvent evaporated, solid precipitate was crystallized from toluene. A colorless needle-shaped crystals were obtained; yield 232 mg (87 %), MP: 161 °C.

b) Tri(*o*-tolyl)antimony (150 mg, 0.40 mmol) was dissolved in tetrachloromethane (30 mL). Then acetophenonoxime (103 mg, 0.80 mmol) and *tert*-butyl hydroperoxide (49 mg, 70 % aqueous, 0.40 mmol) were added. The solution was left to stand for 24 hours. When the solvent evaporated, fine-cristalline precipitate was crystallized from toluene to give a colorless crystalline substance (248 mg, 98 %, MP: 162 °C).

c) Tri(*o*-tolyl)antimony (100 mg, 0.25 mmol) was dissolved in diethyl ether (30 mL). Then acetophenonoxime (34 mg, 0.25 mmol) and *tert*-butyl hydroperoxide (32 mg, 70 % aqueous, 0.25 mmol) were added. The solution was left to stand for 24 hours. When the solvent evaporated, fine-cristalline precipitate was crystallized from toluene to give a colorless crystals (248 mg, 98 %, MP: 162 °C). After 24 hours the product was washed with small portions of heated toluene. Fine solid toluene insoluble precipitate powder with decomposition heat more than 300 °C weighted 37 mg (35 %). The substance **2** (yield 75 mg, 90 %, MP: 160 °C) was isolated from toluene solution.

IR spectrum (ν, cm^{-1}): 3053, 3006, 2928, 1588, 1494, 1471, 1442, 1364, 1306, 1280, 1206, 1163, 1121, 1029, 994, 927, 761, 748, 693, 679, 554, 518, 487, 437, 411.

For $C_{37}H_{37}N_2O_2Sb$ anal. calcd. (%): C 66.92, H 5.58. Found, %: C 66.87, H 5.69.

Synthesis of bis(furfuraloximato)tri(*m*-tolyl)antimony (3).

a) Tri(m-tolyl)antimony (100 mg, 0.25 mmol) was dissolved in hexane (15 mL). Then furfuraloxime (56 mg, 0.50 mmol) and *tert*-butyl hydroperoxide (23 mg, 70 % aqueous, 0.25 mmol) were added. The solution was left to stand for 24 hours at temperature 20 °C. When the solvent evaporated, white crystalline substance were obtained. The product yield 153 mg (98 %), MP: 133 °C.

b) Tri(*m*-tolyl)antimony (100 mg, 0.25 mmol) was dissolved in diethyl ether (20 mL). Then furfuraloxime (28 mg, 0.25 mmol) and *tert*-butyl hydroperoxide (23 mg, 70 % aqueous, 0.25 mmol) were added. Obtained solid precipitate was crystallized from toluene to give a white crystals **3** (67 mg (87 %), MP: 134 °C). Amorphous toluene insoluble powder had decomposition heat more than 300 °C.

IR spectrum (ν, cm^{-1}): 3234, 3137, 2910, 2804, 2361, 2343, 1609, 1557, 1526, 1477, 1445, 1428, 1361, 1302, 1225, 1186, 1170, 1126, 1066, 957, 868, 813, 736, 571, 528, 493, 442, 424.

For $C_{31}H_{29}N_2O_4Sb$ anal. calcd. (%): C 60.46, H 4.71. Found, %: C 60.28, H 4.83.

IR spectra were recorded on the Bruker Tensor 27 FT-IR (KBr pellets; 4000–400 cm^{-1}).

The X-ray diffraction analyses of crystalline substances **1**–**3** were made 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 [8]. All calculations for structure determination and refinement were performed using the *SHELXL/PC* programs [9]. The structures **1**, **2** and **3** were determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and refinement results for structures **1**, **2** and **3** are listed in Table 1. The 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 (CCDC 1012010, 1013407, 1009237 for compounds **1**, **2** and **3**, respectively; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Table 1

Crystallographic data and the experimental and structure refinement parameters for compounds 1–3

Parameter	Value		
	1	**2**	**3**
Empirical formula	$C_{39}H_{43}N_4O_2Sb$	$C_{37}H_{37}N_2O_2Sb$	$C_{31}H_{29}N_2O_4Sb$
Formula weight	721.53	663.45	615.32
T, K	298	273	296
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	Cc	P1	Cc
a, Å	14.5074(5)	10.2151(3)	20.8574(6)
b, Å	10.9331(3)	10.4979(4)	10.3011(3)
c, Å	22.7362(7)	15.9822(5)	15.3511(5)
α, deg	90.00	99.295(1)	90.00
β, deg	93.198(1)	102.960(1)	119.721(1)
γ, deg	90.00	91.749(1)	90.00
V, $Å^3$	3600.59(19)	1644.32(9)	2864.36(135
Z	4	2	4
$\rho_{(calcd.)}$, g/cm^3	1.331	1.340	1.427
μ, mm^{-1}	0.804	0.872	1.000
F(000)	1488.0	680.0	1248.0
Crystal size, mm	0.50×0.49×0.22	0.40×0.36×0.23	0.75×0.38×0.13
θ Range of data collection, deg	2.9 – 26.098	2.94 – 26.096	3.06 – 26.44
Range of refraction indices	$-17 \le h \le 17$, $-13 \le k \le 13$, $-28 \le l \le 28$	$-12 \le h \le 12$, $-12 \le k \le 12$, $-19 \le l \le 19$	$-26 \le h \le 26$, $-12 \le k \le 12$, $-19 \le l \le 19$
Measured reflections	47631	50217	18330
Independent reflections	7107	12975	5902
R_{int}	0.0237	0.0211	R_{int} = 0.0216
Refinement variables	422	768	346
GOOF	1.119	1.089	1.122
R factors for $F^2 > 2\sigma(F^2)$	R_1 = 0.0259, wR_2 = 0.0651	R_1 = 0.0268, wR_2 = 0.0673	R_1 = 0.0272, wR_2 = 0.0618
R factors for all reflections	R_1 = 0.0289, wR_2 = 0.0665	R_1 = 0.0306, wR_2 = 0.0702	R_1 = 0.0343, wR_2 = 0.0655
Residual electron density (min/max), $e/Å^3$	0.44/–0.30	0.66/–0.42	0.71/–0.49

Table 2

Selected bond lengths and bond angles in the structures of compounds 1–3

Bond	*d*, Å	Angle	ω, deg
1			
Sb(1)–C(1)	2.1108(17)	O(1)Sb(1)O(4)	168.92(5)
Sb(1)–C(11)	2.119(2)	C(1)Sb(1)C(21)	118.90(12)
Sb(1)–C(21)	2.149(3)	C(11)Sb(1)C(21)	115.04(7)

Table 2 (end)

Bond	*d*, Å	Angle	ω, deg
Sb(1)–O(1)	2.1047(18)	C(1)Sb(1)C(11)	126.02(12)
Sb(1)–O(4)	2.0395(19)	N(1)O(1)Sb(1)	112.93(13)
O(1)–N(1)	1.407(3)	O(1)N(1)C(37)	107.4(2)
O(2)–N(3)	1.361(3)	N(3)O(2)Sb(1)	114.86(15)
N(1)–C(37)	1.246(3)	O(2)N(3)C(47)	117.7(2)
N(3)–C(47)	1.334(4)	C(44)N(4)C(48)	117.8(3)
2			
Sb(1)–C(1)	2.114(3)	O(1)Sb(1)O(2)	172.14(6)
Sb(1)–C(11)	2.106(2)	C(1)Sb(1)C(21)	116.68(10)
Sb(1)–C(21)	2.138(3)	C(11)Sb(1)C(21)	126.22(9)
Sb(1)–O(1)	2.0615(14)	C(1)Sb(1)C(11)	117.09(10)
Sb(1)–O(2)	2.0600(13)	N(1)O(1)Sb(1)	115.31(11)
O(1)–N(1)	1.431(2)	O(1)N(1)C(37)	111.02(17)
O(2)–N(2)	1.384(2)	N(2)O(2)Sb(1)	115.19(12)
N(1)–C(37)	1.326(2)	O(2)N(2)C(47)	116.30(19)
N(2)–C(47)	1.289(3)	O(3)Sb(2)O(4)	174.29(7)
Sb(2)–C(61)	2.131(2)	C(61)Sb(2)C(71)	116.03(10)
Sb(2)–C(71)	2.099(3)	C(61)Sb(2)C(81)	116.33(9)
Sb(2)–C(81)	2.154(3)	C(81)Sb(2)C(71)	127.63(10)
Sb(2)–O(3)	2.1000(17)	N(3)O(3)Sb(2)	113.88 (14)
Sb(2)–O(4)	2.0841(15)	O(3)N(3)C(97)	111.8(2)
O(3)–N(3)	1.393(3)	N(4)O(4)Sb(2)	115.98(13)
O(4)–N(4)	1.351(3)	O(4)N(4)C(107)	113.7(2)
N(3)–C(97)	1.226(3)	N(3)C(97)C(91)	114.0(3)
N(4)–C(107)	1.219(3)	N(3)C(97)C(98)	124.3(3)
3			
Sb(1)–C(1)	2.106(9)	O(1)Sb(1)O(2)	174.30(9)
Sb(1)–C(11)	2.106(3)	C(1)Sb(1)C(21)	112.02(10)
Sb(1)–C(21)	2.110(10)	C(11)Sb(1)C(21)	123.3(5)
Sb(1)–O(1)	2.058(6)	C(1)Sb(1)C(11)	124.6(5)
Sb(1)–O(2)	2.107(7)	C(1)Sb(1)O(1)	84.6(3)
O(1)–N(1)	1.358(13)	N(1)O(1)Sb(1)	110.3(6)
O(2)–N(2)	1.374(11)	O(1)N(1)C(37)	117.9(10)
N(1)–C(31)	1.310(14)	N(2)O(2)Sb(1)	109.2(6)
N(2)–C(36)	1.241(15)	O(2)N(2)C(47)	107.4(8)

Results and Discussion

The reactions of tri(*o*-tolyl)antimony with 4-N,N-dimethylbenzaldoxime and acetophenonoxime have been investigated in the present study. The variable factors: the oxidizing agent (hydrogen peroxide or *tert*-butylhydroperoxide), solvent (diethyl ether, heptane, carbon tetrachloride), the molar ratio of the reactants (1:2:1 or 1:1:1). It has been found that the interaction of tri(*o*-tolyl)antimony with oximes at the molar ratio 1:2:1, irrespective of the oxidizing agent nature (hydrogen peroxide or *tert*-butyl hydroperoxide), proceeds as the oxidative addition reaction with the formation of high-yield tri(*o*-tolyl)antimony dioximates.

$$o\text{-Tol}_3\text{Sb} + 2\ \text{HON=CRR'} + \text{R''OOH} \rightarrow o\text{-Tol}_3\text{Sb(ON=CRR')}_2 + \text{R''OOH} + \text{H}_2\text{O}$$

R = H, R' = $C_6H_4N(CH_3)_2$ (**1**); R = Me, R' = Ph (**2**); R'' = H or *t*-Bu.

Tri(*o*-tolyl)antimony dioximates **1** and **2** are crystalline substances which are resistant to the effect of moisture and air oxygen, they are freely soluble in aromatic and aliphatic hydrocarbons. It has been found that the solvent nature does not affect the yield, which remains consistently high.

Previously it was shown that the oxidative addition reaction of triphenyl- or tri(*p*-tolyl)antimony and oxime at the molar ratio 1:1 led to the binuclear organoantimony compound with the bridging oxygen atom of the general formula $(Ar_3SbONCRR')_2O$ [3].

We have found that the reaction of tri(*o*-tolyl)antimony and 4-N,N-dimethylbenzaldoxime or acetophenone oxime in the presence of hydrogen peroxide or *tert*-butyl hydroperoxide at the molar ratio 1:1:1 leads to the formation of the mixture of products: tri(*o*-tolyl)antimony dioximate and tri(*o*-tolyl)antimony oxide with a polymeric structure.

$$o\text{-Tol}_3Sb + HON{=}CRR' + R''OOH \rightarrow o\text{-Tol}_3Sb(ON{=}CRR')_2 + o\text{-Tol}_3SbO + 2\ R''OOH + H_2O$$

R = H, R' = $C_6H_4N(CH_3)_2$ (**1**); R = Me, R' = Ph (**2**); R'' = H или *t*-Bu.

The interaction of tri(*m*-tolyl)antimony and furfuraldoxime at the molar ratios of 1:2:1 and 1:1:1 in the presence of hydrogen peroxide in diethyl ether results in the formation of μ_2-oxo-*bis* [(furfuraldoximato)tri(*m*-tolyl)antimony] with the melting point 235 °C.

$$2\ m\text{-Tol}_3Sb + 2\ HON{=}CHC_4H_3O + 2\ H_2O_2 \rightarrow (m\text{-Tol}_3SbON{=}CHC_4H_3O)_2O + 3\ H_2O$$

At the ratio of tri(*m*-tolyl)antimony to oxime to hydrogen peroxide of 1:2:1 (mol.) an oxime is in excess. Therefore, the fixed residue is the mixture of an organoantimony compound and unreacted oxime. After separation of the mixture by fractional recrystallization method, the desired product yield inevitably decreases, it turns out lower than the yied at the molar ratio 1:1:1 (75 % and 96 % respectively).

But in the presence of *tert*-butyl hydroperoxide, irrespective of the mole ratio of the reactants, *bis*(furfuraldoximato)tri(*m*-tolyl)antimony (**3**) is obtained.

$$m\text{-Tol}_3Sb + 2\ HON{=}CHC_4H_3O + t\text{-BuOOH} \rightarrow m\text{-Tol}_3Sb(ON{=}CHC_4H_3O)_2 + t\text{-BuOH} + H_2O$$

At the molar ratio 1:2:1, the yield is 90–98 %, irrespective of the solvent (diethyl ether, hexane, carbon tetrachloride).

Decrease of the oxime concentration (1: 1: 1 mol.) is followed by the formation of high melting co-product, which, we believe, is the polymeric oxide of tri(*m*-tolyl)antimony $[(m\text{-Tol})_3SbO]_n$.

Triarylantimony dioximates have been identified by infrared spectroscopy and X-ray analysis.

The molecules of all compounds contain the same structure fragments, so their IR spectra are similar to each other. The presence of three aryl fragments in this organoantimony compounds does complicate determination of characteristic bands belonging to the stretching vibrations of C=N and N–O, which are detected in oximes at intervals 1685–1650 and 960–930 cm^{-1}, respectively, because it is the area which contains aryl groups vibrational bands [10, 11].

To assign the absorption bands in the IR spectra of triarylantimony dioximates, we have obtained spectra of oximes, which have been used for synthesis. The absorption bands with frequencies at intervals of 3650–3500 cm^{-1} (OH-groups), 1568–1643 cm^{-1} (C=N bonds), 926–968 cm^{-1} (N–O bonds) have been found in the IR spectra of oximes.

The spectra of the compounds contain the intensive absorption band at 440 cm^{-1}, which, according to the literature, refers to vibrations of SbC_3 fragment, having C_3 symmetry [12]. The absorption bands at 410–425 cm^{-1} characterize the vibrations of the Sb–O [13].

The stretching vibrations of C = N bonds in triarylantimony dioximates (1608, 1588, 1557 cm^{-1} in **1**, **2** and **3**, respectively) slightly shift to the low frequency region of the spectrum compared to the same absorption band in the corresponding oximes.

The absorption band, characterizing N–O bonds vibrations, also shifts to the low frequency region of the spectrum (945, 927, 957 cm^{-1} in **1**, **2** and **3** respectively). This indicates, it seems, that the C=N and N–O bond lengths in triarylantimony dioximates increase compared to oximes.

According to X-ray diffraction data, the molecules of compounds **1**, **2** (the crystal contains two types of crystallographically independent molecules ***a*** and ***b***) and **3**, the antimony atoms have trigonal-bipyramidal coordination with the oximate ligands oxygen atoms in axial positions (Fig. 1–3).

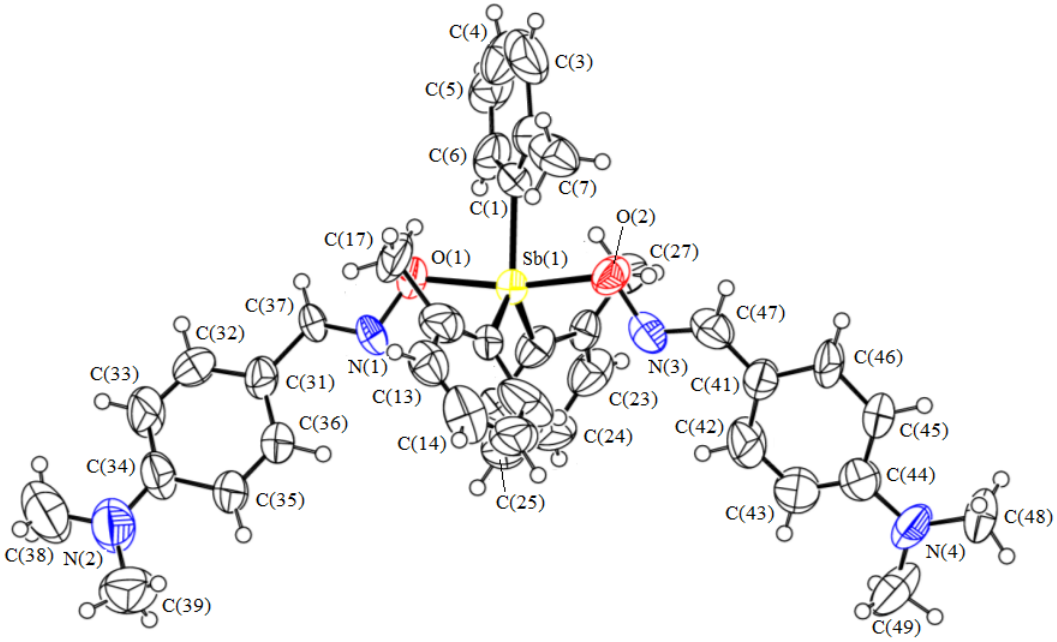

Fig. 1. The structure of compound 1

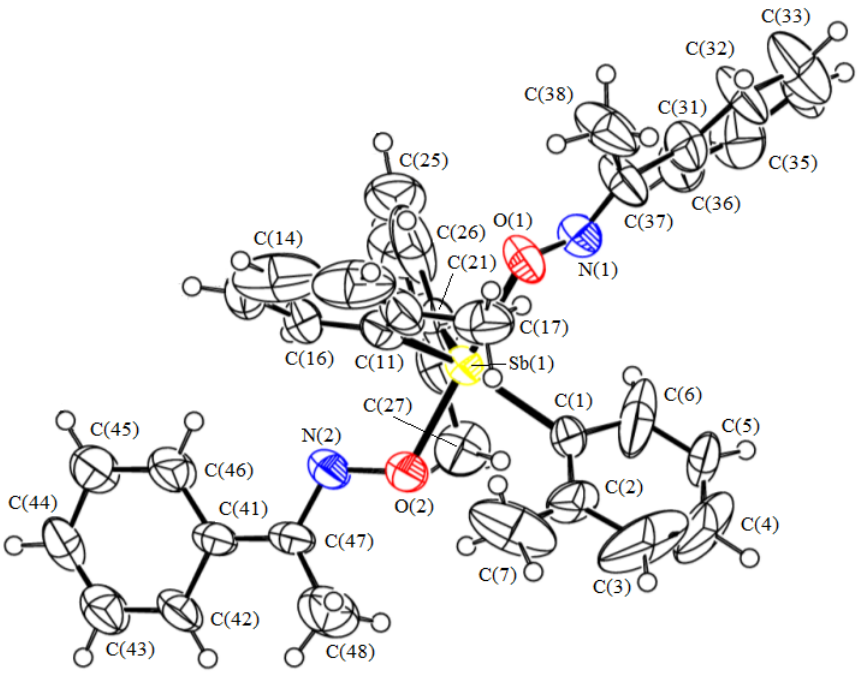

Fig. 2. The structure of compound 2 (molecule a)

The sum of $C_{eq}SbC_{eq}$ bond angles is equal to 360° (within experimental error), at that the values of the individual angles differ from the theoretical angle not more than 8º. The axial OSbO angles are equal to 168.92(5)º (**1**), 172.14(6)° (**2** ***a***), 174.29(7)° (**2** ***b***), 174.30(9)º (**3**). The SbC_3 fragments are almost flat. Antimony atoms are deflected from the C_3 plane through 0.024, 0.007, 0.008, 0.010 Å in **1, 2** ***a***, **2** ***b***, **3** respectively. The OSbC angles vary within the ranges 83.55(11)º–96.07(9)º (**1**), 83.74(7)º–94.55(7)° (**2** ***a***), 83.95(8)º–993.71(9)° (**2** ***b***), 84.6(3)º–93.5(5)º (**3**).

The Sb–C bond intervals are 2.111(2)–2.149(3) Å (the mean value is 2.126(3) Å) (**1**), 2.106(2)–2.138(3) Å (2.119(3) Å) (**2** ***a***), 2.099(3)–2.154(3) Å (2.129(3) Å) (**2** ***b***, 2.106(3)–2110(10) Å (2.107(9) Å) (**3**). Sb–O bond lengths are equal to 2.039(2), 2.105(2) Å (**1**), 2.060(1), 2.061(1) Å (**2** ***a***),

2.084(2), 2.100(2) Å (**2** ***b***), 2.058(6), 2.107(7) Å (**3**). It may be noted that Sb–O distances are significantly different in the molecules (except of molecule **2** ***a***). The average equatorial bond lengths in all the molecules are greater than the average axial bond lengths.

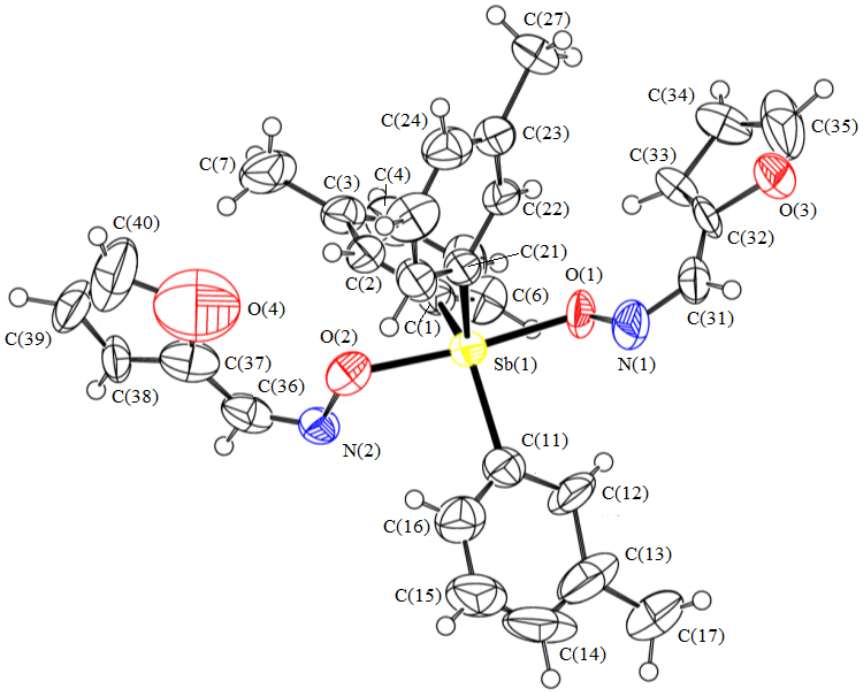

Fig. 3. The structure of compound 3

There are intramolecular contacts between Sb atom and N atoms of oxime groups in molecules **1–3**. The Sb···N distances are 2.952(2), 2.889(2) Å (**1**), 2.970(1), 2.931(2) Å (**2** ***a***), 2.952(2), 2.939(2) Å (**2** ***b***), 2.83(1), 2.87(1) Å (**3**) and considerably less than the sum of Van der Waals radiuses of Sb and N atoms (3.8 Å [14]). Obviously, there is no correlation between Sb–O bond lengths and strength of Sb···N contacts. Decrease of Sb···N distances does not result in the expected N–O bond lengthening [(1.407(3), 1.361(3) Å (**1**), 1.431(2), 1.384(2) Å (**2** ***a***), 1.393(3), 1.351(3) Å (**2** ***б***), 1.358(13), 1.374(11) Å (**3**)], however, it causes a reduction of NOSb valence angles. Thus, in molecule **3**, which has the shortest Sb···N distances, these angles are equal to 109.2(6)º and 110.3(6)º, whereas in molecules **1**, **2** this angles are changed in the range of 112.9(1)º–116.0(1)º.

Note that heteroatoms do not participate in the crystal-packing formation of molecules **1–3**. The structure is formed due to C–H···π intermolecular interactions.

Conclusions

It has been found that the oxidative addition reaction of tri(*o*-tolyl)antimony and 4-N,N-dimethylbenzaldoxime and acetophenonoxime proceed with the formation of tri(*o*-tolyl)antimony dioximates irrespective of the oxidizing agent nature and the molar ratio of the reactants. The direction of the similar reaction of tri(*m*-tolyl)antimony with furfuraldoxime is determined by the type of an oxidizing agent.

Bis[4-N,N(dimethylamino)benzaldoximato]tri(*o*-tolyl)antimony, *bis*(acetophenonoximato)tri(*o*-tolyl)antimony and *bis*(furfuraloximato)tri(*m*-tolyl)antimony molecules have close geometrical parameters. The peculiarity of trigonal bipyramidal polyhedron of antimony atoms is that the equatorial substituents are farther from it than axial ones. The significant reduction of intramolecular distances Sb···N, which we have observed, does not cause significant distortion of bond angles at the central atom, which are close to the theoretical values.

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РЕАКЦИИ ТРИ(*ОРТО*-ТОЛИЛ)- И ТРИ(*МЕТА*-ТОЛИЛ)СУРЬМЫ С ОКСИМАМИ В ПРИСУТСТВИИ ОКИСЛИТЕЛЯ. СТРОЕНИЕ ДИОКСИМАТОВ ТРИ(*ОРТО*-ТОЛИЛ)- И ТРИ(*МЕТА*-ТОЛИЛ)СУРЬМЫ

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Взаимодействием три-*орто*-толил- или три-*мета*-толилсурьмы с оксимами в присутствии *трет*-бутилгидропероксида или пероксида водорода синтезированы диоксиматы триарилсурьмы (o-$CH_3C_6H_4)_3Sb(ON{=}CHC_6H_4N(CH_3)_2$-4)$_2$ (**1**), (o-$CH_3C_6H_4)_3Sb(ON{=}CMePh)_2$ (**2**), (m-$CH_3C_6H_4)_3Sb(ON{=}CHC_4H_3O)_2$ (**3**). По данным РСА, в молекулах **1–3** атомы сурьмы имеют искаженную тригонально-бипирамидальную координацию с атомами кислорода оксиматных лигандов в аксиальных положениях. Особенностью структур является наличие коротких внутримолекулярных расстояний Sb···N, которые примерно на 1 Å меньше суммы ван-дер-ваальсовых радиусов.

Ключевые слова: три-орто-толилсурьма, три-мета-толилсурьма, оксимы, трет-бутилгидропероксид, пероксид водорода, окисление, бис(4-диметиламино-бензальдоксимато)три-орто-толилсурьма, бис(ацетофенонoксимато)три-орто-толилсурьма, бис(фурфуальдоксимато)три(мета-толил)сурьма, молекулярные структуры, рентгеноструктурный анализ.

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БИБЛИОГРАФИЧЕСКОЕ ОПИСАНИЕ СТАТЬИ

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