

THE PECULIARITIES OF TRI(*O*-TOLYL)ANTIMONY AND TRI(*M*-TOLYL)-ANTIMONY REACTIONS WITH 2-HYDROXYBENZALDOXIME. THE MOLECULAR STRUCTURES OF TRI(*O*-TOLYL)ANTIMONY *BIS*(2-HYDROXYBENZALDOXIMATE) AND *BIS*(μ_3 -2-HYDROXYBENZALDOXIMATO-*O,O',N*)-(μ_2 -OXO)-*BIS*[DI(*M*-TOLYL)ANTIMONY]

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Tri(*o*-tolyl)antimony *bis*(2-hydroxybenzaldoximate) (1) and *bis*(μ_3 -2-hydroxybenzaldoximato-*O,O',N*)-(μ_2 -oxo)-*bis*[di(*m*-tolyl)antimony] (2) were obtained by interaction of tri(*o*-tolyl)antimony and tri(*m*-tolyl)antimony with 2-hydroxybenzaldoxime in the presence of an oxidizing agent (hydrogen peroxide or *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 two types of crystallographically independent molecules 1 *a*, *b*. In the binuclear complex 2 antimony atoms are connected by two tridentate bridging ligands and an the oxygen atom; they have the deformed octahedral coordination with C₂O₃N surroundings.

Keywords: tri(*o*-tolyl)antimony, tri(*m*-tolyl)antimony, 2-hydroxybenzaldoxime, *tert*-butylhydroperoxide, hydrogen peroxide, tri(*o*-tolyl)-antimony *bis*(2-hydroxybenzaldoximate), *bis*(μ_3 -2-hydroxybenzaldoximato-*O,O',N*)-(μ_2 -oxo)-*bis*[di(*m*-tolyl)-antimony], molecular structures, X-ray analysis.

Introduction

Oximes are known as amplydentate ligands in the chemistry of coordination compounds. A number of articles are dedicated to exploration of synthesis and structures of organic antimony complexes with oximeligands [1–11]. It has been found that the product of oxidative addition reaction between triarilantimony and oximes is either Ar₃SbX₂ and/or (Ar₃SbX)₂O (Ar = Ph, *p*-Tol, *o*-Tol; X = ONCHR, ONCRR') depending on oxime nature and reaction conditions [6–11]. According to X-ray data analysis, ligand X is characterized by forming only one bond with the antimony atom through an oxygen atom, such molecules have decreased distance between antimony atom and iminoxyl group nitrogen atom, but it doesn't significantly affect trigonal-bipyramidal coordination of the central atom. At the same time, furfuraloxime ligands are bidentate bridging ligands in the molecule of *bis*(μ_2 -furfuraloximato)-(μ_2 -oxo)-*bis*[triphenylantimony]. These ligands are coordinated by an oxygen atom to the first antimony atom and by a nitrogen atom to the second antimony atom. This fact increases antimony coordination number to six [12]. However, the molecule of μ_2 -oxo-*bis*[(furfuraloximato) tri(*o*-tolyl)antimony] is of the regular molecular structure type which includes monodentate ligands [11]. These examples testify that the structure of *bis*[(furfuraloximato) tri(*o*-tolyl)antimony] oxides depends on aryl radical nature.

Systematic investigating oxidative addition reactions of triarilantimony with oximes and molecular structures of the product is of some interest. The present paper studies the reactions of tri(*o*-tolyl)- and tri(*m*-tolyl)antimony with 2-hydroxybenzaldoxime in the presence of hydrogen peroxide or *tert*-butyl hydroperoxide and establishes molecular structures of reaction products.

Experimental

Synthesis of tri(*o*-tolyl)antimony *bis*(2-hydroxybenzaldoximate) (1). Tri(*o*-tolyl)antimony (150 mg, 0.38 mmol) was dissolved in hexane (10 mL). Then 2-hydroxybenzaldoxime (52 mg, 0.38 mmol)

and *tert*-butylhydroperoxide (43 mg, 70 % aqueous, 0.38 mmol) were added. The solution was left at temperature 20 °C to stand for 24 hours. The precipitate was washed with small portions of ether and dried. The product was a colourless transparent crystalline substance **1**; yield 241 mg (95 %), mp: 173 °C.

IR spectrum (ν , cm^{-1}): 3421, 3053, 3006, 2972, 2925, 1617, 1595, 1562, 1488, 1445, 1381, 1333, 1310, 1266, 1238, 1194, 1152, 1112, 1031, 1000, 945, 905, 795, 748, 700, 662, 545, 475, 439, 422.

For $\text{C}_{35}\text{H}_{36}\text{N}_2\text{O}_4\text{Sb}$ anal. calcd. (%): C 62.69, H 5.37. Found (%): C 62.57, H 5.48.

Synthesis of bis(μ_3 -2-hydroxybenzaldoximato-O,O',N)-(μ_2 -oxo)-bis[di(*m*-tolyl)antimony] solvate with toluene (2**).** Tri(*m*-tolyl)antimony (150 mg, 0.38 mmol) was dissolved in ether (10 mL). Then salicylaldehyde oxime (52 mg, 0.38 mmol) and hydrogen peroxide (43 mg, 30 % aqueous, 0.38 mmol) were added. The solution was left at temperature of 20 °C to stand for 24 hours. The precipitate was washed with small portions of ether and dried. The product yield was 121 mg (71 %). After toluene recrystallization a colourless transparent crystalline substance **2** was obtained; mp: 240 °C.

IR spectrum (ν , cm^{-1}): 3049, 3026, 2918, 2361, 2342, 1597, 1555, 1476, 1440, 1320, 1273, 1252, 1200, 1122, 1100, 1044, 1027, 992, 952, 916, 815, 777, 759, 733, 704, 692, 663, 618, 598, 518, 511, 453, 426.

For $\text{C}_{49}\text{H}_{46}\text{N}_2\text{O}_5\text{Sb}_2$ anal. calcd. (%): C 59.63, H 4.66. Found (%): 59.47, H 4.75.

IR spectra were recorded on the Bruker Tensor 27 FT-IR spectrometer (pellets with KBr).

X-ray diffraction of crystal **1** was carried out on the diffractometer *Bruker AXS Smart Apex* (Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$, graphite monochromator). Collection, data editing and refinement of the unit cell parameters, and the accounting for absorption were conducted with the use of programs *SMART* and *SAINT-Plus* [13]. All calculations for structure determination and refinement were carried out by the program *SHELXL/PC* [14]. Structure **1** was 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 structure refinement are given in Table 1, the main bond lengths and angles are in Table 2. Atomic coordinates and their isotropic equivalent temperature factors are given in Table 3.

Table 1

Crystallographic data, parameters of X-ray diffraction experiment, and refinement details for the structures of substances 1–2

Parameter	Compound	
	1	2
Crystal system	Triclinic	Triclinic
Space group	P 1	P 1
<i>a</i> , Å	11.5082(4)	10.7997(3)
<i>b</i> , Å	11.9666(3)	11.8171(4)
<i>c</i> , Å	13.3321(4)	17.5720(5)
α , deg	97.028(1)	97.474(1)
β , deg	111.508(1)	98.084(1)
γ , deg	107.117(1)	95.415(1)
<i>V</i> , Å ³	1576.82(8)	2186.86(11)
<i>Z</i>	2	2
ρ_{calcd} , g/cm ³	1.406	1.496
μ , mm ⁻¹	0.915	1.283
<i>F</i> (000)	680.0	990.0
Crystal shape (size, mm)	0.22×0.20×0.18	0.35×0.27×0.18
θ Data collection range, deg	2.94–26.07	3.24–26.16
Refraction index ranges	–14 ≤ <i>h</i> ≤ 14, –14 ≤ <i>k</i> ≤ 14, –16 ≤ <i>l</i> ≤ 16	–13 ≤ <i>h</i> ≤ 13, –14 ≤ <i>k</i> ≤ 14, –21 ≤ <i>l</i> ≤ 21
Measured reflections	35358	54142
Independent reflections	12530	8746
<i>R</i> _{int}	0.0456	0.0506
Refinement variables	767	521
<i>GOOF</i>	1.044	1.032
<i>R</i> factors for $F^2 > 2\sigma(F^2)$	<i>R</i> ₁ = 0.0368, <i>wR</i> ₂ = 0.0711	<i>R</i> ₁ = 0.0300, <i>wR</i> ₂ = 0.0686
<i>R</i> factors for all reflections	<i>R</i> ₁ = 0.0593, <i>wR</i> ₂ = 0.0782	<i>R</i> ₁ = 0.0458, <i>wR</i> ₂ = 0.0753
Residual electron density (min/max), e/Å ³	0.51/–0.31	0.82/–0.56

Table 2

Selected bond lengths and bond angles in the structures of substances 1–2

Bond	<i>d</i> , Å	Angle	ω , град.	Bond	<i>d</i> , Å	Angle	ω , град.
1				2			
Sb(1)–C(1)	2.152(13)	O(1)Sb(1)O(2)	173.5(4)	Sb(1)–C(1)	2.129(3)	O(1)Sb(1)O(2)	162.86(9)
Sb(1)–C(11)	2.079(13)	C(1)Sb(1)C(21)	115.4(7)	Sb(1)–C(11)	2.123(3)	O(3)Sb(1)C(1)	167.61(11)
Sb(1)–C(21)	2.21(2)	C(11)Sb(1)C(21)	128.2(7)	Sb(1)–O(1)	1.950(2)	C(11)Sb(1)N(1)	165.27(11)
Sb(1)–O(1)	2.076(9)	C(1)Sb(1)C(11)	116.1(5)	Sb(1)–O(2)	2.014(2)	C(1)Sb(1)C(11)	105.07(13)
Sb(1)–O(2)	2.086(10)	N(1)O(1)Sb(1)	116.0(7)	Sb(1)–O(3)	2.094(2)	O(1)Sb(1)O(3)	85.07(13)
O(1)–N(1)	1.419(15)	O(1)N(1)C(37)	115.6(11)	Sb(1)–N(1)	2.276(3)	O(2)Sb(1)O(3)	82.45(9)
O(2)–N(2)	1.320(15)	N(2)O(2)Sb(1)	121.5(8)	O(4)–N(1)	1.374(3)	O(1)Sb(1)C(1)	94.67(11)
N(1)–C(37)	1.259(17)	O(2)N(2)C(47)	112.8(10)	N(1)–C(27)	1.277(4)	O(5)Sb(2)C(41)	94.33(11)
N(2)–C(47)	1.287(14)	O(5)Sb(2)O(6)	172.1(4)	Sb(2)–C(31)	2.128(3)	O(5)Sb(2)O(4)	83.73(9)
Sb(2)–C(51)	2.090(10)	C(51)Sb(2)C(61)	116.2(5)	Sb(2)–C(41)	2.137(3)	C(31)Sb(2)C(41)	103.04(12)
Sb(2)–C(61)	2.139(10)	C(51)Sb(2)C(71)	122.1(4)	Sb(2)–O(1)	1.959(2)	O(1)Sb(2)C(41)	93.38(11)
Sb(1)–C(71)	2.075(7)	C(61)Sb(2)C(71)	121.8(4)	Sb(1)–O(5)	2.023(2)	Sb(1)O(1)Sb(2)	119.25(10)
Sb(2)–O(5)	2.057(10)	N(3)O(5)Sb(2)	121.7(8)	Sb(1)–O(4)	2.098(2)	N(1)O(4)Sb(2)	113.85(16)
Sb(2)–O(6)	2.079(10)	O(5)N(3)C(87)	111.3(11)	Sb(2)–N(2)	2.256(2)	N(2)O(3)Sb(1)	114.55(16)
O(5)–N(3)	1.430(14)	N(4)O(6)Sb(2)	113.4(7)	O(3)–N(2)	1.374(3)	O(4)N(1)C(27)	115.5(3)
O(6)–N(4)	1.341(16)	O(6)N(4)C(97)	113.2(10)	N(2)–C(57)	1.282(4)	O(3)N(2)C(57)	115.7(2)
N(3)–C(87)	1.283(14)						
N(4)–C(97)	1.267(16)						

Table 3

Atomic coordinates ($\times 10^4$) and isotropic equivalent thermal factors ($\text{Å}^2 \times 10^3$) in the structures of substances 1–2

1					2				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)	Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
Sb(1)	3851.2(2)	790.3(2)	2105.7(2)	44.1(2)	Sb(1)	82.30(18)	2619.31(18)	1933.21(12)	30.04(7)
Sb(2)	6406.7(2)	-676.2(2)	-2060.2(2)	44.7(2)	Sb(2)	2500.48(17)	4195.98(17)	3156.62(11)	28.25(7)
O(1)	4755(8)	1947(9)	3696(7)	55(3)	O(2)	-1600(2)	3003(2)	1446.1(14)	41.8(6)
O(3)	1612(10)	1898(9)	4273(10)	77(3)	O(3)	-413.3(19)	3518.4(19)	2932.6(13)	36.2(5)
O(7)	8246(11)	3840(8)	-128(10)	84(3)	N(2)	491(2)	4370(2)	3324.6(15)	31.1(6)
C(61)	6541(12)	-2141(9)	-1308(11)	42(3)	C(41)	2757(3)	3446(3)	4202.5(18)	32.0(7)
N(1)	3879(11)	2266(10)	4094(10)	51(3)	C(42)	2209(3)	2340(3)	4217(2)	38.7(8)
C(51)	8102(11)	303(11)	-2262(11)	44(3)	C(43)	2366(4)	1839(3)	4894(2)	44.9(9)
C(1)	2083(13)	-200(11)	2292(10)	50(3)	C(44)	3090(4)	2475(4)	5550(2)	53.2(10)
C(6)	899(14)	-345(12)	1434(10)	55(4)	C(45)	3646(4)	3561(4)	5544(2)	53.4(10)
C(5)	-289(13)	-952(11)	1436(11)	74(4)	C(46)	3474(3)	4057(3)	4872(2)	43.8(8)
C(4)	-164(16)	-1423(14)	2342(16)	84(5)	C(47)	1731(5)	652(4)	4901(3)	79.7(15)
C(3)	902(12)	-1324(11)	3166(11)	63(4)	O(5)	2783(2)	5831.0(19)	3711.7(14)	39.5(5)
C(2)	2140(13)	-695(10)	3226(9)	47(3)	C(52)	2196(3)	6329(3)	4269.2(19)	34.3(7)
C(7)	3336(14)	-606(13)	4102(11)	75(5)	C(51)	921(3)	6035(3)	4318.2(19)	35.3(7)
O(2)	2972(11)	-196(9)	441(9)	63(3)	C(56)	384(4)	6663(3)	4898(2)	43.0(8)
N(2)	2412(12)	-1388(11)	149(10)	54(3)	C(55)	1078(4)	7523(3)	5424(2)	52.1(10)
C(47)	1539(12)	-1813(10)	-876(11)	56(4)	C(54)	2336(4)	7789(3)	5385(2)	50.3(9)
C(41)	827(14)	-3124(13)	-1390(13)	65(4)	C(53)	2887(3)	7202(3)	4812(2)	43.5(8)
C(42)	992(15)	-4054(12)	-923(12)	61(4)	C(57)	111(3)	5113(3)	3812.1(19)	35.2(7)
C(43)	303(15)	-5239(12)	-1368(18)	94(5)	O(4)	1853.6(19)	4964.7(19)	2187.4(13)	36.9(5)
C(44)	-660(20)	-5501(15)	-2510(20)	114(8)	N(1)	701(2)	4466(2)	1793.6(15)	31.5(6)
C(45)	-1005(17)	-4640(14)	-3161(16)	85(4)	C(27)	134(3)	5068(3)	1332.5(19)	35.8(7)
C(46)	-135(15)	-3438(12)	-2479(13)	72(4)	C(21)	-1073(3)	4686(3)	842.7(19)	37.9(8)
O(4)	1879(13)	-3715(11)	157(10)	114(4)	C(22)	-1478(3)	5366(3)	283(2)	47.7(9)
C(37)	4435(14)	3156(12)	4936(12)	67(4)	C(23)	-2609(4)	5079(4)	-206(2)	61.9(12)
C(31)	3651(13)	3542(12)	5476(12)	49(3)	C(24)	-3366(4)	4118(4)	-129(3)	69.2(13)
C(36)	4242(19)	4549(14)	6332(17)	85(5)	C(25)	-3003(4)	3431(4)	419(2)	57.6(11)
C(35)	3688(19)	4930(16)	6929(16)	102(6)	C(26)	-1852(3)	3701(3)	913(2)	39.8(8)
C(34)	2280(20)	4300(17)	6520(16)	108(6)	C(31)	4344(3)	4356(3)	2855.5(18)	31.3(7)

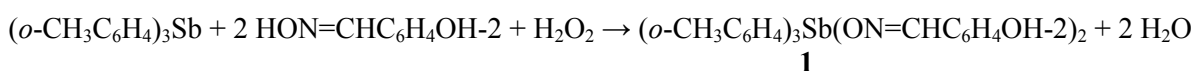
1					2				
Atom	x	y	z	U(eq)	Atom	x	y	z	U(eq)
C(33)	1664(15)	3311(13)	5616(14)	85(5)	C(36)	5206(3)	3688(3)	3173(2)	45.1(9)
C(32)	2399(14)	2921(11)	5134(9)	57(4)	C(35)	6437(3)	3815(4)	3021(2)	53.6(10)
C(11)	3742(12)	2195(11)	1344(11)	47(3)	C(34)	6794(3)	4614(4)	2572(2)	47.9(9)
C(16)	3003(13)	2807(11)	1575(11)	60(4)	C(33)	5953(3)	5304(3)	2258(2)	40.0(8)
C(15)	2781(13)	3730(12)	1104(11)	71(4)	C(32)	4710(3)	5153(3)	2398.6(19)	36.1(7)
C(14)	3379(17)	4023(15)	374(16)	84(5)	C(37)	6368(4)	6191(4)	1778(3)	64.6(12)
C(13)	4113(15)	3428(13)	156(14)	70(5)	O(1)	1775.6(19)	2738.2(18)	2517.4(12)	32.0(5)
C(12)	4258(12)	2483(10)	628(11)	47(3)	C(11)	-734(3)	1105(3)	2286.4(19)	37.6(8)
C(17)	5039(15)	1867(14)	263(13)	78(4)	C(12)	40(4)	288(3)	2498(2)	43.8(8)
C(52)	8116(11)	786(11)	-3077(10)	61(4)	C(13)	-448(5)	-705(3)	2747(2)	58.7(11)
C(53)	9341(14)	1460(10)	-3128(12)	68(4)	C(14)	-1718(5)	-849(4)	2785(3)	70.7(14)
C(54)	10606(14)	1623(14)	-2260(14)	58(3)	C(15)	-2491(4)	-48(4)	2577(3)	70.9(14)
C(57)	6827(13)	676(12)	-4135(9)	69(4)	C(16)	-2009(4)	943(4)	2325(3)	55.2(10)
O(5)	7237(10)	304(9)	-425(8)	55(3)	C(17)	378(6)	-1609(4)	2967(4)	97.0(19)
N(3)	7904(11)	1590(9)	-101(11)	53(3)	C(1)	633(3)	2063(3)	841.7(19)	36.8(7)
C(81)	9506(13)	3216(10)	1508(11)	48(3)	C(6)	-259(4)	1619(3)	203(2)	50.8(9)
C(86)	10473(15)	3597(13)	2605(13)	80(5)	C(5)	118(5)	1262(4)	-504(2)	66.1(12)
O(6)	5482(10)	-1874(9)	-3635(9)	62(3)	C(4)	1363(5)	1331(4)	-571(2)	64.7(12)
N(4)	6351(11)	-2127(10)	-3987(10)	51(3)	C(3)	2268(4)	1766(4)	52(3)	57.6(11)
C(97)	5788(13)	-3002(11)	-4853(10)	52(3)	C(2)	1899(3)	2127(3)	762(2)	45.5(9)
C(91)	6484(14)	-3404(11)	-5377(12)	61(4)	C(7)	3650(5)	1849(6)	-30(3)	101(2)
C(92)	7986(12)	-2766(11)	-5056(12)	61(4)	C(1E)	3505(14)	-543(17)	1567(16)	264(10)
O(8)	8635(10)	-1753(8)	-4224(10)	65(3)	C(1C)	3866(12)	98(18)	2370(11)	234(11)
C(93)	8595(15)	-3200(15)	-5659(15)	82(5)	C(1T)	3955(7)	-1606(6)	2941(7)	140(4)
C(94)	7850(20)	-4226(14)	-6536(14)	96(6)	C(1Q)	4290(8)	-542(8)	3510(9)	204(6)
C(95)	6570(20)	-4829(16)	-6804(16)	124(7)	C(1R)	4186(11)	356(8)	3255(16)	351(15)
C(96)	5810(20)	-4436(17)	-6312(16)	83(5)	C(1U)	3592(12)	-1750(12)	2144(9)	192(6)
C(62)	5951(13)	-2409(12)	-529(11)	54(3)					
C(67)	5112(14)	-1761(12)	-280(13)	64(4)					
C(63)	6217(15)	-3338(12)	-50(12)	59(4)					
C(64)	6928(12)	-3981(12)	-305(14)	62(4)					
C(65)	7454(14)	-3711(11)	-1048(13)	70(5)					
C(66)	7277(11)	-2803(11)	-1566(12)	50(3)					
C(77)	3013(13)	-2405(11)	-3188(13)	124(5)					
C(55)	10556(12)	1072(11)	-1428(11)	73(5)					
C(56)	9348(15)	420(14)	-1393(13)	62(4)					
C(72)	3429(10)	-1117(11)	-3017(10)	72(3)					
C(76)	4750(8)	954(6)	-2560(6)	53.3(19)					
C(27)	7141(14)	1890(20)	3138(12)	175(12)					
C(71)	4690(9)	-256(7)	-2559(7)	39.2(19)					
C(22)	6440(40)	650(30)	2902(17)	250(20)					
C(21)	5480(15)	60(30)	2602(14)	155(9)					
C(75)	3630(30)	1400(18)	-2961(15)	152(10)					
C(24)	7340(20)	-618(14)	3251(16)	122(7)					
C(26)	4712(12)	-1502(16)	2378(7)	132(5)					
C(84)	11010(20)	5662(16)	2587(19)	100(5)					
C(83)	10080(20)	5289(15)	1580(18)	97(5)					
C(82)	9256(16)	4052(14)	892(17)	87(5)					
C(87)	8716(14)	1970(12)	939(10)	55(4)					
C(25)	6050(30)	-1560(30)	2738(18)	237(18)					
C(85)	11133(18)	4821(16)	3025(16)	100(6)					
C(73)	2216(18)	-900(20)	-3385(19)	160(11)					
C(74)	2630(30)	280(30)	-3210(20)	194(17)					
C(23)	8000(20)	520(30)	3437(18)	139(9)					

Results and Discussion

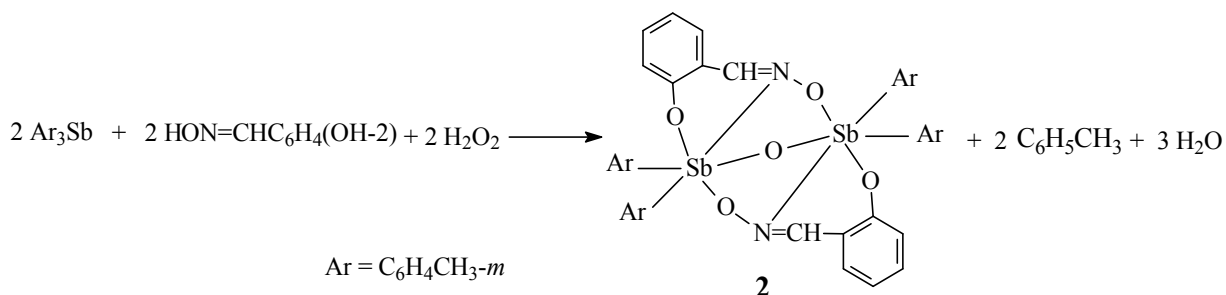
Previously it has been found that the interaction of triphenylantimony with 2-hydroxybenzaloxime, having two functional groups containing mobile hydrogen atoms, in the presence of hydrogen peroxide (1:2:1 mol, diethyl ether) proceeds with the participation of oxime group and the formation of triphenylantimonybis(2-hydroxybenzaloximate) (95 %) [7]. The antimony atom in the molecule of the complex is bound to the ligand *via* an oxygen atom (Sb–O 2.0768(11) Å), the intramolecular distances Sb···N are equal to 2.882(14) Å, the oximate ligand aromatic ring hydroxy groups are involved in the formation of intramolecular O–H···N hydrogen bonds.

To study the possible ways of 2-hydroxybenzaloxime coordination we investigated its interaction with tri(*o*-tolyl) and tri(*m*-tolyl) antimony in the presence of an oxidizing agent. The structures of the obtained products were determined by IR spectroscopy and X-ray diffraction analysis.

The reactions of tri(*o*-tolyl)antimony with 2-hydroxybenzaloxime, going at room temperature in diethyl ether in the presence of 30 % aqueous hydrogen peroxide solution or in heptane in the presence of *tert*-butylhydroperoxide, resulted in the formation of tri(*o*-tolyl)antimony dioximates, as in the case of triphenylantimony.



As it has been found out, the interaction of tri(*m*-tolyl)antimony with hydroxybenzaloxime in the presence of an oxidizing agent (hydrogen peroxide or *tert*-butylhydroperoxide), irrespective of the mole ratio of the reactants (1:2:1 or 1:1:1), proceeds by another scheme – with the formation of a binuclear organoantimony compound **2** with the bridging oxygen atom:



In papers [9, 10] it is reported that the oxides with the general formula (Ar₃SbX)₂O were obtained instead of the expected triaryl antimony dioximates Ar₃SbX₂. Thus, the reaction of triphenylantimony with diacetylmonooxime in the presence of *tert*-butylhydroperoxide, irrespective of the mole ratio of the reactants, led to the formation of μ₂-oxo-bis(oximate)triarylantimony with the yield of 86 % [9]. The mixture of products with different structures – (Ar₃SbX)₂O and Ar₃SbX₂ – was prepared by the oxidative addition reaction of triarylantimony with oximes (hydrogen peroxide was the oxidizing agent) in 1:2 molar ratio, whereas sometimes μ₂-oxo-bis(oximate)triarylantimony prevailed [10]. The singularity of our results is in the fact that 2-hydroxybenzaloxime reacts as a bifunctional compound and both oxidation and dearylation of tri-*m*-tolylantimony take place.

In the IR-spectrum of the compound **1** there is an absorption band at 475 cm⁻¹ due to the Sb–C(Ar) vibration of the C₃-symmetric SbC₃ fragment [15], in the IR spectrum of the compound **2** there is the band at 453 cm⁻¹ due to the same vibrations. The band at 700 cm⁻¹ is related to the stretching Sb–O vibration in the compound **1**, the IR-spectrum of the compound **2** has the bands at 692 and 704 cm⁻¹ which are related to the same stretching vibrations. The characteristic bands assigned to C=N (1595 and 1596 cm⁻¹ for **1** and **2** compounds, respectively), are lower than the band of pure 2-hydroxybenzaloxime. The broad absorption band of OH-groups of pure oxime with the maximum at 3380 cm⁻¹ is absent in the spectrum of the compound **2** and it is shifted to higher frequencies (3421 cm⁻¹) in the spectrum of the compound **1**.

According to the X-ray diffraction data, the crystal of the compound **1** includes two types of crystallographically independent molecules (**a** and **b**), in which the antimony atoms have trigonal-bipyramidal coordination with the oximate ligand oxygen atoms in axial positions (Fig. 1). The sum of $C_{eq}Sb(1, 2)C_{eq}$ bond angles is equal to $359.7(7)^\circ$ (**a**) and $360.0(4)^\circ$ (**b**), at that the value of the individual angles has small difference with the theoretical 120° . The axial angles $OSb(1, 2)O$ are equal to $173.5(4)^\circ$ and $172.1(4)^\circ$, respectively. The SbC_3 fragments are flat. The $Sb(1, 2)-C_{eq}$ bond length intervals are $2.08(1)-2.15(1)$ Å (**a**) and $2.08(1)-2.14(1)$ Å (**b**). The $Sb(1, 2)-O$ bond lengths are equal to $2.076(9)$, $2.086(10)$ Å (**a**) and $2.057(10)$, $2.079(10)$ Å (**b**). There are intramolecular contacts between Sb atom and N atoms of oxime groups in **a** and **b** molecules, the intramolecular distances $Sb(1, 2)\cdots N$ are equal to $(2.98(1), 2.99(1)$ Å and $2.89(1), 3.06(1)$ Å) which are considerably less than the sum of Van der Waals radiuses of Sb and N atoms (3.8 Å) [16]. Note that all basic geometric characteristics of the molecules **1 a** and **b** are close to analogous parameters of the triphenylantimonybis(2-hydroxybenzaldoximate) [7].

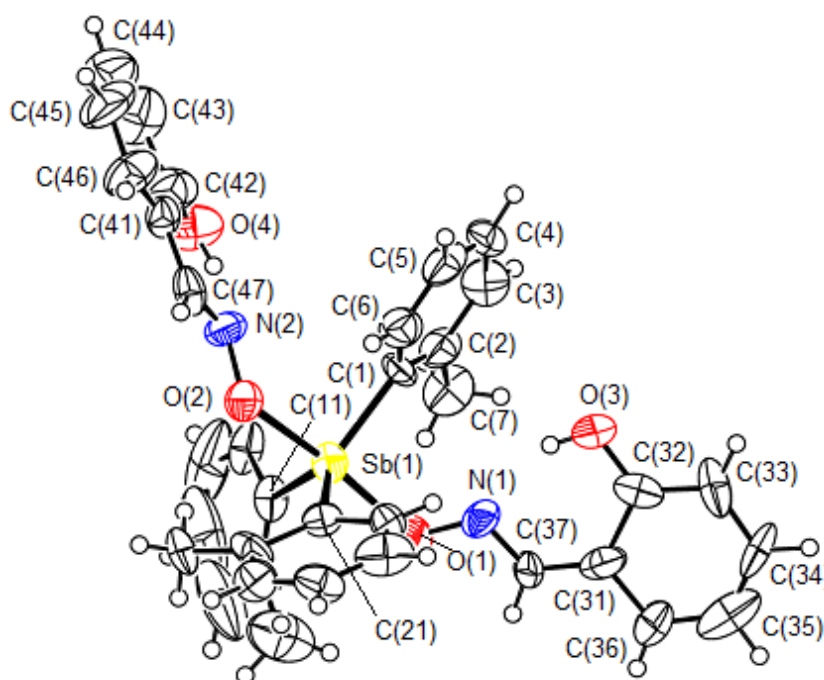


Fig. 1. The structure of the compound **1** (molecule **a**)

In the crystal **2** there is the solvated toluene, the molecules of which are disordered. Binuclear complex has the $Sb-O-Sb$ bridge bond. Every ligand is a tridentate chelating-bridging one, it is coordinated to one antimony atom by the oxygen atom of iminoxy group and to another atom of antimony by the oxygen atom of hydroxyl group and nitrogen atom (Fig. 2). $Sb(1,2)$ atoms have octahedral C_2O_3N surrounding.

Trans angles of octahedron are skewed – $CSb(1,2)O$ $167.6(1)^\circ$, $167.5(1)^\circ$; $CSb(1,2)N$ $165.3(1)^\circ$, $168.3(1)^\circ$; $OSb(1,2)O$ $162.86(9)^\circ$, $164.27(9)^\circ$. $Sb(1,2)-C$ bond lengths change in the interval $2.123(3)-2.137(3)$ Å. There are three types of $Sb(1,2)-O$ distances in the molecule: with the bridging atom of oxygen $1.950(2)$, $1.959(2)$ Å, with oxygen atoms of hydroxyl groups $2.014(2)$, $2.023(2)$ Å, with oxygen atoms of oxime groups $2.094(2)$, $2.098(2)$ Å, which do not differ very much and are comparable with the sum of covalent radiuses of antimony and oxygen atoms (2.07 Å [16]). The coordination bond $Sb(1,2)-N$ ($2.276(3)$, $2.256(2)$ Å) is rather short and it indicates high binding stability.

The angle $Sb(1)O(1)Sb(2)$ is equal to $119.3(1)^\circ$ and this is the minimal value of the angle at bridging atom of oxygen, which has been found in the structures of the general formula $(Ar_3SbX)_2O$ [17]. For example, the analogous angle of the bis(μ_2 -furfuraloximate)-(μ_2 -oxo)-bis(triphenylantimony) is equal to $125.5(3)^\circ$ [12]. The rigid structure of bicyclo[2.2.1]heptane fragment causes the approaching of antimony atoms up to the distance 3.373 Å, which is considerably less than doubled Van der Waals radius of an atom (4.4 Å [16]).

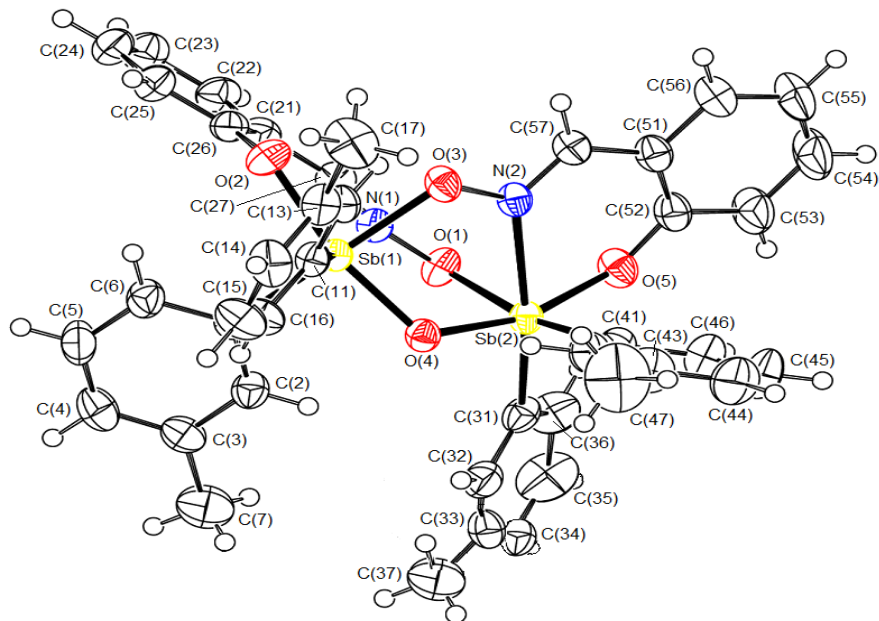


Fig. 2. The structure of the compound 2 (solvating toluene molecule are not shown)

Conclusions

Thus, it has been found that the direction of the oxidative addition reaction of 2-tritolylantimony with 2-hydroxybenzaldehyde in the presence of oxidizing agent is determined by the position of the methyl groups in phenyl radicals at antimony atom.

2-Hydroxybenzaldehyde exhibits structural diversity in tolyl derivatives of antimony due to changes its denticity, acting as the terminal or bridging ligand.

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ОСОБЕННОСТИ ВЗАИМОДЕЙСТВИЯ ТРИ(ОРТО-ТОЛИЛ) И ТРИ(МЕТА-ТОЛИЛ)СУРЬМЫ С 2-ГИДРОКСИБЕНЗАЛЬДОКСИМОМ. МОЛЕКУЛЯРНЫЕ СТРУКТУРЫ БИС(2-ГИДРОКСИ- БЕНЗАЛЬДОКСИМАТА) ТРИ(ОРТО-ТОЛИЛ)СУРЬМЫ И БИС(μ_3 -2-ГИДРОКСИБЕНЗАЛЬДОКСИМАТО-О,О',N)-(μ_2 -ОКСО)- БИС[ДИ(МЕТА-ТОЛИЛ)СУРЬМЫ]

В.В. Шарутин, О.К. Шарутина, Е.В. Артемьева, М.С. Макерова

Взаимодействием три-орто-толил- и три-мета-толилсурьмы с 2-гидроксибензальдоксимом в присутствии окислителя (пероксида водорода или

трет-бутилгидропероксида) синтезированы бис(2-гидроксибензальдоксимат) три-орто-толилсурьмы (1) и бис(μ_3 -2-гидроксибензальдоксимато-О,О',N)-(μ_2 -оксо)-бис[ди(мета-толил)сурьма] (2). По данным РСА, в двух типах кристаллографически независимых молекул (а, б) соединения 1 атомы сурьмы имеют тригонально-бипирамидальную координацию с атомами кислорода оксиматных лигандов в аксиальных положениях. В биядерном комплексе 2 атомы сурьмы связаны двумя тридентатно-мостиковыми лигандами и атомом кислорода и имеют искаженную октаэдрическую координацию с окружением C_2O_3N .

Ключевые слова: три-о-толилсурьма, три-м-толилсурьма, 2-гидроксибензальдоксим, третбутилгидропероксид, пероксид водорода, окисление, бис(2-гидроксибензальдоксимат) три-о-толилсурьмы, бис(μ_3 -2-гидроксибензальдоксимато-О,О',N)-(μ_2 -оксо)-бис[ди(м-толил)сурьмы], молекулярные структуры, рентгено-структурный анализ.

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