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Synthesis and Structure of the Organoantimony Peroxide Solvates $[Sb_4(\mu_2\text{-}O)_4(O_2)_2(C_6H_3MeO\text{-}2,Br\text{-}5)_8]\cdot 1.5C_4H_8O_2$ and $[Sb_4(\mu_2\text{-}O)_4(O_2)_2(C_6H_3MeO\text{-}2,Br\text{-}5)_8]\cdot 6C_4H_8O_2$

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Abstract—The organoantimony peroxide $(Ar_2SbO)_4(O_2)_2$ (Ar = C_6H_3OMe-2, Br-5) was synthesized by the oxidation of Ar_3Sb with hydrogen peroxide in the presence or acetoxime or acetophenone oxime in dioxane. The product crystallizes with various content of the solvent molecules in the crystal unit cell [1.5 (**I**) and 6 (**II**), respectively]. An X-ray diffraction analysis of the solvates was performed. Four antimony atoms in the peroxide are in the octahedral coordination, and are linked through bridging oxygen atoms and two peroxide groups. The distances Sb–C, Sb–O_{bridge}, Sb–$O_{peroxide}$, O–O and Sb···Sb are 2.117–2.122, 1.960–1.972, 2.193–2.235, 1.461, 1.465 and 3.223–3.237 Å in **I,** and 2.112, 2.119, 1.957, 1,966, 2.204, 2,246, 1,467, and 3.2439 Å in **II**.

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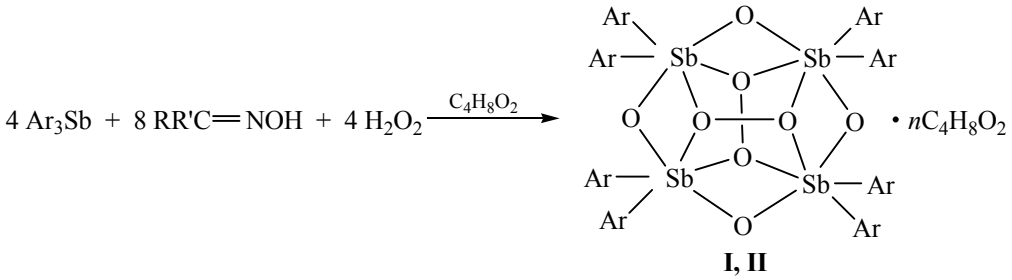
Structure of the antimony aryl derivatives whith the antimony atoms linked by four oxygen and two peroxide bridges has been described in [1, 2]. The organoantimony peroxides $(Ar_2SbO)_4(O_2)_2$ (Ar = Ph, *p*-Tol) were synthesized by oxidation triarylantimony with hydrogen peroxide in the presence of 4-chlorophenol or 4-nitrosophenol in ether [2].

In this work the peroxide $(Ar_2SbO)_4(O_2)_2$ (Ar = C_6H_3OMe-2, Br-5) were obtained by the reaction of triarylantimony with hydrogen peroxide in dioxane in the presence of oximes.

Previously was found that reaction of triphenyl- and tri-*p*-tolylantimony with hydrogen peroxide in ether in the presence of oximes leads to the formation of the triarylantimony dioximates, or μ-oxo-bis(oximatotriarylantimony) [3–5]. However, when the reaction of tris(2-methoxy-5-bromophenyl) antimony with hydrogen peroxide and acetoxime or acetophenone oxime is carried out in dioxane, the products are not the triarylantimony dioximeates, but some colorless high-melting crystals of the organoantimony peroxide:



I, II

Ar = C_6H_3OMe-2, Br-5; **I**, R = R' = Me, *n* = 1.5; **II**, R = Me, R' = Ph, *n* = 6.

X-ray diffraction (XRD) analysis revealed that, depending on the nature of the oxime the peroxide crystallizes as a solvate of different composition $(Ar_2SbO)_4(O)_2\cdot 1.5C_4H_8O_2$ (**I**) and $(Ar_2SbO)_4(O)_2\cdot 6C_4H_8O_2$ (**II**), respectively. Crystallographic parameters of the solvates **I** and **II** are significantly different (Tables 1, 2).

Table 1. Crystallographic data and the results of refinement of structures **I** and **II**

Parameter	Value	
	I	II
Formula	$C_{62}H_{60}Br_8O_{19}Sb_4$	$C_{80}H_{96}Br_8O_{28}Sb_4$
M	2235.38	2631.85
Crystal system	Triclinic	Rhombic
T, K	150	123
Space group	*P*-1	*Fddd*
Unit cell parameters:		
a, Å	14.4329(3)	19.2164(4)
b, Å	14.9705(3)	25.6245(5)
c, Å	18.9302(4)	37.7258(9)
α, deg	86.5490(10)	90
β, deg	69.1900(10)	90
γ, deg	76.1970(10)	90
V, Å^3	3711.60(13)	18576.6(7)
Z	2	8
d_{calc}, g cm^{-3}	2.000	1.882
μ, mm^{-1}	5.811	13.788
F(000)	2136	10272
The crystal shape, mm	Chip (0.33×0.25×0.18)	Chip (0.33×0.25×0.18)
θ, deg	2.23–34.46	3.10–73.07
Reflection indices range	$-22 \le h \le 16$, $-23 \le k \le 22$, $-27 \le l \le 28$	$-21 \le h \le 23$, $-31 \le k \le 20$, $-46 \le l \le 26$
Total reflections	6321421033	10970
Independent reflections	24856	4534
Numer of refined variables	864	271
GOOF	1.021	0.955
R-factors over $F^2>2\sigma(F^2)$	R_1 0.0248, wR_2 0.0545	R_1 0.0447, wR_2 0.1154
R-factors over all reflections	R_1 0.0392, wR_2 0.0589	R_1 0.0572, wR_2 0.1215
Residual electron density (min/max), e A^{-3}	1.223/–1.136	1.533/–0.652

According to XRD (Figs. 1, 2), in **I** and **II** the coordination of the antimony atoms linked through the bridging oxygen atoms and peroxy groups is a distorted octahedron. Each peroxy group is tetradentate, and coordinates simultaneously four antimony atoms. The *trans*-vertices of the octahedron are occupied by the aryl carbon atoms and the oxygen atoms of the peroxy groups ($O_{peroxide}$) and bridging oxygen atoms (O_{bridge}). The corresponding $CSbO_{peroxide}$ and $O_{bridge}SbO_{bridge}$ angles at the antimony atoms in **I** vary in the range 156.40(7)º–162.71(7)º and 151.69(6)º–153.09(5)º respectively. In structure **II** owing to the equivalence of pairs of antimony atoms located opposite each other the angles $CSb(1,2)O_{peroxide}$ and $O_{bridge}Sb(1,2)O_{bridge}$ take the values 160.5(2)°, 159.7(2)°, 154.8(2)°, and 152.0(2)º, respectively.

Four antimony atoms in the eight-membered ring $[Sb_4O_4]$ are almost in the same plane. On both sides of the plane are located the bridging oxygen atoms and

Table 2. The bond lengths and angles in structures **I** and **II**

Bond	*d*, Å	Angle	ω, deg	Bond	*d*, Å	Angle	ω, deg
			I				
Sb^1–Sb^2	3.2301(2)	$Sb^2Sb^1Sb^4$	89.193(5)	Sb^4–C^{421}	2.118(2)	$O^6Sb^2Sb^1$	119.70(4)
Sb^2–Sb^4	3.2332(2)	$O^1Sb^1Sb^2$	42.73(3)	O^1–O^2	1.4608(18)	$O^6Sb^2Sb^3$	34.67(4)
Sb^1–O^1	2.2344(13)	$O^1Sb^1Sb^4$	65.60(3)	O^3–O^4	1.4652(18)	$O^6Sb^2O^1$	82.30(5)
Sb^1–O^3	2.2350(13)	$O^1Sb^1O^3$	73.83(5)	O^{11}–C^{116}	1.361(3)	$O^6Sb^2O^4$	76.15(5)
Sb^1–O^5	1.9691(13)	$O^5Sb^1O^1$	75.89(5)	O^{11}–C^{117}	1.434(3)	$O^6Sb^2C^{211}$	97.85(7)
Sb^1–O^8	1.9600(13)	$O^5Sb^1O^3$	81.68(5)	O^{12}–C^{126}	1.360(3)	$O^6Sb^2C^{221}$	93.57(7)
Sb^1–C^{111}	2.1189(19)	$O^5Sb^1C^{111}$	97.36(7)	O^{12}–C^{127}	1.424(3)	$C^{211}Sb^2Sb^1$	99.95(5)
Sb^1–C^{121}	2.1163(19)	$O^5Sb^1C^{121}$	95.41(7)	O^{21}–C^{216}	1.368(3)	$C^{211}Sb^2Sb^3$	124.23(6)
Sb^2–Sb^3	3.23746(19)	$O^8Sb^1Sb^2$	118.14(4)	O^{21}–C^{217}	1.424(3)	$C^{211}Sb^2O^1$	83.99(6)
Sb^2–O^1	2.1963(13)	$O^8Sb^1Sb^4$	34.61(4)	O^{22}–C^{226}	1.360(3)	$C^{211}Sb^2O^4$	158.60(7)
Sb^2–O^4	2.2213(13)	$O^8Sb^1O^1$	81.33(5)	O^{22}–C^{227}	1.422(3)	$C^{221}Sb^2Sb^1$	128.24(6)
Sb^2–O^5	1.9674(13)	$O^8Sb^1O^3$	75.98(5)	O^{31}–C^{316}	1.359(3)	$C^{221}Sb^2Sb^3$	99.59(6)
Sb^2–O^6	1.9727(13)	$O^8Sb^1O^5$	151.71(6)	O^{31}–C^{317}	1.432(3)	$C^{221}Sb^2O^1$	161.60(6)
Sb^2–C^{211}	2.121(2)	$O^8Sb^1C^{111}$	96.94(7)	O^{32}–C^{326}	1.359(3)	$C^{221}Sb^2O^4$	86.69(6)
Sb^2–C^{221}	2.120(2)	$O^8Sb^1C^{121}$	98.94(7)	O^{32}–C^{327}	1.437(3)	$C^{221}Sb^2C^{211}$	114.39(8)
Sb^3–Sb^4	3.22388(18)	$C^{111}Sb^1O^1$	84.53(6)	O^{41}–C^{416}	1.362(3)	$Sb^4Sb^3Sb^2$	89.226(5)
Sb^3–O^2	2.2306(13)	$C^{111}Sb^1O^3$	157.95(6)	O^{41}–C^{417}	1.429(3)	$O^2Sb^3Sb^2$	65.64(3)
Sb^3–O^4	2.2246(13)	$C^{121}Sb^1O^1$	156.40(7)	O^{42}–C^{426}	1.356(3)	$O^2Sb^3Sb^4$	42.76(3)
Sb^3–O^6	1.9665(13)	$C^{121}Sb^1O^3$	83.30(6)	O^{42}–C^{427}	1.427(3)	$O^4Sb^3Sb^2$	43.22(3)
Sb^3–O^7	1.9670(13)	$C^{121}Sb^1C^{111}$	118.64(8)	Br^{11}–C^{113}	1.907(2)	$O^4Sb^3Sb^4$	66.58(3)
Sb^3–C^{311}	2.117(2)	$Sb^1Sb^2Sb^3$	90.685(5)	Br^{12}–C^{123}	1.901(2)	$O^4Sb^3O^2$	74.07(5)
Sb^3–C^{321}	2.122(2)	$O^1Sb^2O^4$	74.90(5)	Br^{21}–C^{213}	1.905(2)	$O^6Sb^3Sb^2$	34.79(4)
Sb^4–O^2	2.1931(13)	$O^5Sb^2O^1$	76.83(5)	Br^{2A}–C^{223}	1.890(3)	$O^6Sb^3Sb^4$	118.04(4)
Sb^4–O^3	2.2193(13)	$O^5Sb^2O^4$	82.00(5)	Br^{2B}–C^{223}	1.998(4)	$O^6Sb^3O^2$	81.04(5)
Sb^4–O^7	1.9675(14)	$O^5Sb^2O^6$	153.02(5)	Br^{31}–C^{313}	1.901(2)	$O^6Sb^3O^4$	76.19(5)
Sb^4–O^8	1.9656(14)	$O^5Sb^2C^{211}$	96.77(7)	Br^{32}–C^{323}	1.897(2)	$O^6Sb^3O^7$	151.69(6)
Sb^4–C^{411}	2.120(2)	$O^5Sb^2C^{221}$	100.85(7)				
			II				
Sb^1–Sb^2	3.2439(4)	$Sb^2Sb^1Sb^{2a}$	91.578(15)	Sb^2–O^2	1.957(3)	$C^{11b}Sb^1O^1$	160.54(17)
Sb^1–Sb^{2a}	3.2439(4)	$O^1Sb^1O^{1b}$	75.08(17)	Sb^2–O^{2c}	1.957(3)	$C^{11}Sb^1O^1$	87.65(17)
Sb^1–O^1	2.204(3)	$O^2Sb^1O^1$	75.29(13)	Sb^2–C^{21c}	2.119(5)	$C^{11b}Sb^1O^{1b}$	87.65(17)
Sb^1–O^{1b}	2.204(3)	$O^{2b}Sb^1O^1$	84.69(13)	Sb^2–C^{21}	2.119(5)	$C^{11}Sb^1O^{1b}$	160.54(17)
Sb^1–O^2	1.966(3)	$O^2Sb^1O^{1b}$	84.69(13)	O^1–O^{1a}	1.467(6)	$C^{11b}Sb^1C^{11}$	110.7(3)
Sb^1–O^{2b}	1.966(3)	$O^{2b}Sb^1O^{1b}$	75.29(13)	O^3–C^{1M}	1.420(7)	$Sb^1Sb^2Sb^{1c}$	88.422(15)
Sb^1–C^{11b}	2.112(5)	$O^2Sb^1O^{2b}$	154.76(19)	O^3–C^{26}	1.361(7)	$O^1Sb^2Sb^1$	42.70(8)
Sb^1–C^{11}	2.112(5)	$O^2Sb^1C^{11b}$	94.54(18)	O^4–C^{2M}	1.431(7)	$O^{1c}Sb^2Sb^1$	65.44(8)
Sb^2–Sb^{1c}	3.2439(4)	$O^{2b}Sb^1C^{11b}$	99.75(17)	O^4–C^{16}	1.369(7)	$O^1Sb^2Sb^{1c}$	65.44(8)
Sb^2–O^1	2.246(3)	$O^2Sb^1C^{11}$	99.75(17)	Br^1–C^{23}	1.903(6)	$O^{1c}Sb^2Sb^{1c}$	42.70(8)
Sb^2–O^{1c}	2.246(3)	$O^{2b}Sb^1C^{11}$	94.54(18)	Br^2–C^{13}	1.899(6)	$O^1Sb^2O^{1c}$	73.25(17)

Symmetry transformations: [a] $-x + 5/4, y, -z + 1/4$; [b] $x, -y + 5/4, -z + 1/4$; [c] $-x + 5/4, -y + 5/4, z$.

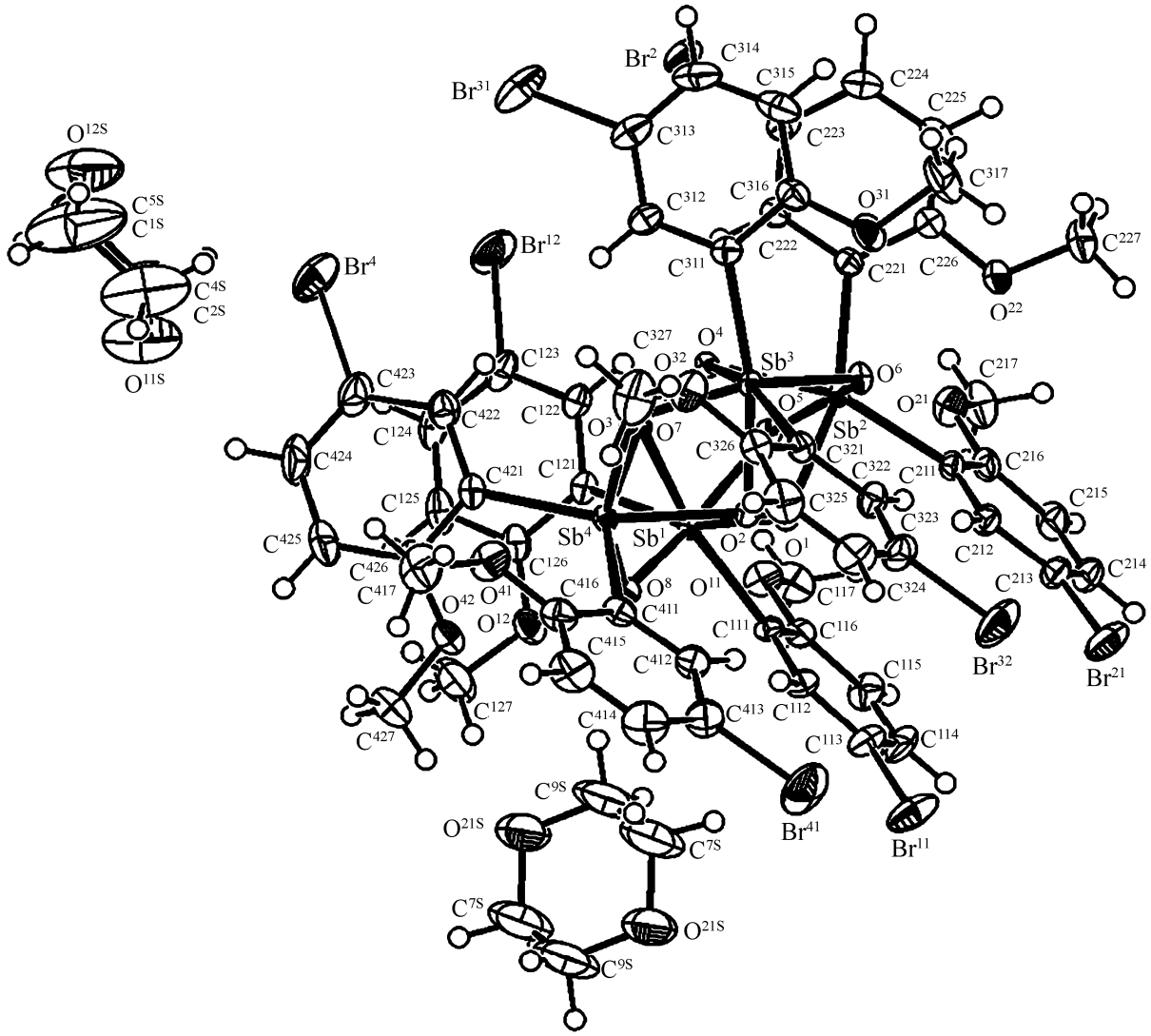


Fig. 1. The general view of the molecule **I**.

peroxy groups. In structure **I**, the distance Sb···Sb are slightly different [3.2239(2)–3.2375(2) Å], in structure **II** the antimony atoms occupy the vertices of a somewhat distorted square [all distances Sb···Sb equal to 3.2439(4) Å]. The SbSbSb angles are 89.193(5)° to 90.873(5)° (**I**) and 88.42(2)°, 91.58(2)° (**II**). The observed Sb···Sb distances are larger than doubled covalent radius of the Sb atom (2.82 Å), but less than doubled van der Waals radius (4.40 Å). Shortening of the distance between the antimony atoms probably due to the rigid structure of the central fragment formed by the peroxy groups.

The $SbO_{bridge}Sb$ angles in the metallocyclic structures **I** [110.05(6)°–110.89(6)°] and **II** [111.5(2)°] vary in a narrow range and are close to the tetrahedral angle. The $Sb–O_{bridge}$ bonds 1.960(1)–1.973(1) Å (**I**) and 1.957(3), 1.966(3) Å (**II**) are shorter than the sum of the antimony and oxygen covalent radii (2.07 Å).

The $SbO_{peroxide}Sb$ angles at the peroxide oxygen atoms are 93.08(5)°–93.60(5)° (**I**) and 93.60(1)° (**II**). In **I** the $Sb–O_{peroxide}$ distance falls to the range 2.196(1)–2.235(1) Å, in **II** the $Sb(1)–O_{peroxide}$ and $Sb(2)–O_{peroxide}$ distances take the values 2.204(3) and 2.246(3) Å respectively. The SbOO angles in **I** are almost identical [113.09(9)°–113.98 (9)°], in **II** they are equal to 112.8(2)° and 114.3(2)°. The OO distances in the bridging peroxy groups in the structures of **I** and **II** are 1.461(2), 1.465(2), and 1.467(6) Å, respectively.

The aryl rings at each antimony atoms are located on the opposite sides of the $[Sb_4]$ plane. The CSbC

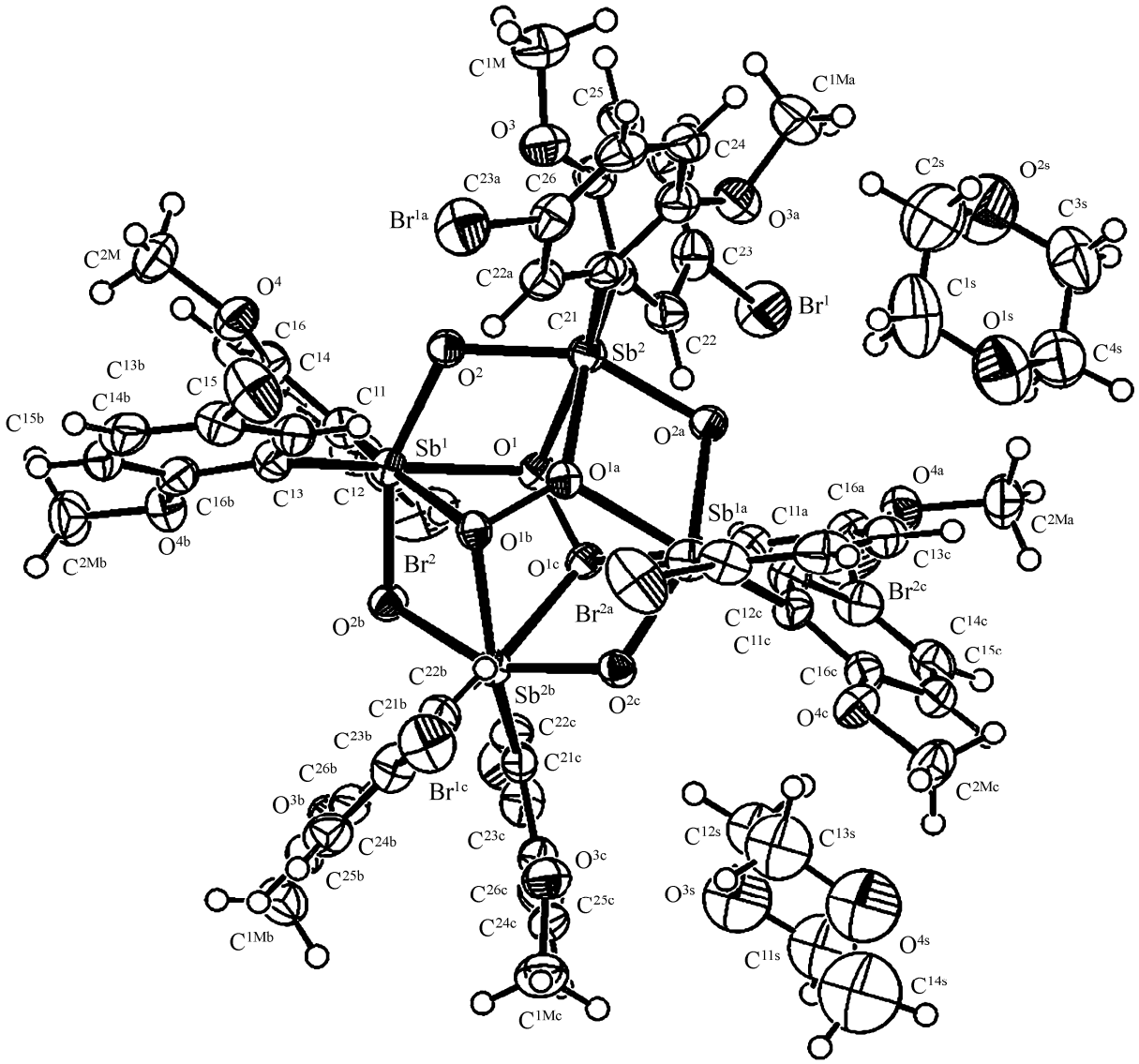


Fig. 2. The general view of the molecule **II**.

bond angles in **I** are 112.23(8)–118.64(8)°, in **II** the $CSb^{1,2}C$ are equal within experimental error [110.7(3)°, 110.4(3)°]. The Sb–C bond lengths in **I** vary within 2.116(2)–2.122(2) Å, in **II** 2.112(5), 2.119(5) Å, which differs little from similar bonds in the structures described in [2].

A feature of the structure **I** is nearly parallel arrangement of the planes of phenyl rings connected with the neighboring antimony atoms C^{111}–C^{116} and C^{211}–C^{216}, C^{121}–C^{116} and C^{421}–C^{426}, C^{211}–C^{226} and C^{311}–C^{316}, C^{321}–C^{326} and C^{411}–C^{416}. In the crystal, compound **II** contains two types of crystallo-graphically in-dependent solvent molecules, and one of them is symmetrically disordered over two positions with equal weight.

Intermolecular interactions in the crystals **I** and **II** are caused mainly by weak hydrogen bonding of C(Ph)–H···Br, C(Me)–H···Br, C(Ph)–H···O_{solv}, C (Me)–H···O_{solv}, etc., type. In addition, in the structure **II** there is π–π-interaction between the aromatic systems of neighboring molecules.

Thus, the composition of the antimony solvate peroxy complexes $(Ar_2SbO)_4(O_2)_2 \cdot n C_4H_8O_2$ obtained by oxidation of tris(2-methoxy-5-bromophenyl) antimony with hydrogen peroxide in the presence of

oximes determines the lattice crystallographic parameters and the geometric characteristics of molecules.

EXPERIMENTAL

Synthesis of I. To a mixture of 0.30 g (0.4 mmol) of tris(2-methoxy-5-bromophenyl)antimony solvate with benzene and 0.06 g (0.8 mmol) of acetoxime in 30 ml of dioxane was added 0.05 ml of 30% aqueous hydrogen peroxide (0.4 mmol), and the mixture was kept for 12 h at 20°C. Precipitated crystals were filtered and dried. 0.10 g (45%) of compound **I** was obtained, mp 290°C. IR spectrum (ν, cm^{-1}): 2958, 2938, 2844, 1570, 1470, 1435, 1374, 1283, 1264, 1247, 1120, 1050, 1020, 872, 807, 680, 660, 618, 442.

Similarly was prepared compound **II** (yield 47%, mp 292°C).

At increasing the hydrogen peroxide amount twice, the diarylantimony peroxide yield in the above reactions reaches 98%.

XRD study of the crystals of compounds **I** and **II** was performed on a SMART 1000 CCD diffractometer (graphite monochromator, MoK_α-radiation). Structures were determined by direct methods and refined by least-squares procedure, anisotropically for nonhydrogen atoms. The H atoms positions were calculated geometrically and included in the refinement in the "rider" model.

Data acquisition and edition, and refinement of the cell parameters was carried out with the programs SMART and SAINT Plus [6]. All calculations to determine and refine the structures were performed with the SHELXTL/PC program [7].

The crystallographic data and the refinement results for **I** and **II** are listed in Table 1, atomic coordinates and thermal parameters in Table 2, bond lengths and angles in Tables 2 and 3.

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