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Synthesis and Structure of Triphenylantinony Dimethacrylate

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Abstract—Triphenylantinony dimethacrylate $Ph_3Sb(O_2CMe{=}CH_2)_2$ was obtained in the reaction of triphenylantimony with methacrylic acid in the presence of hydrogen peroxide. The structure of the product was confirmed by elemental analysis, IR and ^{1}H NMR spectroscopy. According to X-ray diffraction analysis the substance is a trigonal bipyramidal complex of antimony with three phenyl groups in its basis and two methacrylate groups at the bipyramid vertices.

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In the recent period the chemistry of polymers containing a metal, including antimony, in the main chain is widely developed [1–2]. Now the studies are performed of their biological properties, including antibacterial, thermooxidative stability, and optical properties. Some of well-known unsaturated antimony compounds (acrylates, vinyl benzoates) already are used for the synthesis of organic polymers containing antimony atoms as substituents [3–5]. These polymers exhibit fungicidal and biocidal activity. In this regard, the synthesis of new monomers and the antimony-containing (co)polymers based on them is urgent.

The aim of this work is the synthesis of a new organoantimony compound, the triphenylantimony dimethacrylate, and the study of its molecular and crystal structure.

Triphenylantimony dimethacrylate was obtained by the oxidative addition of methacrylic acid to triphenylantimony in the presence of hydrogen peroxide:

$$Ph_3Sb + 2CH_2{=}CMeCO_2H + H_2O_2$$
$$\rightarrow Ph_3Sb(O_2CCMe{=}CH_2)_2 + H_2O$$

Earlier by this method using hydrogen peroxide [6] or *tert*-butylhydroperoxide [7] triphenylantimony diacetate was obtained. Later on, this method was applied to the synthesis of other antimony compounds of the general formula Ar_3SbX_2 (where X is an electronegative group) [7, 8].

The IR spectrum of triphenylantimony dimethacrylate contains an absorption band of medium intensity at 465 cm^{-1} corresponding to the Sb–Ph stretching vibrations, and an absorption band at 690 cm^{-1} belonging to the Sb–O stretching vibrations. The bands of high intensity with peaks at 1605 cm^{-1} and 1357 cm^{-1} are assigned respectively to the antisymmetric and symmetric stretching vibrations of COO group. An absorption band with the maximum at 3080 cm^{-1} corresponds to stretching vibrations of the C–H bonds of phenyl groups. The absorption band in the region of 3000–2900 cm^{-1} is assigned to the stretching vibrations of C–H bonds of methyl groups.

The data of elemental analysis agree well with the calculated values. Found, %: C 59.92, 59.97; H 5.00, 4.90; Sb 23.54, 23.00. $C_{26}H_{25}O_4Sb$. Calculated, %: C 59.68; H 4.82; Sb 23.27.

In the ^{1}H NMR spectrum of triphenylantimony dimethacrylate in the weak field a multiplet signal of the protons of Ph groups (δ 7.39–8.12 ppm) is observed, in the strong field there are two singlets corresponding to the protons of methylene groups (δ 5.93 ppm and δ 5.35 ppm) and a singlet of the protons of methyl groups (δ 1.78 ppm).

According to X-ray diffraction analysis of a single crystal of the product grown from a mixture of benzene and hexane, the antimony atom in triphenyl-

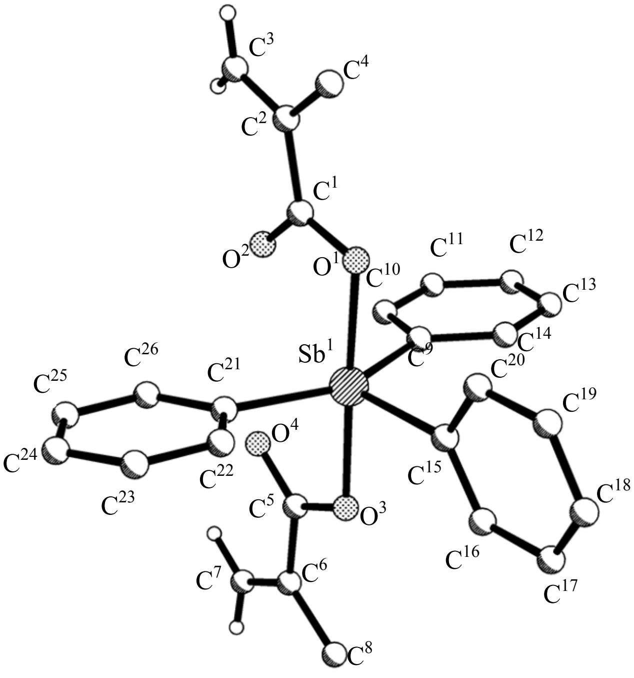

Fig. 1. The geometry of the triphenylantimony dimethacrylate molecule in a crystal.

antimony dimethacrylate has a trigonal–bipyramidal coordination, which is typical of the pentacoordinated antimony compounds (Fig. 1). The methacrylate groups are in axial positions, the phenyl groups occupy equatorial positions.

Bond lengths (*d*) and bond angles (ω) in the triphenylantimony dimethacrylate molecule

Bond	*d*	Bond	*d*	Bond	*d*
Sb^1–O^1	2.1308(16)	O^3–C^5	1.303(3)	O^1–C^1	1.301(2)
Sb^1–O^3	2.1087(16)	O^4–C^5	1.234(3)	O^2–C^1	1.226(3)
Sb^1–C^9	2.104(2)	C^5–C^6	1.475(3)	C^1–C^2	1.482(3)
Sb^1–C^{15}	2.107(2)	C^6–C^8	1.453(3)	C^2–C^4	1.423(4)
Sb^1–C^{21}	2.107(2)	C^6–C^7	1.360(4)	C^2–C^3	1.366(4)
Angle	ω	Angle	ω	Angle	ω
$C^9Sb^1C^{15}$	105.14(9)	$O^3C^5O^4$	121.2(2)	$O^1C^1O^2$	120.6(2)
$C^9Sb^1C^{21}$	149.81(8)	$O^3C^5C^6$	116.1(2)	$O^1C^1C^2$	118.0(2)
$C^{15}Sb^1C^{21}$	105.05(9)	$O^4C^5C^6$	122.7(2)	$O^2C^1C^2$	121.3(2)
$O^3Sb^1O^1$	176.70(6)	$C^5C^6C^7$	118.4(2)	$C^1C^2C^3$	119.2(2)
		$C^7C^6C^8$	124.3(2)	$C^3C^2C^4$	123.5(3)
		$C^5C^6C^8$	117.3(2)	$C^1C^2C^4$	117.3(2)

The sum of the angles C(Ph)SbC(Ph) in the equatorial plane is 360° (see the table). The axial angle O^1–Sb^1–O^3 is 176.70(6)°, close to the ideal value of 180°. The phenyl fragments C^9–C^{14} and C^{21}–C^{26} are almost in one plane (the angle between them is 4.2°). The third Ph group, C^{15}–C^{20}, is turned by approximately 90° to the other two phenyl rings, the angles between them are 85.7° and 81.5°, respectively.

The atoms O^1, O^2, C^1–C^4 of methacrylate fragment lie in the same plane, all angles are close to 120°, which confirms the participation of all the atoms of acrylate groups in the formation of a single conjugated system of *p*-electrons. The C^2–C^3 bond length is 1.366(4) Å, in agreement with the known values for tetraphenylantimony cinnamate (1.34 Å) [9]. A similar structure has the second methacrylate fragment. Methacrylate groups are virtually flat, the average deviation of atoms from the planes $O^1O^2C^1C^2C^3C^4$ and $O^3O^4C^5C^6C^7C^8$ are 0.036 Å and 0.013 Å, respectively. The angle between the methacrylate fragments $O^1O^2C^1C^2C^3C^4$ and $O^3O^4C^5C^6C^7C^8$ is 5.0°.

In the studied compound an intramolecular contact is found between the antimony atom and the oxygen atom of the carbonyl group. The $Sb^1\cdots O^2$ and $Sb^1\cdots O^4$ distances are 2.677(4) Å and 2.861(3) Å, respectively, significantly shorter than the sum of the van der Waals radii of these atoms (3.60 Å [10]). A similar interaction was observed in tetraphenylantimony cinnamate (the Sb···O distance is 3.00 Å) [9]. The interaction between the atoms $Sb^1\cdots O^2$ and $Sb^1\cdots O^4$ is confirmed by the increase in the equatorial angle C^9–Sb^1–C^{21} (at the side of the contact) to 149.81(8)° and the decrease in the angles C^7–Sb^1–C^{15} and C^{15}–Sb^1–C^{21} to 105.14(9)° and 105.05(9)°, respectively, compared with the ideal value of 120°.

Figure 2 shows a fragment of the one-dimensional chain of the molecules of the triphenylantimony–dimethacrylate complex observed in the crystal. The distance between the centers of the double bonds $C^{6A}{=}C^{8A}\cdots C^{2B}{=}C^{3B}$ and $C^{6B}{=}C^{8B}\cdots C^2C{=}C^3C$ is 3.67 Å, which indicates the existence of the interaction between the double bonds of neighboring molecules in the complex.

Thus, as a result of the investigation we for first time synthesized triphenylantimony dimethacrylate, confirmed the product composition by elemental analysis, IR and ^{1}H NMR spectroscopy, and revealed the molecular structure of the crystalline substance by the X-ray diffraction method.

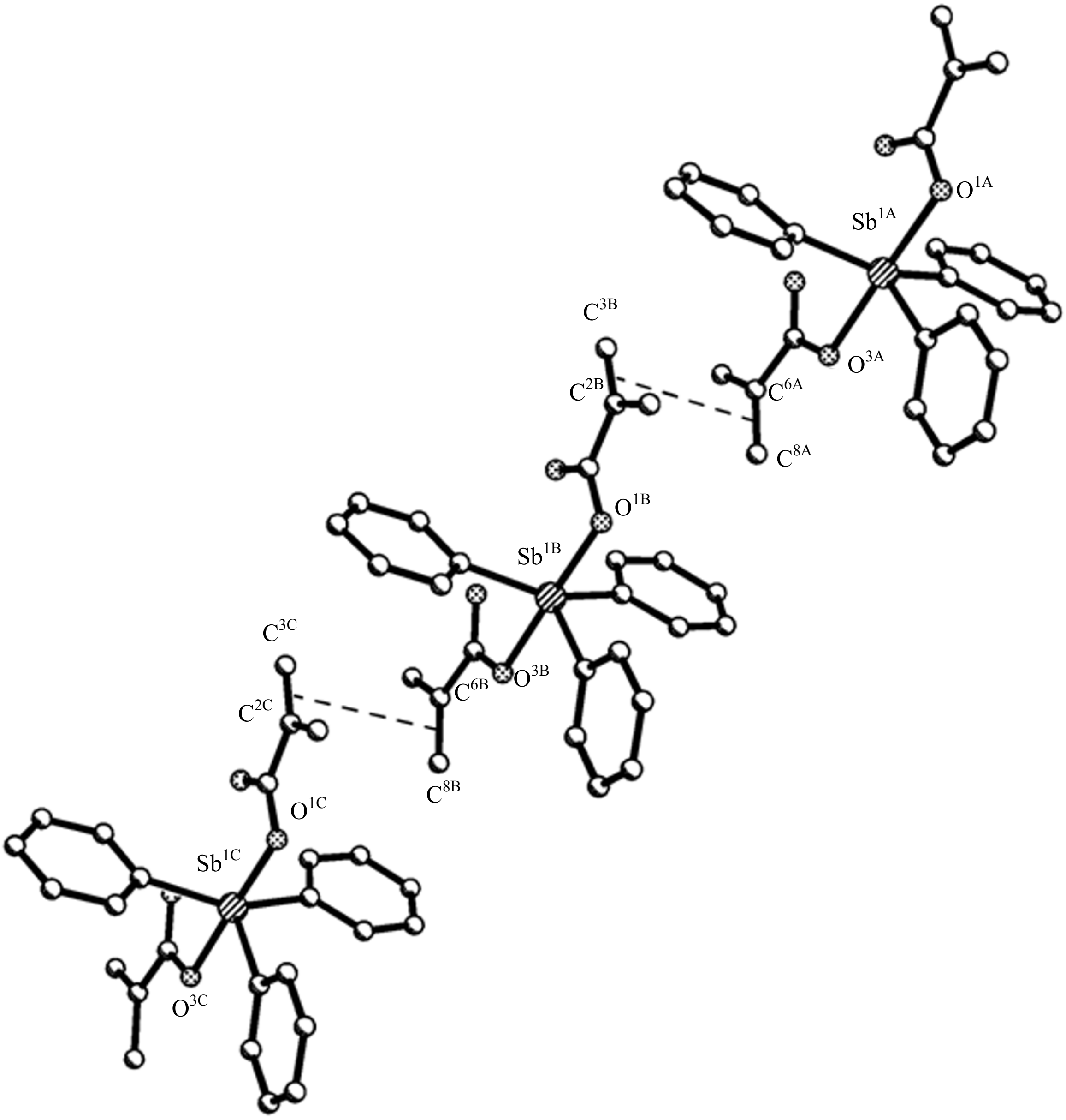

Fig. 2. Fragment of crystal packing of triphenylantimony dimethacrylate.

EXPERIMENTAL

Synthesis of triphenylantimony dimethacrylate. To a solution of 1.2 ml of 29% aqueous hydrogen peroxide and 2.5 ml of methacrylic acid in 40 ml of isopropyl alcohol was added a solution of 3.53 g of triphenylantimony in 10 ml of diethyl ether. The mixture was kept for 12 h at room temperature. The colorless crystals formed were filtered off and dried to obtain 4.13 g (79%) of triphenylantimony dimethacrylate. The product was twice recrystallized from chloroform–hexane mixture, 1:4. For the recrystallized compound, mp 156°C.

X-ray analysis of crystals of triphenylantimony dimethacrylate. A single crystal of triphenylantimony dimethacrylate was grown at room temperature from a mixture of benzene and hexane. The intensities of 6851 reflections observed, of which 3186 with $I > 2\sigma$, were measured on an automatic X-ray diffractometer Oxford Diffraction Gemini S with a χ-goniometer (MoK_α radiation, graphite monochromator, the tube setting 50/40 kV/mA) and a CCD detector SAPPHIRE III. The X-ray experiment was performed at room temperature, *T* = 298(2) K. The crystals of triphenylantimony dimethacrylate with benzene, $C_{29}H_{28}O_4Sb$, are triclinic, at 25°C: a = 9.3700(19), b = 9.4100(19), c = 15.050(3) Å; α = 77.04(3)°, β = 89.38(3)°, γ = 88.53(3)°; V = 1292.7 (5) Å^3; d_{calc} = 1,445 g cm^{-3}.

The solving and refinement of the atomic structure of the crystals was carried out using the software package SHELX-97 [11]. The initial fragment of the atomic structure was found by the direct method and then refined by the least squares method for the full matrix of parameters. The positions of the hydrogen atoms were calculated geometrically in a *rider* model. The final values of divergence factors: R_1 = 0.0373, wR_2 = 0.0455 for 4863 independent reflections.

In the crystal of the triphenylantimony dimethacrylate complex solvate benzene molecules were detected located in the inversion center of the crystal lattice. The ratio of the antimony molecular complex and benzene molecules in the crystal is 1:0.5.

IR spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer (Japan). To record the IR spectrum a KBr tablet was prepared containing 1% of the studied compound.

The ^{1}H NMR spectrum was recorded from a solution of the substance in deuterochloroform. For registration of the NMR spectra a spectrometer Bruker DPX-200 Fourier transform NMR was used (Germany). The spectrum assignment was carried out using the program Mestrec NMR (demo version).

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