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Synthesis and structure of a new tetranuclear macrocyclic antimony(V) complex

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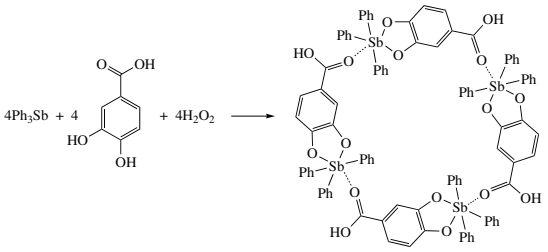
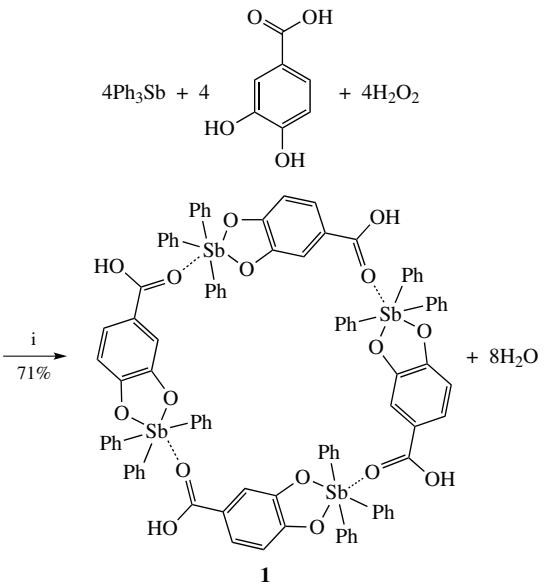
The reaction of triphenylantimony with 3,4-dihydroxybenzoic acid in diethyl ether in the presence of hydrogen peroxide afforded a tetranuclear macrocyclic complex, which was characterized by X-ray diffraction data.



Keywords: triphenylantimony, macrocycle, 3,4-dihydroxybenzoic acid, molecular structure, X-ray diffraction analysis.

Arylantimony compounds exhibit selective action against cancer cells,[1] and they possess antibacterial, fungicidal and general cytotoxic effects[2–4] as well as photocatalytic activity.[5] Organoantimony compounds are of fundamental interest because they typically have unusual structure. Thus, binuclear macrocycles have been synthesized in a reaction between triphenylantimony dichloride and dicarboxylic acids.[6] Metallocycles with different number of antimony atom have been obtained by the reaction of triarylantimony compounds with peroxides in the presence of polyfunctional compounds,[7–10] as well the antimony complexes with heterofunctional ligands have been investigated.[11,12]



Scheme 1 *Reagents and conditions*: i, 30% H_2O_2, Et_2O, room temperature, 24 h.

In this work, we studied the interaction of triphenylantimony with 3,4-dihydroxybenzoic acid in the presence of hydrogen peroxide. It is known that triarylantimony dicarboxylates with intra- and intermolecular hydrogen bonds in the crystals can be formed with chemically passive hydroxyl groups in the presence of the carboxyl ones, for example in reactions with 2-hydroxy- and 5-bromo-2-hydroxybenzoic acids.[13,14]

In our case, in the reaction with triphenylantimony and an oxidizing agent, 3,4-dihydroxybenzoic acid plays the role of a chelate-bridging ligand providing the additional coordination of the antimony atom with the carboxylate oxygen atom to form tetranuclear macrocycle **1** (Scheme 1).†

The IR spectrum of compound **1** exhibited an intense absorption band at 457 cm^{-1} due to Sb–O bond[15] and a medium-intensity absorption band at 568 cm^{-1} due to Sb–C bond.[16] The intense band of carbonyl group vibration at 1641 cm^{-1} disappeared in the low-frequency area, as compared to the similar band in the spectrum of 3,4-dihydroxybenzoic acid at

† *Tetrakis[μ2-4-carboxypyrocatecholato(2–)-O,O′,O″]-tetrakis[triphenylantimony(V)]* **1**. A mixture of triphenylantimony (0.2 g, 0.57 mmol) and 3,4-dihydroxybenzoic acid (0.09 g, 0.57 mmol) was dissolved in diethyl ether (30 ml) and 30% aqueous solution of hydrogen peroxide (0.096 g, 0.86 mmol) was added. The mixure was kept at room temperature for 24 h, then diethyl ether was evaporated and the precipitate was recrystallized from *o*-xylene. Evaporation of the solvent afforded 0.205 g (71%) of compound **1** as yellow crystals, mp 145 °C. IR (ν/cm^{-1}): 1641 (C=O), 457 (Sb–O). ^{1}H NMR (DMSO-d_6) δ: 7.12 [d, 3H, $O_2C_3H_3C(O)O$, *J* 2.7 Hz], 7.14 [d, 3H, $O_2C_3H_3C(O)O$, *J* 2.7 Hz], 7.19 [d, 3H, $O_2C_3H_3C(O)O$, *J* 2.7 Hz], 7.28 [d, 24H, *m*-protons, Sb–C(Ph), *J* 3 Hz], 7.32 [s, 12H, *p*-protons, Sb–C(Ph)], 7.67 [s, 24H, *o*-protons, Sb–C(Ph)]. ^{13}C NMR (DMSO-d_6) δ: 112.92; 113.12, 121.15 [12C, $O_2C_3H_3C(O)O$], 119.81 (4C, C–COOH), 134.56 [24C, *o*-carbons, Sb–C(Ph)], 130.09 [12C, *p*-carbons, Sb–C(Ph)], 129.26 [24C, *m*-carbons, Sb–C(Ph)], 154.18, 148.62 (8C, C–OH), 168.34 (s, 4C, C=O). Found (%): C, 59.50; H, 3.57. Calc. for $C_{100}H_{76}O_{16}Sb_4$ (%): C, 59.44; H, 3.80.

1670 cm^{-1}. Two intense absorption bands of C–O stretching vibrations were found at 1290 and 1265 cm^{-1} (*cf.* with 1287 and 1244 cm^{-1} in the spectrum of the starting acid).

According to the X-ray data (Figure 1),‡ each bridging ligand in macrocycle **1** participates in the coordination of carbonyl group oxygen atoms with the antimony atoms and the oxygen atoms of two hydroxyl groups with the nearby antimony atom resulting in chelate ring formation (Figure S1, see Online Supplementary Materials). The four Sb atoms have a distorted octahedral coordination with their [O_3C_3] surroundings, three carbon atoms being in *fac*-configuration, likewise the three oxygen atoms. The *trans*-angles involving the carbonyl oxygen atoms O(1)Sb(1)C(11), O(5)Sb(2)C(61), O(9)Sb(3)C(81) and O(13)Sb(4)C(131) are 174.41(11), 171.78(12), 174.38(11) and 171.72(12)°, respectively, that is somewhat smaller than the theoretical value, while the *trans*-angles OSbC involving phenolic oxygen atoms vary in a range of 154.87(12)–159.94(13)°. The bridging ligands have a nearly planar structure, the distance from all their oxygen and carbon atoms to the [O_4C_7] middle plane does not exceed 0.100 Å. The [SbO_2C_2] five-membered cycles possess a little inflection on the O–O diagonal. The Sb–C bonds [2.125(4)–2.143(4) Å] are longer than their typical values in triphenylantimony dicarboxylates,[20] which can be explained by an increase in the coordination number to six. The Sb–O bonds in the metallocycles differ from one another [2.023(2)–2.117(2) Å]

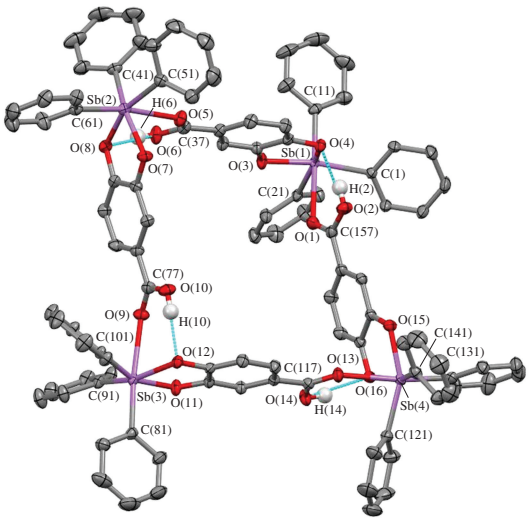


Figure 1 Molecular structure of compound **1** (the hydrogen atoms of benzene rings are omitted for clarity).

‡ *Crystal data for* **1**. $C_{100}H_{76}O_{16}Sb_4$ (M = 2020.61), triclinic, space group $P\bar{1}$ at 293.15 K: a = 10.115(2), b = 23.833(9) and c = 24.065(6) Å, α = 75.312(13)°, β = 77.960(9)°, γ = 77.852(11)°, V = 5412(3) Å^3, Z = 2, d_{calc} = 1.240 g cm^{-3}, μ(MoKα) = 1.042 mm^{-1}, F(000) = 2016.0. Total of 303480 reflections were collected (31639 independent reflections, R_{int} = 0.0730) and used in the refinement, which converged to wR_2 0.1169, GOOF 1.070 for all independent reflections [R_1 = 0.0444 was calculated for 31639 reflections with $I > 2\sigma(I)$].

The X-ray diffraction analysis was carried out on a Bruker D8 QUEST diffractometer (MoKα radiation, λ = 0.71073 Å, graphite monochromator). Collection, editing of data and refinement of the unit cell parameters, as well as accounting for absorption, were carried out using the SMART and SAINT-Plus programs.[17] All calculations were performed using the SHELXTL/PC[18] and OLEX2[19] software. The structure was solved by the direct method and refined by the least squares method in the anisotropic approximation for non-hydrogen atoms.

CCDC 1901680 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

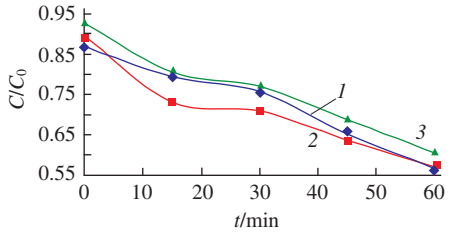


Figure 2 (*1*), (*2*) and (*3*): cycling runs for the photocatalytic decomposition of MB by compound **1** under UV irradiation. C is the concentration, and C_0 is the initial concentration of MB, mg dm^{-3}.

being close to similar bonds in antimony catecholate complexes.[21–23] The distances between the antimony and oxygen atoms of carbonyl groups Sb(1)–O(1), Sb(2)–O(5), Sb(3)–O(9) and Sb(4)–O(13) are 2.536(3), 2.490(3), 2.533(3) and 2.489(3) Å, respectively, that is significantly greater than the sum of the covalent radii,[24] thus these bonds can be considered as coordinating ones. Note that the Sb–O distances are known to be 2.109(4)–2.161(3) Å in the triphenylantimony dicarboxylate molecules obtained by the deprotonation of carboxylic acid groups, where the bonding of the central antimony atom is realized through the carboxylic oxygen atom.[14] The Sb–O distances reported in another work[6] [2.116(7)–2.151(6) Å] are comparable with the sum of the covalent radii of the corresponding atoms. For complex **1**, the distances between antimony and oxygen atoms of carboxylic groups Sb···O–H [3.649(3)–3.659(3) Å] are comparable with the sum of van der Waals radii of the antimony and oxygen atoms (3.7 Å),[24] which confirms the monodentate binding of the carboxyl groups. The O(1)–C(157), O(5)–C(37), O(9)–C(77) and O(13)–C(117) double carbonyl bonds [1.234(6)–1.239(3) Å] are significantly shorter than the corresponding single O(2)–C(157), O(6)–C(37), O(10)–C(77) and O(14)–C(117) bonds [1.319(5)–1.328(5) Å].

In macrocycle **1**, the hydrogen bonds O(2)–H(2)···O(4), O(6)–H(6)···O(8), O(10)–H(10)···O(12) and O(14)–H(14)···O(16) are observed. The H···O distances are 1.87–1.89 Å, and the corresponding O–H···O angles are 162.8–167.8°.

The photocatalytic activity of complex **1** was evaluated by the photodegradation of methylene blue (MB) in an aqueous solution at ambient temperature. The photocatalytic reactions were carried out in accordance with a known procedure.[5] The decomposition of MB reached 42% upon an exposure of its solution to complex **1** for 60 min. To investigate the reusability of the photocatalyst, we separated compound **1** by centrifugation after the first cycle of the dye decomposition, decanted the solvent and used the precipitate for the next cycle (Figure 2). As a result of two photodegradation cycles, the photocatalytic activity of the compound changed only slightly.

In summary, the reaction of triphenylantimony with 3,4-dihydroxybenzoic acid in the presence of hydrogen peroxide in diethyl ether at a molar ratio of 1 : 1 : 1.5 leads to the formation of tetranuclear macrocyclic complex, which was characterized by IR and NMR spectroscopy as well as X-ray diffraction. The photocatalytic activity of the complex was elucidated using the photodegradation of methylene blue.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.032.

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