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Molecular structure and photocatalytic properties of the pentaphenylantimony–3,5-dinitrosalicylic acid reaction product

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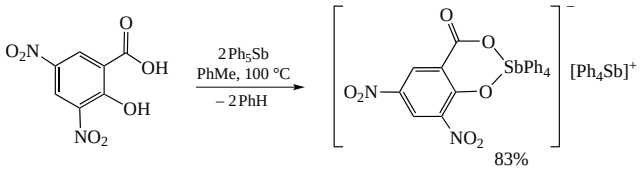
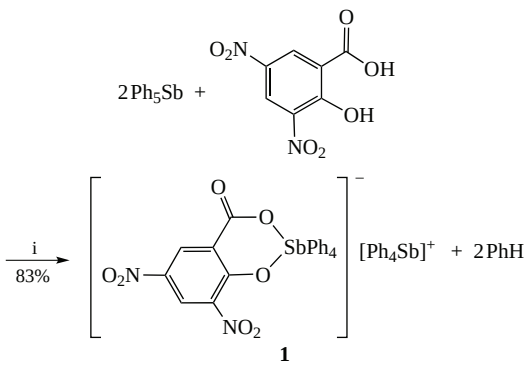
Reaction between pentaphenylantimony and 3,5-dinitrosalicylic acid involves both hydroxy and carboxy groups to form the complex containing an anion with the six-membered metallocycle and Ph_4Sb^+ counter-cation. The molecular structure of the reaction product has been established by X-ray analysis. The photocatalytic properties have been studied by the methylene blue photodegradation.



Keywords: pentaphenylantimony, 3,5-dinitrosalicylic acid, organoantimony compounds, X-ray analysis, molecular structure, photocatalytic properties.

Arylantimony(V) compounds attract interest due to application areas, for example polymer synthesis,[1] fine organic synthesis[2–4] or photocatalytic methods.[3] Such compounds have shown anti-leishmanial[5–7] and anticancer[8–10] activity. Fundamentally, arylantimony(V) compounds exhibit structural variety provided by inclusion of a polyfunctional ligand. For example, some reactions of triarylantimony or their dihalides with polyfunctional carboxylic acids produce bi-[11] or tetranuclear[12,13] macrocyclic compounds. Reactions between pentaphenylantimony (tetraphenylantimony halides) with polyfunctional carboxylic acids can also form binuclear products.[14,15]

In this study, it has been found that 3,5-dinitrosalicylic acid reacts with pentaphenylantimony involving both hydroxy and carboxy groups with formation of ionic complex, namely, tetraphenylstibonium 3,5-dinitrosalicylato-*O*,*O*′-tetraphenylstibotate **1** possessing a six-membered metallocycle in the anion (Scheme 1, for synthetic details see Online Supplementary Materials). It is necessary to note that the excess of pentaphenylantimony (or tetraphenylantimony halide) did not lead to participation of hydroxy group in the analogous synthesis of tetraphenylantimony salicylate and 5-bromosalicylate.[16,17]



Scheme 1 *Reagents and conditions*: i, toluene, 100 °C, 24 h.

The carbonyl group absorption band (1624 cm^{-1}) in the IR-spectrum of compound **1** is displaced in the low-frequency area compared to the IR-spectra of the initial acid (1680 cm^{-1}). The intense Sb–O band at 444 cm^{-1} together with a rather intense Sb–C band at 540 cm^{-1} are also present in the spectrum. The C–O absorption band correlates with the 1325 cm^{-1} frequency (1340 cm^{-1} – in the acid).

According to X-ray study, two antimony atoms in molecule **1**·PhMe (solvate with toluene) have different coordination. The Sb(1) atom has a distorted octahedral coordination while the Sb(2) atom can be described as possessing a distorted tetrahedral coordination (Figure 1).† Two oxygen atoms and two carbon atoms of the phenyl ligands are located in the Sb(1) equatorial plane, two other carbon atoms of phenyl ligands are located in the axial positions. The C(1)Sb(1)C(21) axial angle equals 163.33(16)°, while the C(11)Sb(1)O(1) and C(31)Sb(1)O(3) *trans*-angles in the equatorial plane are 169.69(15)° and 165.23(14)°. The sum of angles in the equatorial plane approach 360°. The Sb(1) atom deviates from [O(1)O(3)C(11)C(31)]

† *Crystal data for* **1**. $C_{62}H_{50}N_2O_7Sb_2$ (M = 1178.54), monoclinic, space group $P2_1/n$, at 293.15 K; a = 12.28(2), b = 34.17(8) and c = 13.07(2) Å, α = 90.00(11)°, β = 93.09(7)°, γ = 90.00(8)°, V = 5476(18) Å^3, Z = 4, d_{calc} = 1.429 g cm^{-3}, $\mu(MoK_\alpha)$ = 1.041 mm^{-1}, $F(000)$ = 2376.0. Total of 107910 reflections were collected (9644 independent reflections, R_{int} = 0.0843) and used in refinement which converged to wR_2 = 0.0906, GOOF 1.069 for all independent reflections [R_1 = 0.0657 was calculated for 9644 reflections with $I > 2\sigma(I)$]. 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.[18] All calculations were performed using the SHELXTL/PC[19] and OLEX2[20] software. The structure was solved by the direct method and refined by the method of least squares in the anisotropic approximation for non-hydrogen atoms.

CCDC 2048156 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.

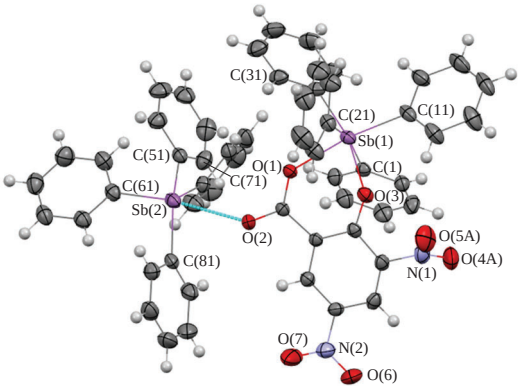


Figure 1 Molecular structure of compound **1** (the solvate molecule of toluene is not shown).

plane by 0.010 Å. The [CCCOOSb] six-membered metallocycle is not planar and has an inflection along the O(1)···O(3) diagonal. The lengths of Sb(1)−C(1), Sb(1)−C(21) axial bonds are 2.181(6), 2.174(6) Å and those of the Sb(1)−C(11), Sb(1)−C(31) equatorial ones are 2.173(5), 2.186(4) Å. It is interesting to note that the ligand is coordinated with the antimony atom practically symmetrically in spite of the different nature of the functional groups [the Sb(1)−O(1), Sb(1)−O(2) distances equal 2.240(4), 2.200(4) Å]. The Sb(2) atom probably has a distorted tetrahedral coordination: the CSb(2)C angles equal 98.1(2)−120.0(2)°, the Sb(2)−C distances are 2.111(5)−2.135(5) Å. The tetrahedron distortion is caused by the presence of the Sb(2)···O(2) contact [2.691(5) Å].

Photocatalytic activity of compound **1** has been evaluated by photodegradation of the methylene blue (MB) aqueous solution in its presence at room temperature. High pressure mercury lamp (125 W) was used as a UV-radiation source. The change of MB concentration was controlled by UV-spectroscopy according to the shift of the peak intensity (λ = 665 nm, for details see Online Supplementary Materials). In the control experiment without addition of compound **1**, MB water solutions did not decompose upon the UV irradiation. It has been established that compound **1** actually influenced the MB photocatalytic activity. Thus, the decomposition of MB has reached 38% by exposure its solution with compound **1** during 60 min.

For the evaluation of photocatalyst reusability, the process of circulating photocatalysis of MB in the presence of compound **1** has been studied. After the first cycle of dye decomposition, compound **1** was precipitated by centrifugation, the solvent was decanted, and the precipitate was used in the next cycle (Figure 2). As a result of two photodegradation cycles, the photocatalytic activity of the compound was slightly changed. It should be noted that comparing with triphenylantimony 2-(trifluoromethyl)benzoate,[3] the photocatalytic activity of compound **1** is higher in the corresponding time gap.

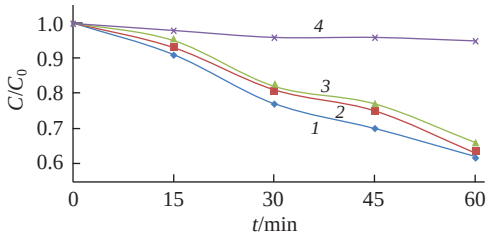


Figure 2 Cycling runs for the MB photocatalytic decomposition by compound **1** under UV irradiation (*C* is the concentration, C_0 is the initial concentration of MB, mg dm^{-3}). Curve *1* stands for cycle 1, curve *2* for cycle 2, curve *3* for cycle 3, curve *4* for cycle without catalyst.

In summary, the reaction of pentaphenylantimony with 3,5-dinitrosalicylic acid in toluene using 2 : 1 mole ratio leads to the formation of tetraphenylstibonium 3,5-dinitrosalicylato-*O*,*O'*-tetraphenylstibotate, which was confirmed by IR, NMR and X-ray diffraction methods. The photocatalytic activity has been established by photodegradation of the methylene blue. The obtained results will be useful for expanding the knowledge of arylantimony(V) compounds structural diversity while catalyzed photodegradation of the methylene blue in the presence of compound **1** can be an important contribution for the environmental maintenance.

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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.2022.05.028.

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