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Synthesis and Structure of Tetraphenylstibonium and Tetraphenylphosphonium Hydrogen Sulfates

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Abstract—Reactions of pentaphenylantimony and pentaphenylphosphorane with sulfuric acid yielded tetraphenylstibonium and tetraphenylphosphonium hydrogen sulfates, respectively; their crystal and molecular structure was determined.

The structures of antimony(V) derivatives Ar_4SbX (X = acid residue) are described in numerous papers [1–20]. In these compounds, the Sb–X bond lengths vary within wide limits, with the antimony coordination polyhedron varying from virtually ideal tetrahedron [17] to trigonal bipyramid [1–4, 10–20] and octahedron [5–9]. Among compounds of this series, organoantimony derivatives of strong acids are the least studied. To determine the structural features of such compounds, we have prepared tetraphenylstibonium (**I**) and tetraphenylphosphonium (**II**) hydrogen sulfates from pentaphenylantimony and pentaphenylphosphorane, respectively:

$$Ph_5E + H_2SO_4 \longrightarrow \underset{\mathbf{I,\ II}}{Ph_4EOSO_2(OH)} + PhH,$$

$$E = Sb\ (\mathbf{I}),\ P\ (\mathbf{II}).$$

According to single crystal X-ray diffraction, the molecules of **I** and **II** (Figs. 1, 2) consist of hydrogen sulfate anions $(HOSO_3)^-$ and Ph_4E^+ cations [E = Sb (**I**), P (**II**)]. The Sb atom in the cation of **I** has a distorted tetrahedral coordination. The CSbC angles vary in the range 99.23(7)°–120.25(6)°, and the Sb–C bond lengths are 2.090(2), 2.102(2), 2.110(2), and 2.116(2) Å. It should be noted that, in tetraphenylstibonium perchlorate having a similar structure, the Sb coordination is virtually ideal tetrahedral: The CSbC angles are 109.44(8)°–109.49(8)°, and the average Sb–C distance, 2.095 Å [13].

The P–C bond lengths [1.7882(16)–1.7947(16) Å] and CPC angles [106.48(8)°–112.67(7)°] in the cation of **II** vary within narrower limits than in **I**, suggesting more regular tetrahedral structure of the Ph_4P^+ cation. Note that the difference between the average distances Sb–C (2.100 Å) and P–C (1.793 Å) in **I** and **II** virtually coincides with the difference between the covalent radii of the Sb and P atoms (d^{Sb}_{cov} 1.41 Å, d^{P}_{cov} 1.10 Å [21]). Although the anions in both complexes are the same, the S–O bonds in them somewhat differ. In **I**, the S=O bond lengths are 1.419(2), 1.436(2), and 1.473(1) Å (average 1.443 Å), and the S–O(H) bond length is 1.522(1) Å. These distances are shorter than in **II** [S=O, 1.440(1), 1.444(2), and 1.474(1) Å (average 1.453 Å); S–O(H) 1.574(1) Å]. The OSO angles are in the range 105.69(8)°–112.29(9)° for **I** and 104.49(8)°–114.16(8)° for **II**. The SOH angle in **I** [120.6(1)°] is larger than in **II** [110.2(1)°]. The difference between the geometries of the anions in **I** and **II** may be due to the effect of the pyridine solvation

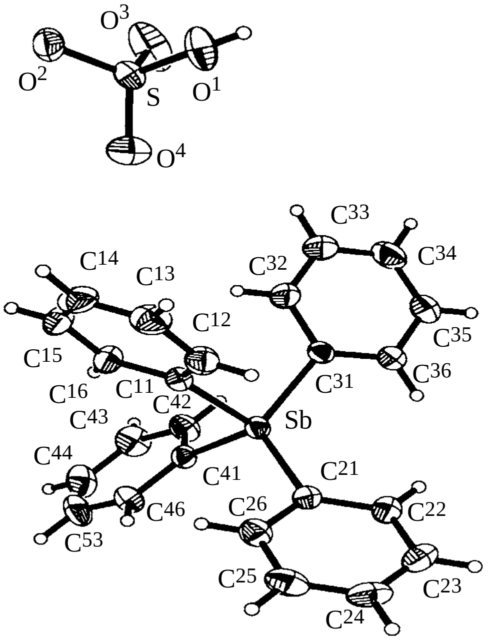

Fig. 1. Molecular structure of tetraphenylstibonium hydrogen sulfate.

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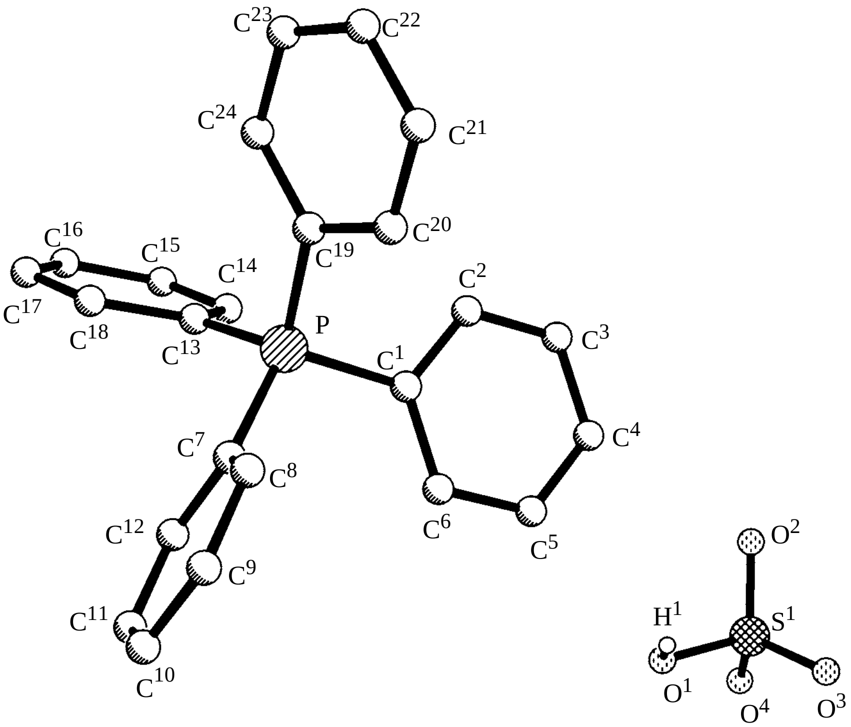

Fig. 2. Molecular structure of tetraphenylphosphonium hydrogen sulfate (the pyridine solvation molecule is not shown).

molecule present in the crystal of **II**. The cation, anion, and pyridine molecule in **II** are linked by weak intermolecular hydrogen bonds H···O···H (Fig. 3). Hydrogen atoms in the *p*-position of the phenyl rings of the tetraphenylphosphonium ions also participate in weak hydrogen bonding. The H···O distances vary within 2.433–2.579 Å (with the C···H···O angles varying within 145.2°–157.6°), which appreciably exceeds the distance typical of hydrogen bonds {*d*(O···H) < 2.1 Å [22]} but is less than the sum of the van der Waals radii of the O and H atoms (2.7 Å [21]).

We found that keeping of a solution of pentaphenylantimony in liquid SO_2 in the absence of H_2SO_4 for 12 h at 20°C, followed by removal of the solvent and recrystallization of the residue from water, results in quantitative formation of tetraphenylantimony benzenesulfonate **III**; the reaction apparently involves insertion of SO_2 into the Sb–C bond with the formation of tetraphenylantimony benzenesulfinate **IV**, which is subsequently oxidized with atmospheric oxygen to tetraphenylantimony benzenesulfonate:

$$\mathrm{Ph_5Sb + SO_2 \longrightarrow \underset{\textbf{IV}}{[Ph_4SbOS(O)Ph]} \xrightarrow{O_2} \underset{\textbf{III}}{Ph_4SbOSO_2Ph}.}$$

EXPERIMENTAL

Single crystal X-ray diffraction study of I and II was performed with Bruker SMART-1000CCD (for **I**; MoK_α radiation, graphite monochromator, θ/2θ scanning, 2θ ≤ 30.03°) and Siemens P3/PC (for **II**; MoK_α radiation, graphite monochromator, θ/2θ scanning, 2θ ≤ 32.41°) diffractometers. $C_{24}H_{21}O_4SSb$ (**I**): monoclinic system; at 20°C *a* 12.308(2), *b* 10.273(1), *c* 18.093(2) Å; β 105.850(2)°, *V* 2200.8(5) $Å^3$, space group $P2_1/c$, *Z* 4, d_{calc} 1.591 g cm^{-3}. $C_{29}H_{26}NO_4PS$ (**II**): triclinic system; at 20°C *a* 9.727(5), *b* 10.859(6), *c* 13.167(7) Å; α 69.232(10)°, β 76.251(10)°, γ 87.221(10)°; *V* 1262.2(12) $Å^3$, space group $P\bar{1}$, *Z* 2, d_{calc} 1.356 g cm^{-3}. The H atoms in aryl substituents in **I** and **II** were localized by differential electron density syntheses and refined isotropically. The X-ray absorption was taken into account with the SADABS program [23]. The structures of **I** and **II** were solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for all nonhydrogen atoms to *R* 0.0475, R_W 0.0690 using 6414 reflections with $I > 2\sigma(I)$ for **I** and to *R* 0.0764, R_W 0.1868 using 8160 reflections with $I > 2\sigma(I)$ for **II**. X-ray diffraction study of **II** revealed a disordered solvation molecule of pyridine.

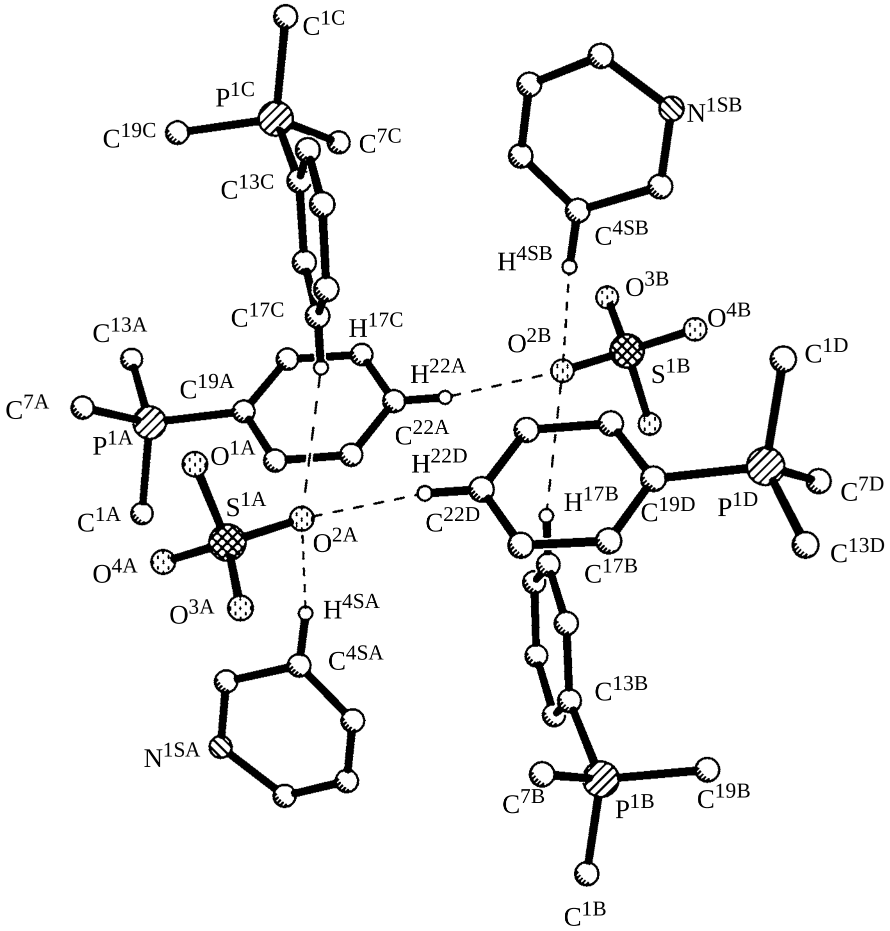

Fig. 3. System of intermolecular hydrogen bonds in the crystal of tetraphenylphosphonium hydrogen sulfate pyridine solvate (the phenyl substituents that do not participate in intermolecular interactions are not shown).

Selected interatomic distances (*d*) and bond angles (ω) in **I** and **II**

Compound **I**		Compound **II**		Compound **I**		Compound **II**	
bond	*d*, Å	bond	*d*, Å	angle	ω, deg	angle	ω, deg
Sb–C^{41}	2.090(2)	P^1–C^1	1.7945(17)	C^{41}SbC^{21}	118.99(6)	C^{13}P^{1}C^7	108.22(7)
Sb–C^{21}	2.102(2)	P^1–C^7	1.7926(17)	C^{41}SbC^{31}	111.05(6)	C^{13}P^{1}C^{19}	108.60(8)
Sb–C^{31}	2.110(2)	P^1–C^{13}	1.7882(16)	C^{21}SbC^{31}	120.25(6)	C^{7}P^{1}C^{19}	112.67(7)
Sb–C^{11}	2.116(2)	P^1–C^{19}	1.7947(16)	C^{41}SbC^{11}	99.23(7)	C^{13}P^{1}C^1	111.17(7)
S–O^4	1.419(2)	S^1–O^1	1.5743(13)	C^{21}SbC^{11}	101.58(6)	C^{7}P^{1}C^1	109.72(7)
S–O^2	1.436(2)	S^1–O^2	1.4442(15)	C^{31}SbC^{11}	100.47(6)	C^{19}P^{1}C^1	106.48(8)
S–O^3	1.473(1)	S^1–O^3	1.4734(13)	O^{4}SO^2	112.29(9)	O^{4}S^{1}O^2	114.16(8)
S–O^1	1.522(1)	S^1–O^4	1.4402(13)	O^{4}SO^3	111.2(1)	O^{4}S^{1}O^3	112.76(7)
O^1–H^1	0.78(2)	O^1–H$^{1'}$	0.86(2)	O^{2}SO^3	110.1(1)	O^{2}S^{1}O^3	112.30(8)
				O^{4}SO^1	109.41(9)	O^{4}S^{1}O^1	104.49(8)
				O^{2}SO^1	107.86(8)	O^{2}S^{1}O^1	106.65(7)
				O^{3}SO^1	105.69(8)	O^{3}S^{1}O^1	105.58(7)
				SO^{1}H^1	120.6(1)	S^{1}O^{1}H$^{1'}$	110.2(1)

The data collection and editing and the refinement of the unit cell parameters were performed by the SMART and SAINT Plus programs [24]. All the calculations for structure determination and refinement were performed by SHELXTL/PC programs [25]. The selected bond lengths and bond angles in the molecules of **I** and **II** are listed in the table.

Tetraphenylstibonium hydrogen sulfate I. A mixture of 1.00 g of pentaphenylantimony and 0.19 g of sulfuric acid in 10 ml of liquid SO_3 was kept for 12 h at room temperature. The solvent was removed, and the residue was recrystallized from water. Yield 0.93 g (89%), mp 213–214°C.

Tetraphenylphosphonium hydrogen sulfate II was prepared similarly to **I** from pentaphenylphosphorane and sulfuric acid in liquid SO_2. The solvent was removed, and the residue was recrystallized from benzene. The crystal solvate $[Ph_4P]^+[SO_4H]^- \cdot 1/2C_6H_6$ was isolated; yield 92%, mp 143°C. Found, %: C 68.63; H 5.20; P 6.10. $C_{27}H_{24}O_4PS$. Calculated, %: C 68.21; H 5.05; P 6.53. The single crystal X-ray diffraction study was performed with a yellow crystalline compound obtained by recrystallization of **II** from pyridine.

Reaction of pentaphenylantimony with SO_2. A mixture of 1 g of pentaphenylantimony and 10 ml of liquid SO_2 was kept for 12 h at room temperature. The solvent was removed, and the residue was recrystallized from water. Tetraphenylantimony benzenesulfonate crystal hydrate was obtained; yield 1.05 g (88%), mp 100°C (101°C [16]).

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