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LETTERS TO THE EDITOR

Synthesis and Structure of μ-Oxobis[(isocyanato)triphenylantimony] (1,4)-Dioxane Solvate

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Reactions of organoantimony(V) compounds with urea have been described only in [1, 2]. Thus, melting (130–140°C) tri-*n*-butyl- or triisobutylantimony dihydroxide or oxide with urea in a vacuum resulted in trialkylantimony diisocyanates [1]. We have studied the interaction of tetraphenylantimony chloride and bromide with urea in the melt at 180°C. The reaction product was tetraphenylantimony cyanamide, whose structure was established by X-ray diffraction analysis [2]. It was of interest to continue studying the interaction of urea with arylantimony(V) compounds.

The reaction of triphenylantimony dibromide with urea was performed in the melt at 155°C. The reaction mixture was treated with dioxane (3 × 15 mL) to isolate the desired product. After evaporation of the solvent μ-oxobis[(isocyanato)triphenylantimony] (1,4)-dioxane solvate **I** was obtained as colorless crystals with a 58% yield.

It should be noted that the compounds of general formula $(NCO)R_3SbOSbR_3(NCO)$, where R = *i*-Bu, *n*-Bu, Me, Ph, have been previously prepared by reacting triorganylantimony dichloride with silver (potassium) cyanate in methanol or acetone. The compounds were characterized by elemental analysis and IR spectroscopy [1, 3].

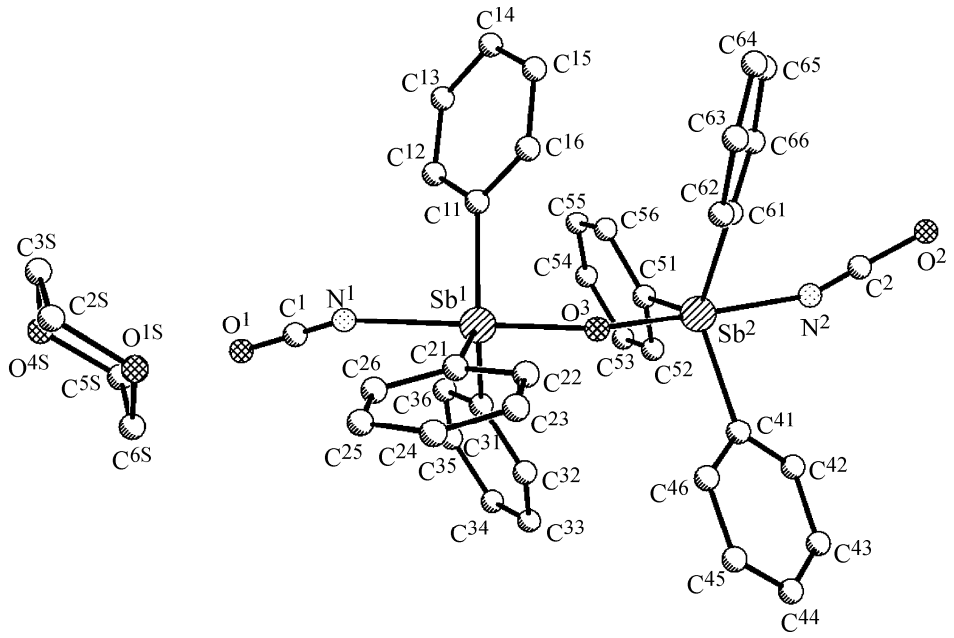
Compound **I** obtained by us is the first specimen of triorganylantimony μ-oxobis(isocyanates), the structure of which has been proved by XRD.

The crystal structure of **I** is based out of binuclear molecules with antimony atoms having distorted trigonal–bipyramidal coordination (see figure).

The apical positions are occupied by a bridging oxygen atom and an isocyanate group. Axial angles NSbO are 177.30(19)° and 179.12(19)°. Phenyl substituents lie in the equatorial plane. In the organoantimony fragment Ph_3Sb^1 the equatorial substituents are arranged more symmetrically [CSbC = 119.0(2)°, 120.1(2)°, 120.2(2)°]. In another fragment the corresponding angles vary in the range 116.9(2)°–122.4(2)° with the sum of the equatorial angles 359.3° and 359.1°, respectively. The planar phenyl rings were tilted with respect to the [SbC3] bipyramid base, the corresponding dihedral angles being 41.06°, 46.69°, and 82.38° (the substituents at the Sb1 atom) and 19.10°, 40.62°, and 65.17° (the substituents at the Sb^2 atom).

Note a similarity of the average values of axial angles, equatorial angles sums, and bond Sb–C lengths [2.092(6)–2.115(6) Å] in **I** and triphenylantimony diisocyanate [178.6(6), 360.0°, 2.110(6)–2.115(6) Å] [4].

For antimony(V) halides and pseudohalides of general formula $XPh_3SbOSbPh_3X$ the average Sb–O bond lengths and angles SbOSb are as follows: 1.958 Å, 173.1° (X = Cl [5]); 1.983 Å, 138.99° (X = Cl [6]); 1.944 Å, 173.4° (X = Br [7]); 1.921 Å, 180° (X = I [8]); 1.985 Å, 139.8° ($X = N_3$ [9]); 1.982 Å, 146.2° [X = NCO, **I**]. These values indicate a lack of correlation between the electronegativity of the substituent X and the value of the angle at the oxygen atom. The Sb–O bond lengths are significantly smaller than the sum of covalent radii of the antimony and the



General view of complex **I**. Hydrogen atoms are not shown.

oxygen atoms (2.14 Å) [10]. As the distance Sb–O decreased, the angle SbOSb increases. This dependence is attributed in [11–13] to overlapping of vacant *d*-orbitals of the metal atom with the lone electron pairs of the oxygen atom. This is reflected in the elongation of Sb–N [2.250(5), 2.258(7) Å] and C–O bonds [1.232(8), 1.285(9) Å] along with reducing the distances N–C [0.973(8), 1.110(8) Å] compared to those in triphenylantimony diisocyanate [Sb–N 2.122(4), 2.125(4) Å; C–O 1.186(7), 1.189(8) Å; N–C 1.111(7), 1.146(7) Å] and isocyanic acid {C–O 1.184 Å, N–C 1.183 Å [14]}. The bonds N–C and C–O are almost collinear. The presence of organoantimony fragments does not distort NCO angles whose values {178.1(8)°, 178.0(9)° (**I**); 178.4(5)°, 177.8(10)° [4]} are comparable with the angle in the isocyanic acid, where the deviation of the carbon atom from N–C–O axis is 0.011 Å.

In the molecule of **I** there is an additional interaction Sb···Sb at a distance of 3.754 Å, which is less than the double value of the van der Waals radius of the antimony atom (4.4 Å) [10]. Such contacts (3.707–3.909 Å) take place in the non-linear molecular fragments SbOSb of $XPh_3SbOSbPh_3X$ (X = Cl, Br, N_3) [15]. Compound **I** is readily soluble in dioxane from which it crystallized as a solvate.

X-Ray diffraction study of compound I. Unit cell parameters of the single crystal of **I** of a prismatic shape (0.18 × 0.10 × 0.06) and the intensity of 27437 reflections, 9075 of which are independent, were measured on a Bruker SMART APEX II diffractometer at 120(2) K (Mo*K*-radiation, graphite monochromator). The processing of the experimental data and the averaging of equivalent reflections were carried out by means of Bruker APEX II program package [16]. The structure was solved by the direct method and refined by full-matrix anisotropic approximation with respect to F^2_{hkl}. Semiempirical accounting for extinction was done with the aid of the SADABS program [17]. The hydrogen atoms were placed to the geometrically calculated positions and refined using the *rider* model. For reflections with $I > 2\sigma(I)$: R_1 0.0513, wR_2 0.1066, *GOF* 1.008, $\Delta\rho_{min}/\rho_{max}$ = –1.366/1.636 *e*/Å^3. All calculations were performed with the use of SHELXTL PLUS software package [18].

The crystals of compound **I** are triclinic, $C_{38}H_{30}N_2O_3Sb_2 \cdot C_4H_8O_2$, *M* 894.24, *a* 9.9797(17), *b* 13.469(2), *c* 15.558(3) Å, α 72.944(3), β 79.586(3), γ 71.323(3)°, *V* 1885.1(6) Å^3, *Z* 2, d_{calc} 1.575 g cm^{-3}, space group *P*-1. The XRD data were deposited in the Cambridge Crystallographic Data Centre (CCDC 1048364).

μ-Oxobis[(isocyanato)triphenylantimony] (1,4)-dioxane solvate. A mixture of 1.00 g (1.95 mmol) of triphenylantimony dibromide [19] and 2.34 g (39.00 mmol)

of urea was heated at 155°C with stirring for 10 min. The product was extracted with dioxane (3 × 15 mL). After evaporation of the solvent, colorless crystals were obtained. Yield 1.01 g (58%), mp 161°C. Found, %: C 56.56; H, 4.01; N 2.94. $C_{38}H_{30}N_2O_3Sb_2 \cdot C_4H_8O_2$. Calculated, %: C 56.36; H, 4.25; N 3.13.

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