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Synthesis and Structure of Tetraphenylantimony Cyanamide

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Abstract—The reactions of tetraphenylantimony chloride and bromide with carbamide were used to obtain tetraphenylantimony cyanamide in yields of 52 and 48%, respectively. According to X-ray diffraction data, the antimony atom has a distorted trigonal bipyramidal coordination with axial cyanamide and aryl groups [axial CSbN angle 177.76(7)°, Sb–C 2.107(2)–2.167.2, Sb–N 2.3383(18) Å].

Keywords: tetraphenylantimony cyanamide, synthesis, X-ray diffraction analysis, trigonal bipyramidal coordination

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Organic compounds of Sb(V) are known to act as O,N-arylating agents: benzodioxastibolanes react with primary and secondary amines, alcohols, and phenols in the presence of copper salts to form corresponding N- and O-aryl derivatives [1].

Organoantimony compounds $Alk_3(PhCH_2)SbBr$ (Alk = Me, Bu) react with aldehydes RCHO (R = Ph, $4-ClC_6H_4$, $4-MeC_6H_4$, PhCH=CH, pyridin-2-yl) to form adducts whose hydrolysis provides benzyl alcohols $RCH(OH)CH_2Ph$ [2–5]. In the present work we studies the reaction of tetraphenylantimony halides with carbamide.

It was found that Ph_4SbHlg (Hlg = Cl, Br) react with carbamide under heating to form previously unknown tetraphenylantimony cyanamide (**I**). The structure of compound **I** was established by X-ray diffraction analysis.

Antimony cyanamides were structurally characterized using the example of two compounds. Tetraphenylantimony benzoylcyanamide $Ph_4Sb[NCNC(O)C_6H_5]$ was prepared by the reaction of tetraphenylantimony bromide with silver benzoylcyanamide in acetonitrile. The other compound $[C_7H_{14}N_2]SbCl_5$ was synthesized from antimony pentachloride and diisopropylcyanamide in dichloroethane [6–8].

The antimony atom in compound **I** has a distorted trigonal bipyramidal coordination with three equatorial phenyl ligands (Fig. 1). The phenyl rings have a pseudopropeller arrangement with respect to the $[SbC_3]$ bipyramid base plane, forming dihedral angles of 9.20°, 37.53°, and 59.11° with the latter.

The cyanamide substituent is in an axial position, in complete agreement with the valence shell electron pair repulsion theory [9]. The axial $C^{20}Sb^1N^1$ angle is 177.76(7)° and the $C^2Sb^1C^8$, $C^8Sb^1C^{14}$, and $C^2Sb^1C^{14}$ angles are close to 120° [115.02(8)°, 119.90(8)°, and 122.22(8)°, respectively], which is characteristic of angles between equatorial bonds with such structures. The equatorial bonds $C^2–Sb^1$, $C^8–Sb^1$, and $C^{14}–Sb^1$ [2.107(2), 2.113(2), and 2.118(2) Å, respectively] are not coplanar: the sum of angles between these bods is smaller than 360° (357.14°). The axial bond $C^{20}–Sb^1$ [2.167(2) Å] is slightly longer then equatorial C–Sb bonds.

The trigonal bipyramidal geometry of $Ph_4Sb[NCN·C(O)C_6H_5]$ is even more distorted: the sum of equatorial angles is 323.9° and the Sb–C bond lengths span the range 2.07(2)–2.13(2) Å [7]. The Sb–N distance [2.3383(18) Å] in **I** is shorter than in $Ph_4Sb[NCNC(O)C_6H_5]$ [2.67(2) Å], at the sum of the covalent radii of these atoms equaling 2.15 Å [10].

The cyanamide hydrogen was not located but was included in the summary formula. The $C^1–N^1$ and $C^1–N^2$ bonds are virtually collinear: the $N^1C^1N^2$ angle is 178.3(3)°. Comparison of the C–N bond lengths in unsubsituted cyanamide [1.152(1) and 1.315(1) Å] [11], complex $Ph_4Sb[NCNC(O)C_6H_5]$ considered as an addition product of the benzoylcyanamide ion to a tetrahedral Ph_4Sb^+ [1.15(3) and 1.27(3) Å], and

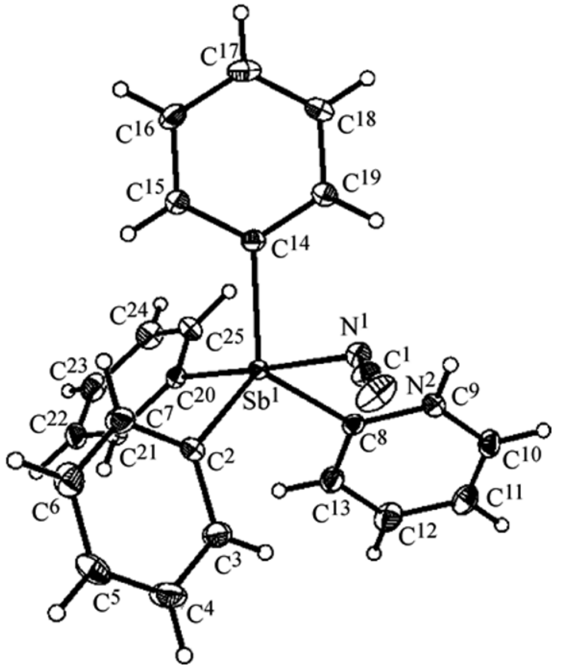

Fig. 1. General view of molecule **I** (50% thermal ellipsoids).

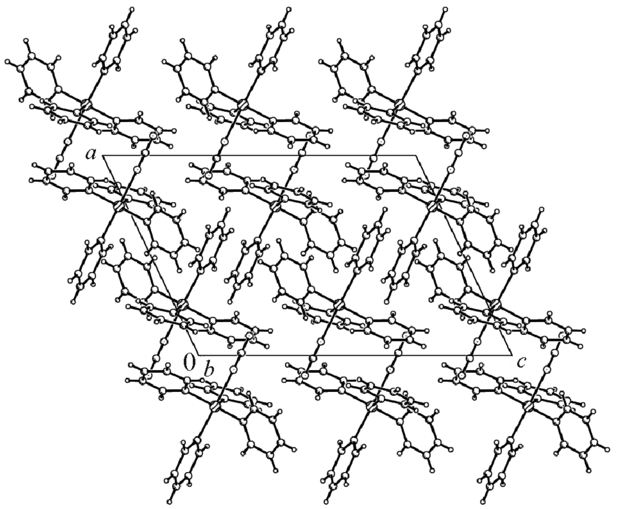

Fig. 2. Crystal packing of molecules **I**.

compound **I** [1.188(3) and 1.196(3) Å] reveals their essential equalization in the latter compounds. The delocalization of electron density makes the C–N distance shorter compared to standard *sp*-C bond lengths (1.16 Å) [12]. The antimony-containing substituents in **I** and $[C_7H_{14}N_2]SbCl_5$ almost do not distort the NCN angle [178.3(3)° and 177(1)°, respectively] compared to that in cyanamide [178.1(1)°].

Neighboring formula units in the unit cell are held together by van der Walls forces. Along the *c* axis, molecules **I** form chains (Fig. 2) due to $H^{16}C^9$ intermolecular contacts (2.744 Å; the sum of the van der Walls of H and C is 2.9 Å). The chains form layers. The intermolecular contacts N^1H^{18} are 2.618 Å (the sum of the van der Walls of H and N is 2.8 Å) [10].

EXPERIMENTAL

X-ray diffraction analysis of compound I. The unit cell parameters of a plate-like single crystal of compound **I** (0.55 × 0.34 × 0.10) and intensities of 25699 reflections, of which 5940 are unique, were measured on a Bruker APEX II CCD diffractometer at 120(2) K (Mo*K* radiation, graphite monochromator). A hemisphere of data was collected over the range $2.32° < \theta < 30.00°$. Data processing and averaging equivalent reflections were performed using the Bruker Apex II software package [13]. The structure was solved by a direct method and refined by full-matrix least squares on F^2 in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were located geometrically and refined isotropically by the rider model: R_1 0.0256, wR_2 0.0618, $F^2 > 2\sigma(F^2)$, *GOF* 1.007, $\Delta\rho_{\min}/\rho_{\max}$ –0.585/0.919 $e/Å^3$. All calculations were performed using SHELXTL [14].

Crystals of compound **I** $[C_{25}H_{21}N_2Sb]$ (*M* 471.19), monoclinic, *a* 12.3001(6), *b* 10.5763(5), *c* 17.3557(7) Å; β 115.689(3)°; *V* 2034.63(16) $Å^3$, *Z* 4, d_{calc} 1.538 g/cm^3, space group *P*21/*c*.

The X-ray diffraction data were deposited in the Cambridge Crystallographic Database (CCDC 969921).

Tetraphenylantimony cyanamide (I). A mixture of 1.00 g (2.15 mmol) of tetraphenylantimony chloride [15] and 1.29 g (21.50 mmol) of carbamide was heated at 180° and stirred for 10 min. The reaction product was successively washed with water (3 × 15 mL) and acetone (30 mL). As acetone evaporated, compound **I** formed as colorless crystals, yield 0.53 g (52%), mp 206°C. Found, %: C 63.92; H 4.22. $C_{25}H_{21}N_2Sb$. Calculated, %: C 63.72; H 4.46.

The same conditions were used to synthesize compound **I** from tetraphenylantimony bromide and carbamide in 48% yield.

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