Preliminary communication

Recognition of linear and bent forms of solid μ-oxo-bis[iodotriphenylantimony(V)] (Ph₃SbI)₂O

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Abstract

Two quite different shapes of the $(Ph_3SbI)_2O$ molecule are found in separate crystals, namely **1a**, in which the Sb–O–Sb bridge is linear with bond distances of 1.9410–1.9437(6) Å and **1b** in which the Sb–O–Sb angle is 144.6(4)° and the Sb–O bonds are longer, averaging 1.971(8) Å. The two species also give distinct vibrational spectra. Both arise from the reaction of triphenylantimony with iodine in moist acetonitrile, **1a** as the initial crop of colourless crystals and **1b** as orange crystals left when the solution is allowed to evaporate to dryness.

Keywords: Phenylantimony(V) halides; Antimony; Crystal structure; Stiboxane

Of twenty stiboxane compounds structurally characterised to date most are bent, with the Sb–O–Sb angle in the range 135–140°, but several are close to linear [1]. The bromide $(Ph_3SbBr)_2O$ is of the latter type, having bond angles of 170.2 and 176.6° in a pair of crystallographically distinct molecules [2], whereas the chloride $(Ph_3SbCl)_2O \cdot 2C_6H_6$ (a benzene solvate) has a bent Sb–O–Sb linkage with an angle of 139.0° [3].

We obtained colourless crystals of $(Ph_3SbI)_2O$, **1a**, from the reaction Ph_3Sb with I_2 in dichloromethane when we used reagents that had not been specially dried. X-ray crystallography [4] revealed centrosymmetric molecules with the dimensions shown in Fig. 1. The antimony centre has trigonal bipyramidal coordination with equatorial phenyl groups, an axial iodine atom, and a rather short bond to the bridging oxygen. The lengths of the Sb–O bonds, which average 1.942 Å, are almost the same as those in $(Ph_3SbBr)_2O$ [2].

The original target of our work, Ph_3SbI_2, was obtained as yellow flakes formed from a solution of equimolar amounts of Ph_3Sb and I_2 in anhydrous CH_2Cl_2. This material was positively identified by its vibrational [5] and NMR [6] spectra, and by an X-ray diffraction examination that showed the solid to be isostructural with Ph_3SbBr_2 [7]. It is not the same as the solid Ph_3SbI_2 described, that was obtained recently from ether solution under strictly anaerobic and anhydrous conditions [8]. Our product also contained a few orange crystals and one was mounted for crystallographic study [9]. The result was very surprising. Like **1a**, the new solid **1b** consists of $(Ph_3SbI)_2O$ molecules, but these have a V-shaped frame, as shown in Fig. 1.

The geometry around antimony, though generally similar to that of **1a**, differs significantly ($> 3\sigma$) in having greater distances to both of the axial atoms, the Sb–O bonds averaging 1.971 and the Sb–I bonds averaging 2.993 Å. The Sb atoms are separated by 3.755 Å. For comparison, $(Ph_3SbCl)_2O$ with a bond angle of 139° has Sb–O bonds of 1.983 Å and an Sb · · · Sb separation of 3.715 Å [3]. Neither crystal of $(Ph_3SbI)_2O$ includes solvent. A small residual electron density is concentrated close to the antimony atoms and probably arises from the need to correct for absorption. Non-hydrogen atoms of adjacent molecules are separated by more than 3 Å. There are no counter anions in either structure, so bridging by an OH group is ruled out.

If Ph_3Sb is treated with I_2 in CH_3CN containing 5% of water, colourless crystals of **1a** separate initially, and then evaporation leaves a residue of the orange solid **1b**.
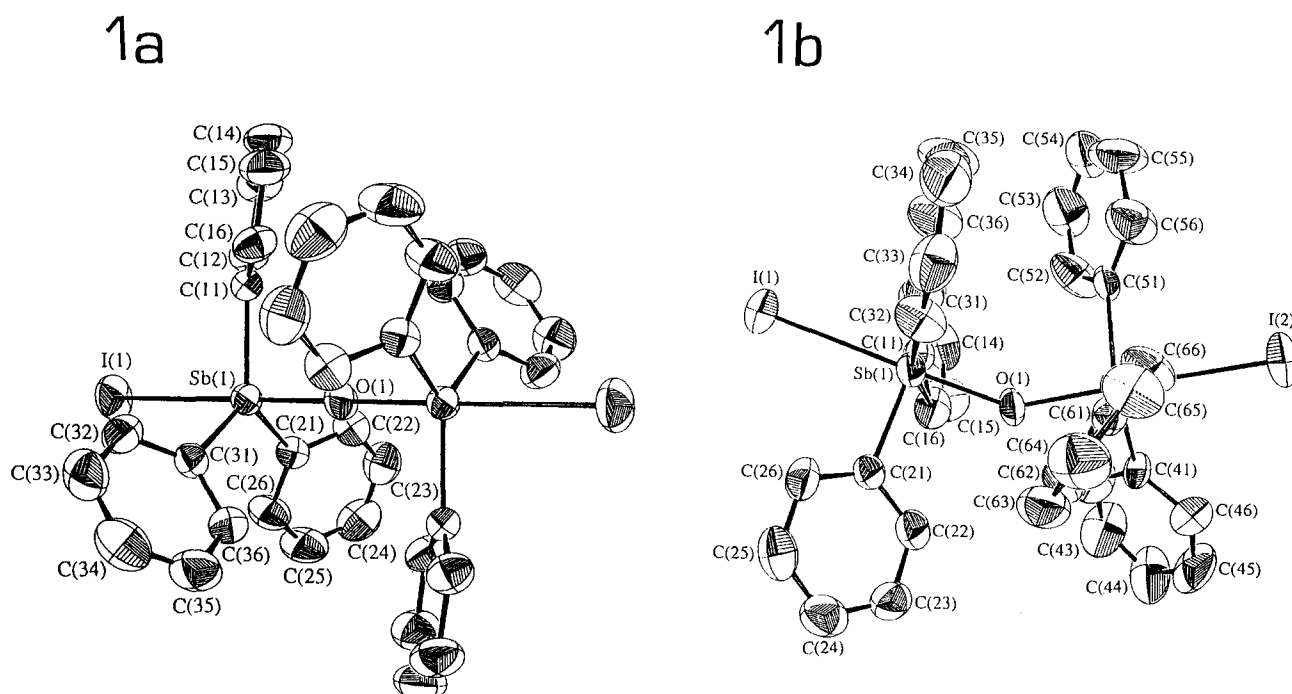
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Fig. 1. The molecular structures of $(Ph_3SbI)_2O$ in the colourless crystal **1a** and the orange crystal **1b**. Selected dimensions: **1a** contains two independent, centrosymmetric molecules with Sb–O = 1.9410(6) or 1.9437(6) Å, Sb–I = 2.954(1) or 2.968(1) Å, Sb–C$_{(av)}$ = 2.105(5) Å, Sb–O–Sb = 180°, C–Sb–O$_{(av)}$ = 90.6(1)°; **1b** consists of molecules with Sb–O = 1.986(8) and 1.956(8) Å, Sb–I = 2.991(3) and 2.995(1) Å, Sb–C$_{(av)}$ = 2.107(10) Å, Sb–O–Sb = 144.6(4)°, C–Sb–O$_{(av)}$ = 91.9(4)°.

Each form melts at 195–198 °C. Their vibrational spectra are distinct; **1a** has a single strong IR band at 780 cm^{-1}, whereas **1b** gives a pair of bands, 771 (strong) and 803 cm^{-1} (medium) associated with the Sb–O–Sb bridge [10]. The Raman spectrum [11] of **1b** displays ν(Sb–I) bands at 112 (strong) and 145 cm^{-1} (weak). For **1a** ν(Sb–I)$_{sym}$ appears as a Raman band at 89 cm^{-1} and ν(Sb–I)$_{asym}$ is conspicuous in the far IR at 114 cm^{-1}, which matches the spectrum of $(Ph_3SbBr)_2O$, in which the Sb–Br stretches appear at 119 cm^{-1} (Raman) and 144 cm^{-1} (IR). Vibrational coupling with the antimony atoms can account for the low values of the ν(Sb–X) modes in the linear case. In diffuse reflection spectra **1a** absorbs only below 350 nm, whereas **1b** has broad absorption below 450 nm which tails off through the visible region to 700 nm.

The NMR spectra [12] of the solution that gives rise to **1a** and **1b** indicate the presence of a pair of phenylantimony species in equilibrium. These give separate sets of signals, whose relative intensities change with concentration and temperature. They are thought to belong to $Ph_3SbI(OH)$ and its dimer $Ph_3SbI(\mu$-OH)$_2ISbPh_3$ from which the linear and bent forms of $(Ph_3SbI)_2O$ may be produced by condensation.

Molecular structures that differ slightly as the result of crystal packing are commonplace. However the change from **1a** to **1b** is substantial; the colour alters and the bond lengths differ significantly (the co-linear Sb–O bonds being shorter), reinforcing the view that

rehybridisation accompanies the change from the linear to the V-shaped isomer.

References and notes

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[4] Elemental analysis for $C_{36}H_{30}I_2OSb_2$: Calc. C 44.31%, H 3.10%; Found: C 44.34%, H 2.81%.

[5] Crystal data for **1a**: $C_{36}H_{30}I_2OSb_2$, $M = 975.90$ g mol^{-1}, colourless cuboid, $0.25 \times 0.20 \times 0.15$ mm, triclinic, space group, $P\bar{1}$, $a = 9.771(4)$, $b = 19.286(4)$, $c = 9.819(4)$ Å, $\alpha = 96.69(1)$, $\beta = 103.20(2)$, $\gamma = 75.46(2)°$, $V = 1740.3(8)$ Å^3, $Z = 2$, $D_c = 1.862$ g cm^{-3}, $F(000) = 924$, $\mu = 3.35$ mm^{-1}. Enraf-Nonius CAD4 diffractometer, graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å, $\omega/2\theta$ scans, $T = 20$ °C. **1a** consists of two half-molecules, each lying on a centre of symmetry. Structure solved by conventional Patterson and heavy-atom electron density synthesis and refined by full least squares on F^2 (SHELXL-93) [13]. Lorentz and polarisation corrections applied

using locally written programs and absorption corrections applied using empirical psi scans [14]. All non-hydrogen atoms were allowed to refine anisotropically and the hydrogen atoms were included in the calculated positions and allowed to ride on the atoms to which they were attached with 20% greater thermal parameter. Final $R = 0.025$, $wR2 = 0.064$, for 4533 observed reflections with cut-off $I > 2\sigma(I)$. For all 5149 reflections, $wR2 = 0.089$. Further details of the crystal structure determination are available from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

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