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Adduct formation between $(Ph_3SbI)_2O$ and I_2

Matthew J. Almond [a,*], Michael G.B. Drew [a], David A. Rice [a], Gavin Salisbury [a], Michael J. Taylor [b,*]

[a] *Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK*
[b] *Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand*

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Abstract

The compound $4[(Ph_3SbI)_2O] \cdot I_2$ (**1**) has been obtained by the addition of an I_2 solution in acetonitrile containing ca. 5% water to a solution of triphenylantimony in the same solvent. **1** crystallises in the rhombohedral crystal system. The unit cell contains 12 molecules of $(Ph_3SbI)_2O$ and four diiodine molecules. The I_2 molecules link $IPh_3SbOSbPh_3I$ molecules to form a one-dimensional chain, while the remaining molecules of $IPh_3SbOSbPh_3I$ are not coordinated to I_2. The geometry of the $IPh_3SbOSbPh_3I$ unit, in which the Sb–O–Sb bridge is linear, is relatively little perturbed upon coordination, but the I_2 unit shows a significant lengthening of the I–I bond compared with free diiodine. This bond lengthening is reflected in the Raman spectrum of **1** which displays ν(I–I) at 174 cm^{-1}, representing a decrease of 40 cm^{-1} from the position of the fundamental vibration of the free diatomic molecule.

Keywords: Antimony; Iodine; Molecular adducts; Stiboxane; Crystal structure

1. Introduction

Oxo-bridged antimony(V) compounds of the type $YPh_3SbOSbPh_3Y$, where Y represents oxyanion, halide or pseudohalide ligands, are of long standing [1]. Of particular interest is the observation that some such compounds contain a linear, and others a bent Sb–O–Sb group [2]. In reviewing these structural types Glidewell [3] proposed a model which predicts that the linear Sb–O–Sb skeleton will be favoured in cases where the terminal Y ligand is tightly bound with a short Sb–Y distance. However, we have encountered a compound of this type, the iodide $(Ph_3SbI)_2O$, which occurs in both forms [4]. Orange crystals of $(Ph_3SbI)_2O$ are monoclinic and consist of molecules with a 'V'-shaped skeleton having an Sb–O–Sb angle of 144.6°; by contrast colourless, triclinic, crystals of the same constitution show the linear version of the molecule.

This unexpected finding suggests that special factors may need to be taken into account to explain the structural variation of μ-oxo-bridged compounds. The conditions of preparation and crystallisation of the product are likely to be important. Packing effects and subtle electronic changes within the Sb–O–Sb bridge may be involved.

Extending the range of well-defined oxo-bridged antimony(V) systems, we now report a crystallographic and spectroscopic study of the compound $4[(Ph_3SbI)_2O] \cdot I_2$ (**1**) which is an iodine adduct containing $IPh_3SbOSbPh_3I$ molecules of the linear kind. The diiodine adduct crystallises alongside $(Ph_3SbI)_2O$ during the reaction of Ph_3Sb with I_2 in the presence of moisture [4]. Under anhydrous conditions, these reagents yield Ph_3SbI_2 in several crystalline modifications [5,6].

Our work on **1** is also of interest in the context of an earlier claim by Boodts and Bueno of complex formation between diiodine and triphenylstibine oxide [7]. However, their reported spectrum cannot be assigned with any confidence because the formulation of the product as a charge transfer complex $Ph_3Sb{=}O \cdot I_2$ was based upon a view of the parent oxide as a monomer $Ph_3Sb{=}O$, analogous to $Ph_3P{=}O$, which has since been shown to be erroneous [8].

* Corresponding authors.

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2. Experimental section

2.1. Preparation of crystals

To a solution of triphenylantimony in acetonitrile containing ca. 5% of water, a dark brown solution of iodine in the same solvent was added dropwise. The mixture was yellow at first, then became orange-brown when equimolar amounts of I_2 and Ph_3Sb were present. The reaction vessel was capped and left overnight, after which the solution was decanted to expose a mixture of well-formed crystals. Some were colourless and others had a greenish-brown cast. An example of each kind was selected for crystallographic study. The colourless solid was shown to be the previously reported compound $(Ph_3SbI)_2O$ (**1a**) in the triclinic form [4] (Fig. 1). The coloured crystals were a new material which proved to be the iodine adduct $4[(Ph_3SbI)_2O] \cdot I_2$ (**1**).

In a similar reaction the solution phase was allowed to evaporate to dryness in air, leaving a dark brown residue. Rinsing with a small volume of acetonitrile exposed crystals, some orange and some of the greenish-brown sort. IR spectroscopy showed the orange crystals to be $(Ph_3SbI)_2O$ in the monoclinic form (in which the Sb–O–Sb framework has a bent configuration). The greenish-brown crystals have a melting point of 194–196°C, which is close to that of both the colourless and orange modifications of $(Ph_3SbI)_2O$ [4].

2.2. Crystallography

Crystal data are given in Table 1 together with refinement details. Diffraction data were collected with Mo Kα radiation using the MAR Research Image Plate System. The crystal was positioned at 75 mm from the image plate. Ninety-five frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [9]. The structure was solved using direct methods with the SHELX86 program [10]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions. An empirical absorption correction was applied using the DIFABS program [11]. The structure was then refined on F^2 using SHELXL [12]. All calculations were carried out on a Silicon Graphics R400 workstation at University of Reading. Table 2 contains the atomic coordinates of **1** and in Table 3 are listed selected bond lengths and angles. Further details are available from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Table 1
Crystal data and structure refinement for **1j**

Formula	$4[IPh_3SbOSbPh_3I], I_2$
Empirical formula	$C_{144}H_{120}I_{10}O_4Sb_8$
Formula weight	4157.40
Temperature (K)	293(2)
Wavelength (Å)	0.71070
Crystal system	rhombohedral
Space group	R-3
Unit cell dimensions (Å)	
a	25.022(7)
b	25.022(7)
c	19.381(7)
Volume (Å^3)	10509(6)
Z	3
Density (calculated) (Mg m^{-3})	1.971
Absorption coefficient (mm^{-1})	3.772
F(000)	5862
θ range for data collection (deg)	2.15 to 25.93
Index ranges	$0 \leq h \leq 30, -30 \leq k \leq 26, -23 \leq l \leq 23$
Reflections collected	10925
Independent reflections	4377 (R(int) = 0.0346)
Data/parameters	4377/253
Goodness-of-fit on F^2	1.092
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0509$, $wR2 = 0.1130$
R indices (all data)	$R1 = 0.0663$, $wR2 = 0.1331$
Largest diff. peak and hole (e Å^{-3})	1.221 and −2.783

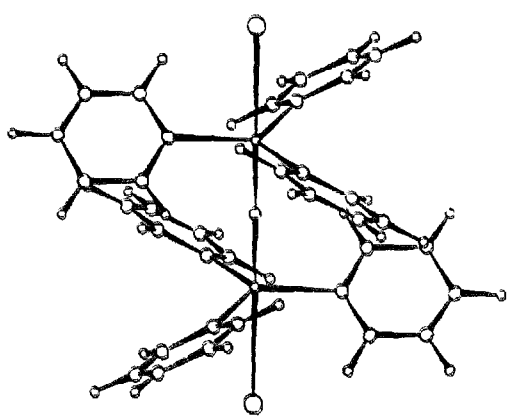

Fig. 1. The structure of the $(Ph_3SbI)_2O$ molecule.

2.3. Spectroscopy

IR spectra were recorded on samples in pressed CsI or polythene discs using a Perkin–Elmer model 1710 (Reading) or Paragon 1000PC and Bio-Rad FTS-60V (Auckland) spectrometers. The lower limit of the far-IR of the latter instrument, which operates with a vacuum bench, is 80 cm^{-1}. Each spectrometer operated with a typical accuracy and resolution of +/−2 cm^{-1}. Raman spectra were obtained from single crystals of **1** at University of Auckland using a Jobin Yvon U1000 spectrometer fitted with a microscope attachment. Excitation employed the green, 514 nm, line of a Spex argon-ion laser operating at powers of 20–50 mW.

3. Results and discussion

3.1. Crystal structure

The unit cell of **1** contains 12 molecules of $(Ph_3SbI)_2O$ and four diiodine molecules. The iodine atoms in the discrete I_2 molecule occupy positions 6c with three-fold symmetry. There are independent molecules of $IPh_3SbOSbPh_3I$ type, which contain Sb(1) and Sb(2). The two molecules have similar geometries with a Sb–O–Sb moiety that is perforce linear. Each Sb is five-coordinate, being bonded to three equatorial carbon atoms and to an iodine atom in an axial position trans to the bridging oxygen atom.

The Sb–C equatorial distances are similar in the two molecules, being 2.098(7) Å around Sb(1) and averaging 2.107(8) Å around Sb(2). In both molecules the angles subtended by axial and equatorial atoms at the metal are within 3° of 90°. The Sb(1)–I distance of 3.035(2) Å is significantly longer than the distance Sb(2)–I (2.964(1) Å), whereas the Sb(1)–O distance is a little less than Sb(2)–O (1.9209(11) as against

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**

	x	y	z	U_{eq}
Sb(1)	0	0	4009(1)	28(1)
I(1)	0	0	2443(1)	56(1)
O(1)	0	0	5000	47(3)
C(11)	412(3)	−552(3)	3961(4)	34(2)
C(12)	963(4)	−352(4)	4286(5)	48(2)
C(13)	1225(5)	−725(6)	4284(6)	71(3)
C(14)	916(6)	−1292(6)	3973(7)	76(3)
C(15)	372(6)	−1481(5)	3660(6)	68(3)
C(16)	117(5)	−1116(4)	3634(5)	53(2)
Sb(2)	5796(1)	165(1)	5349(1)	30(1)
I(2)	7004(1)	417(1)	5905(1)	60(1)
O(2)	5000	0	5000	39(2)
C(21)	5566(3)	331(3)	6342(4)	36(2)
C(22)	5333(4)	727(4)	6392(4)	44(2)
C(23)	5106(5)	789(6)	7000(6)	70(3)
C(24)	5076(6)	445(7)	7559(6)	84(4)
C(25)	5323(7)	74(7)	7509(6)	89(4)
C(26)	5593(6)	22(5)	6904(5)	61(3)
C(31)	5611(4)	−712(3)	5031(4)	35(2)
C(32)	6009(4)	−788(4)	4608(5)	53(2)
C(33)	5830(6)	−1345(6)	4309(6)	77(3)
C(34)	5263(7)	−1834(5)	4470(6)	74(3)
C(35)	4869(5)	−1775(4)	4897(6)	61(3)
C(36)	5044(4)	−1208(4)	5179(4)	40(2)
C(41)	6253(3)	883(3)	4625(4)	34(2)
C(42)	6080(4)	747(4)	3949(5)	45(2)
C(43)	6313(4)	1201(5)	3459(5)	54(2)
C(44)	6711(5)	1799(5)	3655(6)	71(3)
C(45)	6878(6)	1925(5)	4321(7)	81(4)
C(46)	6665(5)	1463(4)	4813(5)	61(3)
I(3)	0	0	705(1)	65(1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths (Å) and angles (deg) for **1**

Sb(1)–O(1)	1.9209(11)
Sb(1)–C(11)	2.098(7)
Sb(1)–I(1)	3.035(2)
C(11)–Sb(1)–C(11)	92.6(2)
C(11)–Sb(1)–C(11)[a]	119.80(3)
C(11)–Sb(1)–I(1)	87.4(2)
Sb(2)–O(2)	1.9425(7)
Sb(2)–C(31)	2.097(7)
Sb(2)–C(21)	2.108(8)
Sb(2)–C(41)	2.109(8)
Sb(2)–I(2)	2.9636(10)
O(2)–Sb(2)–C(31)	90.5(2)
O(2)–Sb(2)–C(21)	90.4(2)
C(31)–Sb(2)–C(21)	122.3(3)
O(2)–Sb(2)–C(41)	90.6(2)
C(31)–Sb(2)–C(41)	116.0(3)
C(21)–Sb(2)–C(41)	121.6(3)
O(2)–Sb(2)–I(2)	179.04(3)
C(31)–Sb(2)–I(2)	89.9(2)
C(21)–Sb(2)–I(2)	88.6(2)
C(41)–Sb(2)–I(2)	90.0(2)
I(3)–I(3)[b]	2.732(3)

Symmetry transformations used to generate equivalent atoms: [a] $-x + y, -x, z$; [b] $-x, -y, -z$.

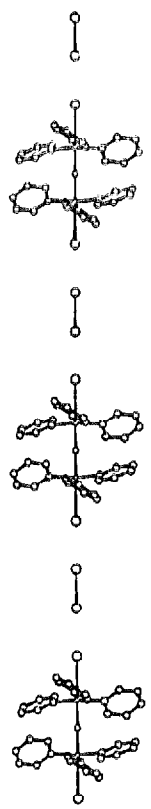

Fig. 2. The structure of the chain $\{\cdots I\text{–}I\cdots IPh_3SbOSbPh_3I\cdots I\text{–}I\cdots IPh_3SbOSbPh_3I\}_x$.

1.9425(7) Å). It seems likely that this difference is due to packing effects. As shown in Fig. 2, the $IPh_3SbOSbPh_3I$ molecules on the three-fold axis are packed alternately with I_2 molecules to form a one-dimensional (1-D) chain. The bond length in the I_2 molecule is 2.732(2) Å, which is towards the low end of the range of values found in many other structures containing the diiodine molecule. A search of the Cambridge Crystallographic database showed more than 60 occurrences of this molecule with a mean distance of 2.80 Å from values between 2.68–3.01 Å. This value is variable partly because it is significantly affected by packing effects. In the 1-D chain the distance between the iodine of the $IPh_3SbOSbPh_3I$ molecule and the diiodine molecule is only 3.370(1) Å so some weak interaction is probably present.

The dimensions of those $IPh_3SbOSbPh_3I$ molecules which are not linked to I_2 can be compared with those of the linear form of $(Ph_3SbI)_2O$, **1a**, reported earlier

Table 4
IR and Raman bands (below 1200 cm^{-1}) of $4[(Ph_3SbI)_2O]\cdot I_2$ (1) and $(Ph_3SbI)_2O$ (1a)

1		1a		Assignment [a]
IR	Raman	IR	Raman	
	45 s		43 s	lattice/
			60 s	bending
	76 s		70 vs	modes
86 vw	91 vs		89 vs	ν_s(Sb–I)
111 m	108 w,sh	114 s		ν_{as}(Sb–I)
136 w				x
		156 m	160 vw	x
	174 vs			ν(I–I)
183 w		190 w	187 w	u
			195 w	u
206 vw	208 w	206 m		u
	215 w		217 wm	u
225 m	225 w	224 s	226 wm	t
260 w	266 w	258 m	262 w	t
295 ms		295 s	293 w	t
	345 vw			w
365 w				w
		390 w	393 vw	w
449 ms		450 s		y
455 w,sh		457 s,sh	460 vw	y
615 w	613 vw	615 w	615 vw	s
	656 m		657 m	r
689 ms		688 s	691 w	v
725 w,sh		727 s		f
738 m	735 vw	736 m	733 w	f
772 s		780 s		ν_{as}(Sb–O–Sb)
803 m				?
		842 w	847 vw	g
915 vw	911 vw	915 vw	913 vw	i
970 vw	970 vw	970 w	970 vw	h
996 m	999 s	996 m	1000 s	p
1018 wm	1020 m	1020 wm	1021 m	b
1060 wm		1063 wm	1068 w	q

[a] Phenyl ring modes are assigned according to Whiffen's notation (see text). The bands of types q, r, t, u, x and y are sensitive to the nature of X in a molecule of the kind PhX.

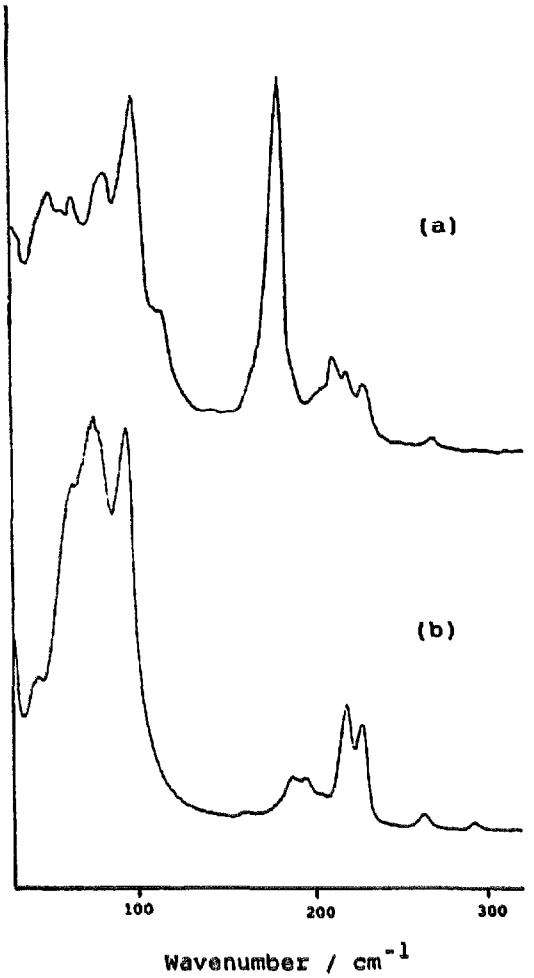

Fig. 3. Raman spectra of the crystalline solids: (a) $4[(Ph_3SbI)_2O]\cdot I_2$ (1); (b) $(Ph_3SbI)_2O$ (1a).

[4]. Taking for **1a** the average measurements of its two crystallographically independent molecules (which have very similar dimensions) gives Sb–O 1.9424(6), Sb–I 2.9610(10), Sb–C(av) 2.105(5) Å, O–Sb–C(av) 90.6(1)°, O–Sb–I 180°. The corresponding figures for the present structure are almost identical, namely Sb–O 1.9425(7), Sb–I 2.9636(10), Sb–C(av) 2.105(8) Å, O–Sb–C(av) 90.5(2)°, O–Sb–I 179.04(3)°. We have also compared the twist angles of the phenyl groups in the different versions of $(Ph_3SbI)_2O$. In the crystal of **1**, the phenyl rings about Sb(1) make angles of 31.5° with the SbC_3 equatorial plane. For the other molecules the angles around Sb(2) are 38.4, 40.1 and 36.2°, respectively. For the molecules of crystal **1a**, the corresponding angles are 38.5, 41.7 and 37.1°.

3.2. Vibrational spectra

The IR and Raman spectra of **1** and **1a** are compared in Table 4, while in Fig. 3 the Raman spectra are compared. The intense Raman scattering exhibited by **1** at 174 cm^{-1} (see Fig. 3(a)) almost certainly arises from

ν(I–I) of the I_2 portion of the adduct. This position represents a 40 cm^{-1} shift to low frequency compared with the fundamental for the I_2 molecule itself: for the isotope $^{127}I_2$ $\omega_e = 214.6$ and $\omega_e x_e = 0.61$ cm^{-1} [13]. The intense Raman band at 91 cm^{-1} may be assigned to ν_{sym}(Sb–I) of the $(Ph_3SbI)_2O$ units of **1** and is almost unchanged in position from the corresponding vibration of **1a** whose spectrum is shown in Fig. 3(b). There is no obvious feature which may be attributed to ν_{sym}(Sb–I) of the adducted $(Ph_3SbI)_2O$ units of **1**. This vibration may give rise to the indistinct shoulder on the flank of the 91 cm^{-1} band. All of the Raman scattering above 200 cm^{-1} may be attributed to vibrations of the Ph_3Sb moiety of either adducted or free $(Ph_3SbI)_2O$ units and may be assigned with more-or-less certainty as in Table 4, according to the scheme of Whiffen [14].

Most of the IR absorptions of **1** find counterparts in the spectrum of **1a** with modest wavenumber shifts. The IR band at 111 cm^{-1} is likely to belong to ν_{as}(Sb–I). Strong bands of **1a** at 680 and 727 cm^{-1}, assigned to ν and f modes [14–16] of the Ph_3Sb moiety, respectively, are replaced in **1** by bands at 689 and 738 cm^{-1}, the latter feature showing a weak shoulder at 725 cm^{-1}. The asymmetric (Sb–O–Sb) vibration gives rise to a single, strong feature at 772 cm^{-1} in the spectrum of **1**, close to the corresponding feature at 780 cm^{-1} in the spectrum of **1a**. An extra IR band at 803 cm^{-1} of medium intensity in the spectrum of **1** may arise from the ν_{as}(Sb–O–Sb) mode of the adducted $(Ph_3SbI)_2O$ molecule, wherein the Sb–O bond is slightly shorter compared with the remaining molecules.

It is instructive to comment briefly on the intermolecular bonding in **1**. The main point concerns the I–I bond length of the diiodine molecule and the vibrational frequency of this unit. The magnitude of the shift to low frequency of ν(I–I) and the degree of lengthening of the I–I bond reflect the level of donation of electronic charge into the σ^* LUMO of the I_2 unit and are usually taken as a measure of the strength of adduct formation [17]. The data quoted here suggest that there is a significant donation of charge from the $(Ph_3SbI)_2O$ unit to the I_2 in **1** but that the adduct is not very strong. The position of the visible absorption of I_2 adducts may also be taken as a measure of the strength of donation by the Lewis base (see for example Ref. [17]). The colour of **1** (a greenish-brown) is consistent with these observations.

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