Pergamon

PII : S0277-5387(96)00602-X

Polyhedron Vol. 16, No. 15, pp. 2643–2649, 1997

0277-5387/97 $17.00+0.00

Triorganoantimony(V) diorganophosphinates. Crystal and molecular structure of (diphenylphosphinato)(hydroxo)trimethylantimony(V), exhibiting a polymeric chain supramolecular self-assembly through hydrogen bonds

Cristian Silvestru,[a]* Anca Silvestru,[a] Ionel Haiduc,[a] D. Bryan Sowerby,[b] Klaus H. Ebert[c] and Hans J. Breunig[c]

[a]Facultatea de Chimie, Universitatea "Babes-Bolyai", RO-3400 Cluj-Napoca, Romania

[b]Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K.

[c]Fachbereich 2 der Universität Bremen, Postfach 330440, D-28334 Bremen, Germany

(Received 22 November 1996; accepted 4 December 1996)

Abstract—The reaction between R_3SbCl_2 (R = Me, Ph) and R'_2PO_2Na (R′ = Me, Ph) afforded $R_3Sb(O_2PR'_2)_2$ derivatives, which were investigated by IR and multinuclear (^1H, ^{13}C, ^{31}P) NMR spectroscopy. Attempts to grow crystals of $Me_3Sb(O_2PPh_2)_2$ led to colorless needles identified by X-ray diffractometry as $Me_3Sb(OH)[O(O)PPh_2]$, produced by partial hydrolysis. Coordination around the central metal atom is distorted trigonal bipyramidal with carbon atoms of the $SbMe_3$ unit in equatorial positions and two oxygen atoms occupying the axial positions [O—Sb—O 175.7(1)°]. The two antimony-oxygen distances are significantly different [Sb—O(H) 1.967(3) Å, Sb—O(P) 2.235(2) Å], as are the phosphorus–oxygen bond lengths in the basically monodentate diphenylphosphinato ligand [P—O 1.528(3) Å, P=O 1.490(3) Å]. The molecules are associated into polymeric chains through intermolecular hydrogen bonds between hydrogen of the hydroxo group and oxygen double bonded to phosphorus. © 1997 Elsevier Science Ltd

Keywords: organometallic compounds; hydroxo-organoantimony; diorganophosphinates; supramolecular.

In recent years inorganic and organic antimony derivatives of dithiolato ligands $[R_2PS_2]^-$ (R = alkyl, aryl, alkoxy, aroxy) have received some attention and the structural patterns of these compounds have been recently reviewed [1]. However, antimony(V) derivatives of oxo ligands $[R_2PO_2]^-$ were scarcely investigated. Only the structures of $[Cl_4Sb(O_2PR_2)]_2$ (R = OMe [2], Me [3]) and $[Cl_3Sb(O_2PMe_2)]_2O$ [4], and more recently, of some phenylantimony(V) derivatives, i.e. $[Ph_3Sb(O_2PMe_2)]_2O$ [5], $[Ph_2SbCl\{O_2P(C_6H_{11})_2\}]_2O$ [6], $[Ph_2Sb(O_2PR_2)O]_2\cdot 2CH_2Cl_2$ (R = *cyclo*-C_6H_{11}, *cyclo*-C_8H_{15}), $Ph_8Sb_4O_4(OH)_2[O_2P(\textit{cyclo}\text{-}C_6H_{11})_2]_2\cdot HO_2CMe\cdot CH_2Cl_2$ [7], were described. In all cases these dinuclear and tetranuclear compounds contain bridging diorganophosphinato moieties.

Within the frame of our interest in the structural patterns of metal–thiophosphorus ligand complexes, we reported on the molecular structures of monomeric compounds $Me_3Sb(S_2PPh_2)_2$ [8], and $Me_3Sb(OSPPh_2)_2$ [9], both containing basically monodentate thio ligands. This behavior of the thio ligands led us to attempt the preparation of similar derivatives containing diorganophosphinato groups, i.e. $R_3Sb(O_2PR'_2)_2$. Such compounds might also be mononuclear species with the phosphorus ligand acting as a monodentate moiety, in contrast to the usual bridging behavior.

We report here the synthesis and spectroscopic characterization of the new $R_3Sb(O_2PR'_2)_2$ (R, R′ = Me, Ph) compounds, as well as the crystal and molecular structure of the unexpected Me_3Sb

---

* Author to whom correspondence should be addressed.

(OH)[O(O)PPh$_2$] derivative. The latter appears to be the first compound of the type Me$_3$Sb(OH)Y for which the presence of the hydroxo group has been proved by a single-crystal X-ray diffraction study (for a recent survey of the literature, see [10]).

EXPERIMENTAL

The starting materials used in this work were prepared according to published procedures: R$_3$SbCl$_2$ (R = Me [11], Ph [12]), R$'_2$P(O)OH (R$'$ = Me [13], Ph [14]). Infrared spectra were recorded as Nujol mulls using a Perkin-Elmer 983 spectrometer. ^{1}H, ^{13}C and ^{31}P NMR spectra were obtained in CDCl$_3$ solutions on a Varian Gemini 300 instrument operating at 299.5, 75.4 and 121.4 MHz, respectively. Chemical shifts are reported in ppm relative to TMS and H$_3$PO$_4$ 85%, respectively. Elemental analyses (carbon, hydrogen) were performed on a Perkin-Elmer 240B analyser. Melting points are listed in Table 1 and are uncorrected. Table 1 also summarizes the analytical and other preparative details.

Preparation of bis(dimethylphosphinato)trimethylantimony(V), Me$_3$Sb(O$_2$PMe$_2$)$_2$

A mixture of Me$_3$SbCl$_2$ (0.792 g, 3.33 mmol) and Me$_2$PO$_2$Na (0.773 g, 6.66 mmol) in 30 cm^3 acetonitrile was stirred for 2 h under reflux. The hot reaction mixture was filtered to remove the resulting NaCl. The colorless oily product, obtained after the removal of the solvent *in vacuo* from the clear filtrate and crystallized on standing over P$_4$O$_{10}$ in a dessicator.

Preparation of bis(diphenylphosphinato)trimethylantimony(V), Me$_3$Sb(O$_2$PPh$_2$)$_2$

Me$_3$SbCl$_2$ (0.594 g, 2.5 mmol) was added to a solution of Ph$_2$PO$_2$Na [prepared *in situ* from Ph$_2$P(O)OH (1.09 g, 5 mmol) and NaOMe (0.115 g, 5 mmol)] in 50 cm^3 methanol. The clear reaction mixture was stirred for 2 h under reflux, when the solution became slightly turbid. The hot reaction mixture was filtered and after concentration of the solution *in vacuo* the desired compound deposited as colorless crystals, insoluble in nonpolar solvents and soluble in water.

Preparation of bis(dimethylphosphinato)triphenylantimony(V), Ph$_3$Sb(O$_2$PMe$_2$)$_2$

A mixture of Ph$_3$SbCl$_2$ (0.847 g, 2 mmol) and Me$_2$PO$_2$Na (0.464 g, 4 mmol) in 30 cm^3 acetonitrile was stirred for 4 h under reflux. The resulting solid product was filtered from the hot reaction mixture and the crude solid extracted several times with acetonitrile. The clear filtrate, on cooling, deposited white crystals of the title compound.

Preparation of bis(diphenylphosphinato)triphenylantimony(V), Ph$_3$Sb(O$_2$PPh$_2$)$_2$

Ph$_3$SbCl$_2$ (0.847 g, 2 mmol) was added to a solution of Ph$_2$PO$_2$Na [prepared *in situ* from Ph$_2$P(O)OH (0.87 g, 4 mmol) and NaOMe (0.09 g, 4 mmol)] in 50 cm^3 methanol and the reaction mixture stirred for 2 h under reflux, when the solution became clear. The reaction mixture was cooled to room temperature and then kept overnight in the refrigerator. Colorless crystals deposited and were filtered off (0.75 g). A further crop of crystals (0.65 g) was obtained when the solvent was gradually removed under vacuum. The compound was recrystallized several times from methanol to remove the resulting NaCl.

X-Ray crystal determination of Me$_3$Sb(OH)[O(O)PPh$_2$]

Molecular formula/asymmetric unit C$_{15}$H$_{20}$O$_3$PSb, $M = 401.0$, monoclinic, space group $P2_1/c$, $a = 16.450(2)$, $b = 8.671(2)$, $c = 12.228(2)$ Å, $\beta = 107.62(2)°$, $V = 1662.2(3)$ Å^3, $F(000) = 800$, $Z = 4$, $D_c = 1.602$ g cm^{-3}, μ(Mo-K_α) = 1.760 mm^{-1}, crystal size 0.5 × 0.3 × 0.2 mm.

Data were collected on a Siemens P4 four-circle diffractometer at 173 K for 4362 reflections in the 2θ-

Table 1. Analytical data and physical properties of R$_3$Sb(O$_2$PR$'_2$)$_2$

Compound R$_3$Sb(O$_2$PR$'_2$)$_2$ R	R$'$	Formula	%C found (calc.)	%H found (calc.)	Yield (%)	m.p. (°C)	Recryst. solvent
Me	Me	C$_7$H$_{21}$O$_4$P$_2$Sb (352.9)	22.3 (23.8)	6.5 (6.0)	85	89–91	CHCl$_3$/*n*-hexane
Me	Ph	C$_{27}$H$_{29}$O$_4$P$_2$Sb (601.2)	53.2 (53.9)	4.0 (4.9)	80	>350	CH$_3$CN
Ph	Me	C$_{22}$H$_{27}$O$_4$P$_2$Sb (539.2)	52.4 (49.0)	4.5 (5.0)	83	213–215	CH$_3$CN
Ph	Ph	C$_{42}$H$_{35}$O$_4$P$_2$Sb (787.4)	63.8 (64.1)	4.6 (4.5)	87	294–296	MeOH

ω mode, of which 3847 were independent reflections ($R_{\mathrm{int}} = 1.46\%$) and 2982 ($F > 6.0\sigma(F)$) were used in the full-matrix least-squares refinement with the SHELXTL PLUS (VMS) [15] program system. The structure was solved by direct methods for the antimony atom and the difference Fourier synthesis revealed the positions for the other non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically, the hydrogen atoms of the phenyl rings were calculated as a riding model with fixed isotropic U, the hydrogen atoms of the methyl groups and the hydrogen of the hydroxo group were calculated in found positions with free isotropic U. An absorption correction was not applied. The final R values are $R = 2.84\%$ and $wR = 3.41\%$ ($R = 4.18\%$ and $wR = 3.82\%$ for all data) with weights $w^{-1} = \sigma^2(F) + 0.0004F^2$; Goodness-of-Fit = 1.18. Residual electron density from a final difference Fourier synthesis was in the range of -1.18 to $0.63\ e\text{Å}^{-3}$.

RESULTS AND DISCUSSION

Bis (diorganophosphinato) triorganoantimony(V), $R_3Sb(O_2PR'_2)_2$ (R, R′ = Me, Ph), were prepared according to eq. (1), by reacting triorganoantimony(V) dichlorides with the sodium salt of the appropriate diorganophosphinic acid:

$$R_3SbCl_2 + 2\,NaO_2PR'_2 \rightarrow R_3Sb(O_2PR'_2)_2 + 2\,NaCl \qquad (1)$$

The compounds are white, crystalline solids, all soluble in chloroform. The trimethylantimony(V) derivatives were also soluble in water; moreover $Me_3Sb(O_2PMe_2)_2$ appeared to be hygroscopic and should be stored under a dried inert atmosphere. Elemental analyses (C, H), melting points, yields and recrystallization solvents are listed in Table 1. All compounds were investigated by IR and multinuclear NMR spectroscopy.

Important infrared bands for the new compounds are summarized in Table 2. The assignments were made using literature data and comparisons with spectra of the starting materials. The geometry of the Me_3Sb unit in the $Me_3Sb(O_2PR'_2)_2$ derivatives is very likely to be planar (D_{3h} point group for the C_3Sb fragment) since only one band at *ca* 580 cm^{-1} (assigned to the asymmetric antimony–carbon stretching vibration) was observed. Additionally, a medium-strong absorption at *ca* 860 cm^{-1} was assigned to the C—H rocking vibration of the Me_3Sb fragment. Both trimethyl- and triphenylantimony(V) diorganophosphinates show strong absorptions in the 1200–1100 and 1060–950 cm^{-1} regions, which were assigned to asymmetric PO_2 and symmetric PO_2 stretching vibrations, respectively. No absorption bands assignable to hydroxy groups were observed in the IR spectra of these compounds.

^1H, ^{13}C, ^{31}P NMR data for the $R_3Sb(O_2PR'_2)_2$ are summarized in Table 3. In the ^1H NMR spectra all compounds contain characteristic resonances for organic groups bonded to antimony and to phosphorus atoms. The proton resonances of the methyl groups, as well as the *ortho* protons in the phenyl groups attached to phosphorus are always split into two components of equal intensity due to phosphorus–proton coupling. For the trimethylantimony(V) derivatives, only singlet ^1H and ^{13}C resonances were observed for the methyl groups bonded to antimony, consistent with their equivalent arrangement in a planar $SbMe_3$ moiety as suggested by the infrared spectra. The ^1H and ^{13}C NMR spectra of the triphenylantimony(V) derivatives also showed only one set of resonances for the carbon atoms of the phenyl groups attached to antimony, suggesting their equivalence on the NMR time scale. All $R_3Sb(O_2PR'_2)_2$ compounds showed a single sharp ^{31}P resonance with carbon satellites, which supports the equivalence of the two phosphorus atoms in these molecules. This might be a consequence of the absence, in solution, of any secondary interactions between the oxygen atoms doubly bonded to phosphorus and the Sb atom, thus allowing free rotation around the Sb—O bonds. It should be mentioned here that for some triorganoantimony(V) dicarboxylates, weak intramolecular interactions between Sb and the carbonyl O atoms were established in solid state by X-ray diffractometry [*cf* Sb$\cdots$O(=C) in $Ph_3Sb(O_2CCH_3)_2$: 2.779(4) Å [16]; $Ph_3Sb(O_2CC_6H_5)_2$: 2.70(2) and 2.81(2) Å [17]; $Me_3Sb(O_2CC_4H_3S\text{-}2)_2$: 3.066(7) and 3.093(7) Å [18]], which led to distortion of the basically trigonal bipyramidal coordination at antimony.

Subsequent attempts to grow X-ray quality crystals

Table 2. Infrared data for $R_3Sb(O_2PR'_2)_2$ derivatives (in cm^{-1})

Compound					
R	R′	$\nu_{as}(PO_2)$	$\nu_s(PO_2)$	$\rho(SbCH_3)$	$\nu_{as}(SbC_3)$
Me	Me	1170s,br	1002s,br	866s,br	584m
Me	Ph	1191vs, 1165vs, 1139s, 1129s	1060s, 1038s, 1019m	852mw	574s
Ph	Me	1116s	1047ms, 1030s		
Ph	Ph	1202s, 1164m, 1125m, 1110m	947s,br		

Table 3. ^{1}H, ^{13}C and ^{31}P NMR data for $R_3Sb(O_2PR'_2)_2$ derivatives

Compound			
R	R′		Chemical shifts (δ, ppm) and coupling constants (J, Hz)
Me	Me	^{1}H	1.24d [12H, P-CH_3, ^2J(PH) = 13.9]; 2.00s (9H, Sb-CH_3)
		^{13}C	15.12s (Sb-CH$_3$); 18.73d [P-CH$_3$, ^1J(PC) = 94.8]
		^{31}P	42.4s [^1J(PC) = 95.3]
Me	Ph	^{1}H	2.05s (9H, Sb-CH_3); 7.36m (12H, P-C$_6H_5$ meta+para); 7.48dd [8H, P-C$_6H_5$ ortho, ^3J(PH) = 11.9, ^3J(HH) = 7.2]
		^{13}C	15.21s (Sb-CH$_3$); 128.31d [C_m, ^3J(PC) = 12.6]; 130.92d [C_O, ^2J(PC) = 9.9]; 131.06s (C_p); 136.42d [C_i, ^1J(PC) = 135.3]
		^{31}P	23.2s[^1J(PC) = 134.3]
Ph	Me	^{1}H	1.00d [12H, P-CH_3, ^2J(PH) = 13.7]; 7.58m (9H, Sb-C$_6H_5$ meta+para); 8.25dd [6H, Sb-C$_6H_5$ ortho, ^3J(HH) = 7.3, ^4J(HH) = 2.9]
		^{13}C	18.39d [P-CH$_3$, ^1J(PC) = 95.6]; 129.65s (C_m); 131.80s (C_p); 134.16s (C_O); 139.99s (C_i)
		^{31}P	38.9s
Ph	Ph	^{1}H	7.30m (29H, Sb-C$_6H_5$ meta+para, P-C$_6H_5$); 8.06d [6H, Sb-C$_6H_5$ ortho, ^3J(HH) = 8.0]
		^{13}C	127.87d [C_m(P), ^3J(PC) = 13.0]; 129.65s [C_m(Sb)]; 130.51s [C_p(P)]; 130.95d [C_o(P), ^2J(PC) = 10.0]; 131.95s [C_p(Sb)]; 134.34s [C_O(Sb)]; 135.35s [C_i(Sb)]; 136.09d [C_i(P), ^1J(PC) = 136.9]
		^{31}P	22.1s [^1J(PC) = 136.4]

of $Me_3Sb(O_2PPh_2)_2$ from a methanol/acetonitrile mixture, without precautions to excluded moisture, led to a crystalline product whose spectroscopic behavior clearly indicates the hydrolytic transformation of one phosphinato group to a hydroxo group. The IR spectrum of this product exhibits the strong bands characteristic of the PO_2 group [$\nu_{as}(PO_2)$ 1180vs, 1118s; $\nu_s(PO_2)$ 1030vs, 1011vs; 992s cm^{-1}], but also a broad and very strong band at 3190 cm^{-1}. This was considered to be indicative of the presence of a hydrogen bonded hydroxo group, and an X-ray diffractometry study (see below) confirmed this compound to be the partially hydrolised species $Me_3Sb(OH)[O(O)PPh_2]$.

The molecular structure of $Me_3Sb(OH)[O(O)PPh_2]$

The molecular structure of the title compound with the atom numbering scheme is illustrated in Fig. 1.

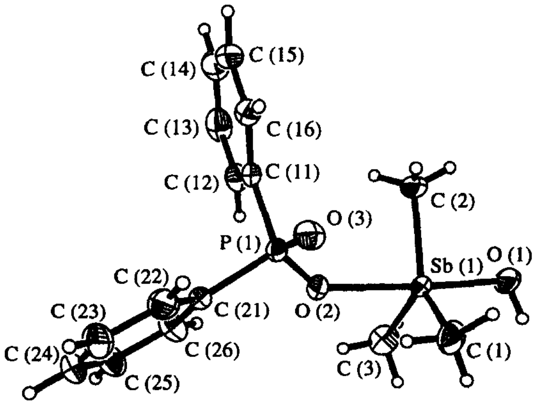


Fig. 1. ORTEP-like view of the $Me_3Sb(OH)[O(O)PPh_2]$ molecule.

Important bond distances and angles are listed in Table 4.

The central antimony atom is in a distorted trigonal bipyramidal coordination environment, with the methyl carbons in equatorial positions. The apical positions are occupied by O(1) (hydroxyl group) and O(2) (the oxygen single bonded to phosphorus in the phosphinato moiety). The O(1)—Sb(1)—O(2) angle [175.7(1)°] is smaller than the ideal value of 180°, but similar deviations were noted for carboxylato analogs, $Mes_3Sb(OH)[O(O)CR]$, or dihydroxo derivatives, $Ar_3Sb(OH)_2$ (for comparative data see Table 5).

There are no inter- or intramolecular interactions between the second O(3) atom of the phosphinato group and antimony atoms [the distances Sb(1c) ··· O(3c) 3.897 Å, Sb(1c) ··· O(3a) 3.602 Å, are larger than the sum of the van der Waals radii for Sb and O, 3.70 Å [23]]. This probably follows from hydrogen-bond formation between O(3) and a hydrogen atom of a neighboring molecule. The short O(1c) ··· O(3a) distance of 2.688 Å is consistent with hydrogen bonding between these two atoms, and this was confirmed by location of the H(1) atom of the hydroxo group. The hydrogen bonds thus formed lead to a chain polymer association (Fig. 2), similar to that observed in $Mes_3Sb(OH)[O(O)CCHCl_2]$ [19]. The resulting chain [—Sb—O—H ··· O=P—O—]$_n$ has a zigzag structure, a view down the polymer axis allowing staggered planes formed by oxygen atoms of the phosphinato ligands, Sb atoms, and oxygen atoms of the hydroxo groups, to be distinguished.

The Sb—O(H) distance of 1.967(3) Å is similar to that in $Mes_3Sb(OH)[O(O)CCHCl_2]$ [19], and is intermediate between those for $Mes_3Sb(OH)[O(O)CR']$ (R′ = 1-adamantyl) [20], $Mes_3Sb(OH)_2$ [21], or $Ph_3Sb(OH)_2$ [22], (which do not display associations

Table 4. Interatomic distances (Å) and angles (°) in $Me_3Sb(OH)[O(O)PPh_2]$

Sb(1)—C(1)	2.093(4)	C(1)—Sb(1)—C(2)	118.5(2)
Sb(1)—C(2)	2.088(5)	C(1)—Sb(1)—C(3)	115.8(2)
Sb(1)—C(3)	2.088(4)	C(2)—Sb(1)—C(3)	124.1(2)
Sb(1)—O(1)	1.967(3)		
Sb(1)—O(2)	2.235(2)	O(1)—Sb(1)—C(1)	96.1(1)
		O(1)—Sb(1)—C(2)	90.3(2)
P(1)—O(2)	1.528(3)	O(1)—Sb(1)—C(3)	96.4(1)
P(1)—O(3)	1.490(3)	O(2)—Sb(1)—C(1)	88.1(1)
P(1)—C(11)	1.813(3)	O(2)—Sb(1)—C(2)	86.9(1)
P(1)—C(21)	1.799(3)	O(2)—Sb(1)—C(3)	82.4(1)
O(1c)—H(1c)[a]	0.869	O(1)—Sb(1)—O(2)	175.7(1)
O(3a)···H(1c)[a]	1.829		
O(1c)···O(3a)[a]	2.688	O(2)—P(1)—O(3)	117.8(1)
Sb(1c)···O(3c) (intramolecular)[a]	3.897	O(2)—P(1)—C(11)	106.2(1)
Sb(1c)···O(3a) (intermolecular)[a]	3.602	O(2)—P(1)—C(21)	106.3(1)
		O(3)—P(1)—C(11)	110.5(2)
		O(3)—P(1)—C(21)	110.1(1)
		C(11)—P(1)—C(21)	105.2(1)
		Sb(1)—O(2)—P(1)	133.9(1)
		Sb(1)—O(1)—H(1)	107.3

[a] For the atom numbering scheme see Fig. 2.

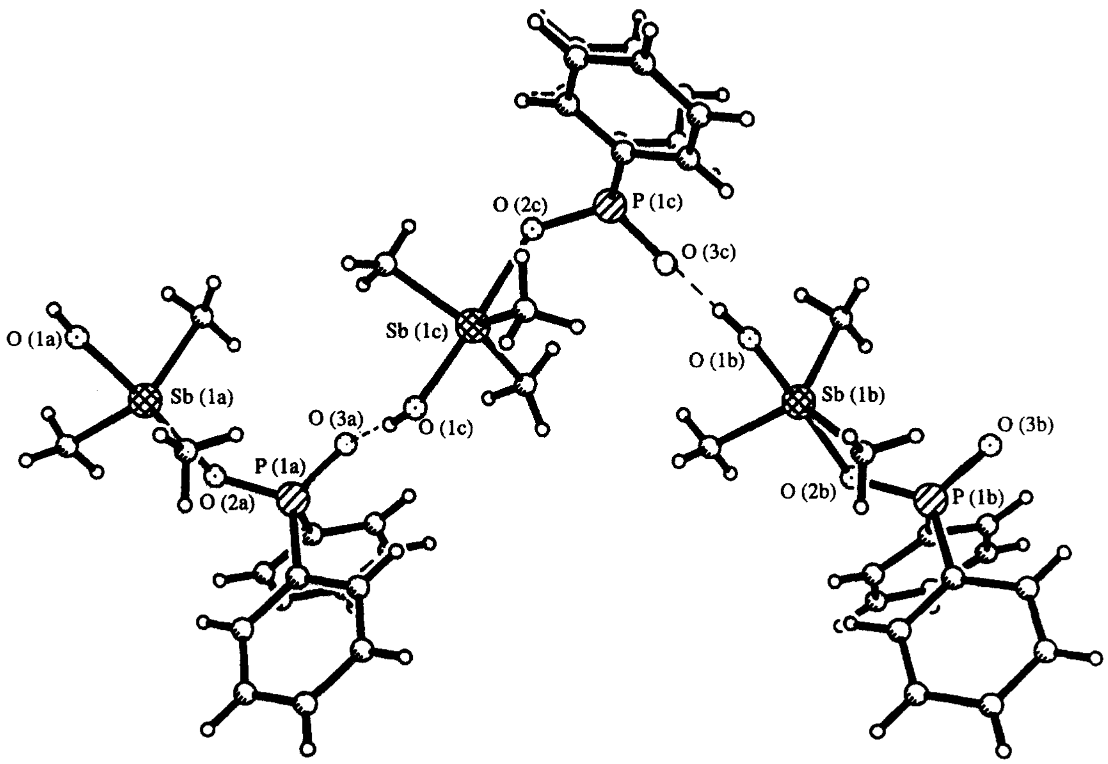


Fig. 2. Chain polymeric self-assembly through H bonding in $\{Me_3Sb(OH)[O(O)PPh_2]\}_n$.

through hydrogen bonds; see Table 5), and (2,4-$Me_2C_6H_3)_3Sb(OH)I$ [Sb—O 1.907(2) Å] [24] and $Mes_3SbO \cdot HO_3SPh$ [Sb—O 1.894(5) Å] [25] (the latter displaying substantial double-bond character). As a result of this short Sb(1)—O(H) bond, although the C—Sb(1)—C angles are in the range of 115.8(2)–124.1(2)° and their sum is close to 360° i.e. 358.4°, the Sb(1) atom lies above the C(1)C(2)C(3) plane and two of the axial-equatorial O(1)—Sb—C angles are larger than 90° (Table 4).

Table 5. Comparative molecular dimensions for $Me_3Sb(OH)[O(O)PPh_2]$ and some related compounds

	$Me_3Sb(OH)[O(O)PPh_2]^a$ [this work]	$Mes_3Sb(OH)[O(O)CR']^a$ $R' = CHCl_2$ [19]	$Mes_3Sb(OH)[O(O)CR']$ R' = 1-adamantyl [20]	$Mes_3Sb(OH)_2$ [21]	$Ph_3Sb(OH)_2$ [22]
Sb—O(—H)	1.967(3)	1.975(3)	2.026(3)	2.027(3)	1.963(3) 2.079(7)
Sb—O(—X)^b	2.235(2)	2.280(3)	2.121(3)		
O(—H)···O(=X)	2.688	2.915(6)			
O—Sb—O	175.7(1)	177.5(1)	175.5(2)	176.7(1)	178.5(5)
C—Sb—C	115.8(2)–124.1(2)	114.3(1)–123.5(1)	119.1(2)–121.1(2)	118.2(1)–120.9(1)	117.4(7)–122.5(5)
(H)O—Sb—C	90.3(2)–96.4(1)	92.1(1)–94.1(1)	90.3(2)–91.6(2)	88.3(1)–91.2(1)	89.2(4)–90.7(4)
(X)O—Sb—C	82.4(1)–88.1(1)	85.1(1)–88.9(1)	86.6(2)–94.2(2)	88.3(1)–91.2(1)	89.3(5)–90.8(4)

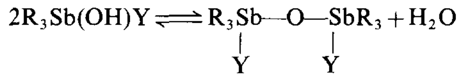
[a] Associated into polymeric chains through hydrogen bonds.

[b] X = P or C.

By contrast to the short Sb—O(H) bond, the distance between Sb(1) and the O(2) atom of the phosphinato group is longer [2.235(2) Å] than values for the typical covalent Sb—O bonds in $Mes_3Sb(OH)[O(O)CR']$ (R′ = 1-adamantyl) [2.121(3) Å] [20], triorganoantimony dicarboxylates [e.g. Sb—O(—C) in $Me_3Sb(O_2CC_4H_3S\text{-}2)_2$: 2.136(6) and 2.124(6) Å] [18] or $Me_3Sb[O(S)PPh_2]_2$: [2.114(5) and 2.107(5) Å [9]. On the other hand it is close to the values observed in $Mes_3Sb(OH)[O(O)CCHCl_2]$ [Sb—O(—C) 2.280(3) Å [19], or $[Ph_3Sb(O_3SC_2H_4OH\text{-}2)]_2O$ [2.276(4) Å] [26], for which some ionic character was assumed. In the title phosphinato derivative, an increase in the ionic character might be also suggested by the axial-equatorial O—Sb—C angles (Table 4) [the Sb atom is displaced from the C(1)C(2)C(3) plane towards the hydroxo O atom]. This is consistent with a certain tendency for the Sb(1) atom to achieve the tetrahedral geometry of a hydroxostibonium cation in the ionic structure $[Me_3SbOH]^+[O_2PPh_2]^-$.

In the diphenylphosphinato group, the phosphorus-oxygen distances can be clearly assigned to single P—O [P(1)—O(2) 1.528(3) Å] and double P=O [P(1)—O(3) 1.490(3) Å] bonds as found in the free acid, $Ph_2P(O)OH$, which is also associated into polymeric chains through —O—H···O=P—hydrogen bonds [P—O 1.526(6) Å and P=O 1.486(6) Å] [27].

Several authors have reported the isolation of compounds formulated as hydroxo derivatives $R_3Sb(OH)Y$, but most of them were found to be dinuclear species of the type $[R_3SbY]_2O$ in solid state, although IR evidence was obtained in favor of the mononuclear hydroxo form in solution [28,29].



$$2R_3Sb(OH)Y \rightleftharpoons \underset{\displaystyle Y}{\underset{|}{R_3Sb}}—O—\underset{\displaystyle Y}{\underset{|}{SbR_3}} + H_2O$$

A (solution) **B** (solid state)

It was suggested that bulky organic groups on antimony or bulky Y ligands might stabilize the hydroxo form **A** in solid state too [29]. For example, in the carboxylato series, $R_3Sb(OH)(O_2CR')$, only two compounds, both containing bulky mesityl groups attached to antimony, have been characterized by X-ray diffractometry: $Mes_3Sb(OH)[O(O)CCHCl_2]$, which is associated into polymeric chains through intermolecular hydrogen bonds of the type —O—H···O=C— [19], and $Mes_3Sb(OH)[O(O)CR']$ (R′ = 1-adamantyl), which is monomeric probably as a result of the bulky carboxylato ligand [20]. The role of the hydrogen bonds in the stabilization of the form **A** in solid state was not yet definitely confirmed. Two other interesting cases should also be noted. Thus, the compound formulated as $(2,4\text{-}Me_2C_6H_3)_3Sb(OH)I$ is in fact a stibonium salt with hydrogen bonds between the OH group and I^- [24] while the product of the reaction between $Mes_3Sb(OH)_2$ and $PhSO_3H$ was described as the first solid hydrogen-bonded adduct of a triorganoantimony oxide with an acid [25]. The phosphinate $Me_3Sb(OH)[O(O)PPh_2]$ provides an example of a solid-state stable hydroxo-antimony(V) derivative of the type $R_3Sb(OH)Y$, which does not require bulky organic groups on antimony. Moreover, this is the first example in which a diorganophosphinato group does not act as a bridge between two antimony atoms, but is basically monometallic monoconnective (monodentate), the structure being stabilized through —Sb—O—H···O=P—hydrogen bonds.

Acknowledgements—This work was supported by the Roumanian National Council for University Scientific Research (CNCSU). C.S. thanks DAAD and the University of Bremen for the financial support and hospitality during the research stays spent in Bremen. The Romanian authors also thank the British Council for financial support and travel grants within a ROMLISS program. The financial support provided by Oltchim S.A. (C. Roibu, General Manager) for the service of the Varian NMR equipment (Babes-Bolyai University) is also greatly acknowledged.

REFERENCES

1. Silvestru, C. and Haiduc, I., *Coord. Chem. Rev.* 1996, **147**, 117.
2. Brauninger, M., Schwarz, W. and Schmidt, A., *Z. Naturforsch., Teil B*, 1979, **34**, 1703.
3. Shihada, A.-F. and Weller, F., *Z. Anorg. Allg. Chem.* 1981, **472**, 102.
4. Blösl, S., Schwarz, W. and Schmidt, A., *Z. Naturforsch., Teil B*, 1983, **38**, 143.
5. Gibbons, M. N. and Sowerby, D. B., *Phosphorus, Sulfur & Silicon*, 1994, **93/94**, 305.
6. Said, M. A., Kumara Swamy, K. C., Babu, K., Aparna, K. and Nethaji, M., *J. Chem. Soc., Dalton Trans.* 1995, 2151.
7. Said, M. A., Kumara Swamy, K. C., Ponjary, D. M., Clearfield, A., Veith, M. and Huch, V., *Inorg. Chem.* 1996, **35**, 3235.
8. Silvestru, C., Sowerby, D. B., Haiduc, I., Ebert, K. H. and Breunig, H. J., *Main Group Metal Chem.* 1994, **17**, 505.
9. Silvestru, C., Haiduc, I., Ebert, K. H., Breunig, H. J. and Sowerby, D. B., *J. Organomet. Chem.* 1994, **468**, 113.
10. Sowerby, D. B., in *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*, (edited by S. Patai), Ch. 2, p. 25. John Wiley & Sons Ltd, Chichester (1994).
11. Doak, G. O., Long, G. G. and Key, M. E., *Inorg. Synth.* 1967, **9**, 92.
12. Beveridge, A. D., Harris, G. S. and Inglis, F., *J. Chem. Soc. A*, 1966, 520.
13. Reinhardt, H., Bianchi, D. and Mölle, D., *Chem. Ber.* 1957, **90**, 1656.
14. Higgins, W. A., Vogel, P. W. and Craig, W. G., *J. Am. Chem. Soc.* 1955, **77**, 1864.
15. Siemens SHELXTL PLUS: Release 4.0 for Siemens R3 Crystallographic Research Systems, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, U.S.A. (1989).
16. Sowerby, D. B., *J. Chem. Res.* (*S*), 1979, 80; (*M*), 1979, 1001.
17. Lebedev, V. A., Bochkova, R. I., Kuzubova, L. F., Kuz'min, E. A., Sharutin, V. V. and Belov, N. V., *Dokl. Akad. Nauk SSSR*, 1982, **265**, 332.
18. Preut, H., Domagala, M. and Huber, F., *Acta Cryst.* 1987, **C43**, 416.
19. Preut, H., Westhoff, T. and Huber, F., *Acta Cryst.* 1989, **C45**, 49.
20. Westhoff, T., Huber, F. and Preut, H., *J. Organomet. Chem.* 1988, **348**, 185.
21. Westhoff, T., Huber, F., Rüther, R. and Preut, H., *J. Organomet. Chem.* 1988, **352**, 107.
22. Pankaj, S., Rosas, N., Espinosa-Perez, G. and Cabrera, A., *Acta Cryst.* 1996, **C52**, 889.
23. Bondi, A., *J. Phys. Chem.* 1964, **68**, 441.
24. Ferguson, G., Harris, G. S. and Khan, A., *Acta Cryst.* 1987, **C43**, 2078.
25. Huber, F., Westhoff, T. and Preut, H., *J. Organomet. Chem.* 1987, **323**, 173.
26. Preut, H., Rüther, R. and Huber, F., *Acta Cryst.* 1985, **C41**, 358.
27. Fenske, D., Mattes, R., Löns, J. and Tebbe, K.-F., *Chem. Ber.* 1973, **106**, 1139.
28. Mirbach, M. and Wieber, M., in *Gmelin Handbook of Inorganic Compounds, Part* 5. *Organoantimony Compounds* (Edited by M. Mirbach). Springer Verlag, Berlin (1990).
29. Kawasaki, Y., Yamamoto, Y. and Wada, M., *Bull. Chem. Soc. Jpn*, 1983, **56**, 145.