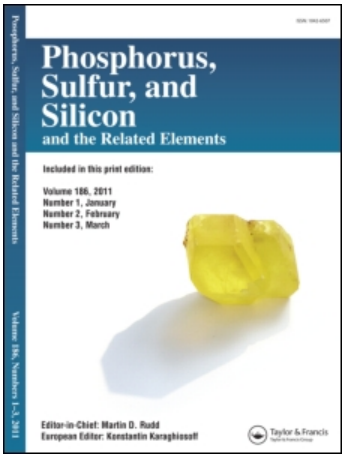


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE CRYSTAL STRUCTURES OF TETRAPHENYLANTIMONY ACETATE AND ITS

Stephen P. Bone[a]; D. Bryan Sowerby[a]
[a] Department of Chemistry, University of Nottingham, Nottingham, (U.K.)

To cite this Article Bone, Stephen P. and Sowerby, D. Bryan(1989) 'THE CRYSTAL STRUCTURES OF TETRAPHENYLANTIMONY ACETATE AND ITS', Phosphorus, Sulfur, and Silicon and the Related Elements, 45: 1, 23 — 29
To link to this Article: DOI: 10.1080/10426508908046072
URL: http://dx.doi.org/10.1080/10426508908046072

Phosphorus, Sulfur, and Silicon, 1989, Vol. 45, pp. 23–29
Reprints available directly from the publisher
Photocopying permitted by license only

THE CRYSTAL STRUCTURES OF TETRAPHENYLANTIMONY ACETATE AND ITS ACETIC ACID ADDUCT

STEPHEN P. BONE and D. BRYAN SOWERBY*
Department of Chemistry, University of Nottingham, Nottingham NG7 2RD (U.K.)

(Received November 8, 1988)

Tetraphenylantimony acetate is basically trigonal bipyramidal with an axial acetate group, but the structure is substantially distorted as a result of secondary Sb . . . O bonding with the formally non-bonded oxygen of the acetate group. A major feature of the distortion is an increase in one of the C–Sb–C equatorial angles to 152.6° at the expense of the other two, which are close to 102.5°. Secondary bonding also leads to a reduction in the angle at the acetate bonded oxygen atom to 108.1°. Addition of a molecule of acetic acid gives $Ph_4SbOAc{\cdot}HOAc$ with trigonal bipyramidal geometry about antimony, but secondary bonding is reduced to almost zero. The non-bonded oxygen of the acetate group forms a strong hydrogen bond (O . . . O 2.581 Å) to the acetic acid molecule but the cyclic structure suggested previously for this compound is not formed.

Crystals of $Ph_4SbOAc{\cdot}HOAc$ belong to the space group $P2_1/n$ (a 8.077(4), b 17.189(6), c 16.095(6) Å, β 98.29(2)°) and those of Ph_4SbOAc to the space group $P2_1/c$ (a 16.261(6), b 10.312(5), c 17.423(6) Å, β 119.13(6)).

Key words: Antimony; organo-antimony acetate crystal structure; hydrogen bonding; secondary bonding

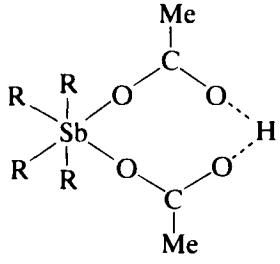
INTRODUCTION

We have previously shown that the geometry in both $Ph_3Sb(OAc)_2$[1] and $Ph_4Sb(O_2CH)$[2] is basically trigonal bipyramidal. In the former, axial positions are occupied by acetate groups but the structure is distorted substantially by intramolecular Sb . . . O secondary bonding (2.779 Å) involving the formally non-bonded oxygens of the acetate groups. The interactions cause both a reduction to 108.1° in the Sb–O–C angles at the primary bonded oxygens and an increase in one of the C–Sb–C angles in the equatorial plane to 148.2°. The acetate groups thus show partial bidentate character which is reflected in C–O stretching modes in the i.r. for solid samples at 1633 and 1302 cm^{-1}.[3] These bands move to 1651 and 1230 cm^{-1} for solutions in chloroform implying a reduction in the extent of the Sb . . . O bonding.

There is much weaker secondary bonding in $Ph_4Sb(O_2CH)$ (Sb . . . O 3.291 Å, cf. *ca.* 3.6 Å for the van der Waals separation), the Sb–O–C angle (120.4°) is normal and C–Sb–C equatorial angles (114.0, 119.0 and 123.9°) deviate far less from 120°. The solid state i.r. spectrum showing C–O stretches at 1630 and 1280 cm^{-1}, is not changed in chloroform solution indicating essentially unidentate character in each phase.[3]

* Author to whom correspondence should be addressed.

The related acetate, Ph_4SbOAc, on the other hand, has i.r. bands at 1555 and 1395 cm^{-1},[4] pointing to partial bidentate character and substantial Sb . . . O secondary bonding and to quantify this we have determined its crystal structure. This compound and Me_4SbOAc each form hydrogen bonded 1:1 adducts with acetic acid for which cyclic structure (**1**) has been proposed.[5] Clearly, any Sb . . . O secondary bonding in the acetate will be modified by incorporating an acetic acid molecule but our solid state i.r. data with C–O stretches at 1570/1310 and 1730/1280 are at variance with structure (**1**) and point to the presence of a terminal C=O system. To clarify this point we have determined the structure of this compound also.



1, R = Me or Ph

EXPERIMENTAL

Tetraphenylantimony acetate

The compound was prepared as described previously[5,6] from pentaphenylantimony and glacial acetic acid in benzene solution and crystals suitable for x-ray analysis were obtained by recrystallisation from ether. M.p. 128°C (lit.[6] 130°C)

Crystal data

$C_{26}H_{23}O_2Sb$, M 488.8, monoclinic, a 8.077(4), b 17.189(6), c 16.095(6) Å, β 98.29(2), U 2211.2 $Å^3$, Z 4, D_c 1.468 g cm^{-3}, F(000) 984, space group $P2_1/n$, Mo-K_α radiation, λ 0.7107 Å, μ(Mo–K_α) 12.8 cm^{-1}, crystal size 0.2 × 0.2 × 0.2 mm.

Structure determination

Data were collected using a Hilger and Watts four circle diffractometer for 4090 reflections of which 2 677 with $I > 3\sigma(I)$ were observed. Intensities were corrected for Lorentz and polarisation effects but an absorption correction was not necessary. Data reduction and subsequent calculations used the CRYSTALS programs;[7] atomic scattering factors were those for neutral atoms.[8] The structure was solved by Patterson and Fourier methods and the refinement by full matrix least squares converged at R 0.057 with isotropic and at R 0.043 after two cycles of refinement with anisotropic thermal parameters. Although the hydrogen atoms of the phenyl groups were placed at their calculated positions and not refined, a difference Fourier synthesis showed positions of the methyl hydrogens, which in subsequent cycles were refined with isotropic thermal parameters. Final convergence occurred at R 0.035. Analysis of the reflection data showed unit weights were most appropriate and a final difference Fourier showed no peaks with intensities greater than 0.4 e $Å^{-3}$. Refined values of the atomic coordinates are collected in Table I.

Tetraphenylantimony acetate-acetic acid adduct

Preparation

Tetraphenylantimony acetate (1.29 g, 3 mmol) was dissolved in benzene (30 ml) and glacial acetic acid (0.18 g, 3 mmol) was added. After 2 h reflux, the solution was reduced to *ca.* 10 ml and ether (10 ml) was added. White crystals were obtained on cooling. M.p. 115°C (lit.[5] 112–3°C). (Found: C, 54.3; H, 4.2. Calc. for $C_{28}H_{27}O_4Sb$: C, 54.8; H, 4.4%). Crystals suitable for x-ray diffraction were obtained by recrystallisation from a 1:1 benzene-ether mixture.

Crystal data

$C_{28}H_{27}O_4Sb$, M 548.8, monoclinic, a 16.261(6), b 10.312(5), c 17.423(6) Å, β 119.13(6), U 2552.0 $Å^3$, Z 4, D_c 1.43 g cm^{-3}, F(000) 1112, space group $P2_1/c$, Mo-K_α radiation, λ 0.7107 Å, μ(Mo–K_α) 11.3 cm^{-1}.

TABLE I

Atomic coordinates ($\times 10^4$), with estimated standard deviations in parentheses, for Ph_4SbOAc

Atom	x/a	y/b	z/c
Sb(1)	4455.6(5)	1270.2(2)	2512.6(2)
O(1)	6352(6)	418(3)	3109(3)
O(2)	7102(6)	81(3)	1910(3)
C(1)	6256(8)	2136(4)	2987(4)
C(2)	6077(8)	2473(4)	3755(4)
C(3)	7120(10)	3080(5)	4075(5)
C(4)	8284(9)	3367(4)	3629(5)
C(5)	8464(9)	3048(4)	2867(5)
C(6)	7460(8)	2429(4)	2549(4)
C(7)	3079(7)	1120(3)	3539(4)
C(8)	3426(7)	521(3)	4106(4)
C(9)	2496(8)	441(4)	4763(4)
C(10)	1252(9)	954(5)	4867(4)
C(11)	912(9)	1557(5)	4297(5)
C(12)	1822(8)	1638(4)	3643(4)
C(13)	3609(8)	322(4)	1702(4)
C(14)	3017(9)	−356(4)	2029(4)
C(15)	2330(10)	−939(5)	1493(6)
C(16)	2230(10)	−859(6)	641(7)
C(17)	2820(10)	−191(6)	308(5)
C(18)	3510(10)	395(6)	840(4)
C(19)	2860(8)	2101(5)	1751(4)
C(20)	3401(9)	2823(4)	1580(4)
C(21)	2370(10)	3345(4)	1110(5)
C(22)	790(10)	3150(4)	833(5)
C(23)	170(10)	2420(5)	983(4)
C(24)	1233(9)	1886(5)	1443(4)
C(25)	7380(9)	408(6)	2574(5)
C(26)	8892(9)	−103(4)	2730(6)

Structure determination

Data were collected as described above for 4554 reflections of which 3250 were observed. The structure was solved by conventional Patterson and Fourier methods and refinement converged at R 0.066 with isotropic and R 0.043 with anisotropic thermal parameters. The hydrogen atoms of the phenyl groups were placed at their calculated positions but not refined. After two further cycles of refinement R was reduced to 0.035 and a difference Fourier synthesis gave positions for the hydrogens of the two methyl groups and for the acidic proton. Further refinement with the C–H distances in the methyl groups constrained at 1.00(2) Å gave final convergence at R 0.033. Unit weights were appropriate. Final refined values of the atomic coordinates are listed in Table II.

Tables of calculated hydrogen atom coordinates, thermal parameters and observed and calculated structure factors can be obtained from DBS.

DISCUSSION

Tetraphenylantimony acetate

Selected bond distances and angles are collected in Table III and the molecular structure and atom numbering scheme are given in Figure 1. The most important feature in this structure is the strong secondary interaction between antimony and the formally non-bonded oxygen of the acetate group effectively *trans* (143.0°) to C(7); at 2.585 Å it is substantially shorter than that in $Ph_3Sb(OAc)_2$ (2.779 Å) and from the Pauling relationship[9] represents a bond order of *ca.* 0.2. The five primary bonds at antimony define a very distorted trigonal bipyramid with the

TABLE II

Atomic coordinates ($\times 10^4$), with estimated standard deviations in parentheses, for $Ph_4SbOAc \cdot HOAc$

Atom	x/a	y/b	z/c
Sb(1)	1975.0(2)	1773.9(4)	1819.2(2)
O(1)	3300(2)	2153(4)	1707(2)
O(2)	4252(3)	1121(5)	2935(3)
O(3)	5937(3)	597(6)	4160(3)
O(4)	6938(4)	1103(7)	5514(3)
C(1)	2278(4)	−166(5)	1697(3)
C(2)	2189(4)	−599(6)	908(4)
C(3)	2349(4)	−1872(8)	807(4)
C(4)	2573(5)	−2737(7)	1474(4)
C(5)	2655(5)	−2313(6)	2264(4)
C(6)	2504(4)	−1039(6)	2378(4)
C(7)	1348(4)	2870(5)	647(3)
C(8)	1836(4)	3807(6)	462(3)
C(9)	1381(4)	4514(8)	−309(4)
C(10)	454(5)	4269(7)	−896(4)
C(11)	−24(4)	3344(7)	−720(4)
C(12)	409(4)	2638(6)	53(4)
C(13)	2665(3)	2844(5)	3000(3)
C(14)	3191(5)	3932(6)	3066(4)
C(15)	3612(5)	4634(8)	3843(5)
C(16)	3522(5)	4221(7)	4553(6)
C(17)	3016(5)	3136(7)	4495(5)
C(18)	2572(4)	2450(6)	3716(4)
C(19)	677(4)	1397(5)	1837(3)
C(20)	223(4)	224(6)	1566(4)
C(21)	−675(5)	70(8)	1467(4)
C(22)	−1111(4)	1087(8)	1642(4)
C(23)	658(5)	2248(7)	1913(4)
C(24)	243(4)	2409(6)	2018(4)
C(25)	4097(4)	1719(8)	2266(4)
C(26)	4880(6)	203(2)	2066(2)
C(27)	6154(5)	1167(8)	4909(4)
C(28)	5379(8)	183(2)	4968(9)

acetate oxygen occupying an axial position. As expected the equatorial Sb–C distances (2.135–2.142 Å) are slightly shorter than that to the axial phenyl group (2.175 Å).

The stronger Sb . . . O interaction in the monoacetate probably follows from reduced competition for the sixth "octahedral" acceptor site at antimony; the reduction in Lewis acidity in going from $Ph_3Sb(OAc)_2$ to Ph_4SbOAc is apparently of less importance. Distortions of the molecular structure consequent on secondary bond formation are similar to those for $Ph_3Sb(OAc)_2$, i.e. opening of the C(1)–Sb(1)–C(13) "equatorial" angle from 120° to 152.6°, and decreases in the angles at the primarily bonded acetate oxygen [Sb(1)–O(1)–C(25)] and the carboxylate carbon [O(1)–C(25)–O(2)] to 108.1 and 118.6 respectively.

Secondary Sb . . . O bonding is even stronger in $[Ph_2Sb(OAc)_2]_2O$, the first hydrolysis product of $Ph_2Sb(OAc)_3$, where the primary and secondary Sb–O bonds average 2.16 and 2.47 Å respectively.[10] The Sb–O–C angles at the primary bonded oxygens are closed even further (mean 99.6°) than in Ph_4SbOAc but the

TABLE III

Bond distances (Å) and angles (deg) for Ph_4SbOAc and $Ph_4SbOAc \cdot HOAc$, with estimated standard deviations in parentheses

	Ph_4SbOAc	$Ph_4SbOAc \cdot HOAc$
Sb(1)–O(1)	2.235(4)	2.290(3)
Sb(1)–C(1)	2.142(6)	2.096(6)
Sb(1)–C(7)	2.135(5)	2.111(5)
Sb(1)–C(13)	2.136(7)	2.112(5)
Sb(1)–C(19)	2.175(6)	2.161(5)
Sb(1)–O(2)	2.585(5)	3.307(6)
O(1)–C(25)	1.289(8)	1.264(7)
O(2)–C(25)	1.258(8)	1.231(8)
C(25)–C(26)	1.487(9)	1.511(10)
O(3)–C(27)		1.314(9)
O(4)–C(27)		1.197(8)
C(27)–C(28)		1.481(12)
O(2) . . . O(3)		2.581(6)
O(3)–H(31)		1.10(8)
O(2) . . . H(31)		1.48(8)
O(1)–Sb(1)–C(1)	85.2(2)	82.9(2)
O(1)–Sb(1)–C(7)	89.5(2)	81.8(2)
O(1)–Sb(1)–C(13)	84.3(2)	85.3(2)
O(1)–Sb(1)–C(19)	169.8(2)	176.4(2)
O(1)–Sb(1) . . . O(2)	53.4(2)	
C(1)–Sb(1)–C(7)	102.1(2)	116.1(2)
C(1)–Sb(1)–C(13)	152.6(2)	123.9(2)
C(1)–Sb(1)–C(19)	93.3(2)	96.3(2)
C(1)–Sb(1) . . . O(2)	77.8(2)	
C(7)–Sb(1)–C(13)	102.9(2)	116.1(2)
C(7)–Sb(1)–C(19)	100.7(2)	95.4(2)
C(7)–Sb(1) . . . O(2)	143.0(2)	
C(13)–Sb(1)–C(19)	92.7(2)	98.0(2)
C(13)–Sb(1) . . . O(2)	75.6(2)	
C(19)–Sb(1) . . . O(2)	116.4(2)	
Sb(1)–O(1)–C(25)	101.8(4)	121.8(4)
Sb(1) . . . O(2)–C(25)	86.2(4)	
O(1)–C(25)–O(2)	118.6(7)	124.6(5)
O(1)–C(25)–C(26)	119.5(8)	114.2(7)
O(2)–C(25)–C(26)	121.9(7)	121.2(7)
O(3)–C(27)–O(4)		120.4(7)
O(3)–C(27)–C(28)		116.7(7)
O(4)–C(27)–C(28)		122.9(8)
O(3)–H(31) . . . O(2)		173(7)
O(2) . . . O(3)–C(27)		113.1(4)
O(3) . . . O(2)–C(25)		122.3(4)

O–C–O angle (mean 118.3°) is effectively the same. In this case, increased Lewis acidity at antimony from the presence of three primary bonded oxygen atoms is dominant and competition for the sixth coordination, which restricted the extent of secondary bonding in $Ph_3Sb(OAc)_2$, is not a factor as, unusually, the effective coordination number of antimony is raised to seven.

In spite of an increase of *ca.* 33° in one C–Sb–C equatorial angle, the C_3Sb system is maintained close to planarity by reduction of the other two angles to *ca.* 102.5°; the antimony atom is displaced 0.17 Å from the C(1) C(7) C(13) plane towards the axial phenyl group. Bond distance and angles within the phenyl

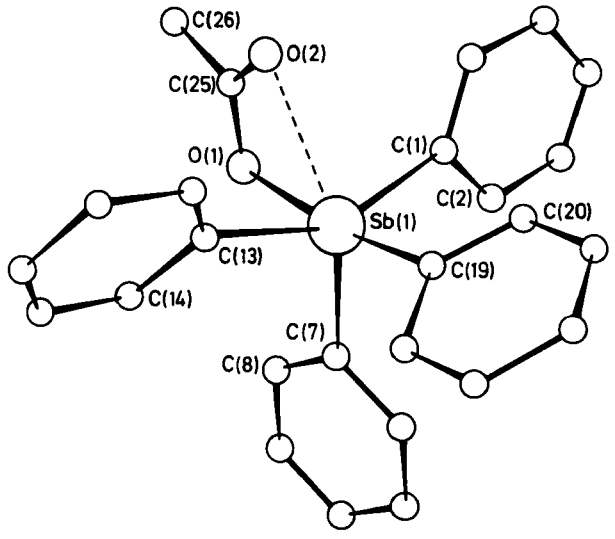


FIGURE 1 Structure of Ph_4SbOAc showing the atom numbering scheme.

groups (mean values 1.39 Å and 120°) are normal and their orientations are defined by angles of 2, 77 and 35° between the C_3Sb equatorial plane and the planes of respectively the C(1) C(7) and C(13) phenyl groups.

The acetic acid adduct

Molecular parameters for $Ph_4SbOAc{\cdot}HOAc$ are listed in Table III and the structure and numbering scheme are illustrated in Figure 2. Geometry about antimony is again basically trigonal bipyramidal with shorter equatorial Sb–C

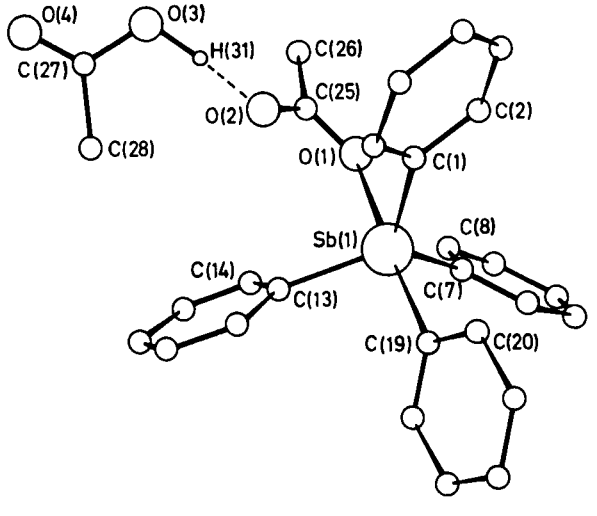


FIGURE 2 Structure of $Ph_4SbOAc{\cdot}HOAc$ showing the atom numbering scheme.

distances, 2.11 Å, than that to the axial group, 2.16 Å. There is an increase in the Sb(1)–O(1) distance to 2.290 Å, cf. 2.235 Å in Ph_4SbOAc, but the major change on introducing a molecule of acetic acid is the great increase in the secondary, Sb(1) . . . O(2), distance to 3.307 Å, cf. 2.585 Å in Ph_4SbOAc. Following this, the angles between the equatorial carbons are closer to 120°, the C(1)–Sb(1)–C(13) angle being increased to 123.9° compensated by reduction of the other two angles to *ca.* 116°. As in the previous structure, the antimony atom does not lie in the plane of the three equatorial carbon atoms but is displaced toward the axial phenyl group, here by 0.24 Å. Reduction in secondary Sb . . . O bonding relieves the strain in the Sb(1)–O(1)–C(25)–O(2) system giving angles of 121.8 and 124.6° at O(1) and C(25) respectively.

Reduced secondary bonding is obviously a consequence of hydrogen bonding between O(2) and the solvate acetic acid molecule. The x-ray data were sufficiently precise to determine all the hydrogen positions in the $H(OAc)_2$ system, showing an asymmetric hydrogen bond with O–H and H . . . O distances of 1.10 and 1.48 Å. The overall O(2) . . . O(3) distance, 2.581 Å, indicates strong hydrogen bonding, but the distance is substantially longer than that (*ca.* 2.44 Å) observed in the dicarboxylate anions, which are often symmetrical and are designated as "very strong".[11] The angle between the planes of the two acetate groups is 122°, which has the effect of orienting the acetic acid molecule away from the Ph_4Sb unit. The cyclic structure (**1**), suggested as a possibility for this compound, is thus not realised; the closest contact to O(4) is, in fact, with a symmetry related antimony atom at 5.05 Å.

In this context, it is interesting to note that the structures of tetramethylantimony hydrogen dibenzoate, hydrogen-o-phthalate and 4-ethoxysalicylate[12] are basically ionic with a distorted tetrahedral Me_4Sb^+ cation and a strongly hydrogen bonded anion.

In keeping with the absence of interaction at O(4), the C(27)–O(4) and C(27)–O(3) distances, 1.197 and 1.314 Å respectively, represent effectively double and single bonds. C–O distances in the bonded acetate group, 1.231 and 1.264 Å, both show evidence of double bond character and surprisingly are shorter than the equivalent distances in Ph_4SbOAc.

REFERENCES

1. D. B. Sowerby, *J. Chem. Res.* (*S*), 80 (1979).
2. S. P. Bone and D. B. Sowerby, *J. Chem. Res.* (*S*), 82 (1979).
3. S. P. Bone, Ph.D Thesis, University of Nottingham, 1979.
4. R. G. Goel, *Can. J. Chem.*, **47**, 4607 (1969).
5. H. Schmidbaur and K.-H. Mitschke, *Angew Chem., Int. Ed. Engl.*, **10**, 136 (1971).
6. H. Schmidbaur, K.-H. Mitschke and J. Weidlein, *Z. Anorg. Allg. Chem.*, **386**, 147 (1971).
7. J. R. Carruthers, CRYSTALS, the Oxford Crystallographic Programs (1975).
8. 'International Tables for X-Ray Crystallography', Kynoch Press, Birmingham (1974), vol. 4.
9. L. Pauling, 'The Nature of the Chemical Bond', 3rd edn., Cornell University Press, Ithaca, 1960, p. 255.
10. D. B. Sowerby, M. J. Begley and P. L. Millington, *J. Chem. Soc., Chem. Commun.*, 896 (1984).
11. J. Emsley, *Quart. Rev.*, **9**, 91 (1980).
12. B. Milewski and H. Schmidbaur, *Z. Naturforsch. Teil B*, **37**, 1393 (1982).