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DIPHENYLANTIMONY(III) ACETATE: SPECTRA AND CRYSTAL STRUCTURE

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Summary

Infrared data suggest that diphenylantimony acetate has a polymeric structure with bridging acetate groups which is partially broken down in carbon tetrachloride solution and completely destroyed in chloroform. The solid state structure has been determined by X-ray crystallography. The compound is triclinic, space group $P\bar{1}$, with a 10.61(1), b 13.36(1), c 11.07(1) Å, α 106.9(1), β 116.7(1), γ 93.7(1)° and $Z = 4$. The two independent antimony atoms are linked into polymeric chains by bridging acetate groups and are in pseudo trigonal bipyramidal coordination. The two phenyl groups (mean Sb—C, 2.155 Å) and the antimony lone pair occupy the equatorial positions while one axial position is occupied by an oxygen of the bonded acetate group (Sb—O, 2.137 Å).

The bridge bonds occupy the second axial position leading to distances of 2.592 and 2.513 Å to Sb(1) and Sb(2).

Introduction

Diphenylantimony(III) acetate, originally prepared in 1944 [1] has been little investigated beyond noting its melting point and that it has antibacterial and fungicidal [2] properties. Our interest in the compound stems from the presence within the molecule of a coordinatively unsaturated central atom and a ligand with a marked tendency to behave as either a chelating or bridging group. In a number of organoantimony(V) acetates, there is evidence for the acetate showing chelate behaviour [3,4] but no data are available for antimony(III) acetates.

Results and discussion

The compound can be obtained by metathesis between diphenylantimony chloride and potassium acetate in methanol [2] as a white crystalline solid soluble in, among others, benzene, toluene, glacial acetic acid, methanol and chloroform; it is less soluble in carbon tetrachloride. The mass spectrum shows a weak parent ion (1.4%) with the major fragments in the upper *m/e* range being assigned to $PhSbO_2CCH_3^+$ (8.8%), $PhSbOH^+$ (8.0%), $PhSb^+$ (8.5%), $C_6H_4Sb^+$ (6.3%), $SbO_2CCH_3^+$ (11.2%) and Ph_2^+ (17.0%). (Values in parentheses indicate the percentage of the total ion current associated with each species). No ion with *m/e* greater than that of the parent was observed, indicating that if intermolecular Sb···O bonds are present in the solid they do not persist under mass spectrometric conditions. This should be contrasted with the behaviour of the fluorine analogue, Ph_2SbF, which shows high intensity for the $Ph_2SbF_2^+$ ion, and for which a strongly fluorine bridged polymeric structure has been confirmed by X-ray crystallography [5].

Interpretation of the vibrational data (see Experimental Section) was aided by IR measurements on the corresponding deuteroacetate which confirmed the assignment of the 1332 cm^{-1} band in the solid as a methyl deformation mode. The asymmetric and symmetric C—O stretching modes in the solid state can then be assigned to the strong, broad bands in both the Raman and IR at ca. 1540 and 1385 cm^{-1}, respectively (see Fig. 1). The $\Delta\nu$ value, ($\nu_{asym} - \nu_{sym}$), of 155 cm^{-1}, clearly indicates the presence of a chelating or bridging group, but it is difficult to make a clear distinction between these alternatives purely on the basis of vibrational data. In a 0.1 *M* solution in chloroform, the two stretching modes appear again as strong, broad bands but shifted to 1660 and 1285 cm^{-1}; these values are characteristic of a normal unidentate acetate group and the implication is that pyramidal monomers are present. That this is the case is confirmed by molecular weight measurements in chloroform solution when a value of 336 [cf. 334.9 for $Ph_2Sb(O_2CCH_3)$] was obtained.

IR spectra in the less polar solvent, carbon tetrachloride show peaks associ-

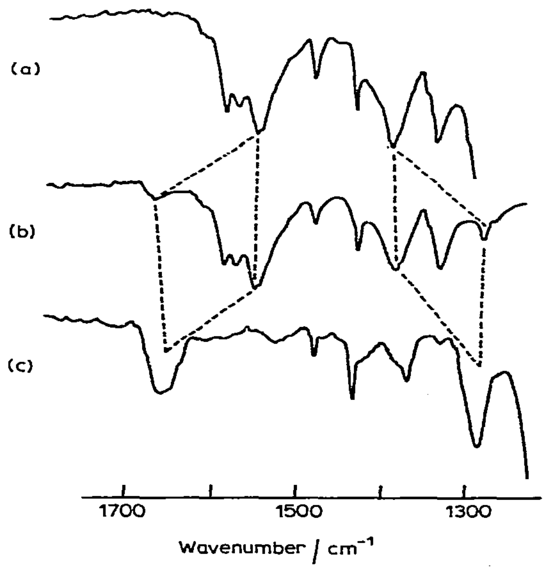

Fig. 1. Infrared spectra of $Ph_2SbO_2CCH_3$ (a) Halocarbon oil mull of the solid, (b) 0.1 *M* solution in carbon tetrachloride, (c) 0.1 *M* solution in chloroform.

ated with both unidentate (1665 and 1280 cm^{-1}) and either bridging or chelating (1546 and 1380 cm^{-1}) acetate groups. One interpretation of these results is that the long chain polymeric structure of the solid is partially broken down to smaller units with terminal acetate groups. There are also changes in the IR spectrum in the 450 cm^{-1} region. In both the solid state and CCl_4 solution spectra this mode shows three components (471, 460 and 448 cm^{-1}) while in chloroform a single band at 457 cm^{-1} is observed. Again these data can be correlated with the progressive breakdown of a polymeric chain in the solid to isolated molecules in chloroform solution.

Structural similarities are to be expected between antimony(III) compounds and the isoelectronic tin(IV) analogues. For example, both Ph_2SbF [5] and Me_3SnF [6] have fluorine bridged linear polymeric structures. Tin carboxylates of the type $R_3SnO_2CCX_3$ [7], where R = Me, X = H or F and R = benzyl, X = H, have similar structures but a four-coordinate monomeric structure has been observed when R = cyclohexyl and X = H. However, the most likely structure for $Ph_2SbO_2CCH_3$ is an acetate bridged polymer and to confirm this a crystal determination has been carried out.

Crystal structure and determination

Crystal Data. $C_{14}H_{13}O_2Sb$, $M = 334.8$, triclinic, a 10.62(1), b 13.36(1), c 11.07(1) Å, α 106.9(1), β 116.7(1), γ 93.7(1)°, U 1307.1 $Å^3$, D_c 1.70 g cm^{-3}, $Z = 4$, $F(000) = 632$, space group $P\bar{1}$, Mo-K_α radiation, λ 0.7107 Å, μ(Mo-K_α) 21.2 cm^{-1}. Crystal size ca. 0.2 × 0.2 × 0.2 mm, $\mu R = 0.21$.

The unit cell dimensions, originally obtained from oscillation and Weissenberg photographs, were refined by a least squares procedure on the positions of 23 strong reflexions accurately measured on a Hilger and Watts four circle diffractometer. Intensity data were collected using an ω—2θ scan for 4160 reflexions in the range $0° \leqslant \theta \leqslant 25°$ using Mo-K_α radiation. The intensities of 4131 reflexions for which $I > 3\sigma(I)$ were corrected for Lorentz and polarization effects but not for absorption or secondary extinction. Data reduction and subsequent crystallographic calculations used the CRYSTALS programs [8]; atomic scattering factors were taken from ref. 9.

The asymmetric unit consists of two complete formula units. A three-dimensional Patterson synthesis showed the expected two single and two double weight peaks and gave probable positions for the two antimony atoms. A difference Fourier synthesis, phased by these two atoms, gave positions for all the non-hydrogen atoms. Three cycles of full matrix, least squares refinement gave convergence at R 7.7% with isotropic thermal parameters and after two cycles with anisotropic thermal parameters R converged at 4.4%. Fixing the hydrogen atoms on the phenyl groups at their calculated positions and two further cycles of refinement led to a reduction of R to 3.8%; this was reduced to 3.5% after the introduction of a weighting scheme of the form: $w = 1/[1 + (F_0 - 18/28)]^2$. A final difference Fourier synthesis showed no peaks with intensity >0.4 e$Å^{-3}$.

Atomic coordinates for the heavy atoms are listed in Table 1. Tables of (i) calculated hydrogen positions, (ii) anisotropic thermal parameters for the heavier atoms, (iii) distances and angles within the phenyl groups, and (iv) observed and calculated structure factors can be obtained from the authors.

TABLE 1

ATOMIC COORDINATES (X 10^4) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x/a	y/b	z/c
Sb(1)	1068.6(2)	807.6(2)	3910.5(3)
O(1)	2048(3)	191(2)	2618(3)
O(2)	4134(3)	1330(2)	4268(3)
C(1)	659(4)	2065(3)	3038(4)
C(2)	—469(5)	1899(3)	1683(5)
C(3)	—714(5)	2714(4)	1139(5)
C(4)	180(5)	3734(4)	1973(6)
C(5)	1316(6)	3904(4)	3327(6)
C(6)	1555(5)	3078(4)	3851(5)
C(7)	—894(4)	—351(3)	2170(4)
C(8)	—2205(5)	—323(4)	2156(5)
C(9)	—3448(5)	—1052(4)	1020(6)
C(10)	—3418(5)	—1809(4)	—97(5)
C(11)	—2124(6)	—1857(4)	—73(6)
C(12)	—858(5)	—1126(4)	1056(5)
C(13)	3379(4)	579(3)	3102(4)
C(14)	3975(5)	50(4)	2150(6)
Sb(2)	6841.9(3)	1876.7(2)	5461.4(3)
O(3)	9072(3)	2689(2)	6657(3)
O(4)	9511(3)	1586(2)	5043(3)
C(21)	6641(4)	2966(3)	7206(4)
C(22)	5589(5)	2681(4)	7551(5)
C(23)	5543(5)	3384(4)	8722(5)
C(24)	6484(5)	4369(4)	9528(5)
C(25)	7518(5)	4661(4)	9177(5)
C(26)	7596(5)	3953(3)	8027(5)
C(27)	6442(4)	2920(3)	4257(4)
C(28)	5356(4)	3491(3)	4120(4)
C(29)	5134(5)	4209(4)	3403(5)
C(30)	6010(5)	4387(4)	2826(5)
C(31)	7064(5)	3823(4)	2933(6)
C(32)	7282(5)	3097(4)	3641(5)
C(33)	9927(4)	2343(3)	6187(5)
C(34)	11468(5)	2943(4)	7126(5)

Discussion of the structure. Relevant bond distances and angles are listed in Table 2, and Fig. 2 shows the relative orientation of the two independent molecules in the asymmetric unit and gives the atom numbering scheme. A projection of the unit cell contents down the *c* axis is shown in Fig. 3. This crystal structure determination confirms the polymeric structure suggested above on the basis of IR evidence. Two structurally independent molecules are present which are linked by bridging acetate groups into infinite chains parallel to the *a* axis. As shown in Table 2, molecular parameters for the two independent molecules are very similar but there are differences in the intermolecular Sb—O distances and in the angles at the bridging oxygen atoms. The torsion angles summarized in Table 3 also show that there are substantial differences in the relative orientation of the two molecules. The overall structure is, however, similar to that of the corresponding fluoride, Ph_2SbF [5] and to that found for the isoelectronic tin(IV) carboxylates, $Me_3SnO_2CCH_3$ and $Me_3SnO_2CCF_3$ [6].

Coordination about each antimony can be considered as distorted pseudo-

TABLE 2

SELECTED BOND DISTANCES (Å) AND ANGLES (deg) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Sb(1)—O(1)	2.137(3)	Sb(2)—O(3)	2.137(3)
Sb(1)—C(1)	2.147(4)	Sb(2)—C(21)	2.160(4)
Sb(1)—C(7)	2.169(4)	Sb(2)—C(27)	2.145(3)
Sb(1)···C(4')[a]	2.592(3)	Sb(2)···O(2)	2.513(3)
O(1)—C(13)	1.273(5)	O(3)—C(33)	1.284(5)
C(13)—O(2)	1.237(5)	C(33)—O(4)	1.231(5)
C(13)—O(14)	1.495(6)	C(33)—C(34)	1.492(6)
O(1)—Sb(1)—C(1)	89.4(1)	O(3)—Sb(2)—C(21)	85.9(1)
O(1)—Sb(1)—C(7)	86.2(1)	O(3)—Sb(2)—C(27)	88.5(1)
C(1)—Sb(1)—C(7)	95.2(1)	C(21)—Sb(2)—C(27)	94.5(1)
O(4')···Sb(1)—O(1)	169.4(1)	O(2)···Sb(2)—O(3)	167.2(1)
O(4')···Sb(1)—C(1)	83.1(1)	O(2)···Sb(2)—C(21)	83.7(1)
O(4')···Sb(1)—C(7)	87.0(1)	O(2)···Sb(2)—C(27)	84.9(1)
Sb(1)—O(1)—C(13)	119.0(3)	Sb(2)—O(3)—C(33)	118.9(2)
O(1)—C(13)—O(2)	123.4(4)	O(3)—C(33)—O(4)	122.9(3)
O(1)—C(13)—C(14)	114.7(4)	O(3)—C(33)—C(34)	114.6(3)
O(2)—C(13)—C(14)	122.0(4)	O(4)—C(33)—C(34)	112.5(4)
C(13)—O(2)···Sb(2)	123.7(3)	C(33)—O(4)···Sb(1)	127.1(2)

[a] Atoms carrying a prime are related to unprimed atoms by the transformations x, y, z → x — 1, y, z.

trigonal bipyramidal with the two phenyl groups and the antimony lone pair occupying the equatorial positions. The axial positions, as expected, are occupied by the more electronegative oxygen atoms, one from each of two acetate groups. The pseudo-trigonal bipyramidal skeleton is confirmed by an angle of 92.3° between the Sb(1)—C(1)—C(7) and Sb(1)—O(1)—O(4') planes and an angle of 89.7° between the Sb(2)—C(21)—C(27) and Sb(2)—O(2)—O(3) planes.

The effect of the lone pair is to reduce both the O—Sb···O angle to ca. 168° and that between the two phenyl groups to ca. 95°. The latter is smaller than the comparable angle in Ph_2SbF (99.9°) [5] and is probably associated with the

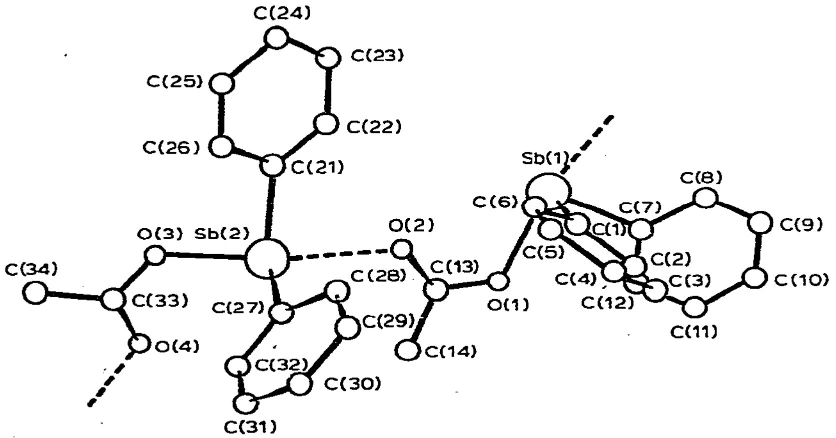

Fig. 2. View showing the two independent molecules and giving the atom numbering scheme.

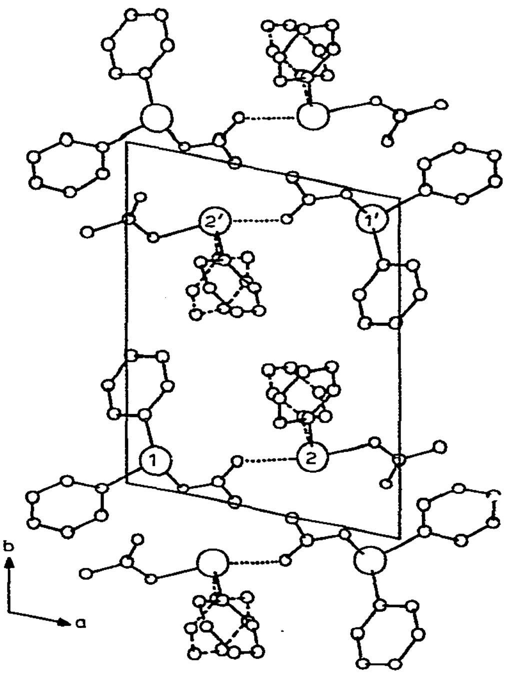

Fig. 3. Projection of the unit cell contents down the *c* axis.

TABLE 3

SELECTED TORSION ANGLES (deg)

C(1)—Sb(1)—O(1)—C(13)	85.1	C(27)—Sb(2)—O(3)—C(33)	−89.9
C(7)—Sb(1)—O(1)—C(13)	−179.5	C(21)—Sb(2)—O(3)—C(33)	175.3
O(4′)—Sb(1)—O(1)—C(13)	130.1	O(2)—Sb(2)—O(3)—C(33)	−149.0
C(7)—Sb(1)—C(1)—C(2)	−8.0	C(21)—Sb(2)—C(27)—C(28)	−42.1
O(4′)—Sb(1)—C(1)—C(2)	−94.1	O(2)—Sb(2)—C(27)—C(28)	40.9
O(1)—Sb(1)—C(1)—C(2)	78.2	O(3)—Sb(2)—C(27)—C(28)	−127.9
C(1)—Sb(1)—C(7)—C(8)	−81.1	C(27)—Sb(2)—C(21)—C(22)	120.3
O(4′)—Sb(1)—C(7)—C(8)	1.7	O(2)—Sb(2)—C(21)—C(22)	35.8
O(1)—Sb(1)—C(7)—C(8)	−170.0	O(3)—Sb(2)—C(21)—C(22)	−151.5
C(1)—Sb(1)—O(4′)—C(33′)	−85.7	C(27)—Sb(2)—O(2)—C(13)	89.9
C(7)—Sb(1)—O(4′)—C(33′)	178.6	C(21)—Sb(2)—O(2)—C(13)	174.4
O(1)—Sb(1)—O(4′)—C(33′)	−131.1	O(3)—Sb(2)—O(2)—C(13)	−149.7
C(14)—C(13)—O(2)—Sb(2)	11.7	C(34)—C(33)—O(4)—Sb(1″)[a]	0.5
O(1)—C(13)—O(2)—Sb(2)	167.5	O(3)—C(33)—O(4)—Sb(1″)	178.7
Sb(1)—O(1)—C(13)—C(14)	176.9	Sb(2)—O(3)—C(33)—C(34)	−178.3
Sb(1)—O(1)—C(13)—O(2)	−2.9	Sb(2)—O(3)—C(33)—O(4)	3.5

[a] Atoms carrying a double prime are related to unprimed atoms by the transformation $x, y, z \rightarrow x + 1, y, z$.

lower Lewis acidity of antimony in the acetate. A further consequence of this reduced Lewis acidity is the relative weakness of the intermolecular bonding as shown by Sb···O distances of 2.592 and 2.513 Å. Using Pauling's equation the intermolecular Sb···O bond (mean 2.55 Å) is equivalent to a partial bond order of 0.19. For comparison, intermolecular interaction in the corresponding fluoride is equivalent to a 0.37 bond order.

Carboxylate groups can sometimes show effectively tridentate behaviour, perhaps better described as bidentate-bridging, where the second oxygen atom in a bridging system interacts also with the first metal atom. This situation occurs here as in addition to the Sb—O distances listed in Table 2, there are Sb(1)···O(2) and Sb(2)···O(4) distances of 3.10 Å, a value which is within the sum of the Van der Waals' radii for antimony and oxygen (3.6 Å).

The four phenyl groups are planar with no atom deviating more than 0.01 Å from the appropriate mean plane. Similarly the CCO_2 skeletons of the acetate groups are planar.

This structure determination provides evidence for the rationalization of the IR data in carbon tetrachloride and chloroform solutions given above in terms of the progressive breakdown of polymeric chains. However, it is somewhat surprising that complete breakdown of the acetate bridged chains in $Me_3SnO_2CCH_3$ occurs in carbon tetrachloride solution where from the Sn—O distances (2.205 and 2.391 Å) stronger intermolecular bonding would be expected [11].

Experimental

Preparation of diphenylantimony acetate. A solution of diphenylantimony chloride was prepared by refluxing together Ph_3Sb (14.1 g, 0.04 mol) and $SbCl_3$ (7.6 g, 0.02 mol) in anhydrous dichloromethane (100 cm^3) for 3 days. The solvent was then removed and replaced by methanol (120 cm^3). Anhydrous sodium acetate (4.9 g, 0.06 mol) was added and the mixture refluxed for 12 h. After filtration, the solvent was removed in a vacuum and the remaining solid extracted with hot toluene. Crystallization from either toluene or glacial acetic acid gave the compound (12.3 g, 61% yield). M.p. 130° C (lit. [2], 131—132° C). (Found: C, 50.1; H, 4.0. $C_{14}H_{13}O_2Sb$ calcd.: C, 50.2; H, 3.9%). Suitable crystals for X-ray investigation were obtained by slow cooling of a benzene solution; crystals obtained from glacial acetic acid were invariably twinned.

Major peaks in the IR from nujol or halocarbon oil mulls together with Raman data in parentheses are: 1583s (1580vs), 1545s (1550m), 1480s (1480s), 1430s (1432m), 1380s (1390s), 1332m (1340m), 1265ms, 1075ms (1068m), 1025m (1023vs), 1001s (1000s), 738vs, 733vs, 669s, 664s (658s), 616mw (616s), 515ms (514ms), 470ms, 460s, 450ms, 290m (284m), 264ms (264s), 254s (252s), 230ms (226s) cm^{-1}.

IR spectra were obtained using a Perkin—Elmer 577 spectrometer and Raman data using a modified Cary 81 spectrometer with an argon ion laser.

References

1 A.N. Nesmeyanov and K.A. Kocheshkov, Bull. Acad. Sci. URSS, Classe S Chim., (1944) 416; Chem. Abstr., 39 (1945) 4320.

2 J.R. Leebrick and N.L. Remes (M. and T. Chemicals Inc.) U.S. Patent 3 367 954; Chem. Abstr., 68 (1968) 105367.
3 D.B. Sowerby, J. Chem. Res. (S), (1979) 80.
4 R.G. Goel, Can. J. Chem., 47 (1969) 4607.
5 S.P. Bone and D.B. Sowerby, J. Chem. Soc. Dalton Trans., (1979) 1430.
6 H.C. Clarke, R.J. O'Brien and J. Trotter, J. Chem. Soc., (1964) 2332.
7 H. Chin and B.R. Penfold, J. Cryst. Mol. Struct., 3 (1973) 285.
8 CRYSTALS — the Oxford Crystallographic Programs, J.R. Carruthers.
9 International Tables for X-ray Crystallography, Kynoch Press, Birmingham, 1974, Vol. 4.
10 L. Pauling, The Nature of the Chemical Bond, 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p. 255.
11 C. Poder and J.R. Sams, J. Organometal. Chem., 19 (1969) 67.