Perfluorophenylantimony acetates(I): synthetic and spectroscopic studies (UV, IR, ^{1}H and ^{19}F NMR) of some new tris(pentafluorophenyl)antimony(V) diacetates

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Abstract

A series of new tris(pentafluorophenyl)antimony(V) diacetates of the type $(C_6F_5)_3Sb(OCOCH_{3-n}R_n)_2$ (R=Cl, F; n=0–3: R=$-OC_6H_5$, $-OC_6H_4Cl$-4, $-OC_6H_3Cl_2$-2,4, $-OC_6H_2Cl_3$-2,4,5; n=1) have been synthesized by the reaction of tris(pentafluorophenyl)antimony(V) dichloride and a carboxylic acid in the presence of triethylamine or the sodium/potassium salt of the carboxylic acid in the presence of 15-crown-5 or 18-crown-6 as a phase-transfer catalyst. A representative alkyl derivative, viz. trimethylantimony(V) diphenoxyacetate, was also synthesised by similar methods for spectral comparisons.

The synthesis of tris(pentafluorophenyl)antimony(V) diacetate was also accomplished by reaction of tris(pentafluorophenyl)antimony(III) with acetic anhydride in the presence of equimolar quantities of periodic acid. These compounds were characterised by spectroscopic and elemental analyses as trigonal bipyramidal with the acetate ligand in all the derivatives behaving as a monodentate ligand. A correlation in the ^{19}F chemical shift and the pK_a values of the acetates has been observed.

Introduction

The literature reveals that acetates in organoantimony derivatives behave both as monodentate and bidentate ligands depending on the oxidation states of antimony (III or V), the physical states of the compounds (solid or solution) and the various substituents present on the acetate ligand itself [1–8]. Such intricacies of behaviour of the acetate group have always evoked the interest of researchers into the coordination chemistry of organoantimony(III and V) derivatives.

Most of the available literature in this area is devoted to hydrocarbon-based organoantimony compounds [1]. Similar studies on pentafluorophenyl-antimony(III and V) are virtually non-existent. Acetates having three coordinating centres, e.g. aryloxy acetates, have also not been studied.

Continuing our interest in the synthesis, reaction and spectroscopic studies of pentafluorophenylantimony(III and V) derivatives [9–11], coupled

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with the markedly different behaviour of the pentafluorophenyl ring relative to the phenyl ring, it was of interest to synthesise a variety of new tris(pentafluorophenyl)antimony(V) diacetates and study their spectral and structural characteristics. With this in mind, we have synthesised a number of α-halo acetates and α-aryloxy acetates of tris(pentafluorophenyl)-antimony(III). The results of these studies are reported in this paper.

Results and discussion

The dual behaviour of an acetate group as a mono- or bi-dentate ligand has been well established in the case of phenylantimony(V) tetraacetate and dimethylantimony(V) triacetate, where one acetate group is bidentate and the remaining act as monodentate ligands [2, 3]. Similarly, antimony in tetramethyl- and tetraphenyl-antimony(V) acetate has been considered to be trigonal bipyramidal in solution with the acetate group exhibiting monodentate behaviour, whereas in the solid state the same antimony compound is hexa-coordinate with the acetate group bidentate [4, 5]. Hence it appears that it is the physical state and nature and number of the organic groups attached to the antimony atom that determines the coordination of the acetate ligand.

In this work, we have synthesised two types of tris(pentafluoro-phenyl)antimony(V) diacetate, viz. $(C_6F_5)_3Sb(OCOCH_{3-n}R_n)_2$ (R = Cl and F; $n = 0$–3) and $(C_6F_5)_3Sb(OCOCH_2OC_6H_{5-n}R_n)_2$ (R = Cl; $n = 0$–3), with a view to studying the coordination behaviour of these ligands, since the latter has one extra donor site, i.e. Ar–Ö–, in addition to the –C=Ö functionality compared to the former, and it is necessary to assess the effect of the pentafluorophenyl rings attached to antimony(V) derivatives on the donor behaviour of the acetate groups.

These derivatives have been synthesised either by the displacement reaction of tris(pentafluorophenyl)antimony(V) dichloride with the sodium/potassium salts of acetates in the presence of 15-crown-5 or 18-crown-6 as a phase-transfer catalyst using benzene as the solvent, or by the reaction of tris(pentafluorophenyl)antimony(V) dichloride with aryloxy acids in the presence of triethylamine using benzene as the solvent. The reaction of acetic acid or α-halogenated acetic acid with tris(pentafluorophenyl)antimony(V) dichloride in the presence of triethylamine yielded only viscous materials. Analytical data relating to the compounds prepared are listed in Table 1.

A representative reaction of tris(pentafluorophenyl)antimony(III), acetic anhydride and periodic acid has been carried out to synthesise tris(pentafluorophenyl)antimony(V) diacetate. The reaction was quick, easy and gave a high yield ($\sim$95%) compared to earlier methods.

All the acetates isolated were white crystalline sharp-melting solids which were fairly stable to air and moisture. The molar conductances of the derivatives were recorded in methanol and were in the order 19–48 Ω^{-1} cm^2 mol^{-1} indicating that the compounds were non-conducting in nature and thus predominantly covalent.

TABLE 1

Analytical data for tris(pentafluorophenyl)antimony(V) diacetates

Comp. No.	Molecular formula	M.p. (°C)	Yield (%)		Analysis	Found (%)	(Calc.) (%)
			a	b	C	H	Sb
I	$C_{34}H_{14}F_{15}O_6Sb$	67	85	72	43.61 (43.66)	1.51 (1.50)	12.99 (13.01)
II	$C_{34}H_{12}F_{15}Cl_2O_6Sb$	110	80	68	41.05 (41.07)	1.20 (1.21)	12.25 (12.24)
III	$C_{34}H_{10}F_{15}Cl_4O_6Sb$	108	84.5	69	38.39 (38.41)	1.00 (0.94)	11.43 (11.45)
IV	$C_{34}H_8F_{15}Cl_6O_6Sb$	89	80.6	67	36.06 (36.07)	0.69 (0.71)	10.72 (10.75)
V	$C_{22}H_6F_{15}O_4Sb$	265–266	–	90	35.64 (35.65)	0.80 (0.81)	16.39 (16.43)
VI	$C_{22}F_{21}O_4Sb$	182	–	88	31.08 (31.12)	–	14.33 (14.34)
VII	$C_{22}F_{15}Cl_6O_4Sb$	252	–	85	25.96 (25.98)	–	12.81 (12.84)
VIII	$C_{22}H_2F_{15}Cl_4O_4Sb$	228	–	86	30.01 (30.06)	0.20 (0.22)	13.80 (13.85)
IX	$C_{22}H_4F_{15}Cl_2O_4Sb$	255	–	88	32.60 (32.62)	0.48 (0.49)	15.00 (15.03)
X	$C_{19}H_{23}O_6Sb$	99–100	86	75	58.60 (58.64)	5.92 (5.95)	31.31 (31.28)

[a] Yields obtained using triethylamine.
[b] Yields obtained using the sodium/potassium salt of the acid.

The van't Hoff factor i (0.98–1.05) calculated from molecular weights determined cryoscopically in nitrobenzene showed that the derivatives were monomeric in nature.

Ultraviolet spectra

The UV spectra of the derivatives I–X and the ligands XI–XIV were recorded in chloroform, with the UV absorption due to the –COO group appearing at λ 262±4 nm in each case. The corresponding data are given in Table 2. The aryloxy acetates exhibited two further absorptions at λ 276±5 nm and λ 290±5 nm due to the aryloxy moieties. As there is no change in the absorption wavelengths between the derivatives and ligands, it appears that the halogenated acetates and aryloxy acetates behaved as monodentate ligands towards antimony in all the compounds prepared.

Infrared spectra

IR spectra of the compounds were recorded both in the solid state and in solution using KBr/CsI pellets and chloroform, respectively.

All the compounds showed characteristic absorption peaks corresponding to the C_6F_5– group at ~1645 (s), 1520 (vs, d) and 1480 (vs) cm^{-1} [due

TABLE 2

UV absorption of tris(pentafluorophenyl)antimony(V) diacetates and the free ligand[a]

Comp. No.	Molecular formula	UV absorption, λ (nm)			
I	$(C_6F_5)_3Sb(OCOCH_2OC_6H_5)_2$	262	266	275 (sh)	—
II	$(C_6F_5)_3Sb(OCOCH_2OC_6H_4Cl\text{-}4)_2$	266	276	284 (sh)	—
III	$(C_6F_5)_3Sb(OCOCH_2OC_6H_3Cl_2\text{-}2,4)_2$	262	—	280	288
IV	$(C_6F_5)_3Sb(OCOCH_2OC_6H_2Cl_3\text{-}2,4,5)_2$	264	—	285	295
V	$(C_6F_5)_3Sb(OCOCH_3)_2$	262	—	—	—
VI	$(C_6F_5)_3Sb(OCOCF_3)_2$	260	—	—	—
VII	$(C_6F_5)_3Sb(OCOCCl_3)_2$	260	—	—	—
VIII	$(C_6F_5)_3Sb(OCOCHCl_2)_2$	259	—	—	—
IX	$(C_6F_5)_3Sb(OCOCH_2Cl)_2$	261	—	—	—
X	$(CH_3)_3Sb(OCOCH_2OC_6H_5)_2$	262 (sh)	267	274	—
XI	$C_6H_5OCH_2COOH$	268	274	—	—
XII	$4\text{-}ClC_6H_4OCH_2COOH$	—	276	284	—
XIII	$2,4\text{-}Cl_2C_6H_3OCH_2COOH$	—	—	280	288
XIV	$2,4,5\text{-}Cl_3C_6H_2OCH_2COOH$	—	—	286	295

[a]Acetic acid and halogen-substituted acetic acids exhibit no absorptions in the UV spectral range.

to ν (C–C) bands] as well as ν(C–F) absorption bands at ~ 1385 (s), 1290 (s), 1088 (vs) and 980 (vs) cm^{-1} [9].

The presence of ν_{asym}(C=O), ν_{sym}(C–O) and deformation bands at 1742 ± 3 cm^{-1} (1685 ± 10 cm^{-1}), 1400 ± 2 cm^{-1} (1395 ± 10 cm^{-1}) for halogenated acetates (aryloxy acetates) confirmed the synthesis of the antimony(V) acetates [1]. The aryloxy acetates exhibited a characteristic ν(–O–C–) absorption band at 800 ± 10 cm^{-1}. The effect of pK_a values can be seen in the ν_{asym}(C=O) peaks where the values increase with a decrease in the pK_a values (Table 3).

The small shift in the IR ν_{asym}(C=O), ν_{sym}(C–O) and ν(C–O–C) deformation absorption bands of the organoantimony(V) derivatives compared with the ligands in the solid state and in solution rules out the likelihood of coordination of antimony through –C=Ö or –C–Ö–Ar groups in the halogenated or aryloxy acetates (Table 3).

¹H NMR spectra

The ¹H NMR spectra of compounds VI–X were recorded in CDCl$_3$ using TMS as an internal standard. The spectra showed a single peak for the –CH$_2$ group at δ 4.50 ± 0.15 ppm, a multiplet at δ 7.14 ± 0.4 ppm for the phenyl protons (compounds VI–IX) and a single peak at 1.89 ppm for –CH$_3$ protons (compound X). The singlet for –CH$_2$ indicates that the ligands were planar. The results thus confirm that the three methyl groups occupy an equatorial position with the ligands being below and above the plane, i.e. apical. The aromatic protons (compounds VI–X) appear as multiplets.

TABLE 3

Characteristic IR absorption bands (cm^{-1}) for tris(pentafluorophenyl)antimony(V) diacetates

Comp. No.	ν_{asym}(C=O)		ν_{sym}(C–O)		ν(C–O–C)	ν(Sb–C)	ν(Sb–O)
	Solid	Solution	Solid	Solution			
I	1680 (vs)	1678 (vs)	1390 (s)	1388 (s)	802 (m)	600 (m)	385 (m)
II	1675 (s)	1680 (s)	1390 (m)	1392 (m)	795 (m br)	605 (m)	385 (m)
III	1678 (m)	1680 (m)	1390 (m)	1390 (m)	808 (m)	600 (m)	388 (m)
IV	1675 (vs)	1678 (vs)	1395 (s)	1392 (s)	800 (m)	592 (m)	390 (m)
V	1725 (m)	1730 (m)	1388 (s)	1385 (s)	–	605 (m)	380 (m)
VI	1745 (m)	1742 (m)	1402 (m)	1400 (m)	–	620 (m)	385 (m)
VII	1740 (m)	1740 (m)	1400 (m)	1398 (m)	–	620 (m)	380 (m)
VIII	1700 (m)	1702 (m)	1388 (m)	1390 (m)	–	618 (w)	385 (m)
IX	1720 (m)	1718 (m)	1385 (m)	1382 (m)	–	610 (m)	385 (w)
X	1685 (vs)	1690 (vs)	1405 (m)	1400 (m)	795 (s)	605 (m)	432 (m)

vs = very strong, s = strong, m = medium, w = weak, br = broad.

^{19}F NMR spectra

The ^{19}F NMR spectra of the tris(pentafluorophenyl)antimony(V) diacetates I–IX have been studied in detail in CDCl$_3$ using trifluoroacetic acid as the external standard at 84.26 MHz (Table 4). In every case, the signals for F$_{2,6}$, F$_{3,5}$ and F$_4$ appeared in the normal range of the spectrum. The F$_{3,5}$ signals appeared at a higher field compared to F$_{2,6}$ and F$_4$, indicating electron donation from the o- and p-positions towards antimony. This seems reasonable since the perfluorinated ring behaves as an electron donor [12–14].

The linear relationship between the ^{19}F NMR chemical shift and the pK_a values of the acids, i.e. α-halogenated acetic acids and aryloxy acetic acids, for the two sets of compounds I–IV and V–IX has been clearly observed, the ^{19}F signals for compounds I–IV appearing at lower fields because of the low pK_a values of the acids compared to compounds V–IX. Such correlation is not very marked for the tris(pentafluorophenyl)antimony(V) compounds of the α-halogenated acetic acids (I–IV) themselves. This may be attributed to the small difference in pK_a values for these acids, which may be further diminished due to the strong donor abilities of the perfluorinated phenyl rings. Whereas the tris(pentafluorophenyl)antimony(V) diaryloxy acetates exhibited a definite pattern in the chemical shifts for F$_{3,5}$ and F$_4$ (Table 4) which can be well correlated with the pK_a values of the acids, the chemical shift values for F$_{2,6}$ do not follow the same general trend in any of the acetates. This may be tentatively attributed to the fact that the o-fluorine chemical shift is not only governed by the electron charge density and bond order, but by the total effect of the intramolecular electric field contribution [13].

Since only one signal appeared for each F$_{2,6}$, F$_{3,5}$ and F$_4$ chemical shift, all the pentafluorophenyl rings seem to be equivalent and in one plane,

TABLE 4

^{1}H and ^{19}F NMR data for tris(pentafluorophenyl)antimony(V) diacetates

Comp. No.	$(C_6F_5)_3SbL_2$; L=	^{1}H NMR δ (ppm)			^{19}F NMR δ (ppm)			
		Ph	CH$_2$	CH$_3$	CF$_3$	F$_{3,5}$	F$_{2,6}$	F$_4$
I	$-OCOCH_3$	—	—	—	—	-156.43 to -157.65 (d)	-126.08 to -127.53	-144.79 to -146.72
II	$-OCOCH_2Cl$	—	—	—	—	-156.14 to -156.37 (d)	-124.81 to -125.97	-143.30 to -144.20 (m)
III	$-OCOCHCl_2$	—	—	—	—	-155.91 to -156.37 (d)	-124.75 to -125.97	-143.75 to -144.96 (t, t)
IV	$-OCOCCl_3$	—	—	—	—	-156.14 to -156.37 (d)	-124.75 to -125.91	-143.63 to -144.79 (t, t)
V	$-OCOCF_3$	—	—	—	-76.39	-155.91 to -156.14 (d)	-124.85 to -125.91	-143.57 to -144.03 (t)
VI	$-OCOCH_2OC_6H_5$	7.21 (m)	4.56 (s)	—	—	-161.26 (d)	-129.00 to -130.70 (m)	-153.61 to -156.20 (t)
VII	$-OCOCH_2OC_6H_4Cl-4$	7.26 (m)	4.58 (s)	—	—	-161.41 (d)	-129.08 to -130.50 (m)	-153.71 to -156.19 (t)
VIII	$-OCOCH_2OC_6H_3Cl_2-2,4$	7.35 to 6.77 (m)	4.65 (s)	—	—	-161.20 (d)	-129.05 to -130.75 (m)	-152.63 to -153.92 (t)
IX	$-OCOCH_2OC_6H_2Cl_3-2,4,5$	7.43 to 6.90 (m)	4.59	—	—	-160.95 to -161.12 (d)	-129.16 to -130.83 (m)	-152.43 to -154.05 (t)
X	$(CH_3)_3Sb(OCOCH_2OC_6H_5)_2$	7.25 to 6.90 (m)	4.47 (s)	1.89 (s)	—	—	—	—

otherwise there would have been two signals in a ratio of 2:1 for each fluorine.

^{13}C NMR spectra

The ^{13}C spectra of the pentafluorophenylantimony(V) derivatives allow no clear interpretation for the positions of the pentafluorophenyl rings and ligands because of the low peak-to-noise ratio as well as the existence of overlapping signals associated with the pentafluorophenyl group attached to antimony and the phenyl rings of the ligand [15, 16]. For this reason, a representative compound, trimethylantimony(V) diphenoxy acetate, has been synthesised with a view to studying the geometry of the methyl groups and ligands.

A comparison of the ^{13}C chemical shifts for C=O, $-CH_2$ and C_1 (Ph) in compound X with those of the phenoxy acetate ligand showed no significant change, thus confirming the lack of coordination between the oxygen of the phenoxy group and the carbonyl of the carboxy group with the antimony atom.

On the basis of above-mentioned spectral data, i.e. ^1H, ^{13}C, ^{19}F NMR, it appears that the methyl and pentafluorophenyl groups are located in one plane and are equivalent. Similarly, the monodentate behaviour of the acetate ligands is confirmed by the UV and IR spectral data and, hence, the structure of the derivatives may be deemed as trigonal bipyramidal with the methyl or the pentafluorophenyl rings being in one plane, i.e. in an equatorial position, and the ligands in an apical position [17].

The donor abilities of the acetate ligands may be reduced since the electropositive nature of the antimony atom with attached pentafluorophenyl/ methyl groups is also reduced. The monodentate behaviour of aryloxy acetate may be attributed to the delocalisation of the $-\overset{..}{O}-$ centre electrons of the aryloxy group to the benzene rings or because of steric factors.

Experimental

All solvents were purified, dried and distilled before use as per the literature methods [18]. The reactants, viz. acetic acid, trifluoroacetic acid, mono-, di- and tri-chloroacetic acid, 2,4-dichlorophenoxy acetic acid and 2,4,5-trichlorophenoxy acetic acid (all BDH), 15-crown-5 and 18-crown-6 (Fluka), were obtained commercially and used as such. Phenoxy and 4-chlorophenoxy acetic acid [18], trimethylantimony(V) dibromide [19] and tris(pentafluorophenyl)antimony(V) dichloride [9] were prepared using reported methods. IR spectra were recorded on a Pye Unicam SP3-300 spectrophotometer over the spectral range 4000–200 cm^{-1}, ^1H, ^{19}F and ^{13}C NMR spectra were recorded on a Joel FX90 Q NMR spectrometer, using TMS, CF_3COOH and $CDCl_3$ as standards, respectively. UV spectra of the compounds and ligands were recorded on a Varian Cary-1000 spectrophotometer (λ 220–400 nm). Antimony was determined according to the method given in

ref. 20. Molecular weights were determined cryoscopically in nitrobenzene using a Beckmann thermometer. All reactions were carried out under inert and dry atmospheres. Typical synthetic procedures are given below.

Preparation of tris(pentafluorophenyl)antimony(V) diphenoxy acetate (I)

Tris(pentafluorophenyl)antimony(V) dichloride (1.36 g, 2.0 mmol) and the potassium salt of phenoxy acetic acid (0.71 g, 4.0 mmol) were stirred together in 75 ml dry benzene in the presence of a catalytic amount of 18-crown-6 as phase-transfer catalyst at room temperature for 6 h, followed by refluxing for 1 h to ensure completion of the reaction. The potassium chloride formed was filtered off and the filtrate on concentration and addition of petroleum ether (40–60 °C) afforded the white amorphous solid **I**, 1.34 g (72% yield). The product was recrystallised from a 1:5 benzene/petroleum ether (40–60 °C) mixture, m.p. 67 °C.

Synthesis of trimethylantimony(V) diphenoxy acetate (X)

Trimethylantimony(V) dibromide (0.65 g, 2.0 mmol), phenoxy acetic acid (0.48 g, 4.0 mmol) and triethylamine (0.40 g, 4.0 mmol) were stirred together in 75 ml dry benzene at room temperature for 6 h, and later refluxed for 1.5 h to ensure completion of the reaction. Triethylamine hydrogen bromide which separated as a flocculent precipitate was filtered off (m.p. 248 °C) and the filtrate on concentration and addition of petroleum ether (40–60 °C; 50 ml) afforded the white crystalline solid **X** which was recrystallised from a 1:5 benzene/petroleum ether (40–60 °C) mixture, 0.66 g (~86% yield), m.p. 99–100 °C. ^{13}C NMR δ: 11.01 (–CH$_3$); 172.88 (–C=O); 65.45 (–CH$_2$); 114.20 (C$_1$, Ph); 121.03 (C$_{2,6}$, Ph); 129.16 (C$_4$, Ph); and 157.71 (C$_{3,5}$, Ph) ppm.

Synthesis of tris(pentafluorophenyl)antimony(V) diacetate (V)

Method 1

Tris(pentafluorophenyl)antimony(V) dichloride (1.38 g, 2.0 mmol) and the potassium salt of acetic acid (0.39 g, 4.0 mmol) were stirred together in 75 ml dry benzene in the presence of 18-crown-6 at room temperature for 8 h, followed by 1 h refluxing to ensure completion of the reaction. The potassium chloride formed was filtered off and the filtrate on concentration and addition of petroleum ether (40–60 °C) afforded the white crystalline solid **V**, 1.34 g (~90% yield). The product was recrystallised from a 1:5 benzene/petroleum ether mixture, m.p. 265–266 °C.

Method 2

Into a flask (100 ml) fitted with an efficient stirrer and condenser was placed tris(pentafluorophenyl)antimony (1.38 g, 2.0 mmol), acetic anhydride (0.20 g, 2.0 mmol) and periodic acid (0.44 g, 2.0 mmol) in n-octane (150 ml) at room temperature (25 °C) and the reaction mixture stirred vigorously for 1 h. The solution was then heated to reflux for 30 min and filtered hot.

After concentration (to 25 ml), the solution was cooled (0 °C, 4 h) to afford a white crystalline product, 1.40 g (±95% yield), m.p. 264–266 °C. The compound was identical in all respects to the product prepared by Method 1. Further details are given in Tables 1–4.

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