Fluorophenylantimony carboxylates(II): synthetic and spectroscopic studies (UV, IR, ^{1}H, ^{19}F and ^{13}C NMR) of pentafluorophenylantimony(V) di- and tetracarboxylates

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Abstract

Pentafluorophenylantimony(V) di- and tetracarboxylates of the molecular formula $C_6F_5SbX_2L_2$ (when $X = L = OCOR$ ($R = -CH_3$, $-CH_2Cl$, $-CHCl_2$, $-CCl_3$, $-CF_3$, $-CH_2OC_6H_3Cl_2$-2,4, $-CH_2OC_6H_2Cl_3$-2,4,5) and when $X = Cl$; $L = -OCOCH_3$, $-OCOCHCl_2$) have been synthesized by the metathetical reaction of pentafluorophenylantimony(V) tetrachloride and (dibromide)dichloride with corresponding sodium salt of carboxylic acids in appropriate molar ratio using 15-crown-5 as phase transfer catalyst. The van't Hoff factor 'i' and molar conductance data of the compounds revealed them to be monomeric and non-conducting in nature. Elemental analysis, UV, IR and NMR (^{1}H, ^{19}F and ^{13}C) were used to characterize the derivatives. Compounds are tentatively assigned as a pentacoordinated square pyramidal structure in which carboxylate ligand behaving as a monodentate ligand. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pentafluorophenylantimony(V); Carboxylates; Monodentate; Synthesis; Characterization

1. Introduction

The coordination behavior of acetate ligands in organoantimony derivatives is determined by various factors like physical state of the compounds, i.e. liquid or solid, the number of ligands and organic groups attached to central metal atom and oxidation state, etc. [1–6]. It has been reported that one acetate ligand in compound dimethylantimony(V) triacetate and phenylantimony(V) tetraacetate behaved as bidentate and others as monodentate [7,8]. Both the acetate and aryloxycarboxylate ligands in trialkyl and triarylantimony(V) derivatives behaved as monodentate ligand [6,9,10]. The acetate ligand in tetramethylantimony(V) acetate also behaved as bidentate when the compound is in solid state while in liquid state it acts as monodentate ligand [2]. These studies are mainly carried out in hydrocarbon based alkyl or aryl derivatives [1], but similar studies are scarcely reported in pentafluorophenyantimony(V) compounds [6,9–11]. As the electronic behavior of pentafluorophenyl ring is markedly different compared to phenyl ring it would be of interest to study the coordination behavior of bi- and tridentate ligands, viz. acetates and aryloxycarboxylates in pentafluorophenylantimony(V) compounds.

Therefore, keeping in view our continued interest in such studies and more particularly with fluorosubstituted arylantimony derivatives [6,9–11], it is considered worth to synthesize some new pentafluorophenylantimony(V) carboxylates with bi- and tridentate ligands to study the coordination behavior of the ligands with central metal atom.

2. Results and discussion

The dual behavior of acetate ligands in organoantimony compounds, i.e. mono- or bidentate always creates interest among researchers to investigate the coordination chemistry of organoantimony derivatives [1,2,7,8].

In view of such intricacies we have synthesized some new pentafluorophenylantimony(V) acetates and aryloxycarboxylates by the metathetical reactions using 15-crown-5 as phase transfer catalyst as shown below to study the coordination behavior of these ligands.

$$C_6F_5SbCl_4 + 4NaOCOR \rightarrow C_6F_5Sb(OCOR)_4$$

where $R = -CH_3$ **1**, $-CH_2Cl$ **3**, $-CHCl_2$ **4**, $-CCl_3$ **6**, $-CF_3$ **7**, $-CH_2OC_6H_3Cl_2$-2,4 **8**, and $-CH_2OC_6H_2Cl_3$-2,4,5 **9**.

$$C_6F_5SbCl_2Br_2 + 2NaOCOR \rightarrow C_6F_5SbCl_2(OCOR)_2$$

where $R = -CH_3$ **2**, and $-CHCl_2$ **5**.

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Table 1
Some physical and analytical data of pentafluorophenylantimony(V) carboxylates[a]

Compound no.	Emperical formula (molecular weight)	m.p. (°C)	Yield (%)	Analysis: found (%) (calculated %)		
				C	H	Sb
1	$C_{14}H_{12}O_8F_5Sb$ (524.87)	181 (d)	85	32.02 (32.04)	2.29 (2.31)	23.18 (23.20)
2	$C_{10}H_6O_4F_5Cl_2Sb$ (477.72)	169	88	25.12 (25.14)	1.25 (1.27)	25.47 (25.48)
3	$C_{14}H_8O_8F_5Cl_4Sb$ (662.63)	196–197	75	25.33 (25.34)	1.30 (1.31)	18.34 (18.36)
4	$C_{14}H_4O_8F_5Cl_8Sb$ (800.40)	119	80	20.98 (20.99)	0.49 (0.51)	15.18 (15.20)
5	$C_{10}H_2O_4F_5Cl_6Sb$ (615.49)	162	82	19.49 (19.51)	0.31 (0.33)	19.76 (19.78)
6	$C_{14}O_8F_5Cl_{12}Sb$ (938.16)	175	76	17.90 (17.92)	–	12.96 (12.97)
7	$C_{14}O_8F_{17}Sb$ (740.64)	201	78	22.69 (22.70)	–	16.41 (16.43)
8	$C_{38}H_{20}O_{12}F_5Cl_8Sb$ (1168.76)	90	86	38.97 (38.99)	1.84 (1.86)	10.38 (10.40)
9	$C_{38}H_{16}O_{12}F_5Cl_{12}Sb$ (1306.52)	106	83	34.87 (34.89)	1.32 (1.33)	9.29 (9.30)

[a] d: decomposition temperature.

All the carboxylates isolated are white crystalline sharp melting solids and are fairly stable to atmospheric oxygen and moisture. The molar conductance values of the compounds were evaluated in methanol (10^{-3} M solution) which were in the range of 13–43 Ω^{-1} mol^{-1} cm^2 showing their non-conducting behavior in solution [12]. The molecular weight and thus, van't Hoff factor 'i' (0.99–1.02) determined cryoscopically in nitrobenzene confirmed their monomeric nature. The elemental analysis were also found satisfactory and within permissible limits (Table 1).

2.1. Ultraviolet spectra

The UV absorption spectra of the compounds **1–9** were recorded in methanol. The acetates (compounds **1–7**) did not show any absorption similar to corresponding ligands [9]. Where as the aryloxy carboxylates (compounds **8** and **9**) have shown an absorption at $\lambda = 292 \pm 5$ nm, which is in the close proximities of the absorption of corresponding aryloxy carboxylate ligands [9]. As very marginal positive shift of absorption ($\lambda = 3$–10 nm) could only be observed in such derivatives, so it may be assumed that the ligands are behaving as monodentate ligands despite the availability of three coordinating sites.

2.2. Infrared spectra

IR spectra of the compounds **1–9** were recorded both in solid state and in solution using KBr/CsI pellets and chloroform, respectively. Some of the characteristic absorption bands of the synthesized pentafluorophenylantimony(V) dichlorodicarboxylates and tetracarboxylates are given in Table 2.

The IR absorptions of $-C_6F_5$ groups in all the derivatives reported here in are in confirmity to those reported earlier [6,13,14], hence, not discussed.

The absence of prominent ν(OH) absorption band at $\sim$3400 cm^{-1} and presence of ν_{asym}(C=O) and ν_{sym}(C–O) bands at 1727–1665 cm^{-1} and 1344–1273 cm^{-1}, respectively, confirmed the formation of reported derivatives. Compounds **8** and **9** also show the presence of an additional ν(C–O–C) deformation band at 808 and 805 cm^{-1}, respectively. The appearance of ν_{asym}(C=O) absorption band relatively at higher frequency, i.e. $\sim$1700 cm^{-1} may be attributed to the changed electronic behavior of pentafluorophenyl ring. The presence of medium to weak absorption bands corresponds to ν(Sb–C) and ν(Sb–O) at 618–572 and 385–425 cm^{-1}, respectively, in all the compounds.

Table 2
Characteristic IR absorption bands (cm^{-1}) for pentafluorophenylantimony(V) carboxylates[a]

Compound no.	Molecular formula	ν_{asym}(C=O)		ν_{sym}(C–O)		ν(C–O–C)	ν(Sb–C)	ν(Sb–O)
		Solid	Solution	Solid	Solution			
1	$C_6F_5Sb(OCOCH_3)_4$	1679 (s)	1683 (s)	1287 (s)	1291 (s)	–	586 (m)	405 (m)
2	$C_6F_5SbCl_2(OCOCH_3)_2$	1672 (m)	1675 (m)	1273 (s)	1276 (s)	–	585 (w)	425 (m)
3	$C_6F_5Sb(OCOCH_2Cl)_4$	1690 (m)	1686 (m)	1291 (m)	1290 (m)	–	582 (m)	395 (m)
4	$C_6F_5Sb(OCOCHCl_2)_4$	1700 (s)	1700 (s)	1318 (s)	1315 (s)	–	580 (m)	390 (m)
5	$C_6F_5SbCl_2(OCOCHCl_2)_2$	1727 (s)	1725 (s)	1284 (s)	1280 (s)	–	572 (m)	395 (m)
6	$C_6F_5Sb(OCOCCl_3)_4$	1690 (m)	1687 (m)	1291 (s)	1291 (s)	–	585 (m)	385 (m)
7	$C_6F_5Sb(OCOCF_3)_4$	1707 (s)	1702 (s)	1278 (m)	1275 (m)	–	608 (m)	388 (m)
8	$C_6F_5Sb(OCOCH_2OC_6H_3Cl_2\text{-}2,4)_4$	1715 (m)	1711 (m)	1344 (m)	1348 (m)	808 (m)	618 (w)	388 (m)
9	$C_6F_5Sb(OCOCH_2OC_6H_2Cl_3\text{-}2,4,5)_4$	1665 (m)	1662 (m)	1305 (m)	1302 (m)	805 (m)	587 (m)	392 (m)

[a] s: strong, m: medium, w: weak.

Table 3
^{1}H and ^{19}F NMR data of pentafluorophenylantimony(V) carboxylates

Compound no.	Carboxylic ligands	^{1}H NMR, δ (ppm)			^{19}F NMR, δ (ppm)			
		Ph	CH$_2$	CH$_3$	CF$_3$	F$_{3,5}$ (J_{3-4}(Hz))	F$_{2,6}$ ($J_{2,3}$(Hz))	F$_4$
1	–OCOCH$_3$	–	–	3.57 (s)	–	−164.9 (t) (19.53)	−132.2 (d) (20.54)	−158.9(t)
2	–OCOCH$_3$	–	–	3.69 (s)	–	−164.7 (t) (19.53)	−132.1 (d) (20.54)	−158.4 (t)
3	–OCOCH$_2$Cl	–	–	3.62 (s)	–	−164.8 (t) (19.53)	−132.1 (d) (20.54)	−158.6 (t)
4	–OCOCHCl$_2$	–	–	3.71 (s)	–	−163.9 (t) (19.53)	−131.7 (d) (20.53)	−157.2 (t)
5	–OCOCHCl$_2$	–	–	3.73 (s)	–	−163.8 (t) (19.53)	−131.6 (d) (20.53)	−157.1 (t)
6	–OCOCCl$_3$	–	–	–	–	−164.1 (t) (19.53)	−131.8 (d) (20.53)	−157.5 (t)
7	–OCOCF$_3$	–	–	–	−79.10 (s)	−163.1 (t) (19.53)	−132.1 (d) (20.54)	−156.1 (t)
8	–OCOCH$_2$OC$_6$H$_3$Cl$_2$-2,4	7.28–6.72 (m)	4.51 (s)	–	–	−161.1 (t) (19.53)	−129.4 (d) (20.54)	−152.6 (t)
9	–OCOCH$_2$OC$_6$H$_2$Cl$_3$-2,4,5	7.42–6.68 (m)	4.48 (s)	–	–	−161.1 (t) (19.53)	−129.1 (d) (20.54)	−152.5 (t)

As no distinct change in ν(C=O) absorption peak could be observed in solution and solid IR spectra which indicates that the ligands are monodentate in nature in such compounds.

2.3. NMR spectra

2.3.1. ^{1}H NMR spectra

The ^{1}H NMR spectra of compounds **1–5**, **8** and **9** were recorded in CDCl$_3$ using TMS as the reference at 400 MHz instrument. The chemical shift values are tabulated in Table 3. The –OH proton signals (at $\delta \sim 9.20$ ppm) of carboxylic acid disappeared in all the compounds indicated the formation antimony(V) adducts. In compounds **1–5**, –CH$_3$ protons signals appeared at $\delta = 3.60 \pm 0.12$ ppm as singlet. Similarly in compounds **8** and **9**, –CH$_2$ protons appeared at $\delta = 4.50 \pm 0.02$ ppm as singlet. The appearance of one signal in each case indicates that all the ligands were present either in one plane or due to fluxionality only one signal is appearing. To rule out the possibility of fluxionality effect, a NMR of the compound **4** was done at lower temperature (-60°C), which also gave one signal and even the broadening of the signal could not be observed. So, it may be concluded that all the ligands were present in one plane and behaving as monodentate ligand.

2.3.2. ^{19}F NMR spectra

The ^{19}F NMR spectra of the compounds **1–9** were recorded in CDCl$_3$ using CF$_3$COOH as reference at 400 MHz instrument (Table 3). The signal due to F$_4$, F$_{3,5}$ and F$_{2,6}$ appeared at δ: -152.5 to -158.9, -161.1 to -164.9 and -129.1 to -132.2 ppm, respectively. The F$_4$ signal may easily be identified due to its half intensity as compared to the signals of F$_{3,5}$ and F$_{2,6}$. The F$_4$ signals also splitted into a triplet due to the F$_{3,5}$ coupling, although expected further splitting as triplet of triplet due to F$_{2,6}$ coupling was not observed in these compounds. The F$_{3,5}$ and F$_{2,6}$ signals appeared as triplet and doublet, respectively. The F$_{3,5}$ chemical shift appeared at higher field as compared to the F$_{2,6}$ and F$_4$ chemical shift, indicating the donation of electron from *ortho* and *para* position towards carbon attached to

antimony atom and this observation is in accordance to previous studies that the C$_1$ carbon of perfluorinated benzene ring feels high electron density due to diminished inductive effect of fluorine atom and donation of electron density from the unshared p electron of fluorine to the π system of the ring (p–π interaction) [9–11,15–17]. The –CF$_3$ group in compound **7** gave one signal at $\delta = -79.1$ ppm which further indicates that all the ligands are present in one plane and monodentate in nature.

2.3.3. ^{13}C NMR spectra

The ^{13}C NMR of two representative pentafluorophenylantimony(V) carboxylates, i.e. pentafluorophenylantimony(V) bis(dichloroacetate)dichloride (**5**) (^{13}C NMR (400 MHz, CDCl$_3$): $\delta = 125.1$ (C$_1$); 138.9 (C$_{3,5}$); 145.5 (C$_4$); 148.7 (C$_{2,6}$); 167.1 (C=O) and 68.8 ppm (–CH)) and pentafluorophenylantimony(V) tetraacetate (**1**) (^{13}C NMR (400 MHz, CDCl$_3$): $\delta = 125.2$ (C$_1$); 139.1 (C$_{3,5}$); 145.6 (C$_4$); 148.8 (C$_{2,6}$); 168.9 (C=O) and 68.8 ppm (–CH$_3$)) have been examined. The ^{13}C NMR of the pentafluorophenylantimony(V) tetrachloride (^{13}C NMR (400 MHz, CDCl$_3$): $\delta = 116$ (C$_1$); 136.8 (C$_{3,5}$); 146.9 (C$_{2,6}$); 143.7 (C$_4$)) has also been done to study the effect of carboxylate group on the chemical shift behavior of the ring carbon centers. In every case C$_1$ position was found to be more shielded than C$_{3,5}$, C$_{2,6}$ or C$_4$ centers. The order of chemical shift was C$_1$ > C$_{3,5}$ > C$_4$ > C$_{2,6}$. These data are in confirmity to ^{19}F NMR data. On comparing the chemical shift behavior of pentafluorophenylantimony(V) tetrachloride to the derivatives, it is evident that there is an invariable lower field shift of all the ring carbon centers due to the decrease in the electronegativity of the ligands. The C$_1$ center felt significant change where the electron density seems decreased while replacing strong electronegative –Cl atom with carboxylate group. The chemical shift behavior seems dependent on the pK_a values of the acids too, where the compound **5**, i.e. less pK_a value showed the position of each C center to be at higher field compared to compound **1**, i.e. high pK_a value. These observations are same as in case of triphenylantimony(V) dihalides where the electron density decreases at C$_1$ center with the decrease of electronegativity of halogens [15].

2.4. FAB mass

The FAB Mass analysis of a representative compound $C_6F_5SbCl_2(OCOCHCl_2)_2$ (**5**), molecular weight 615 has been studied. The spectra showed a cluster ion peak at *m/z* 774 (100%) which may be attributed to the formation of (molecular ion + *m*-nitrobenzyl alcohal + sodium)$^+$ ion. The isotopic peaks of chlorine were obtained in the required intensity ratio. Peak at *m/z* 289 may be due to the formation of $(C_6F_5Sb-H)^+$ moiety. A Peak at *m/z* 454/456 is also appeared which may be attributed due to loss of $(OCOCHCl_2 + Cl)$ moiety from parent molecule.

3. Experimental

3.1. General experimental procedures

All solvents (AR Grade) were purified, dried and distilled before use as per the literature methods [18]. The reactants, viz. acetic acid, trifluoroacetic acid, mono-, di- and trichloroacetic acid, 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxy acetic acid (all BDH) were used as their sodium salt. The 15-crown-5 (Fluka) was used as received. Pentafluorophenylantimony(V) tetrachloride and pentafluorophenylantimony(V) (dibromide)dichloride were prepared by reported method [19].

IR spectra were recorded on a Pye Unicam SP3-300 spectrophotometer over the spectral range 4000–200 cm^{-1} in the solid state and also in solution using KBr/CsI Pellets and chloroform, respectively. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on Jeol JNM-400 NMR spectrometer using TMS, CF_3COOH and $CDCl_3$ as references, respectively. UV spectra of the compounds and ligand were recorded on a Varian Cary-1000 spectrophotometer ($\lambda = 220–400$ nm). Antimony was determined according to a literature method [20]. Molecular weights were determined cryoscopically in nitrobenzene using a Beckman thermometer of ±0.01 accuracy. The molar conductance of 10^{-3} M solution of the compounds was determined at 25°C with a Khera DC610 Digital conductivity meter in methanol.

The FAB mass spectra were recorded on Jeol SX 102 mass spectrometer using DA-6000 data analysis system. Argon was used as bombarding gas at 6 kV, 10 mA. The accelerating voltage was kept at 10 kV. *m*-Nitrobenzyl alcohol (NBA) was used as matrix.

3.2. Representative synthetic procedures

3.2.1. Synthesis of pentafluorophenylantimony(V) tetraacetate (**1**)

Pentaflurophenylantimony(V) tetrachloride (0.86 g, 2.0 mmol) and the sodium salt of acetic acid (0.66 g, 8.0 mmol) were stirred together in 75 ml dry benzene in the presence of a catalytic amount of 15-crown-5 as phase transfer catalyst at room temperature for 6 h. The reaction mixture was further refluxed for 1 h to ensure the completion of the reaction. The sodium chloride formed was filtered off. The filtrate on concentration and addition of petroleum ether (40–60°C) afforded a white amorphous solid **1**, 0.95 g (90% yield). The product was recrystallized from a 1:5 benzene/petroleum ether (40–60°C) mixture; yield 0.89 g (85% yield); m.p. 181°C (d).

3.2.2. Synthesis of pentafluorophenylantimony(V) bis(dichloroacetate)dichloride (**5**)

Pentaflurophenylantimony(V) (dibromide)dichloride (1.04 g, 2.0 mmol) and the sodium salt of dichloroacetic acid (0.61 g, 4.0 mmol) were stirred together in 75 ml dry benzene in the presence of a catalytic amount of 15-crown-5 as phase transfer catalyst at room temperature for 6 h. The reaction mixture was further refluxed for 1 h to ensure the completion of the reaction. The sodium chloride formed was filtered off. The filtrate on concentration and addition of petroleum ether (40–60°C) afforded a white amorphous solid **5**, 1.05 g (86% yield). The product was recrystallized from a 1:5 benzene/petroleum ether (40–60°C) mixture; yield 1.01 g (82% yield); m.p. 162°C.
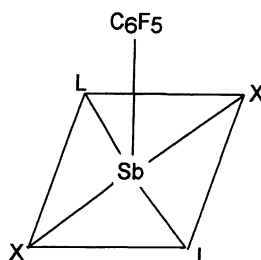
X = L = -OCOCH$_3$ **1**, -OCOCH$_2$Cl **3**, -OCOCHCl$_2$ **4**, -OCOCCl$_3$ **6**, -OCOCF$_3$ **7**,
-OCOCH$_2$OC$_6$H$_3$Cl$_2$-2,4 **8** and -OCOCH$_2$OC$_6$H$_2$Cl$_3$-2,4,5 **9**

X = Cl; L = -OCOCH$_3$ **2**, -OCOCHCl$_2$ **5**

Fig. 1. Configuration of pentafluorophenylantimony(V) di- and tetracarboxylates.

4. Conclusions

From the UV and IR studies it is evident that the carboxylate ligands, whether bidentate or tridentate in nature, behaved as monodentate ligands. This may be attributed to the donation of electron density from unshared p electrons of fluorine to the π system of the ring and thus, increasing electron density at C_1 center, which decreases the lewis acid character of central metal atom and preventing to accept electron from the ligands. The NMR studies (^{1}H, ^{19}F and ^{13}C) showed that the carboxylate ligands were present in one plane. Thus, in such compounds the antimony is assumed to be in pentacoordinated state with a probable square pyramidal structure (Fig. 1).

Acknowledgements

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