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Fluorophenylantimony Carboxylates. I. Synthesis and Spectroscopic (UV, IR, ^{1}H and ^{19}F NMR) Studies of Some New Monofluoro- and Pentafluorophenylantimony(III and V) Derivatives of 2-methoxybenzoic Acid

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FLUOROPHENYLANTIMONY CARBOXYLATES. I. SYNTHESIS AND SPECTROSCOPIC (UV, IR, ^{1}H AND ^{19}F NMR) STUDIES OF SOME NEW MONOFLUORO- AND PENTAFLUOROPHENYLANTIMONY(III AND V) DERIVATIVES OF 2-METHOXYBENZOIC ACID

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ABSTRACT

A series of new mono- and pentafluorophenylantimony(III and V) arylcarboxylates of the type $Ar_nSb(OOCC_6H_4OCH_3\text{-}2)_{3-n}$ and $Ar_3Sb(OOCC_6H_4OCH_3\text{-}2)_2$ (Ar = p-FC_6H_4-, m-FC_6H_4- and C_6F_5-, n =1 or 2) have been synthesized by the reaction of fluorophenylantimony (III or V) chlorides and the sodium salt of 2-methoxybenzoic acid in the presence of 15-crown-5 as phase transfer catalyst. A representative compound, namely trimethylantimony(V) bis(2-methoxybenzoate) has also been synthesized for the sake of spectral comparisons. The van't Hoff factor 'i' and molar conductance data of the compounds revealed them to be monomeric and non-conducting in nature. The compounds were characterised by the usual physicochemical techniques e.g., elemental analyses, UV, IR and NMR (^{1}H, ^{13}C and ^{19}F). Compound (III-VIII) are tentatively assigned as a trigonal bipyramidal structure in which the 2-methoxybenzoate acted as monodentate ligand.

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INTRODUCTION

Past studies revealed that the coordination behavior of organoantimony derivatives with bi- or tridentate ligands depends on the oxidation state of the central metal atom, physical state of the compound i.e., solid or solution and various organic groups attached to the metal[1-7]. Such intricacies always piqued researchers to investigate the coordination chemistry of organoantimony(III and V) derivatives. Sofar, such studies are mainly confined to the Schiff bases and acetate ligands with hydrocarbon-based alkyl or arylantimony derivatives[8-10]. Such studies with fluorophenyl derivatives are rather scarce[11,12].

Henceforth, continuing our interest in the area of synthesis, reactions and spectroscopic studies of fluorophenylantimony(III and V) derivatives[11-15], it is of interest to study the behavior of a tridentate arylcarboxylate ligand i.e., 2-methoxybenzoic acid with mono- and pentafluorinated arylantimony(III and V) derivatives as the behavior of both rings are markedly different. Thus, in the present investigation, new arylcarboxylates of the type Ar_nSbL_{3-n} and Ar_3SbL_2 ($L = -OOCC_6H_4OCH_3$-2) have been synthesized and characterised.

RESULTS AND DISCUSSION

As the physical state i.e., solution or solid and number of organic groups attached to the antimony atom determines the coordination of carboxylate ligands[1], it would be of interest to investigate the behavior of an hitherto unstudied class of arylcarboxylate ligand i.e., 2-methoxybenzoate, with fluorophenylantimony derivatives. In the present investigation a variety of organoantimony(III and V) arylcarboxylates have been synthesized by the reaction of the sodium derivative of 2-methoxybenzoic acid and corresponding organoantimony halides in the presence of 15-crown-5 as PTC.

$$Ar_nSbX_{3-n} + NaOOCC_6H_4OCH_3\text{-}2 \rightarrow Ar_nSb(OOCC_6H_4OCH_3\text{-}2)_{3-n}$$

$$Ar = C_6F_5,\ n = 1\ (I)\ \text{or}\ 2\ (II)$$

$$Ar_nSbX_{5-n} + NaOOCC_6H_4OCH_3\text{-}2 \rightarrow Ar_nSb(OOCC_6H_4OCH_3\text{-}2)_{5-n}$$

Ar = m-FC_6H_4 (IV), p-F C_6H_4 (V) or Me (VI), n = 3
Ar = C_6F_5-, n = 1 (VII and VIII) and 3 (III)

A representative derivative trimethylantimony(V) bis(2-methoxybenzoate) has also been synthesized by the reaction of trimethylantimony dibromide and the sodium salt of the acid for spectral comparisons. The molar conductance of the derivatives were recorded in methanol and found to be of the order of 13- 43 Ω^{-1} cm^2 mol^{-1} indicating their non-conducting nature. Molecular weights and thus van't Hoff factors 'i' (0.98-1.02) determined cryoscopically in nitrobenzene showed their monomeric nature. The elemental analyses were found satisfactory and within permissible limits (Table I).

UV Spectra

The UV absorption spectra of the derivatives (Table II) were recorded in methanol. The appearance of the absorption in the range λ 290 ± 2 nm showed the formation of the compounds. Compounds (IV) and (V) showed additional absorbtions at λ 260 sh, 266, 272 and 258 sh 268 due to m- and p-fluorophenyl moieties, respectively. An additional absorption also appeared at λ 230 nm in compounds (II) and (VI). The absence of any sizable shift in absorption bands of the ligand in these derivatives indicates the absence of coordination through C=O or C-O-Ar groups.

Infrared Spectra

IR spectra of the compounds (I) - (VIII) were recorded in the solid state using KBr/CsI pellets. The main absorption bands of the synthesized organoantimony(III and V) 2-methoxybenzoates are given in Table III.

The disappearance of the characteristic ν(OH) absorption band at 3400 cm^{-1} and the presence of ν_{asy} (C=O), ν_{sy}(C-O) and ν(C-O-C) deformation bands

TABLE I

Some Physical and Analytical Data of Organoantimony(III and V) 2-Methoxybenzoates

Compd. No.	Empirical Formula (Molecular Weight)	M.P. (°C)	Yield (%)	Analysis: Found (Calcd) %		
				C	H	Sb
(I)	$C_{14}H_7F_5ClO_3Sb$	92	85	35.34	1.46	25.59
	(475.39)			(35.37)	(1.48)	(25.61)
(II)	$C_{20}H_7F_{10}O_3Sb$	102	80	39.56	1.15	20.04
	(512.02)			(39.58)	(1.16)	(20.06)
(III)	$C_{34}H_{14}F_{15}O_6Sb$	185	90	44.09	1.51	13.14
	(925.23)			(44.14)	(1.52)	(13.16)
(IV)	$C_{34}H_{26}F_3O_6Sb$	147	88	57.56	3.67	17.15
	(709.15)			(57.58)	(3.69)	(17.16)
(V)	$C_{34}H_{26}F_3O_6Sb$	158	86	57.54	3.68	17.15
	(709.15)			(57.58)	(3.69)	(17.16)
(VI)	$C_{19}H_{23}O_6Sb$	110	88	48.63	4.93	25.94
	(469.14)			(48.64)	(4.94)	(25.95)
(VII)	$C_{22}H_{14}F_5Cl_2O_6Sb$	101	55	39.90	2.12	18.38
	(661.99)			(39.91)	(2.13)	(18.39)
(VIII)	$C_{38}H_{28}F_5O_{12}Sb$	92	62	51.09	3.14	13.60
	(893.33)			(51.09)	(3.15)	(13.62)

at 1705-1605, 1400±15 and 805±10 cm^{-1}, respectively, confirmed the formation of organoantimony(III and V) 2-methoxybenzoates. The major shift to higher frequency of the v_{asy}(C=O) absorption band for the compounds containing pentafluorophenyl groups (I) - (III), (VII) and (VIII) may be attributed to its electron donor behavior as compared to compounds (IV), (V) and (VI) having *m*-, *p*-fluorophenyl and methyl groups, respectively. The pentafluorophenyl-antimony(III and V) derivatives also showed the characteristic v(C-C) bands of the $-C_6F_5$ group at ~1645 (s), 1520 (vs, d) and 1480 (vs) cm^{-1} as well as v(C-F) absorption bands[11,16] at ~1385 (s), 1290 (s), 1088 (vs) and 980 (vs) cm^{-1}.

TABLE II

UV Absorptions of Organoantimony(III and V) 2-Methoxybenzoates

Compd.	Formula	UV (nm) absorption				
No.	L = $OOCC_6H_4OCH_3$-2	λ_{max} [ϵ_M]				
(I)	C_6F_5SbLCl	-	-	266 [12100]	-	292 [11010]
(II)	$(C_6F_5)_2SbL$	230 [25000]	-	-	-	292 [11050]
(III)	$(C_6F_5)_3SbL_2$	-	-	-	-	288 [10310]
(IV)	$(\underline{m}\text{-}FC_6H_4)_3SbL_2$	-	260 sh [12300]	266 [11800]	272 [10900]	290 [6412]
(V)	$(\underline{p}\text{-}FC_6H_4)_3SbL_2$	-	258 sh [12580]	268 [11600]	-	288 [5540]
(VI)	$(CH_3)_3SbL_2$	230 [12110]	-	-	-	290 [5510]
(VII)	$C_6F_5SbCl_2L_2$	-	-	-	-	292 [11120]
(VIII)	$C_6F_5SbL_4$	-	-	-	-	292 [10300]

2-$CH_3OC_6H_4COONa$, λ 282 nm; $(\underline{m}\text{-}FC_6H_4)_3SbCl_2$, λ 262 (sh), 268, 270 nm; $(\underline{p}\text{-}FC_6H_4)_3SbCl_2$, λ 260, 270 nm; $(CH_3)_3SbBr_2$, $C_6F_5SbCl_2$, $(C_6F_5)_2SbCl$, $(C_6F_5)_3SbCl_2$ showed no UV absorption.

NMR Spectra

^{1}H NMR Spectra. ^{1}H NMR spectra of the compounds (I) – (VIII) have been determined in $CDCl_3$ using TMS as the internal standard and chemical shift data are listed in Table IV. The disappearance of the characteristic resonance of the -OH proton at δ ~9.2 ppm and the appearance of $-OCH_3$ protons in compounds (I) – (VII) at δ 3.92 ± 0.15 ppm as singlet showed the formation of organoantimony

TABLE III

Characteristic IR Absorption Bands (cm^{-1}) for Organoantimony(III and V) 2-Methoxybenzoates

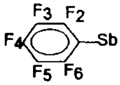
Compd. No.	ν_{asym}(C=O)	ν_{sym}(C-O)	ν(C-O-C)	ν(Sb-C)	ν(Sb-O)
(I)	1685 vs	1398 m	805 m	605 m	385 m
(II)	1680 vs	1395 m	805 m	605 m	380 m
(III)	1705 s	1400 m	800 m	600 m	385 w
(IV)	1618 s	1415 m	805 m	605 m	425 m
(V)	1605 vs	1388 s	802 m	600 m	385 m
(VI)	1645 vs	1395 m	795 m	605 m	430 m
(VII)	1694 s	1408 m	815 m	612 m	405 m
(VIII)	1692 vs	1405 m	815 m	610 m	405 m

(III and V) 2-methoxybenzoates in which the ligands are present in the same plane. In compound (VIII) two singlets of $-OCH_3$ protons appeared at δ 4.05 and 3.68 ppm (1:1). It showed that the two of the four methoxybenzoates were present at the apical position and two at the axial position. This observation further establishes our previous observation that in compounds (III)-(VII), having two methoxybenzoate ligands, only one signal for $-OCH_3$ protons appeared i.e., the ligands are present in one plane and the fluxionality is not playing any role, otherwise in compound (VIII) only one signal would have appeared. The appearance of $-CH_3$ protons at δ 2.07 ppm in compound (VI) as singlet also confirmed that the methyl groups are in one plane and the methoxybenzoate ligands are present in axial positions. The aryl protons of the compounds (I) –

TABLE IV

^{1}H and ^{19}F NMR Data of Organoantimony(III and V) 2-Methoxybenzoates

Compd. No.	^{1}H NMR δ (ppm) Ph	OCH$_3$	CH$_3$	^{19}F NMR δ (ppm) F$_{2,6}$ [J$_{2,3}$(Hz)]	F$_{3,5}$ [J$_{3,4}$(Hz)]	F$_4$
(I)	7.01-8.24 (m)	4.07 (s)	-	-130.59 (d) [20.53]	-163.99 (t) [19.53]	-155.79 (t)
(II)	7.01-8.21 (m)	4.06 (s)	-	-130.53 (d) [20.53]	-163.92 (t) [19.53]	-155.77 (t)
(III)	6.04 -7.45 (m)	4.07 (s)	-	-127.76 (d) [20.54]	-157.36 (t) [19.53]	-144.99 (t)
(IV)	6.04 -7.45 (m)	3.92 (s)	-	-	-110.22 (s)	-
(V)	6.98-8.30 (m)	3.85 (s)	-	-	-	-111.96 (s)
(VI)	6.93-7.78 (m)	3.87 (s)	2.07 (s)	-	-	-
(VII)	6.95-8.30 (m)	3.96 (s)	-	-126.28 (d) [20.53]	-157.32 (t) [19.53]	-144.89 (t)
(VIII)	6.95-8.20 (m)	4.05 (s)	-	-127.69 (d) [20.53]	-157.57 (t) [19.53]	-145.47 (t)



[Structure of the pentafluoropheny ring]

(VIII) appeared at δ 6.04 to 8.30 ppm as multiplet and do not allow any clear interpretation.

<u>^{19}F NMR Spectra.</u> ^{19}F NMR spectra of the compounds (I) – (V), (VII) and (VIII) have been studied in detail in CDCl$_3$ using CF$_3$COOH as an external standard at 84.26 MHz (Table IV). The signal due to F$_4$ (at δ -144.06 to -156.87 ppm) of the pentafluorophenyl ring has been easily identified as compared to F$_{3,5}$ and F$_{2,6}$ due

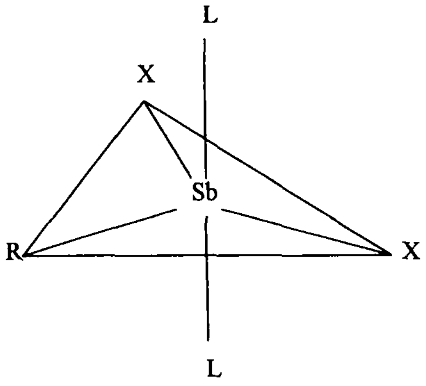
to its half intensity in compounds (I) - (III), (VII) and (VIII). The F_4 signal appeared as a triplet due to $F_{3,5}$ coupling. Further splitting due to ortho coupling ($F_{2,6}$) was not observed although one can expect F_4 to appear as a triplet of triplets. The $F_{2,6}$ signal appeared as doublet at δ -126.65 to -130.69 ppm, while the $F_{3,5}$ signal appeared as triplet at δ -156.86 to -164.22 ppm for the various derivatives. The $F_{3,5}$ chemical shifts were at higher field compared to the $F_{2,6}$ and F_4 chemical shifts indicating the donation of electrons from the o- and p-positions towards antimony. This is in accordance with our previous studies that perfluorinated rings behaves as electron donors [11-14]. Compounds (IV) and (V) gave ^{19}F signals at δ -110.22 and -111.96 for m- and p-fluorophenyl groups, respectively. The single signal of fluorine in these compounds further indicating that all the aryl rings are in one plane and thus the 2-methoxybenzoate groups attained apical positions.

^{13}C NMR Spectra. ^{13}C NMR spectra of a representative compound, trimethylantimony(V) bis(2-methoxybenzoate) (VI), has been studied in detail in which the $-CH_3$, C=O, $-OCH_3$ groups appeared at δ 11.72 , 170.20 and 56.0 ppm, respectively. The phenyl ring carbons i.e., C_1, C_2, C_3, C_4, C_5 and C_6 appeared at δ 120.11, 159.12, 112.21, 132.32, 119.81 and 131.52 ppm, respectively. The single signal of the $-CH_3$ group further confirmed the uniplaner geometrical position of all methyl groups. Similarly, the singlet for the $-OCH_3$ groups also indicated that the ligands are present in one plane in these compounds.

The ^{13}C spectra of the perfluorophenylantimony (V) carboxylates do not lend to any clear interpretation due to high peak to noise ratio.

CONCLUSION

In view of the above spectroscopic data, the structure of the compounds (III) – (VIII) may be tentatively assigned as trigonal bipyramidal in which the 2-methoxybenzoate ligand functions as monodentate ligand.



R = X = C_6F_5, p-FC_6H_4 , m-FC_6H_4 and CH_3; L = $OOCC_6H_4OCH_3$-2 for compounds (III) – (VI).

R = C_6F_5; X = Cl; L = $OOCC_6H_4OCH_3$-2 for compound (VII).

R = C_6F_5; X = L = $OOCC_6H_4OCH_3$-2 for compound (VIII).

FIG. 1. Configuration of Organoantimony(V) 2-Methoxybenzoates.

EXPERIMENTAL

All solvents (AR Grade) were purified, dried and distilled before use. 2-Methoxybenzoic acid (BDH) was used as its sodium salt. The 15-crown-5 (Fluka) was used as such. Bis(pentafluorophenyl)antimony(III) chloride[12], pentafluorophenylantimony(III) dichloride[12], tris(pentafluorophenylantimony(V) dichloride[11], tris(m-fluorophenyl)- and tris(p-fluorophenyl)antimony(V) dichloride[17], trimethylantimony(V) dibromide[18] and pentafluorophenylantimony(III) dichloride dibromide[12] were prepared by reported methods.

IR spectra were recorded on a Pye Unicam SP3-300 spectrophotometer over the spectral range 4000-200 cm^{-1} using KBr pellets. ^1H, ^{19}F and ^{13}C NMR spectra were recorded on a Jeol FX90 Q NMR spectrometer using TMS, CF_3COOH and $CDCl_3$ as standards, respectively. UV spectra of the compounds and ligand were recorded on a Varian Cary-1000 spectrophotometer (λ 220-400 nm). Antimony was determined according to a literature method[19]. Molecular weights were determined cryoscopically in nitrobenzene using a Beckman thermometer of ± 0.01 accuracy. The molar conductance of the compounds was determined in methanol solution. A representative synthesis procedure is given below.

Synthesis of Tris(pentafluorophenyl)antimony(V) Bis(2-methoxybenzoate) (III)

Tris(pentafluorophenyl)antimony(V) dichloride (1.38 g, 2.0 mmol) and the sodium salt of 2-methoxybenzoic acid (0.69 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, followed by 1 h of refluxing to ensure the completion of the reaction. The sodium chloride formed was filtered off and the filtrate on concentration and addition of petroleum ether (40-60° C) afforded a white amorphous solid, (III), 1.67 g (90% yield). The crude product (1.67 g) was recrystallized from a 1:5 benzene/petroleum ether (40-60°C) mixture; yield, 1.42 g (85%); m.p. 185° C.

The other derivatives were synthesized similarly to the above method using the respective reactants in suitable molar ratios.

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