SYNTHESIS AND CHARACTERIZATION OF NEW p-FLUOROPHENYL SUBSTITUTED ARYLANTIMONY (V) CARBOXYLATES

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ABSTRACT

Several new complexes of p-fluorophenylantimony (V) carboxylates, halocarboxylates and pseudohalocarboxylates have been synthesized by the reaction of salt of carboxylic acids, potassium thiocyanate with tris p-fluorophenylantimony dichloride, which in turn was obtained from p-fluorobromobenzene magnesium and antimony trichloride. New compounds were characterized by melting point, elemental analysis, infrared and NMR spectroscopy.

Keywords: Antimony, Carboxylates, Halocarboxylates, Organometallic compounds, Pseudohalocarboxylates.

I. INTRODUCTION

Oragnoantimony (V) compounds are well known and can be represented by general formula R_nSbX_{5-n} where n=1 to 5. Among these the most common, easily prepared and extensively studied are the triorganoantimony compounds (n=3).Organ antimony (V) compounds of formic, benzoic, acetic, propionic, halo and cyano-acetic acids have been prepared by the reaction of antimony halide with (a) the corresponding silver carboxylate or (b) silver oxide and carboxylic acid. The substitution of the Sb-OOCR' bond has been studied with the help of infrared and NMR spectroscopy [1-5].

The first organoantimony carboxylate, $Ph_3Sb(OOCCH_3)_2$ was prepared way back in 1922 by Schmidt et.al. [6] by the oxidation of triphenylantimony with hydrogen peroxide and subsequent reaction with acetic acid. Since then, several triorganoantimony(V) dicarboxylates have been prepared by different methods *e.g.*, by dissolving triphenylantimony dihydroxide in hot formic acid [7].The biocidal activity of a series of tertiary substituted aryl antimony (V) dicarboxylates has also been reported [8, 9].Tertiary substituted arylantimonydipseudohalides of the type R_3SbX_2 (R=*p*-ClC_6H_4, *p*-FC_6H_4; X=N_3, NCO, NCS) have been prepared through replacement reaction between tertiary susbtituted aryl antimony (V) dihalide and the corresponding metallic salt [8].Tetraphenylantimony(V) carboxylates have been used in the Pd-catalysed C-phenylation reaction of methyl acrylate in the presence of peroxides [10]. Several cationic complexes of the general formula $[Ar_2SbL][Y]$ and $[ArSbL_2][Y_2]$ [where Ar= C_6H_5, L= α-Picoline, Pyridine, Ph_3AsO, Hexamethyl phosphoramide(HMPA), Thiourea(TU) and Y= ClO_4^-, BF_4^-] have been synthesized and characterized [11].Muhammad kaleem khosa and coworkers [12] prepared a series of new bis-triphenylgermyl(substituted) propionate triarylantimony(V)

derivatives in order to study the nature of the bonding as well as antibacterial and antifungal activity of organoantimony(V) carboxylates,. V.V.Sharutin and coworkers [13] have synthesized tri and tetraphenylantimony propiolates. Antimony(V) complexes showed antileishmanial, antibacterial and *invitro* cytotoxic activity against murine macrophages showed that antimony(V) complexes were least toxic[14]. Pankaj Sharma and coworkers [15] focused on recent advances in developing antimony anticancer agents with an emphasis on antimony coordination complexes as Sb(III) and Sb(V).

In view of these observations new tris(p-fluoro)antimony dicarboxylates, halocarboxylates and pseudohalo carboxylates has been prepared by simple metathetical reactions. New complexes have been characterized on the basis of melting point, elemental analysis, infrared and NMR spectroscopy. Tentative structures for these complexes have been assigned on the basis of solid state IR spectra and some solution phase studies.

II. MATERIAL AND METHODS

The melting points of the compounds were determined in a Toshniwal electric melting point bath and are uncorrected. IR spectra were recorded on Perkin- Elmer 577 spectrophotometer in the range 4000-400 cm^{-1} using KBr. Special precautions were taken to exclude moisture. Anhydrous benzene (Aldrich) was used as the solvent.

2.1. Synthesis Of Tris P-Fluorophenylantimony(V) Dichloride

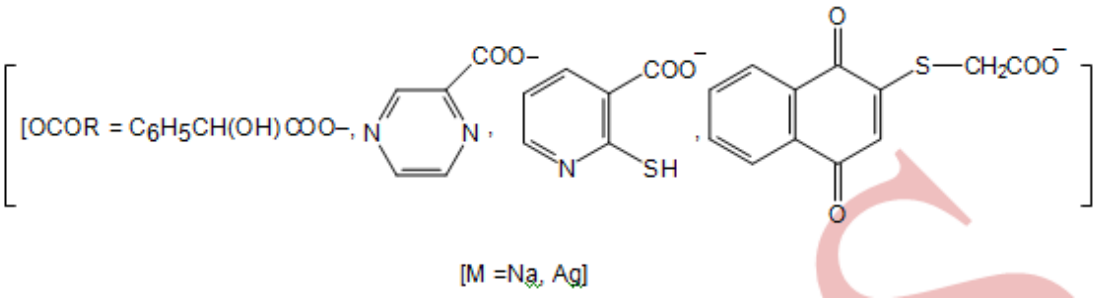
p-Fluorobromobenzene (0.5 mole) dissolved in dry ether was added dropwise to 12.5 g magnesium turnings at 0^oC. The resulting Grignard solution was cooled to -12^oC and $SbCl_3$ (22.8gm.) dissolved in dried benzene is slowly added in that solution. This mixture was stirred for an additional hour at room temperature and after completion of the reaction it was treated with a saturated ammonium chloride solution. The ether layer was separated and dried over sodium sulphate. The solvent was then reduced and then treated with alcohol. The residue recrystallized from alcohol.All operations was undertaken in a protective Nitrogen atmosphere to avoid moisture. Melting Point: 90^oC (Lit. 91.8^oC) [16]. The organic solution of tris p-fluorophenyl antimony was bubbled with chlorine for half an hour. The reaction mixture was hydrolysed by addition of 10% HCl in cold water. The organic layer was separated and dried over sodium sulphate. Removal of solvent followed by crystallization from absolute alcohol.

2.2. Synthesis of Tris P-Fluorophenylantimony Dicarboxylates

Tris *p*-fluorophenylantimony(V) dicarboxylates can conveniently be prepared by the interaction of tris *p*-fluorophenyl antimony (V) dichloride with the corresponding carboxylic acids in presence of Et_3N as hydrogen chloride acceptor or by the interaction of tris *p*-fluorophenylantimony(V) chloride with the sodium or silver salt of the corresponding ligand under anhydrous oxygen free conditions [Table-1].

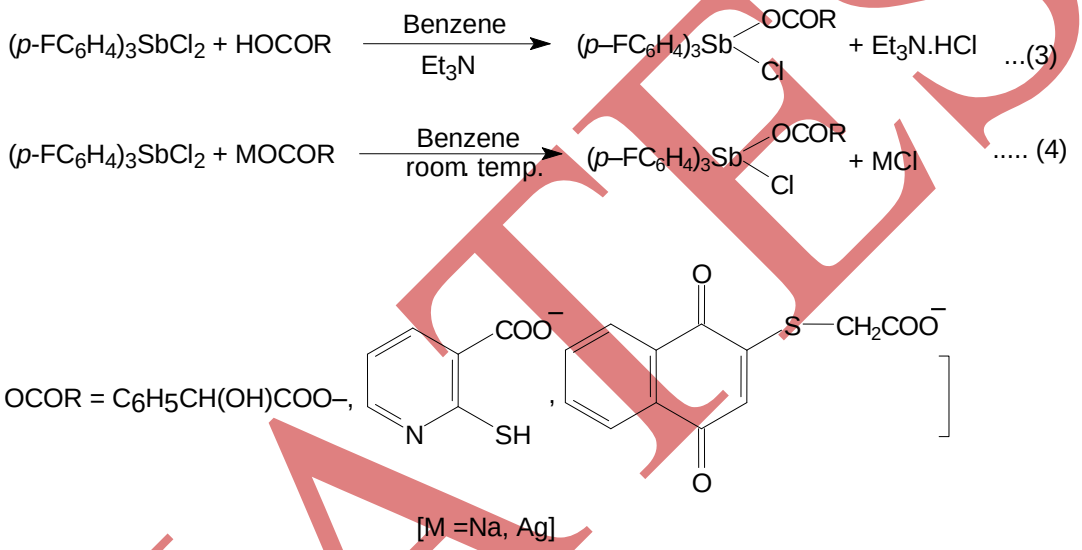
$$(p\text{-}FC_6H_4)_3SbCl_2 + 2HOCOR \xrightarrow[Benzene]{Et_3N} (p\text{-}FC_6H_4)_3Sb(OCOR)_2 + 2Et_3N.HCl \quad \ldots\ldots (1)$$

$$(p\text{-}FC_6H_4)_3SbCl_2 + 2MOCOR \xrightarrow[room\ temp.]{Benzene} (p\text{-}FC_6H_4)_3Sb(OCOR)_2 + 2MCl \quad \ldots\ldots (2)$$



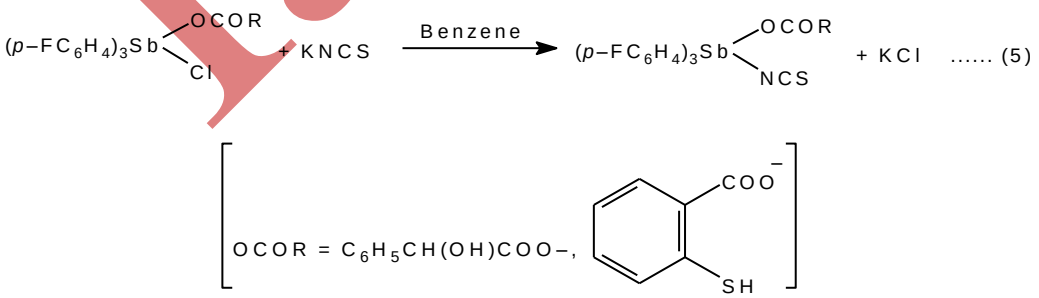
2.3. Synthesis Of Tris P-Fluorophenylantimony Halocarboxylates

The equimolar reaction of tris(*p*-fluorophenyl)antimony(V) dihalide with the corresponding carboxylic acid in presence of Et_3N (or with the sodium or silver salt of the corresponding acid) afforded a series of tris (*p*-fluorophenyl) halocarboxylates [Table-1].



2.4. Synthesis Of Tris P-Fluorophenylantimony Pseudohalocarboxylates

Pseudohalo carboxylates were obtained through replacement of halogen group by pseudohalide of the corresponding halocarboxylate. These equimolar reactions were carried out in an anhydrous oxygen free condition (Table-I).



All the compounds reported herein are white, off white or brown solids, stable at room temperature and are unaffected by atmospheric moisture. These compounds are soluble in common organic solvents. Molecular

weights determined by cryoscopic method, show that these compounds exist as monomeric molecular species in benzene.

Suggested Structures of Tris (*p*-fluorophenyl) Antimony (V) Derivatives

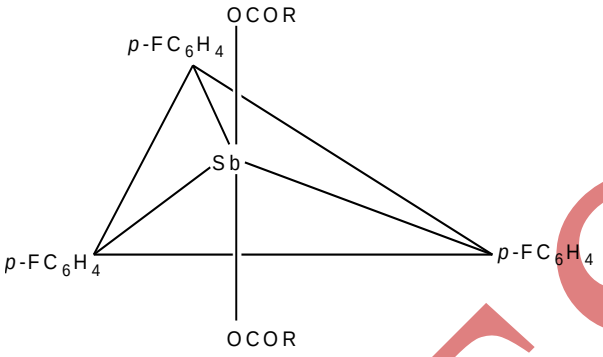


Fig. 1: Tris (*p*-fluorophenyl) antimony dicarboxylates.

$(p\text{-}FC_6H_4)_3Sb(OOCR)_2$

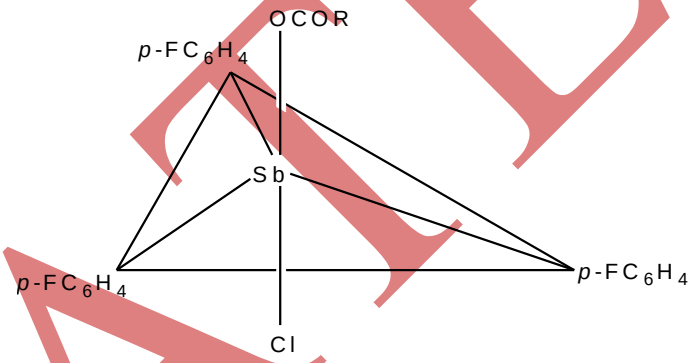


Fig. 2: Tris (*p*-fluorophenyl) antimony halocarboxylates

$(p\text{-}FC_6H_4)_3Sb(Cl)(OCOR)$

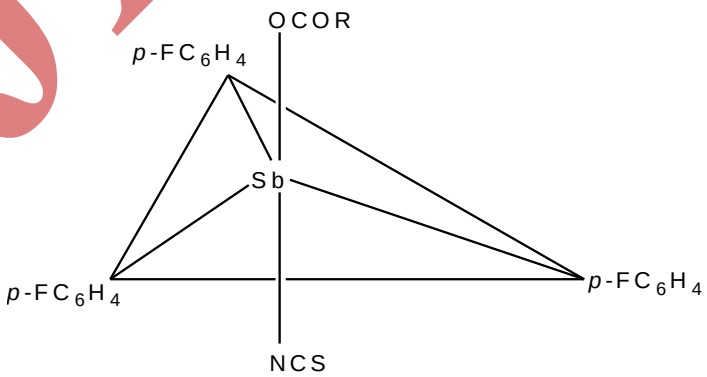
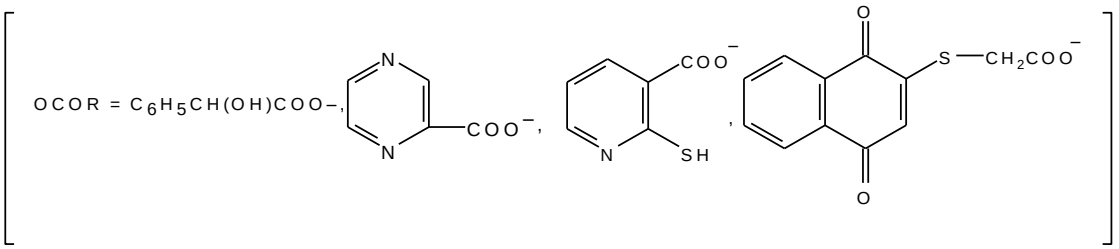


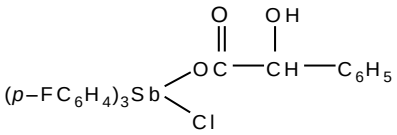
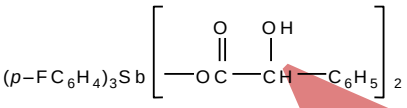
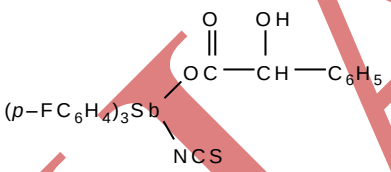
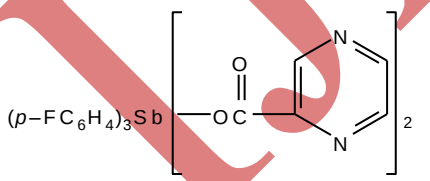
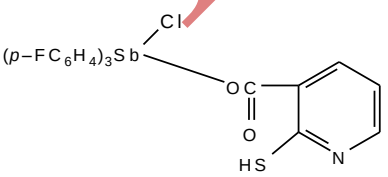
Fig. 3: Tris (p-fluorophenyl) antimony pseudohalocarboxylates.

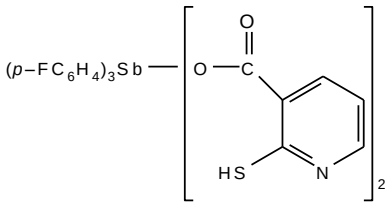
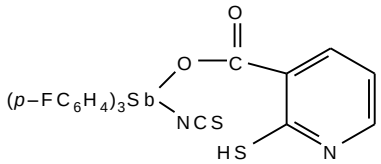
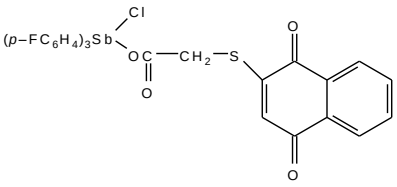
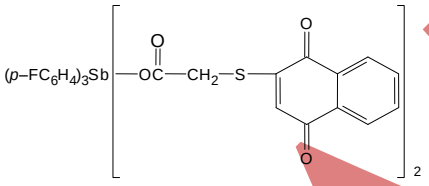
$(p\text{-}FC_6H_4)_3Sb(NCS)(OCOR)$



[M =Na, Ag]

TABLE-I: Analytical data of Tris(*p*-f phenyl) antimony Derivatives of Dicarboxylates, Halocarboxylates and Pseudohalocarboxylates

S.No.	Compound	Molecular* Formula (Molecular Weight)	Solvent	M.P. (Colour)	Analysis Found (Calcd.) %		
					C%	H%	N%
1.		$C_{26}H_{19}O_3F_3ClSb$ (593.45)	Benzene	74°C (off white)	52.56 (52.62)	3.20 (3.20)	
2.		$C_{34}H_{26}O_6F_3Sb$ (709)	Benzene	53°C (dirty yellow)	57.53 (57.59)	3.66 (3.67)	
3.		$C_{27}H_{19}O_3F_3SNSb$ (616.02)	Benzene	90°C (off white)	52.57 (52.64)	3.06 (3.08)	2.26 (2.27)
4.		$C_{28}H_{18}O_4F_3N_2Sb$ (624.96)	Benzene	102°C (off white)	53.75 (53.81)	2.87 (2.88)	4.47 (4.48)
5.		$C_{24}H_{16}O_2F_3SNClSb$ (696.50)	Benzene	134°C (white)	41.30 (41.38)	2.27 (2.29)	2.00 (2.01)

S.No.	Compound	Molecular* Formula	Solvent	M.P. (Colour)	Analysis Found (Calcd.) %		
6.		$C_{30}H_{20}O_4F_3SN_2Sb$ (683.04)	Benzene	158°C (white)	52.69 (52.75)	2.92 (2.93)	4.09 (4.10)
7.		$C_{25}H_{16}O_2F_3N_2S_2Sb$ (619.06)	Benzene	160°C (off white)	48.42 (48.50)	2.58 (2.58)	4.51 (4.52)
8.		$C_{30}H_{19}O_4F_3SClSb$ (689.54)	Benzene	120°C (dark brown)	52.18 (52.25)	2.75 (2.76)	
9.		$C_{42}H_{26}O_8F_3S_2Sb$ (901.18)	Benzene	65°C (dark brown)	55.91 (55.97)	2.89 (2.89)	

*Molecular weight and conductance of 10^{-3}M solution (ohm^{-1} cm^2 mole^{-1}) was found in satisfactory range.

III. RESULT AND DISCUSSION

All the compounds reported herein are white, off white or brown solids, stable at room temp. and are unaffected by atmospheric moisture. These compounds are soluble in common organic solvents. IR spectra of all the compounds were run in the solid state in the region 4000-400 cm^{-1}in KBr. IR absorption due to p- fluorophenyl group bonded to antimony do not differ significantly from those reported in the in the literature and hence not discussed here [1, 17].

3.1. Infrared Spectra Of (Tris *P*-Fluorophenyl)Antimony (V) Dicarboxylates

In the solid state vibrational spectra of tris-*p*-fluorophenyl antimony dicarboxylate, the peaks due to ν_{asym} (OCO) stretching mode appear in the range 1580-1720 cm^{-1} and ν_{sym}(OCO) appear in the range 1200-1340 cm^{-1} as a medium strong bond. Since the difference $\Delta\nu$ between ν_{asym} (OCO) and ν_{sym} (OCO) is quite larger {$\Delta\nu$ [ν_{asym}(OCO)-ν_{sym}(OCO) > 250cm^{-1}]} in all the cases, it seems reasonable to conclude that the carboxylate moiety behaves as unidentate, ester type –OCO group. This observation is in confirmity with the earlier reported conclusions on similar compounds [1].

3.2. Infrared Spectra Of Tris (*P*-Fluorophenyl)Antimony(V) Halocarboxylates

The charateristic IR absorptions associated with the various modes of vibrations of carboxylate groups have been identified and the possible assignments for the representative compounds are listed in Table-II.

In solid state vibrational spectra of $(p\text{-}FC_6H_4)_3Sb(Cl)COOR$, the $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$ stretching mode appear in the range 1587-1725 cm^{-1} and 1230-1350 cm^{-1}, respectively, as a medium strong bond, which indicates the presence of monodentate 'ester type' COO group with the penta-coordinate geometry around antimony atom. The absence of evidence for carboxylate ions in IR spectra and the non-conducting nature of these derivatives strongly rules out the possibility of an ionic structure Table-III.

3.3 .Infrared Spectra Of Pseudo-Halocarboxylates

The thiocyanate group in tris(*p*-fluorophenyl)antimony thiocyanate carboxylates shows a very strong bond due to asymmetric stretching ν(–NCS) which centres at 1950-2050 cm^{-1} and readily suggest the bonding to be iso (–NCS) *i.e.* the group is attached through the nitrogen atom with antimony. Apart from the shape and intensity of the band which has been used to distinguish between the two isomers in the past [17]., other important features in the favour of nitrogen linkage are the appearance of ν(C-S) symmetric stretching at 1050-1070 cm^{-1} of very weak intensity and a strong band due to bending δ(NCS) at 495-480 cm^{-1}. All these modes of vibrations are in favour of an iso-structure.Compound 5, 6 and 7 exhibit a weak absorption attributed to SH group around 2550 cm^{-1} indicating that hydrogen of mercapto is not displaced and thus lending support that only one hydrogen is replaced and as well as to the absence of Sb–S bond Table-IV.

3.3.1 Other Important Factors In Favour Of –N Linkage Are

a) The smaller size and greater electronegativity of N which permits a stronger dπ - pπ bond between antimony and nitrogen than with diffuse *p*-orbitals of the atom.
b) R_3Sb^{++}(V) being a hard acid according to HSAB concept would prefer to attach itself to the hard base that is N rather than S of the thiocyanate [18].
c) Unlike the organometallics of transition metals, group [18]metal thiocyanates in general do not have a S-bonded linkage.

A medium but sharp band appearing at 435 cm^{-1} may tentatively be assigned to Sb-N band. In the vibrational spectra of $(p\text{-}FC_6H_4)_3Sb(NCS)(OCOR)$, the ν_{asym} (OCO) and $\nu_{sym}(OCO)$ stretching modes appear in the range 1582-1735 cm^{-1} and 1230-1320 cm^{-1}, respectively.

Based on IR, molecular weight data of the present compounds $(p\text{-}FC_6H_4)_3Sb(OCOR)_2$, $(p\text{-}FC_6H_4)_3Sb(Cl)(OCOR)$, $(p\text{-}FC_6H_4)_3Sb(NCS)(OCOR)$ can be assigned a trigonal bipyramidal structure with the *p*-fluorophenyl group at the equatorial position and the more electronegative groups occupying the axial positions.

3.4 NMR Spectra

^{1}H NMR

The ^{1}H NMR spectra of representative compounds 4,6,7,8 and 9 was recorded at room temperature in $CDCl_3$. The spectra of all the compounds showed multiplets in the range δ 7 to 8.32 ppm attributed to aromatic proton.

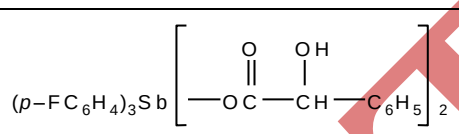
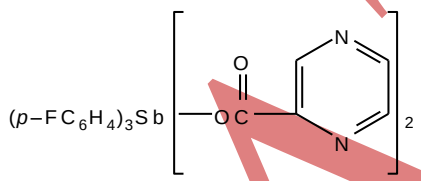
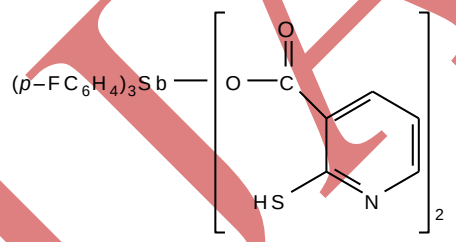
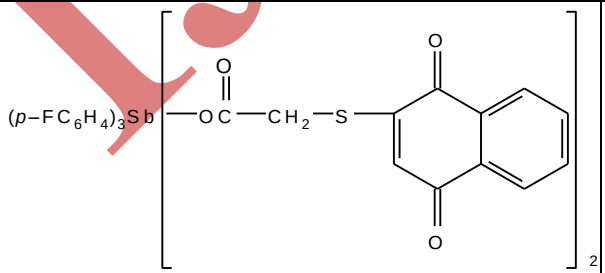
The spectra of compound 9 showed a peak at δ 2.50 ppm due to CH_2 proton, while for compound 8it appered at δ 3.40 ppm. the appearance of a peak between δ 1-2 ppm in compunds 6 and 7 indicate the presence of mercapto group. The integration of the peak is consistent with the proposed formulation of the compounds.

^{19}F

The ^{19}F spectrum of all the compound was carried out at room temperature. The spectra of *p*-fluorophenyl derivatives showed triplet of a triplets in case of all the five compounds appearing in the range 106-107 is consistent with the levels of three *p*-fluorophenyl group in equatorial position. Such observation has earlier been made for analogous arsenic and antimony dihalides [19].

IV CONCLUSION

Table-II: Infrared Spectral Data of Tris (*p*-fluorophenyl) antimony(v) Dicarboxylates

S. No.	Compounds	ν_{asym} (OCO)	ν_{sym} (OCO)	νS-H
1.		1670(m), 1640(sh)	1234(m)	-
2.		1585(ms), 1630 (sh)	1302(m)	-
3.		1583(ms), 1634(ms), 1704(w)	1312(m)	-
4.		1650(ms), 1664(sh), 1700(w)	1330(m)	1552(w)

Fluoro and thio group substituents present in organometallic compounds have an added advantage of water and lipid solubility and also show biocidal activities, therefore a series of new *p*-fluorophenyl antimony dicarboxylates $(p\text{-}FC_6H_4)_3Sb(OCOR)_2$, halo-carboxylates $(p\text{-}FC_6H_4)_3Sb(Cl)(OCOR)$, and pseudohalo

carboxylates (p-$FC_6H_4)_3Sb(Y)(OCOR)$ [Y=NCS] were synthesized and characterizwd by spectral studies in order to study their biocidal study, which is under progress.

Table-III: Infrared Spectral Data of Tris (p-fluorophenyl) antimony(v) Halocarboxylates

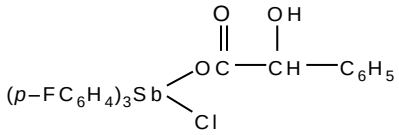
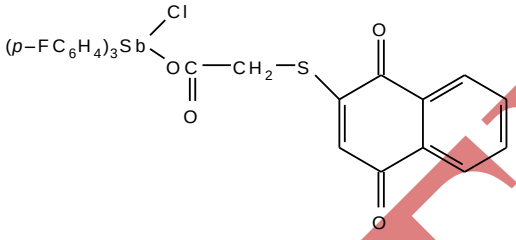
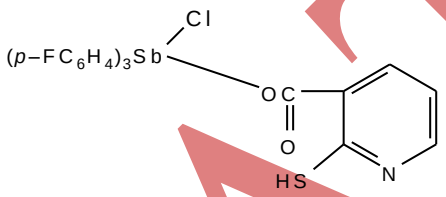
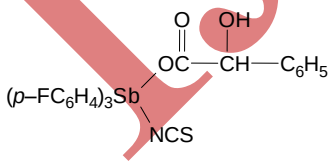
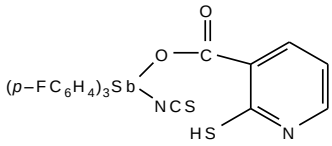
S. No.	Compounds	ν_{asym} (OCO)	ν_{sym} (OCO)	νS-H
5.		1587, 1700(w)	1233 1261	-
6.		1664(s), 1705(w)	1232 1273 1299	-
7.		1803(w), 1636		2550(w)

Table-IV: Infrared Spectral Data of Tris (p-fluorophenyl) antimony(v) Pseudohalocarboxylates

S. No.	Compounds	ν_a (NCS)	ν_{sym} (NCS)	δ(NCS)	ν_{asym} (OCO)	ν_{sym} (OCO)	νS-H
8.		2047	865	480	1645, 1582	1310, 1261 1231	
9.		2020	824	485	1702	1311 1398 1442	2553(w)

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