

# Tris(pentafluorophenyl)bismuth(V) carboxylates and cyclobismuthates

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**Abstract-** Tris(pentafluorophenyl)bismuth(V) carboxylates;  $(C_6F_5)_3Bi(OCOR)_2$  and tris(pentafluorophenyl)cyclobismuthates have been synthesized. These compounds are monomeric in benzene and non electrolyte in acetonitrile. The formation of ring compounds were established on the basis of IR spectra, melting points, elemental analysis.

**Keywords—** Perfluoro organic moieties, anticacterial, antifungal, insecticidal, acaricidal, hydrolytic stability.

## 1 INTRODUCTION

Interest in pentafluorophenyl derivatives of metal and non-metals started as early as in 1960's and a number of pentafluorophenyl derivatives of boron were reported by wall et al. in a preliminary communication [1]. This was followed by the preparation of a number of fluoro alkyl derivatives of metal and non-metal by chamber and chives [2-7] and some of them showed unusual properties. Detailed studies on the synthesis of perfluoroaryl derivatives of group 14 and 15 elements were almost simultaneously taken by American and Spanish workers [5,6]. The studies, in fact were stimulated due to the unusual characters of fluorine and intrinsic properties shown by fluorocarbon based organo metallic derivatives. In addition to this pentafluoroaryl metallic derivatives provide an instructive comparison with compounds based on hydrocarbon verdure. It was subsequently established that the electronic effects due to the presence of fluorine atom rather than steric effect play an important role in determining the properties and chemical behaviors of pentafluoroaryl substituted metallic and non-metallic compounds. During the best decade pentafluorophenyl based organo metallic derivatives of group 15 and bismuth antimony have shown promising trends in biological activity [7].

They have been found not only to be potent antimicrobial agent but also potent cytotoxic antagonist. This property is probably associated due to the solubility of fluorophenyl based organo bismuth derivatives in water as well as in lipids. These studies were encouraged by the reported anti-tumor activities during the best decade by Italian and Chinese workers on organo antimony derivatives [8-11]. However phenyl based derivatives could not succeed as pro-metal drug due to the insolubility in water as well as in lipid.

The short coming could more or less be made up by the presence of fluorine substituent's which make their studies

worthwhile Endeavour commercial interest in fluoro carbon chemistry is still based mainly on the high chemical and thermal stability of fluoroorganometallics.

Academic interest in fluoro carbon derivatives has further been stimulated by the challenge of finding newer methods of synthesis and study of their chemical behavior. An easy way to synthesize such compounds was opened up by the discovery of pentafluorophenyl magnesium bromide and pentafluorophenylbismuthines. Within a short term numerous new compounds were prepared which enhanced our insight into the fluorine carbon based moieties linked to the metal atom.

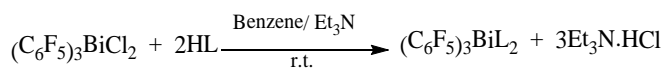
This investigation includes new perfluoro organic derivatives of bismuth which are relatively less studied but more potent due to reduced toxicity of bismuth compound as compared to organo-arsenic and organo antimony compound 8-12 (MP). Further due to enhanced lipophilicity and hydrophilicity as in case of perthoroorgano antimony compounds, bismuth compounds are expected to display significant biological activity. An added advantage with organo bismuth compound is that Bi-C bond is biodegradable and inorganic bismuth is now toxic. Taking due to the fact, that organotin and organo antimony carboxylates along with corresponding organo arsenic derivatives (non-platinum group metals) are potential biocides and can act as proactive metal drugs, if they continue partially or fully substituted fluoro or chloro substituent on to the metal atom, present both in organic group as well as ligand' it was considered worth while to come-out parallel reaction with tris (pentafluorophenyl) bismuth. The main aim of the study was focused to synthesize a variety of carboxylic acid derivatives with  $\alpha$  and  $\beta$  hydroxycarboxylic acid and also to synthesize agro derivatives which have not reported till date. The formation of ring compound is more fascinating from structure point of view and also to compare their chemical behaviors with unidentate carboxylate moiety. In this chapter the author has accomplished the synthesis with salicylic acid, benzoic acid, mandelic acid, p (bifluoromethyl) mandelic acid and p-methoxy mandelic acid. The cyclic moieties were obtained with mandelic acid and its derivatives.

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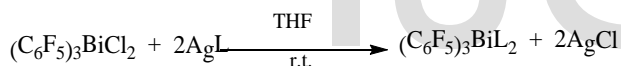
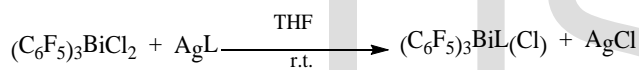
The chemical behavior and constitution of the compounds has been ascertained on the basis of solid state IR spectra and  $^1\text{H}$ -,  $^{19}\text{F}$ -,  $^{13}\text{C}$ -NMR spectra. The solution phase studies have been carried out to establish nonnumeric and non-elderolyte behavior of bismuth compounds. This study inturn also provide a instructive comparison with those of bismuth compounds based on phenyl moieties. We have proffered the metathetical reaction with silver salt of some spending carboxylic acid because it facilitates the replacement of both the endocrine, which other wise quite stable in case of fluoro derivatives.

## 2 RESULTS AND DISCUSSION

In an anhydrous oxygen free atmosphere tris (pentafluorophenyl) bismuth (V) carboxyl ate can be conveniently prepared by the interaction of tris (pentafluorophenyl) bismuths (V) dichloride  $(\text{C}_6\text{F}_5)_3\text{BiCl}_2$  with a carboxylic acid in 1 : 2 and 1 : 1 molar ratio in presence of lewis base, triethylamine ( $\text{Et}_3\text{N}$ ), as hydrogen halide acceptor. Alternatively, these could also be obtained by simple metathesis of  $(\text{C}_6\text{F}_5)_3\text{BiCl}_2$  with an appropriate silver salt of corresponding carboxylic acid.



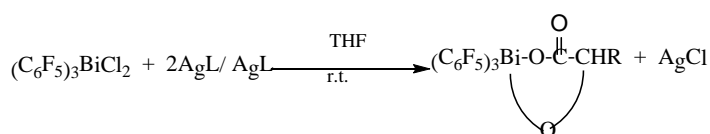
Where L =  $\text{HOC}_6\text{H}_4\text{COO}^-$  and  $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{COO}^-$



Where L =  $\text{HOC}_6\text{H}_4\text{COO}^-$  and  $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{COO}^-$ ,  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COO}^-$ ,  $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}(\text{OH})\text{COO}^-$

The reaction were carried out in dried becomes or THF at room temperature (R.T.) with constant stemming for almost 24h. The yields of the products were nearly quantitative except. for the losses deeming workup poor. In case of salicylic acid ( $\beta$ hydroxy acid), benzilic acid ( $\alpha$ -hydroxy acid) moieties both 1: 2 and 1 :1 molar ratio reaction proceeded smoothly. However with mandelic acid and its derivatives instead of simple carboxyl ate derivatives, cyclic derivatives were obtained parallel to those obtained in the reaction of  $\text{Ph}_3\text{BiCl}_2$  with these acids.

The reaction representing cyclic product may be shown in sense of equation shown below.



Where L =  $\text{RCH}(\text{OH})\text{COO}^-$ ; R =  $\text{C}_6\text{H}_5^-$ ,  $p\text{-CF}_3\text{-C}_6\text{H}_4^-$  and  $p\text{-CH}_3\text{O-C}_6\text{H}_4^-$

The formation of ring compound was established on the basis of IR spectra and the formation of silver telluride. It is also interesting to note that both 1 : 1 and 1 : 2 molar ratio reaction resulted in the formation of some cyclic produced as confirmed by melting points elemental analysis and super imposable IR-spectra.

The compounds are freely soluble in most of the organic solvents except petroleum ether and n-hexane. They are off white, light brown or grey crystalline solids with sharp melting points. The complexes remain unoffered by air and atmospheric moisture and can be stored for several makes without decomposition. All these derivatives were found non-electrolytes and monomeric in nature.

## 3 IR Spectroscopy

The IR spectra of all the tries (pentafluorophenyl) bismuth carboxylates

were recorded in the range of  $4000\text{-}400\text{cm}^{-1}$  scale using KBr pellets. The characteristic absorptions associated with the organic group band to bismuth correspond well with those reported earlier [29,30,45]<sup>RM</sup>. The IR absorption frequencies are listed in Table (3). C-C stretching corresponding to k-mode was observed in the rang  $1648\text{-}1601\text{ cm}^{-1}$  as a modicum or strong bond. the C-C stretching corresponding to m- and n-mode were observed at lower frequency ranging from  $1520\text{-}1495\text{ cm}^{-1}$  and  $1520\text{-}1445\text{ cm}^{-1}$  as strong and very strong stretching bond respectively. The C-F stretching frequency corresponding to  $Z_1$ -,  $Z_2$ - and  $Z_3$ - mode were also found in the reported range for similar compound.  $Z_1$ - mode appears between  $1394\text{-}1301\text{ cm}^{-1}$ . while  $Z_2$ - mode appears between  $1297\text{-}1246\text{ cm}^{-1}$ . The C-F stretching frequency corresponding to  $Z_3$ -mode generally appears as strong or very strong intercity bond and was found in the range  $1174\text{-}1083\text{ cm}^{-1}$ . Bi-C stretching frequency corresponding to  $\gamma$ -mode appears in the range  $455\text{-}449\text{ cm}^{-1}$  as a medium peak.

The O-H group in compound (1-4) does not participate in the reaction as has been observed by appearance of  $\nu(\text{O-H})$  frequency in the IR spectra as a medium to strong bond in the reported range. The disappearance of  $\nu(\text{OH})$  peak from spectra of compound (5-10) is a guarantee that the hydrogen of OH group is actively involved in metathetical reaction.

The IR absorption of carboxyl ate derivatives of diagnostic value are given in table, the Vasym (oco) frequency appear in the range  $1724\text{-}1659\text{cm}^{-1}$  and the corresponding Vasym (oco) appears in the range  $1450\text{-}1320\text{ cm}^{-1}$ . The difference between these two frequencies  $\Delta V(\text{OCO}) = \text{Vasym}(\text{OCO}) - \text{Vasym}(\text{OCO})$  has been reported in past [13, 46-49]<sup>RM</sup> early indicates that the carboxyl ate moiety behave as unidentate legend. and the appearances of Vasym (OCO) absorption bond relatively at higher frequency may be attributed to the changed eldrmic behavior of pentaflorophenyl ring.

## 4 $^{19}\text{F}$ NMR SPECTRA

The  $^{19}\text{F}$  NMR spectra of all the compounds were recorded in  $\text{CDCl}_3$  at  $\approx 282\text{MHz}$  on  $300\text{ MHz}$  instrument and the data are

listed in Table (4). The signals due to  $F_4$ ,  $F_{3,5}$  and  $F_{2,6}$  appeared at  $\delta$  : -1471 to -149, -155 to -162 and -124 to -133ppm, respectively.

The  $F_4$  signals may easily be identified due to its half intensity as compared to the signals of  $F_{3,5}$  and  $F_{4,6}$ . 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  $F_{2,6}$  signals appeared as triplet and doublet' respectively.  $F_{3,5}$  chemical shift appeared at higher field as compared to the  $F_{2,6}$  and  $F_4$  chemical shift, indicating the donation of electron from other and para position forward carbon attached to Bi atom and this observation is in accordance to previous studies that the CI carbon of per fluorinated 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  $\lambda$  system of the ring ( $p\pi$  interaction) [34,35,30,50,51]<sup>RM</sup>. The  $CF_3$  group in compound (7,8) give on signal at -65 pm which further confirm the coordination of legend to the metal.

### 5 $^1H$ NMR SPECTRA

The  $^1H$  NMR spectra of all the compounds were recorded in  $CDCl_3$  using TMS as the reference at 300 MHz on 300 MHz FT NMR (Bruker DRX - 300) instrument. The chemical shift values are tabulated in table (5). the -OH proton signals of carboxylic acid disappeared in all the compounds indicating the formatin of Bismuth (V) carboxylates [39,44,53]<sup>RM</sup>. in compounds (1, 2) m-H and p -h were appeared at  $\delta$ (7.80, 7.84) ppm,  $\delta$ 6.86ppm and  $\delta$  (7.37,7.38)ppm, respectively. where as, a musltiplet was centered around  $\delta$ 7.53 ppm and  $\delta$ 7.44 ppm for both the phenyl rings of bemillic acid. In case if bismuth (V) carboxylates of mandelic acid and its derivatives (5-10) the signals of all appeared in the range  $\delta$ (5.38-5.41)ppm, the  $\alpha$ -H mandelic acid derivatives appeared as singlet -OCH<sub>3</sub> proton singals appeared at  $\delta$ 3.79 ppm for compound (9,10) as singlets. All the results thus obtained are in good agreement with the  $^1HNMR$  spectra of free acid used.

### 6 $^{13}C$ NMR SPECTRA

The  $^{13}C$  NMR of all compounds were recorded in  $CDCl_3$  at  $\approx$ 75 MHz on 300 MHz FT NMR (Bruker DRX-300) instrument and the data are summarized in table (6). in every case i-c  $\delta$ (100.02-101.72) ppm of penta fluorophenyl ring (i.e. Bi-c) was frome to be more shielded the O-C'  $\delta$ (152.0-152.74)ppm' m-C,  $\delta$ (126.09-126.80) ppm and p-c,  $\delta$ (145.00-146.10) ppm. the order of chemical shift ( $\delta$ ppm values) was found as O-C > p- C > m-C > i-C. it is evident from the  $^{13}C$  NMR data that these is an invariable lower field shift of all the penta fluorophenyl ring carbon centers due to the decrease in the electronegativity of the legends [25,39]<sup>RM</sup>. Due to this the pentafluorophenyl ring carbon enter of compounds,  $(C_6F_5)_3BiCl(L)$  (1,3) experience higher field in comparison to compounds,  $(C_6F_5)_3Bi(L)^2$  (2,4). The i-c center felt significant change where the electron density seems decreased while replacing string eliding live ehionine atom with

carboxylate group. The data are in conformity to  $^{19}F$  NMR data discussed above. The observation are some as in case of triphenyl (bismuth (V) dihalides where the elcteron density decrease at i-c center with the decrease of elctronegativity of halogen or carboxylate attached to the metal [52]<sup>RM</sup>.

The chemical shift behavior of carbon centers of pentafluorophenyl ring us also dependent on the  $pK_a$  values of the carboxylic acids i.e. less  $pK_a$  value shows the positions of each carbon center to be at higher side compared to acids having higher  $pK_a$  value [39]<sup>RM</sup>. But, this effect was bominal in case of the present work because the carboxylic acid ligends were having almost some  $pK_a$  values.

The position of the carbon centers of legends were identified and have the chemical shift values in range. In most of the cases the chemical shifts values of carboxylates were showing marginal difference from the chemical shift values of carbon of free carboxylic acids [43,44,53]<sup>RM</sup>. The position of carboxyl ate carbon in alls the complexes shift to lower field as compared to the free acid indicating the participation of carboxyl ate group in coordination to metal [54]<sup>RM</sup>.

Thus, from the IR and NMR ( $^1H, ^{19}F, ^{13}C$ ) spectral data aided by molecular weight and conductance mearsument it is evident that mono-and di-carboxylic acids, behave as monodentate ligends. This may be attributed to the presence of penta fluorophenyl ring resulting in the do action of electron density from unshared peledrons of fluorine to system ring and thus, in erasing electron density at jpsocarbon, which ultimately decreases the hewis acid character of central metal atom (Bismuth) and deersase the tendency to accept the elctron from the ligends. Thus, in these newly synthsised carboxyl ate derivatives the bismuth is in penta coordinated state imparting trigonal bipyzamidal (TBP) structure around the Bismuth atom in which electrongative group. (Carboxylate order) occupy opical position and the three penta fluoro phenyl groups  $C_6F_5(Rf)$  are situated at the equitorial position.

The preferred geometry of five coordinate group 15 element is trigonal Bi pyramides which is a fluxional stereochemically non-rigid or pseudorotating argonsment rapidly intercenverting with square pgrmidal (JP) structure.

Thus, in case of cyclometallates following geometries (Fig.2) are possible, which are already been established in case of anti-mony [44]<sup>RM</sup> and the same is expected for pentafluorophenyl bismuth (V) carboxylates resulting in the formations of cyclometallates.

## 7 EXPERIMENTAL

Preparation of tris (pentafluorophenyl) bismuth (V) dichloride  $(C_6F_5)_3 BiCl_2$  has already been disenzsed in chapter-2. the carboxylic acid used ware converted to corresponding silver salt. detailed example of tris (penta fluorophenyl bismuth (V) carboxylates preparation are summarized below and the condi-

tions for the reactions are summarised in Table (1). Physico-chemical data are given in Table (2-5).

Tris(pentafluorophenyl)antimony(V) dichloride,  $(C_6F_5)_3SbCl_2$  and tris(pentafluorophenyl)antimony(V) diisothiocyanate,  $(C_6F_5)_3Sb(NCS)_2$  was prepared by the reported methods [9], [10]. All the ligands were of reagent grade and used without further purification. The solvents were purified and dried before use. All manipulations were conducted in an atmosphere of nitrogen and stringent precautions were taken to exclude moisture. Conductivity data were obtained in acetonitrile with the help of Philips magic eye type PR 950 Conductivity Bridge using a dip type conductivity cell. Molecular weights were determined cryoscopically in benzene. IR spectra were recorded on a Perkin Elmer 577 spectrophotometer in the range 4000-200  $cm^{-1}$ . Typical experimental details of the reactions are described below. All other complexes/adducts were prepared in similar fashion. Analytical data are given in Table 1, 2, 3.

### 7.1 1:2 Molar Ratio Reaction of Tris (Pentafluorophenyl) bismuth (V) dichloride with silver salt of salicylic Acid (1)

A solution of tris (penta fluorophenyl) bismuth (V) diehlride (0.390g, 0.5 mmol) and freshly prepared anhychrous silver salt of salicydic acid (0.245g, 1.0 mmol) in THF (15ml) was stimed together in an oxygen and moisture free atmosphere at room temperature for 24 h. The white precipitute of Agcl thus formed was filtered off. The fietrate on can centrabion under vaccuum yielded off white solid characterised as tris (pentafluori phenyl) bismuth (V) di-salicylate (1). It was crystallized from a mixture of THF and hexane (1:2).

similarly, 1:1 molar reaction of tris (penta fluoriphenyl bismuth (V) dienorivde (0.390g, 0.5mmol and silver salt of salisyl-ic acid (0.122g, 0.5mmol) in THF (10ml) was stirred for 24h and yielded off white amorphous solid. The compound was recrystallised from a mixture of THF and n-hexane and characterised as tris (pentafluorophenyl) bismuth (V) (eltoro) (sali-cylate) (2).

### 1:2 Molar Ratio Reaction of Tris (penta fluorophenyl) bismuth (V) dichloride with silver salt of Benzilic Acid (3)

Tris (penta fluorophenyl) bismuth (v) diehlride (0.390g, 0.5mmol) and silver salt of benzilic acid add (0.335g, 1.0mmol) were stirred in THF (15m<sup>2</sup>) at room temperature for 24h in an oxygen moisture free atmosphere. after removing Agcl the fietate containing compound was concentrated in vaec (≈ 2ml) followed by the addition of n-hexone (2ml) afforded off white amorphous solid. The solid thus formed was crystallised from a mixture of THF an petroleum ether (60-80)<sup>o</sup>C (1:3) and indentified as tris (pontafloorophenyl) bismuth (V) dibernilate (3). In the same manner 1:1 molar ratio of tris (pentafluoro-phenyl) bismuth (V) diehlride (0.390g, 0.5mmol) and silver salt of benzilic acid (0.167g, 0.5mmol) in THF (10ml) afforded

off white solid. The compound thus formed was crystallised from a mixture of THF and petroleum ether (60-80<sup>o</sup>C) (1:3 and cauterized as tris (penta fluorophenyl) bismuth (V) (eltoro) (benzilate) (4).

M.P. 118<sup>o</sup>

### 1:2 Molar Ratio Reaction of Tris (pentafluorophenyl) bismuth (v) Dichloride with silver salt of (RS) Mandelic Acid (5)

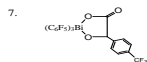
In oxygen and moisture free atmosphere; a solution of tris (penta florophenyl) bismuth (V) diehlride (0.390g, 0.5mmol) and silver salf of (RS) mondalic acid (0.25g, 1.0mmol) in THF (15ml) were stirred together at room temperature for 24h. Agcl thus formed was filtered off. The fietrate on can contraction in vaeuo followed by addition of petr ether (60-80)<sup>o</sup> (2ml) yielded a light brown solid which was crystallised from a mixture of petroleum ether (60-80<sup>o</sup>) and diehloro methane (4:1) to af-fored a cyclometallate (RS)  $(C_6C_5)_3Bi O_2 (CH(O) Ph (5)$ .

In the similar fashion , 1:1 molar ratio reaction of trise pentafluorophenyl bismuth (V) dichloride (0.323g, 0.5mmol) and silver salt of (RS)-mandelic acid (0.129g, 0.5 mmol) in THF (15mL) stirred for 24h and afforded the same cyclometal- led complex. (RS)-  $(C_6F_5)_3 BiO_2 (CH(O)Ph(6)$ .

## 5 TABLES

Table 1 Preparation And Properties Of Tris (Pentafluorophenyl)bismuth(V) Carboxylate And Cyclometalla

Comp. No.	Complex	$(C_6F_5)_3BiCl_2$ (g)	Ligand (g)	Molar Ratio/ Solvent (mL)	M.P. (°C)	Colour	Recryst. solvent
1.		0.390		1:2 THF (15)	144	off white	THF/ n-Hexane
2.		0.390		1:1 THF (10)	144	off white	THF/ n-Hexane
3.		0.390		1:2 THF (15)	122	off white	THF/ Pet ether (60-80 <sup>o</sup> C)
4.		0.390		1:1 THF (10)	118	off white	THF/ Pet ether (40-60 <sup>o</sup> C)
5.		0.390		1:2 THF (15)	104	Light Brown	DCM/ Pet ether (60-80 <sup>o</sup> C)
6.		0.390		1:1	104	Light Brown	DCM/ Pet ether (60-80 <sup>o</sup> C)



**Table-3 Characteristic IR absorption bands (cm<sup>-1</sup>) for tris(pentafluorophenyl)bismuth(V) derivati**

Compound No.	$\gamma$ (OCO)			C-C Stretching			C-F Stretching			Bi-C Stretching			$\gamma$	S	
	$\gamma_{asym}$	$\gamma_{sym}$	$\Delta\gamma$	K	M	N	Z <sub>1</sub>	Z <sub>2</sub>	Z <sub>3</sub>	$\gamma$	r	y			
(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> Bi	-	-	-	1642 (s)	1515 (VS)	1460 (VS)	1381 (S)	<b>1282</b> (s)	1083 (s)	972 (s)	625 (m)	455 (m)	756 (vw)	723 (w)	4
(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> BiCl <sub>2</sub>	-	-	-	1647 (s)	1520 (S)	1476 (vs)	1391 (VS)	<b>1292</b> (m)	1094 (vs)	1017 (s)	622 (m)	452 (m)	758 (w)	723 (w)	4
(1)	1659 (S)	1323 (m)	336 (O)	1495 (S)	1445 (S)	1395 (s)	<b>1293</b> (m)	1155 (s)	1030 (s)	650 (s)	450 (w)	759 (s)	697 (m)	5	
(2)	1664 (S)	1330 (m)	334 (S)	1648 (S)	1518 (VS)	1450 (VS)	1393 (m)	<b>1297</b> (m)	1096 (vs)	1020 (m)	622 (w)	450 (s)	759 (s)	722 (w)	5
(3)	1719 (VS)	1368 (m)	351 (O)	1517 (W)	1477 (S)	1341 (S)	<b>1246</b> (m)	1053 (s)	976 (m)	625 (m)	453 (m)	771 (m)	721 (m)	5	
(4)	1719 (S)	(O)	-	1643 (m)	1510 (S)	1475 (VS)	1391 (m)	<b>1291</b> (m)	1094 (m)	982 (s)	623 (m)	451 (m)	760 (m)	722 (m)	5
(5) & (6)	1719 (S)	(O)	-	1647 (m)	1522 (S)	1494 (VS)	1394 (w)	<b>1290</b> (m)	1095 (s)	981 (m)	624 (m)	458 (s)	795 (w)	724 (m)	4

**Table-2 Elemental Analysis Of Tris(Pentafluorophenyl)Bismuth(V) Carboxylate And CycloBismuthates.**

Comp. No.	Empirical Formula	Weight	Found ( calcd. )%	
			C	H
1.	C <sub>32</sub> H <sub>10</sub> BiF <sub>15</sub> O <sub>6</sub>	984.37	41.01 (39.04)	1.01 (1.02)
2.	C <sub>25</sub> H <sub>5</sub> BiClF <sub>15</sub> O <sub>3</sub>	882.71	34.0 (34.02)	0.55 (0.57)
3.	C <sub>46</sub> H <sub>22</sub> BiF <sub>15</sub> O <sub>3</sub>	1164.62	48.44 (47.44)	1.89 (1.90)
4.	C <sub>32</sub> H <sub>11</sub> BiClF <sub>15</sub> O <sub>3</sub>	972.84	41.02 (39.51)	2.12 (1.14)
5.	C <sub>26</sub> H <sub>6</sub> BiF <sub>15</sub> O <sub>3</sub>	860.28	37.05 (36.30)	0.68 (0.70)
6.	C <sub>26</sub> H <sub>6</sub> BiF <sub>15</sub> O <sub>3</sub>	860.28	37.05 (36.30)	0.68 (0.70)
7.	C <sub>27</sub> H <sub>3</sub> BiF <sub>18</sub> O <sub>3</sub>	928.28	37.51 (34.93)	0.71 (0.54)
8.	C <sub>27</sub> H <sub>3</sub> BiF <sub>18</sub> O <sub>3</sub>	928.28	37.15 (34.93)	0.71 (0.54)
9.	C <sub>27</sub> H <sub>3</sub> BiF <sub>15</sub> O <sub>4</sub>	890.31	37.12 (36.42)	0.88 (0.91)
10.	C <sub>27</sub> H <sub>3</sub> BiF <sub>15</sub> O <sub>4</sub>	890.31	37.12 (36.42)	0.88 (0.91)

(7) & (8)	1723 (S)	1440 (w)	283 (m)	1646 (m)	1520 (VS)	1491 (VS)	1390 (w)	<b>1295</b> (s)	1093 (vs)	978 (s)	628 (w)	450 (m)	780 (m)	720 (m)	510 (vw)	-
(9) & (10)	1675 (S)	1460 (m)	215 (s)	1610 (s)	1511 (S)	1480 (S)	1334 (s)	<b>1302</b> (m)	1173 (m)	986 (m)	622 (m)	454 (s)	770 (w)	734 (w)	529 (vw)	-

vs = very strong, s = strong, m = medium, w = weak, vw = very weak, o = overlapped, k, m, and n = C—C stretching modes, z<sub>1</sub>—z<sub>3</sub> = C—F stretching modes, q and r = mass sensitive Bi—C vibration, v = out of plane ring deformation, s = In plane ring deformation

**Table – 4 <sup>19</sup>F NMR data of Tris(pentafluorophenyl)bismuth(V) Derivatives**

S. No.	Compound No.	<sup>19</sup> F	
		F <sub>2,6</sub>	F <sub>3,4,5</sub>
1	(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> Bi	-129 (d)	-149 (t)
2	(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> BiCl <sub>2</sub>	-132 (d)	-142 (t)
3	(1)	-132 (d)	-143 (t)
4	(3)	-127 (d)	-142 (t)
5	(5) & (6)	-133 (d)	-141 (t)
6	(7) & (8)	-131 (d)	-141 (t)
7	(9) & (10)	-133 (d)	-141 (t)

S. No.	Compound No.	F <sub>2,6</sub>	F <sub>3,4,5</sub>
1	(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> Bi	-129 (d)	-149 (t)
2	(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> BiCl <sub>2</sub>	-132 (d)	-142 (t)
3	(1)	-132 (d)	-143 (t)
4	(3)	-127 (d)	-142 (t)
5	(5) & (6)	-133 (d)	-141 (t)
6	(7) & (8)	-131 (d)	-141 (t)
7	(9) & (10)	-133 (d)	-141 (t)



Where s = singlet, d = doublet, t = triplet

Table – 5  
<sup>1</sup>H NMR Data of Tris(Pentafluorophenyl)bisbismuth(V) Derivatives in  $\delta$ ppm

Compound No.	H $\alpha$	Phenyl			OCH <sub>3</sub>
		O-H	m-H	p-H	
(1)	-	7.80 (m)	6.86 (m)	7.37 (m)	-
(2)	-	7.84 (m)	6.86 (m)	7.38 (m)	-
(3)	-	-	7.43 (m)	-	-
(4)	-	-	7.93 (m)	-	-
(5) & (6)	5.51 (s)	7.48 (m)	7.22 (m)	-	-
(7) & (8)	5.41 (s)	7.52 (m)	-	-	-
(9) & (10)	5.38 (s)	7.54 (m)	7.40 (m)	-	3.79 (s)

Where S = singlet, d = doublet, m = multiplet

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Table – 6 <sup>13</sup>C NMR Data of Tris(pentafluorophenyl)bisbismuth(V) Derivative in  $\delta$ (ppm)

<sup>13</sup> C NMR Peaks	Comp. No.						
	(1)	(2)	(3)	(4)	(5) & (6)	(7) & (8)	(9) & (10)
o-C	152.42	152.68	152.04	152.9	152.4	152.71	152
m-C	126.71	127.09	126.63	126.93	126.81	126.76	126
p-C	145.82	146.15	145.05	145.82	145.15	145.21	145
o-C'	130.4 & 161.11 (OH)	130.61 & 161.19 (OH)	127.91	127.98	128.02	126.23	129
m-C'	118.21 117.03	118.43 117.12	127.24	127.39	126.16	126.24	128
p-C'	134.62	134.94	127.22	127.38	127.24	128.08	129
>C=O	173.60	173.88	174.86	175.28	174.10	173.00	175
i-C	100.12	100.30	100.41	101.64	101.55	101.70	101
i-C'	114.8	114.8	134.05	134.27	139.32	140.11	140
C $\alpha$	-	-	81.52	81.72	83.41	73.24	77
CF <sub>3</sub>	-	-	-	-	-	125.07	-
OCH <sub>3</sub>	-	-	-	-	-	-	53

## Conclusion

These compounds are hydrolytically stable due to presence of pentafluorophenyl and coordinatively saturated due to bulness and cyclisation of carboxylate ligands. These complexes are monomeric and stable to atmospheric moisture and oxygen.

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