Research Article

Preparation and Characterization of Some New Tris (*p*-fluorophenyl) Bismuth (iii) and Bismuth (v) Halides and Pseudohalides

Kiran Singhal[*] and Neeraj Kumar Verma

Department of Chemistry, University of Lucknow, Lucknow, Uttar Pradesh – 226007, India.

ABSTRACT

Several new substituted triarylbismuth(v) dihalide and pseudo halide of the general formula Ar_3BiX_2 and mixed halides $Ar_3BiIY[Ar=p-FC_6H_4, p-ClC_6H_4$ and $p-CH_3C_6H_4$; $X=Cl,Br,N_3,NCS,NCO$ and $Y=Cl$ and Br],have been prepared and characterized.As compared to triorganobismuth(v)dihalides mixed halides and pseudohalides of the general formula R_3BiX_2 or $R_3BiXY(R=Ph,Me,CF$; X=halo or pseudohalo group) similar triarylbismuth dihalides Ar_3BiX_2(where Ar= substituted phenyl ring having electron with drawing or electron donating groups) have not received much attention. Here in we report the synthesis and characterization of triarylbismuth(V)dihalide,Ar_3BiX_2 (Ar= $p-FC_6H_4$, $p-ClC_6H_4$;X=Cl,Br) mixed halides, Ar_3BiIY (Y=Cl,Br), pseudohalides Ar_3BiX_2 (X=N,NCO,NCS).

Keywords: Organobismuth, tris-parafluorophenylbismuth, Corbonylsulphide.

INTRODUCTION

Despite a voluminous work appearing in the literature concerning the synthesis and characterization of partially and fully halophenyl substituted Groups 15 Organometallics, (M = As, Sb and Bi) the studies are mainly centered on antimony compounds[1-2]. The latter compounds in recent years have been studied not only from synthetic point of view but also for their potential biological activity[3]. As in case of Organotin compounds, fluorine substituted organic groups or the ligands bound to metal atoms enhance the water and lipid solubility and as a result of this, their bioavailability increases. No wonder many of fluoro substituted organoantimony show significant antimicrobial and antitumour activity. However, the studies on organoantimony compounds are hindered due to their toxic nature. The retention period of antimony compounds, in human organs is again greater than the corresponding bismuth compounds and the Sb–C bond is not biodegradable unlike bismuth-carbon bond(s)[4,5].

A perusal of literature reveals that in contrast to Organoantimony compounds, corresponding Organobismuth compounds in which organic group is studded with a fluoro substituent have been little studied, while halo substituted phenyl antimony compounds are well known in literature and have been studied by our research group and others[6-8]. However, *p*-fluorophenylgroup(s) containing organo-bismuth compounds are very little known. Exploratory work reveals that the synthesis of tris(*p*-fluorophenyl) bismuth(III) alongwith arylstibines was reported as early as in 1971 by De Ketelaere et, al.[9-10] together with their ^{1}H and ^{19}F NMR spectra followed by vibrational studies reported (Both IR and Raman) by the same authors in 1974[10].It may be noted that inorganic bismuth compounds e.g. bismuth subsalicylate, bismuth subcitrate and bismuth subcarbonate have been used over a long period for treatment of gastroentitis, peptic ulcer and duodenal illness and are frequently administered for stomach related ailments despite the prevalence of so many antibiotics[10-13].The introduction of fluoro group in the organic group bound to the metal atom or in the anionic ligand is known to enhance both hydrophilicity and lipophilicity and thereby make them better candidates for biological activity. This observation is well substantiated in our finding on pentafluoro phenyl antimony compounds on which we have got issued a patent for potential insecticidal activity[14-17].

Experimental

Tertiary substituted_arylbismuth Ar_3Bi [Ar= ($p-FC_6H_4$)] were synthesized through the reported method. Thiocyanogen was generated in CCl_4 by the reaction of bromine upon lead thiocyanate. Moisture was excluded from thiocyanogen solution in order to prevent its hydrolysis. The reaction of Bromine was carried out in dark at lower temperature (-5^oC) to retard its polymerization, which is induced due to the presence of light, heat and hydrolysis products. A few representative experiments are described below further details are listed in tables[2-4].

Reaction of (p-FC$_6$H$_4$)$_3$Bi with Br$_2$

Tris(p-fluorophenylantimony)dibromide was prepared by the addition of bromine in slight excess to a solution of tri(p-fluorophenyl)bismuth in petroleum-ether (60-80°C). The reaction mixture was stirred for 3-4 h. Subsequent filtration and recrystallization from benzene yielded tri(p-fluorophenyl)bismuth dibromide, m.p.109°C;yield 65%.

Reaction of (p-FC$_6$H$_4$)$_3$Bi with (SCN)$_2$

Tris(p-fluorophenyl)bismuth (0.912 g, 2 mmol) was taken in CCl$_4$ (~30 ml) and kept stirring. To this was then added a freshly prepared solution of thiocyanogen (0.24 g, 2 mmol) in CCl4 (~50 ml) at –5°C during 15 minutes. The reaction mixture was subsequently stirred for 1 h and warmed to room temperature. The removal of the solvent under reduced pressure afforded a brownish-yellow solid. After recrystallization from ethanol it was characterized as tris(p-fluorophenyl) bismuth dithiocyanate, m.p. 173°C;yield 76%.

Reaction of (p-FC$_6$H$_4$)$_3$Bi with IBr

To a stirred solution of tris(p-fluorophenyl)bismuth (0.456 g, 1 mmol) in acetonitrile at 0oC, added iodine monobromide (0.207 g, 1 mmol) in the same solvent dropwise within 30 minutes. The reactants were stirred further for 30 minutes at 0°C and then for 2 h at room temperature, solution on concentration afforded tris(p-fluorophenyl)bismuth iodine bromide which was recrystallized from petroleum-ether,m. p. 95°C ,yield 65%.

Reaction of (p-FC$_6$H$_4$)$_3$Bi with Sulphur

A solution of tris(p-fluorophenyl) bismuth (0.912 g, 2 mmol) in acetonitrile (~50 ml) was refluxed with elemental sulphur (0.064 g, 2 mmol) for 1 h under nitrogen atmosphere. The solution was concentrated and cooled overnight to afford off white crystalline solid. It was characterized as tris(p-fluorophenyl)bismuth sulphide,m.p. 138°C,yield 62%.

Reaction of (p-FC$_6$H$_4$)$_3$BiICl with NaN$_3$

A freshly generated solution of iodine azide (0.338 g, 2 mmol) in acetonitrile (~50 ml) at –10°C was added to a precooled (–10°C) stirring solution of tris(p-fluorophenyl)bismuth chloride iodide (0.618 g, 2 mmol) in the same solvent (~50 ml) during 15 minutes under nitrogen atmosphere. The reactants were stirred for 1 h at initial temperature and then at room temperature. The solution was evaporated under reduced pressure and cooled overnight after adding petroleum-ether (40-60°C) (~10 ml). A brownish yellow crystalline solid of tris(p-fluorophenyl)bismuth Iodideazide was obtained, m.p.280°C yield 58%.

Reaction of (p-FC$_6$H$_4$)$_3$BiICl with KNCO

A suspension of potassium cyanate (1 g, 1.24 mmol) in acetonitrile was added to a solution of tris(p-fluorophenyl)bismuth chloride iodide (0.618 g, 1 mmol) in the same solvent (~60 ml) and refluxed for 3-4 h. The mixture was then filtered to remove potassium chloride and unreacted potassium cyanate. The filtrate was concentrated under vaccum to afford white solid which was recrystallized from petroleum-ether (40-60°C) and characterized as tris(p-fluorophenyl)bismuth(V) iodide isocyanate, m. p. 148°C,yield: 68%.

RESULTS AND DISCUSSION

Tris (p-fluorophenyl) bismuth dichlorides and dibromides were prepared almost in quantitative yields through the direct chlorination or bromination respectively, from the corresponding tertiary substituted aryl bismuth (III) compounds in petroleum-ether (40-60°C) at –10°C.

$$(p\text{-}FC_6H_4)_3Bi \ + \ X_2 \xrightarrow[\text{-10}^{o}\text{C}]{\text{pet ether}} (p\text{-}FC_6H_4)_3BiX_2 \quad ....(1)$$

$$(X = Cl, Br)$$
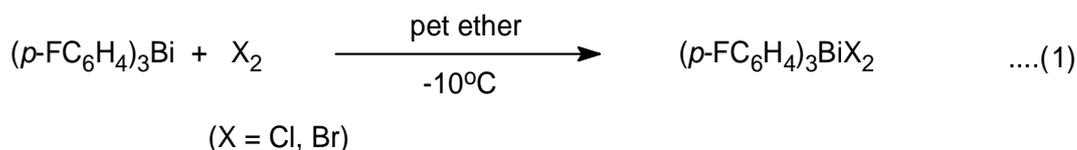
The products are white crystalline solids with sharp melting point and are soluble in common organic solvents. Being hygroscopic in nature they were stored in vacuum desiccators. The analytical data of the newly synthesized compounds are given in Table 2 and 3.

Similarly, under oxygen free conditions interhalogens, ICl and IBr were found to add oxidatively to tertiary substituted p-fluorophenylbismuth(III) compounds to give tertiary substituted aryl bismuth mixed halides in high yield and high purity at $-10^{\circ}C$ in dried carbon tetrachloride.

$$(p\text{-}FC_6H_4)_3Bi + IX \xrightarrow[-10^oC]{CCl_4} (p\text{-}FC_6H_4)_3Bi\begin{smallmatrix}I\\X\end{smallmatrix} \quad ....(2)$$

$$(X = Cl, Br)$$

No traces of p-F(C_6H_4I) or p-C_6H_4BiX were found in any of these reactions. The products normally expected from the bismuth-aryl bond cleavage. This observation is in conformity with the earlier observed reactions of interhalogens with triorganobismuth, R_3Bi (R= Ph, Me, C_6F_5) compounds.
Elemental sulphur was also found to add oxidatively to the tertiary aryl substituted compound in refluxing benzene in dry nitrogen atmosphere in the sense of equation shown below:

$$(p\text{-}FC_6H_4)_3Bi + S \xrightarrow[\Delta]{Benzene} (p\text{-}FC_6H_4)_3BiS \quad ....(3)$$
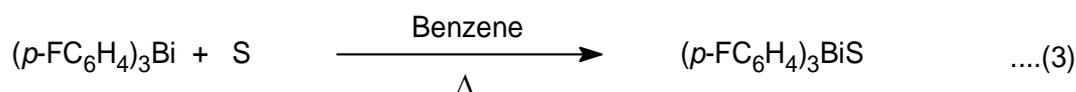
The sulphide derivatives could be obtained by passing H_2S gas to an ammonical solution of tertiary arylbismuth(V) dihalide in alcohol.

$$(p\text{-}FC_6H_4)_3BiX_2 + H_2S \xrightarrow[room\ temp.]{Alcohol} (p\text{-}FC_6H_4)_3BiS + 2HX \quad ....(4)$$
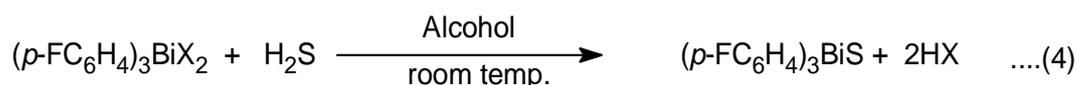
The compounds obtained by equation (3) and (4) are identical in nature. They had similar melting points (no depression in melting point on mixing) and had super imposable infrared spectra. The molecular weight of sulphide derivative determined cryoscopically in benzene suggests that they exist as a monomer. It is not surprising since triphenylbismuthsulphide triphenylantimony and tris-pentafluorophenylsulphide have also been reported to be monomolecular on the basis of molecular weight and dipole moment data[2,3].
Freshly generated solution of IN_3 and INCO were found to add oxidatively to tris(p-fluorophenyl)bismuth at $-10^{\circ}C$ in carbon tetrachloride in the sense of equation shown below:

$$(p\text{-}FC_6H_4)_3Bi + IN_3 \xrightarrow[-10^oC]{CCl_4} (p\text{-}FC_6H_4)_3Bi\begin{smallmatrix}I\\N_3\end{smallmatrix} \quad ....(5)$$

$$(p\text{-}FC_6H_4)_3Bi + INCO \xrightarrow[-10^oC]{CCl_4} (p\text{-}FC_6H_4)_3Bi\begin{smallmatrix}I\\NCO\end{smallmatrix} \quad ....(6)$$
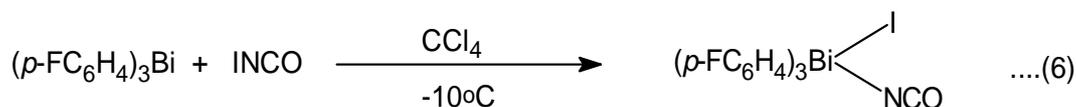
The reactions with these interhalopseudohalides were performed in dark because at room temperature and in sunlight polymerization retarded oxidative addition. Mixed pseudohalides can also be obtained by the selective replacement reactions as shown below.

$$(p\text{-}FC_6H_4)_3BiICl + NaN_3 \xrightarrow[r.t.]{Benzene} (p\text{-}FC_6H_4)_3BiIN_3 + NaCl \quad ....(7)$$

$$(p\text{-}FC_6H_4)_3BiIBr + KNCO \xrightarrow[r.t.]{Benzene} (p\text{-}FC_6H_4)_3BiI(NCO) + KBr \quad ....(8)$$
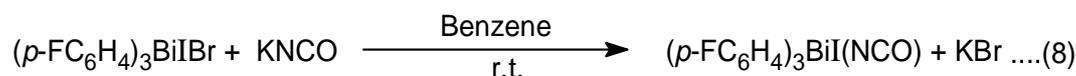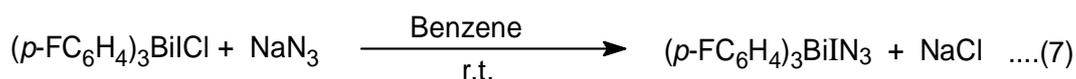
Further, $(p\text{-}FC_6H_4)_3BiCl_2$ forms an important source for obtaining various disubstituted tris(p-fluorophenyl)bismuth(V) derivatives. Thus, the treatment with the corresponding sodium salts in

benzene under moderate condition leads to the replacement of both the chloride atoms. The metallic chlorides separate immediately in each case after mixing the reactants.

$$(p\text{-}FC_6H_4)_3BiCl_2 + 2MY \longrightarrow (p\text{-}FC_6H_4)_3BiY_2 + 2MCl \quad ....(9)$$

$$M = Na, Ag, Y = NCO, N_3$$
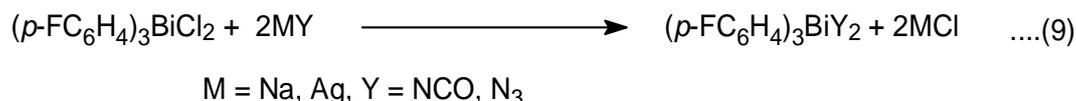
Reaction of freshly generated solution of thiocyanogen[6] in carbon tetrachloride proceeded in the same fashion at -10^oC.

$$(p\text{-}FC_6H_4)_3Bi + (SCN)_2 \xrightarrow[-10^oC]{CCl_4} (p\text{-}FC_6H_4)_3Bi(SCN)_2 \quad ....(10)$$
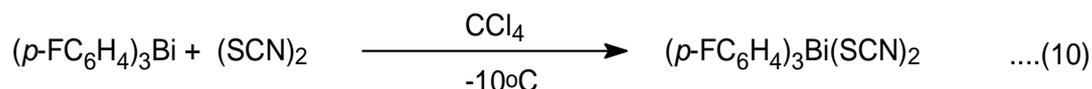
Reaction of thiocyanogen was carried in dark to retard its polymerization. No cleavage of any group however was observed.

IR Spectra

The IR absorptions associated with the various modes of vibrations due to the *p*-fluorophenyl groups bound to the bismuth in the newly synthesized tertiary substituted arylbismuth(V) dihalides and pseudo-halides correspond well with those reported for tertiary substituted aryl bismuth, R_3Bi (R = *p*-FC_6H_4)[9]. No appreciable change or shifting in the positions of none mass sensitive modes was observed and hence not discussed here. IR absorptions associated with the various modes of vibrations of azido, thiocyanato and cyanato groups have been identified and a conclusion regarding the mode of bonding of these pseudohalide groups to bismuth atom has been arrived at and is discussed below.

The chalcogenate group has three fundamental modes of vibrations $\nu C=N$, $\nu C–X$ and δNCX. Out of these modes the $C\equiv N$ has been most frequently studied because its intensity and position in infrared spectra does not vary significantly from one pseudohalogen to another and from one metal to the other. The position of the corresponding $\nu C–X$ and bending mode of vibration, δNCX greatly depends upon the nature of the pseudohalogen and its mode of bonding to the metal atom[18].Approximate frequency range for the different type of chalcogenate coordination are listed in Table 1.

Tertiary substituted arylbismuth (V) diisothiocyanate

Absorption frequencies of diagnostic values of NCS group and their possible assignments are given inTable 4.

Reported spectra of various isothiocyanates place the asymmetric isothiocyanate stretching at $2075+35$ cm^{-1} and the corresponding vibrations of the thiocyanate (–SCN) at $2155+15$ cm^{-1}[19-22]. In the present investigation the asymmetric stretching vibrations appear as a broad band of strong intensity at $2140+10$ cm^{-1} which is closer to the normal form than the isothiocyanate. It has been reported[23, 24] that the intensity of the asymmetric –NCS group is 50-100 times stronger than the –SCN group and the shape is broad for the former. The shape and intensity of the –NCS stretching absorption observed in thepresent investigation, suggest normal structure for (p-$FC_6H_4)_3Bi$ (SCN)$_2$[20].The symmetric NCS stretching, which is virtually ν C-S stretching mode, according to the established views, lies at distinctly higher frequency in the isothiocyanates (760 cm^{-1} to 880 cm^{-1}) and offers more promise in the deciding the nature of these compounds[25-29]. Thus, the appearance of a medium intensity band at 800 cm^{-1} suggests no bonding through sulphur bonding.

The IR spectra of azido derivatives exhibit three fundamental bands in the region 2100-400 cm^{-1}. The band around 2090 cm^{-1}, assignable to νas N=N$^+$=N$^-$ mode, is the strongest and the only one in the triple bond region above 2000 cm^{-1}. A second band of weak intensity is located at $1270+10$ cm^{-1} and is assigned to symmetric N=N$^+$=N$^-$, while bending δN_3 was identified at $655+5$ cm^{-1}. The spectral data thus suggest the presence of a covalently bonded linear N=N$^+$=N$^-$ in the azide derivatives[2,3,28]. The ν Bi-C bond corresponding to *y* mode of vibration appears 440-450cm^{-1}.

All the compounds are stable at room temperature and are less hygroscopic as compared to phenyl or alkyl analogs. The molecular weight determined in nitrobenzene indicates their monomeric behaviour. They were also found non-conducting in acetonitrile and, the conductivity ranges between 8 to 20 ohm^{-1}cm^{2}mole^{-1} for 10^{-3} M solution[29].

NMR Spectra

The ^{1}H NMR of the representative compounds showed a multiplet in the range δ 7.82 ppm to δ 8.12 ppm which could be assigned to aromatic protons. The ^{19}F NMR spectra of the compound (3 & 4) were carried out at room temperature. Both the compounds showed a triplet of triplets appearing in the range δ –108.30 ppm to δ –112.30 ppm and is consistent with the presence of three *p*-fluorophenyl groups in equatorial positions.

Thus on the basis of IR and NMR spectra, molecular weight and non-ionic nature of the compounds the newly synthesized triarylbismuth halo-pseudohalides and dipseudohalides may be assigned a trigonalbipyramidal structure in which three *p*-fluorophenyl groups occupy equatorial positions. Halo and pseudohalo group being more electronegative would occupy axial positions. Similar conclusions have earlier been arrived at in case of triphenylbismuth(V) compounds.
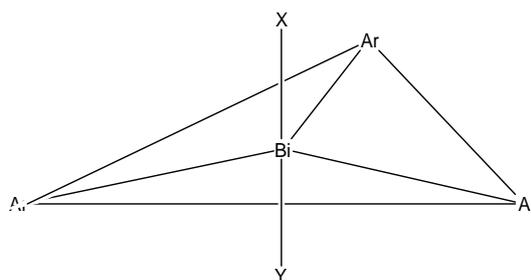
Ar = *p*-FC$_6$H$_4$; X = Y = NCS, N$_3$, NCO

X, Y = ICl, IBr, IN$_3$, INCO
X, Y = I, Cl, Br; I, N$_3$; I, NCO

Table 1: Approximate frequency ranges for different types of chalcogenate co-ordination to metal

Compound type	ν CN (cm-1)	ν CX (cm-1)	δ NCX (cm-1)
NCS–	2053	746	486, 471
M–NCS	2100-2050	870-820	485-475
M-SCN	2130-2085	760-700	470-430
M-NCS-M	2165-2065	800-750	470-440
NCSe–	2070	558	424-416
M-NCSe–	2090-2050	650-600	460-410
M-SeCN	2130-2070	550-520	410-370
M-NCSe-M	2150-2100	640-550	410-390
NCO–	2165	1254	637, 628
M-NCO	2240-2170	1350-1320	640-590
M-OCN	2240-2200	1320-1250	630-590

Table 2: Analytical data of tertiary substituted aryl bismuth (v) derivatives

S. No.	Compound	M.P. ^{o}C	Yield %	Colour	Recrystallisation solvent
1.	(*p*-FC$_6$H$_4$)$_3$BiBr$_2$	109	65	Off white	Petroleum-ether/ benzene (60-80 ^{o}C)
2.	(*p*-FC$_6$H$_4$)$_3$BiCl$_2$	117	70	Off white	Petroleum-ether (60-80°C)
3.	(*p*-FC$_6$H$_4$)$_3$Bi(N$_3$)$_2$	163	70	Off white	Petroleum-ether/ hexane
4.	(*p*-FC$_6$H$_4$)$_3$Bi(NCO)$_2$	184	68	Off white	Petroleum-ether (60-80°C)
5.	(*p*-FC$_6$H$_4$)$_3$Bi(SCN)$_2$	173	67	Light brown	Petroleum-ether (60-80°C)
6.	(*p*-FC$_6$H$_4$)$_3$BiICl	127	60	Light brown	Petroleum-ether (60-80°C)
7.	(*p*-FC$_6$H$_4$)$_3$BiIBr	143	62	Brown	Petroleum-ether (60-80°C)
8.	(*p*-FC$_6$H$_4$)$_3$BiS	138	78	Off white	Petroleum-ether/ Hexane
9.	(*p*-FC$_6$H$_4$)$_3$BiINCO	148	68	White	Petroleum-ether (40-60°C)
10.	(*p*-FC$_6$H$_4$)$_3$BiIN$_3$	280	58	Brownish crystalline	Petroleum-ether (40-60°C)

Table 3: Elemental analysis of tertiary substituted aryl bismuth (v) derivatives

S. No.	Empirical formula	Molecular weight	Found (Calcd) %		
			C	H	N
1.	$C_{18}H_{12}F_3Br_2Bi$	654.07	33.05 (33.10)	1.85 (1.90)	–
2.	$C_{18}H_{12}F_3Cl_2Bi$	565.17	38.05 (38.11)	2.14 (2.16)	–
3.	$C_{18}H_{12}F_3N_6Bi$	578.30	37.38 (37.40)	2.09 (2.10)	14.53 (14.68)
4.	$C_{20}H_{12}F_3N_2O_2Bi$	578.30	41.54 (41.56)	2.09 (2.10)	4.84 (4.92)
5.	$C_{20}H_{12}N_2S_2F_3Bi$	610.43	39.35 (39.38)	1.98 (2.00)	4.59 (4.65)
6.	$C_{18}H_{12}F_3IClBi$	656.62	32.93 (33.00)	1.84 (1.92)	–
7.	$C_{18}H_{12}F_3IBrBi$	701.07	30.84 (30.90)	1.73 (1.80)	–
8.	$C_{18}H_{12}F_3SBi$	526.33	41.08 (41.10)	2.30 (2.32)	–
9.	$C_{19}H_{12}F_3NOI$	334.10	32.35 (32.38)	3.62 (3.68)	4.19 (4.22)
10.	$C_{18}H_{12}F_3N_3BiI$	663.19	32.60 (32.68)	1.82 (1.90)	6.34 (6.38)

Table 4: Relevant IR absorptions of tertiary substituted aryl bismuth (V) derivatives

Compound No.	ν_{asy}Pseudohalide	ν_{sym}Pseudohalide	δ Pseudohalide	Bi-N
3	2090 s	1280 w	650 w	346 w
4	2160 s	1365 w	655 mw	422 vw
5	2150 s	800 w	440 w	355 vw
9	2075 s	880 w	450 w	418 w
10	2000 s	1270 w	655 w	423 w

s = strong; w = weak; mw = medium weak; vw = very weak

CONCLUSION

The introduction of fluoro group in the organic bound to the metal atom or in the anionic ligand is known to enhance both hydrophilicity and lipophilicity and thereby make them better candidates for biological activity. However, the studies on organoantimony compounds are hindered due to their toxic nature. The retention period of antimony compounds, in human organs is again greater than the corresponding bismuth compounds and the Sb–C bond is not biodegradable unlike bismuth-carbon bond(s).

ACKNOWLEDGEMENT

REFERENCES

1. Doak GO and Freedman LD. Organometallic compounds of Arsenic Antimony and Bismuth. Wiley-Interscience. New York. 1970;318.
2. Maslowsky E.Vibrational spectra of the organic derivatives of the group VB elements. J. Organometal. Chem.1974;70:153-227.
3. Wardell JL, Wilkinson G, Stone FG and A Abel EW.(Eds.). Arsenic, Antimony, Bismuth in Comprehensive Organometallic Chemistry Vol. 2. Pergamon. London.1995;321-347.
4. Sharma P, Rosas N, Cabrea A and Toscano A. Substituted thienyl stibines and bismuthines: syntheses, structures and cytotoxicity. App. Organometal Chem.2005;19:1121-1126.
5. Klapötke T. Synthese, spektroskopische Charakterisierung und bakterizide Wirksamkeit neuer Organylbis(thiophenolato)bismut(III)-Komplexe. J Organometal Chem.1987;331:299-307.
6. Kant R, Singhal K, Sanjeev S, Chandrashekar K, Saxena AK, Ranjan A and Raj P. Synthesis and Biological Activity of a Novel Compound: (C6F5)2SbPh .Phosphorous, Sulphur, Silicon and Related Elements. 2008;183(8):2029-2039.
7. Singhal K, Misra R and Raj P. Synthesis, characterization, and in vitro antimicrobial and antitumor activities of some tetraphenylstibonium(V) carboxylates. Heteroatom Chem.2008; 19(7):688-693.
8. De Ketelaere RF, Delbeke FT and Van Der Kelen GP. Organo group VB chemistry III. Synthesis and NMR spectra of some tertiary substituted arylstibines and arylbismuthines. J Organometal Chem. 1971;30:365-368.
9. De Ketelaere RF and Vander Kelen GP. Organo group VB chemistry: IV. vibrational study of some tertiary substituted aryl-group VB compounds J Organometal Chem.1974;73:251-257.

10. Soran A, Breunig HJ, Lippotis V, Arca M and Silverstru C.Monoorganobismuth(III) dihalides. J Chem Soc. Dalton Trans I.2009;77-84.
11. Gielen M. Metal based anti-tumor drugs. Freund Publishing Company London. 1988;1(2): 1992.
12. Burrell RE, Corke CT and Goel RG. Fungitoxicity of organoantimony and organobismuth compounds. J. Agricultural Food Chemistry. 1983;31:85-88.
13. Suzuki (Ed.).H. Organobismuth Chemistry. Elsevier Amsterdam.2001.
14. Singhal K. Triorganoantimony compounds for Pesticidal Use. International Patent WO/2006/067800 June 28. 2006.
15. Tiekink ERK. Critical Review. Oncology Hematology. 2002;42:217-224.
16. Sharma P, Perez D, Cabrera A, Rosas N and Arias JL. Perspectives of antimony compounds in oncology .ActaPharmacologicaSinica. 2008;29(8):881-896.
17. Singhal K, Misra R and Raj P. Synthesis, characterization, antifungal, antibacterial, and antitumor activities of some tris(pentafluorophenyl)arsenic(V) derivatives.Heteroatom Chemistry. 2010;21:181-187.
18. Norbury AH. Advances Inorg Chem Radio Chem. Academic Press, New York. 1975;17:231.
19. Ham NS and Willis JB. The vibrational spectra of phenyl thiocyanate and benzoyl isothiocyanate. Spectrochimica. Acta. 1960;16:393-395.
20. Lieber E, Rao CNR and Ramchandran J. The infrared spectra of organic thiocyanates and isothiocyanates. Spectrochimica Acta. 1959;13:296-299.
21. Mitchell PCH. and Williams RJP. The infrared spectra and general properties of inorganic thiocyanates. J Chememical. Society (resumed)1960;1912
22. Caldow GL and Thompson HW. Vibrational bands of isothiocyanates, thiocyanates and isocyanates. Spectrochimica Acta. 1958;13: 212-216.
23. Ham NS and Wills JB. The vibrational spectra of organic isothiocynates Spectrochimica. Acta. 1960;16:279-301.
24. Lewis J, Nyholm RS and Smith PW.The structure of complex molybdenum(iii) thiocyanates. J. Chemical. Society (resumed) 1961;4590.
25. Cummins RA and Dunn P. Tributytin isothiocyanate and isocyanide. Australian Journal of Chemistry.1964;17:411-418.
26. Sabatini A and Bertini T. Infra spectra between 100 and 2500cm^{-1} of some complex metal Cynate, Thiocyanates and Selenocyanates. Inorganic Chemistry.1965;4:959-961
27. Clark RJH and Williams CS. Infrared spectra (3000-200cm^{-1}) of metal-isothiocyanate complex Spectrochim. Acta.1966;22:1081-1090.
28. Bertazzi N, Alonzo G, Silvestri A and Consiglio G. Complexes of organometallic compounds: XXXI. Studies on organolead(IV) thiocyanate compounds. J Organometal Chem. 1972;37: 281-284.
29. Geary WJ. The use of conductivity measurement in organic solvents for the characterization of co-ordination compounds. Coordination Chemistry Reviews.1971;7:81-122.