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Neutral Adducts of Tri Arylantimony Mixed Halides with Oxygen, Nitrogen and Sulphur Donors

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ABSTRACT

A series of molecular adducts of $(p\text{-}FC_6H_4)_3SbCl_2$ *and* $(p\text{-}FC_6H_4)_3SbIX$ *(X = Cl, Br) with Lewis bases having oxygen, nitrogen and sulphur donor have been synthesized. The complexes isolated as solid compounds were characterized by elemental analysis, molar conductance, IR and* ^1H *and* ^{19}F *NMR spectroscopy. Elemental analysis, molar conductance and molcular weight data have been used to the proposed formulation of the complexes. The observed values of molecular weight indicate their monomeric constitution. While the values of molar conductance shows the absence of ionic species in the solution. IR- and NMR spectra reflected octahedral structure of these neutral adducts in which three R groups (R =* $p\text{-}FC_6H_4$*,* $p\text{-}ClC_6H_4$*) and one L (L = DMSO, DMF, Py,* Ph_3PO*, TU) occupied the equatorial positions with trans IX groups at axial positions.*

Keywords: Tri arylantimony Mixed Halides, Lewis bases, molar conductance IR- and NMR data

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INTRODUCTION

Lewis acidity of antimony(V) pentahalides with a variety of Lewis bases which may be oxygen donors (Ph_3PO, R_2SO, Cl_2SO), sulphur donors (R_2S, RSH), nitrogen donors (C_5H_5N, R_3N) and chlorine donors (NOCl, $TeCl_4$, Me_3SbCl_2) has been reported and the majority of the adducts conform 1:1 stoichiometry [1,2]. SbX_5 act as acceptor towards halide ion forming the complex of the type $M[SbX_6]$ [M = alkali metal, R_4N^+], in which antimony moiety acts as anion. Substitution of one or two chlorine atom(s) by phenyl group(s) in $SbCl_3$ still leaves the molcules with acceptor properties. Substitution of three chlorine atoms by organic group also leaves the molcules with some acceptor properties provided that the substituted group should be strongly electronegative for e.g. $(CF_3)_3SbCl_2$ which forms weak complexes with pyridine [3]. The Lewis acidity of pentavalent organoantimony compounds R_nSbX_{5-n} has extensively investigated by various groups of workers in the last four decades [4-9]. These studies are not confined to R_2SbCl_3 and $RSbCl_4$ having more chlorine content but has been extended to R_3SbCl_2 derivatives as well. The Lewis acidity of R_nSbX_{5-n} forwards various ligands increases with decreasing value of n [4]. With monodentate oxygen donors, viz., DMSO Popov and Kondratenko establishes the sequence on $RSbF_4 > R_2SbF_3 > R_3SbF_2$ (10). Attempts to demonstrate the existence of $Ph_3SbCl_2.L$ have not yet been successful [1, 3]. However, complex formation with organic groups containing CF_3 or C_6F_5 groups on to the metal atom (Sb) considerably enhances the Lewis acidity as is evident by the formation of hexacoordinate complexes of the type $(CF_3)_3$ $SbCl_2.L$ and $(C_6F_5)_3SbCl_2.L$ [5]. The synthesis and stereochemistry of $(C_6F_5)_3SbCl_2L$ with a number of ligands viz., DMF, DMSO, α-, β- and γ-picolines, HMPA, TU, Ph_3PO, Ph_3AsO, thiourea, pyridine has been reported in the past [8-10]. An octahedral environment around antimony has tentatively been proposed for such complexes, on the basis of analytical and spectroscopic data. It may be noted that except for a single reference on the formation and characterisation of $(C_6F_5)3SbCl_2.L$, no other study related to the synthesis of molecular adducts has been reported todate [11]. Substituted aryl groups viz. (p-FC_6H_4) are also expected to enhance the Lewis acidity of (p-$FC_6H_4)_3SbCl_2$ as compared to Ph_3SbCl_2 and thus could form molecular adduct with oxygen, nitrogen and sulphur donors. In view of our interest in the chemistry, and various aspects of fluoro-carbon based organoantimony compounds including their antimicrobial and antitumor activity, coupled with the paucity of published data in the field, we considered it worthwhile to synthesise a series of molecular adducts of (p-$FC_6H_4)_3SbCl_2$ and (p-$FC_6H_4)_3SbIX$ (X = Cl, Br) with oxygen, nitrogen and sulphur donor Lewis bases. The complexes isolated as solid compounds were characterized by elemental analysis, IR and ^{1}H and ^{19}F NMR spectroscopy.

EXPERIMENTAL SECTION

The details of the preparation of the neutral adducts are given below. The mixed halogenoderivatives of antinomy were characterised by the formation of their complexes with oxygen, nitrogen and sulphur donors for example Dimethyl sulphoxide, Dmethyl formamide, Pyridine, Triphenyl phosphine oxide and Thiourea in 1:1 molar ration. Further details are given in Table 1 to 4.

2.1. Reaction of Tri-(*p*-fluoro phenyl)antimony dichloride with Dimethyl sulphoxide (1:1): (4.77 g, 0.01 mol) of tri-(*p*-fluoro phenyl)antinomy dichloride in dichloro methane in 50 ml was refluxed with (0.78 g, 0.01 mol) of dimethyl sulphoxide for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum which afforded the complex, tri-(*p*-fluoro phenyl)antimony dichloride dimethyl sulphoxide.

M.p : 173°C Yield : 63%

2.2. Reaction of Tri-(*p*-fluoro phenyl)antimony dichloride with Dimethyl formamide (1:1): (4.77 g, 0.01 mol) of tri-(*p*-fluoro phenyl)antinomy dichloride in dichloro methane in 50 ml was refluxed with (0.73 g, 0.01 mol) of dimethyl formamide for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum which afforded the complex, tri-(*p*-fluoro phenyl)antimony dichloride dimethyl formamide.

M.p : 131°C Yield : 56%

2.3. Reaction of Tri-(*p*-fluoro phenyl)antimony dichloride with Pyridine (1:1): (4.77 g, 0.01 mol) of tri-(*p*-fluoro phenyl)antinomy dichloride in dichloro methane in 50 ml was refluxed with (0.79 g, 0.01 mol) of pyridine for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum which afforded the complex, tri-(*p*-fluoro phenyl)antimony dichloride pyridine.

M.p : 167°C Yield : 63%

2.4. Reaction of Tri-(*p*-fluoro phenyl)antimony dichloride with Triphenyl Phosphine Oxide (1:1): (4.77 g, 0.01 mol) of tri-(*p*-fluoro phenyl)antinomy dichloride in dichloro methane in 50 ml was refluxed with (2.78 g, 0.01 mol) of triphenyl phosphine oxide for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum which afforded the complex, tri-(*p*-fluoro phenyl)antimony dichloride triphenyl phosphine oxide.

M.p : 155°C Yield : 62%

2.5. Reaction of Tri-(*p*-fluoro phenyl)antimony dichloride with Thiourea (1:1): (4.77 g, 0.01 mol) of tri-(*p*-fluoro phenyl)antinomy dichloride in dichloro methane in 50 ml was refluxed with (0.76 g, 0.01 mol) of thiourea for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum which afforded the complex, tri-(*p*-fluoro phenyl)antimony dichloride thiourea.

M.p : 137°C Yield : 67%

2.6. Reaction of Tri-(*p*-fluoro phenyl)antimony bromo iodide with Dimethyl sulphoxide (1:1): (6.13 g, 0.01 mol) of tri-(*p*-fluoro phenyl)antinomy bromo iodide in dichloromethane (CH_2Cl_2) in 50 ml was refluxed with (0.78 g, 0.01 mol) of dimethyl sulphoxide for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum which afforded the complex, tri-(*p*-fluoro phenyl)antimony bromo iodide dimethyl sulphoxide.

M.p : 124°C Yield : 65%

2.7. Reaction of Tri-(*p*-fluoro phenyl)antimony bromo iodide with Pyridine (1:1): (6.13 g, 0.01 mol) of tri-(*p*-fluoro phenyl)antinomy bromo iodide in dichloromethane (CH_2Cl_2) in 50 ml was refluxed with (0.79 g, 0.01 mol) of pyridine for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum which afforded the complex, tri-(*p*-fluoro phenyl)antimony bromo iodide pyridine.

M.p : 106°C Yield : 60%

2.8. Reaction of Tri-(*p*-fluoro phenyl)antimony chloro iodide with Dimethyl sulphoxide (1:1): (5.69 g, 0.01 mol) of tri-(*p*-fluoro phenyl)antinomy chloro iodide in dichloromethane (CH_2Cl_2) in 50 ml was refluxed with (0.78 g, 0.01 mol) of dimethyl sulphoxide for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum, which afforded the complex, tri-(*p*-fluoro phenyl)antimony chloro iodide dimethyl sulphoxide.

M.p : 144°C Yield : 55%

2.9. Reaction of Tri-(*p*-fluoro phenyl)antimony chloro iodide with Pyridine (1:1): (5.69 g, 0.01 mol) of tri-(*p*-fluoro phenyl)antinomy chloro iodide in dichloromethane (CH_2Cl_2) in 50 ml was refluxed with (0.79 g, 0.01 mol) of pyridine for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum which afforded the complex, tri-(*p*-fluoro phenyl)antimony chloro iodide pyridine.

M.p : 158°C Yield : 69%

2.10. Reaction of Tri-(*p*-chloro phenyl)antimony chloro iodide with Dimethyl sulphoxide (1:1): (6.18 g, 0.01 mol) of tri-(*p*-chloro phenyl)antinomy chloro iodide in dichloromethane (CH_2Cl_2) in 50 ml was refluxed with (0.78 g, 0.01 mol) of dimethyl sulphoxide for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum which gives the complex, tri-(*p*-chloro phenyl)antimony chloro iodide dimethyl sulphoxide.

M.p : 148°C Yield : 61%

2.11. Reaction of Tri-(*p*-chloro phenyl)antimony chloro iodide with Pyridine (1:1): (6.18 g, 0.01 mol) of tri-(*p*-chloro phenyl)antinomy chloro iodide in dichloromethane (CH_2Cl_2) in 50 ml was refluxed with (0.79 g, 0.01 mol) of pyridine for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum which gives the complex, tri-(*p*-chloro phenyl)antimony chloro iodide pyridine.

M.p : 176°C Yield : 61%

2.12. Reaction of Tri-(*p*-chloro phenyl)antimony chloro iodide with Triphenyl phosphine oxide (1:1): 6.18 g, 0.01 mol) of tri-(*p*-chloro phenyl)antinomy chloro iodide in dichloromethane (CH_2Cl_2) in 50 ml was refluxed with (2.78 g, 0.01 mol) of triphenyl phosphine oxide for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum which gives the complex, tri-(*p*-chloro phenyl)antimony chloro iodide triphenyl phosphine oxide.

M.p : 103°C Yield : 64%

2.13. Reaction of Tri-(*p*-chloro phenyl)antimony bromo iodide with Dimethyl sulphoxide (1:1): (6.63 g, 0.01 mol) of tri-(*p*-chloro phenyl)antinomy bromo iodide in dichloromethane (CH_2Cl_2) in 50 ml was refluxed with (0.78 g, 0.01 mol) of dimethyl sulphoxide for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum which gives the complex, tri-(*p*-chloro phenyl)antimony chloro iodide dimethyl sulphoxide.

M.p : 136°C Yield : 60%

2.14. Reaction of Tri-(*p*-chloro phenyl)antimony bromo iodide with Dimethyl formamide (1:1): (6.63 g, 0.01 mol) of tri-(*p*-chloro phenyl)antinomy bromo iodide in dichloromethane (CH_2Cl_2) in 50 ml was refluxed with (0.78 g, 0.01 mol) of dimethyl formamide for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum which gives the complex, tri-(*p*-chloro phenyl)antimony bromo iodide dimethyl formamide.

M.p : 112°C Yield : 58%

2.15. Reaction of Tri-(*p*-chloro phenyl)antimony bromo iodide with Pyridine (1:1): (6.63 g, 0.01 mol) of tri-(*p*-chloro phenyl)antinomy bromo iodide in dichloromethane (CH_2Cl_2) in 50 ml was refluxed with (0.78 g, 0.01 mol) of pyridine for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum which gives the complex, tri-(*p*-chloro phenyl)antimony bromo iodide pyridine.

M.p : 122°C Yield : 49%

2.16. Reaction of Tri-(*p*-chloro phenyl)antimony bromo iodide with Triphenyl phosphine oxide (1:1): (6.63 g, 0.01 mol) of tri-(*p*-chloro phenyl)antinomy bromo iodide in dichloromethane (CH_2Cl_2) in 50 ml was refluxed with (0.78 g, 0.01 mol) of triphenyl phosphine oxide for one hr. After refluxtion, excess of CH_2Cl_2 was distilled off. The residue was recrystallised with pet. ether and hexane and finally dried in vacuum, which afforded the complex, tri-(*p*-chloro phenyl)antimony bromo iodide triphenyl phosphine oxide.

M.p : 138°C Yield : 61%

Table 1: Experimental Data of R_3MX2 and R_3MXX' Complexes with Lewis Bases

S.N.	Compound	Ligand	Molar-ratio	Complex (a, b)	M.p. (°C)	Yield (%)
1	R_3SbCl_2	Dimethyl sulphoxide	1:1	R_3SbCl_3.DMSO	173	63
2	R_3SbCl_2	Dimethylformamie	1:1	$R_3SbCl_{2.}$DMF	131	56
3	R_3SbCl_2	Pyridine	1:1	R_3SbCl_2.Py	167	63
4	R_3SbCl_2	Triphenyl phosphine oxide	1:1	$R_3SbCl_2.Ph_3Po$	155	62
5	R_3SbCl_2	Thiourea	1:1	R_3SbCl_2.TU	137	67
6	R_3SblBr	Dimethyl sulphoxide	1:1	R_3SblBr..DMSO	124	65
7	R_3SblBr	Pyridine	1:1	R_3SblBr.Py	106	60
8	R_3SblCI	Dimethyl sulphoxide	1:1	R_3SblCI.DMSO	144	55
9	R_3SblCI	Pyridine	1:1	R_3SblCI.Py	158	69

where R = p-FC_6H_4, [a]*Conductance values in CH_3CN indicated non-electrolyte behaviour,* [b]*Molecular wt. data in freezing nitrobenzene indicated monomeric nature of the adducts.*

Table 2: Analytical Data of R_3MX_2 And R_3MXX' Complexes with Lewis Bases

S. No.	Complexes	Empirical formula	Analysis Found (Caled.) %			
			C	H	N	Sb
1	R_3SbCl_2.DMSO	$C_{20}H_{18}F_3SbCl_2SO$	43.18	3.21		21.88
			(43.20)	(3.23)	-	(21.90)
2	R_3SbCl_2.DMF	$C_{21}H_{19}F_3SbCl_2NO$	45.74	3.41	2.50	22.07
			(45.77)	(3.44)	(2.54)	(22.10)
3	R_3SbCl_2.Py	$C_{23}H_{17}F_3SbCl_2N$	49.55	3.01	2.50	21.82
			(49.59)	(3.05)	(2.51)	(21.86)
4	$R_3SbCl_2.Ph_3PO$	$C_{36}H_{27}F_3SbCl_2PO$	57.15	3.54		16.07
			(57.18)	(3.57)		(16.10)
5	R_3SbCl_2.TU	$C_{19}H_{16}F_3SbCl_2N_2S$	41.17	2.84	5.01	21.92
			(41.19)	(2.88)	(5.05)	(21.98)
6	R_3SblBr.DMSO	$C_{20}H_{18}F_3SblBrSO$	34.70	2.58	-	17.56
			(34.72)	(2.60)	-	(17.60)
7	R_3SblBr.Py	$C_{23}H_{17}F_3SblBrN$	39.85	2.40	2.00	17.51
			(39.87)	(2.45)	(2.02)	(17.57)
8	R_3SblCI.DMSO	$C_{20}H_{18}F_3SblCISO$	37.06	2.72		(18.76)
			(37.10)	(2.78)	-	(18.80)
9	R_3SblCI.Py	$C_{23}H_{17}F_3SblCIN$	42.58	2.60	2.11	
			(42.60)	(2.62)	(2.15)	(18.78)

where R = p-FC_6H_4, [a]*Conductance values in CH_3CN indicated non-electrolyte behaviour,* [b]*Molecular wt. data in freezing nitrobenzene indicated monomeric nature of the adducts.*

Table 3: Experimental Data of R_3MXX' Complexes with Lewis Bases

S.No.	Compound	Ligand	Molar-ratio	Complex (a, b)	M.p. (°C)	Yield (%)
1	R_3SblCl	Dimethyl sulphoxide	1:1	R_3SblCl.DMSO	148	61
2	R_3SblCl	Dimethyl formamide	1:1	R_3SblCl.DMF	163	66
3	R_3SblCl	Pyridine	1:1	R_3SblCl.Py	176	61
4	R_3SblCl	Triphenyl phosphine oxide	1:1	$R_3SblCl.Ph_3PO$	103	64
5	R_3SblBr	Dimethylsulphoxide	1:1	R_3SblBr.DMSO	136	60
6	R_3SblBr	Dimethyl formamide	1:1	R_3SblBr.DMF	112	58
7	R_3SblBr	Pyridine	1:1	R_3SblBr.Py	122	49
8	R_3SblBr	Triphenyl phosphine oxide	1:1	$R_3SblBr.Ph_3PO$	138	61

where R = p-ClC_6H_4, [a]*Conductance values in CH_3CN indicated non-electrolyte behaviour,* [b]*Molecular wt. data in freezing nitrobenzene indicated* *monomeric nature of the adducts.*

Table 4: Analytical Data of R_3MXX' Complexes with Lewis Bases

S.No.	Complexes	Emperical formula	Analysis Found (Caled.) %			
			C	H	N	Sb
1	$R_3SbICl.DMSO$	$C_{20}H_{18}Cl_4SbISO$	34.44	2.55		17.45
			(34.46)	(2.58)	-	(17.47)
2	$R_3SbICl.DMF$	$C_{21}H_{19}Cl_4SbION$	36.40	2.71		1.98
			(36.45)	(2.74)	(2.02)	(17.59)
3	$R_3SbICl.Py$	$C_{23}H_{17}Cl_4SbIN$	39.54	2.40		1.95
			(39.58)	(2.43)	(2.00)	(17.44)
4	$R_3SbICl.Ph_3PO$	$C_{36}H_{27}Cl_4SbIPO$	48.15	2.98		
			(48.20)	(3.01)	-	(13.57)
5	$R_3SbIBr.DMSO$	$C_{20}H_{18}Cl_3SbBrISO$	32.35	2.40		-
			(32.40)	(2.42)	-	(16.42)
6	$R_3SbIBr.DMF$	$C_{21}H_{19}Cl_3SbBrION$	34.22	2.55		1.85
			(34.25)	(2.58)	(1.90)	(16.53)
7	$R_3SbIBr.Py$	$C_{23}H_{17}Cl_3SbBrIN$	37.19	2.25		1.86
			(37.21)	(2.29)	(1.88)	(16.40)
8	$R_3SbIBr.Ph_3PO$	$C_{36}H_{27}Cl_3SbBrIPO$	45.90	2.84		12.90
			(45.92)	(2.86)	-	(12.93)

where R = p-CIC_6H_4

RESULTS AND DISCUSSION

Tri-(*p*-fluorophenyl)antimony dichloride obtained by the oxidative reaction of (*p*-$FC_6H_4)_3Sb$ with ICI/CI_2, recrystallised and dried before use. It was treated with the desired ligand in equivalent molar ratio (1:1) in dichloromethane.

$$(p\text{-}FC_6H_4)_3SbCl_2 + L \rightarrow (p\text{-}FC_6H_4)_3SbCl_2.L \qquad (1)$$

$$(p\text{-}FC_6H_4)_3SbIX + L \rightarrow (p\text{-}FC_6H_4)_3SbIX.L \qquad (2)$$

where L = Dimethy sulphoxide (DMSO), Dimethyl formamide (DMF), Pyridine (Py), Triphenyl phosphine oxide (Ph_3PO) and Thiourea (TU) and IX = ICI, IBr.

All the reactions were found to proceed smoothly under mild conditions. The completion of the reaction takes place within 2 to 3 hrs. In most of the cases, the products were obtained as solid after evaporating the solvent which were crystallised with petroleum ether/ether (neat or mixture). The complexes are soluble in common organic solvent such as chloroform, acetonitrile, etc. They show monomeric constitution in freezing benzene. The complexes are stable, non-susceptible to oxygen and can be stored for several weeks without decomposition. The constancy in melting point after the repeated crystallization as well as TLC run in polar solvent with a single spot excluded the presence of mixture of reactants. Elemental analysis, conductance and molcular weight data correspond well to the proposed formulation of the complexes. The observed values of molecular weight indicate their monomeric constitution. While the values of molar conductance of 10^{-3} M solution in acetonitrile ranges between 20-30 ohm^{-1} cm^{2} at room temperature, which shows the absence of ionic species in the solution.

3.1. Infrared Spectra:

All the complexes, listed in Table-1, were characterised in the solid state by their IR spectra in the region 4000-200 cm^{-1}. Important IR frequencies for the complexes together with their assignments are also identified. These assignments have been made by comparing the spectra in 4000-200 cm^{-1} region in the solid state of the complexes. With those of free ligands the infrared absorptions due to (*p*-FC_6H_4) groups bound to antimony are almost identical and do not differ significantly from those observed for other (*p*-fluoro phenyl) antimony compounds reported earlier from this laboratory [13, 16] and elsewhere.

3.1.1. Infrared Spectra of Adducts with Oxygen Donors:

The υC=0) modes in various amide bases appearing at 1650 ± 15 cm^{-1} undergo negative shift and identified at 1608 cm^{-1} in the spectra of adducts, suggesting weakening of the (C=0) bond and coordination through oxygen atom of the base [12-18]. An absorption of strong intensity for υ(S=0) and υ(P=0) lying at 1045 and 1195 cm^{-1}, respectively, in the spectra of free ligand, undergoes a distinct negative shift on complexation. The corresponding absorption in the spectra of adducts appear at 940 and 1162 cm^{-1} suggesting coordination from oxygen atom of the base. On the basis of present and some previous studies a medium strong band at 380 ± 5cm^{-1} is assigned to υ(Sb-O) stretching frequency [16-18]

3.1.2. Infrared Spectra of Adduct with Nitrogen Donors:
The υ(C=N) frequency in (p-$FC_6H_4)_3SbCl_2$.Py is decreased significantly to 1605 cm^{-1}. In addition to this a band at 3310 ± 10 cm^{-1} assignable to υNH mode in free ligand is shifted to lower frequency 3010 cm^{-1}. In the IR spectra of the ligand the assignment of the Sb-N bond is tentatively assigned at 380 cm^{-1}.

3.1.3. Infrared Spectra of the Adduct with Sulphur Donors:
In sulphur donor ligand (TU), an absorption at 1069 cm^{-1} reported to possess equal contribution from υC=N) and υ(C-S). This remains unaffected on adduct formation and appears at 1075 cm^{-1}. When coordination occurs through sulphur atom, the υ(C=N) suffers a positive shift while the υ(C=S) suffers an almost equal negative shift. As a consequence to this the resulting absorption remains apparently unchanged [17]. The positive shift of υ(NH) from 3360 cm^{-1} to 3300 cm^{-1} in free ligand to 3410 and 3370 cm^{-1} in its adduct indicates the absence of coordination through N-atom of the ligand and indirectly suggests Sb ← S bonding [17]. On the basis of some previous observation and present studies, the (Sb-S) bond is assigned at 380 cm^{-1} [19]. (Sb-C) bond for the above complexes corresponding to Y mode appears in the range 445-465 cm^{-1} [19, 20].

3.2. ^{1}H NMR Spectra:

^{1}H NMR spectra of (p-$FC_6H_4)_3SbCl_2$.DMSO was recorded at room temperature in $CDCl_3$. Aromatic protons exhibited doublet of multiplets centered at δ 7.90 ppm and 8.20 ppm. A singlet centered at δ 2.36 ppm is due to methyl protons (-CH_3 of DMSO).

3.3. ^{19}F Spectra:

The ^{19}F spectra of (p-$FC_6H_4)_3SbCl_2$.L were recorded in $CDCl_3$ using trifluoroacetic acid as the external standard at 84.26 MHz. The spectra consists a doublet for F_4, triplet for $F_{3,5}$ and a doublet for $F_{2,6}$ indicating that all the three (p-FC_6H_4) groups are equivalent and in one plane.

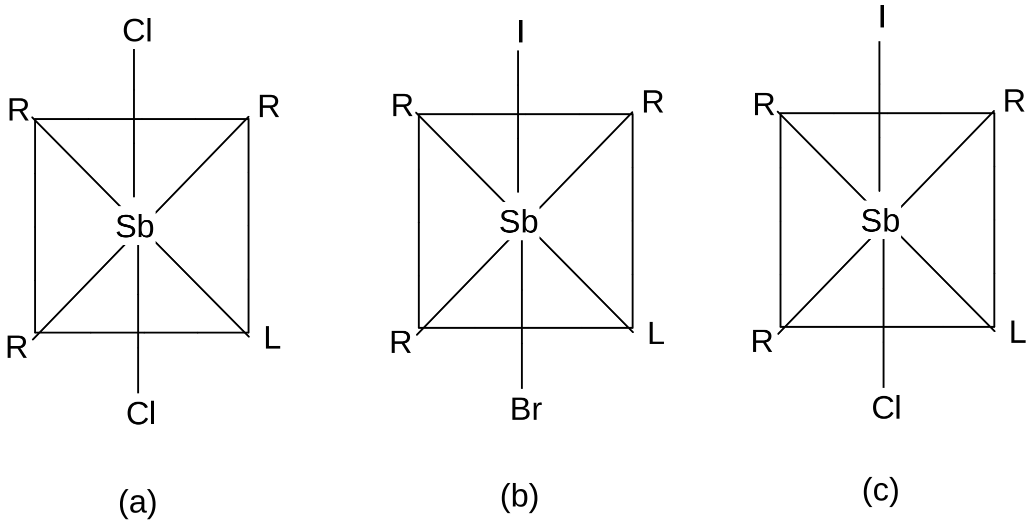

Figure 1. Structure of R_3SbCl_2.L and R_3SbIX.L and L = DMSO, DMF, Py, Ph_3PO, TU; IX = ICl, IBr

3.4. Stereochemistry of the Neutral Molcular Adducts

It has been assumed that the addition of a Lewis base L to the central metal atom in a trigonal bipyramidal molecule takes place in a trigonal plane and steric and electrostatic factor play an important role in determining the position of entry of L. It is well established that more electronegative groups goes to the axial position and less electronegative on equatorial position. Therefore, base L should settle in equatorial position. It is also suggested by a tentative assignment of Sb-Cl bond at 330 cm^{-1} appearing in the spectra and attributed to axial chlorine. In view of the above idea, the nucleophilic attacks at the position between the two (p-FC_6H_4) groups to produce octahedral structure with trans chloro groups appear to be most favourable. Similar structure can be suggested for (p-$FC_6H_4)_3SbIX$.L (X = Cl, Br) [Fig. 1). Nishii et al. have suggested similar structure for R_2SbCl_3.L [7-9].

CONCLUSION

The study concluded following points:
(a) Molecular weight of the complexes indicates their monomeric constitution
(b) Molar conductance show the absence of ionic species in the solution and

(c) IR- and NMR spectra reflected octahedral structure of these neutral adducts in which three R groups (R = *p*-FC_6H_4, *p*-ClC_6H_4) and one L (L = DMSO, DMF, Py, Ph_3PO, TU) occupied the equatorial positions with trans IX groups at axial positions.

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