

Molecular adducts of pentafluorophenylantimony (III) chlorides $(R_f)_n SbCl_{3-n}$ with neutral monodentate oxygen, nitrogen and sulphur donors

Isha Rizvi, Amarika Singh, Navneet Singh, Dharmendra K. Srivastava

Abstract—Penta-coordinated and Tetra-coordinated neutral adducts $(C_6F_5)_2SbCl.L$, $(C_6F_5)SbCl_2.L$ and $(C_6F_5)SbCl_2.L_2$ [L= Pyridine, Thiourea, Triphenylarsenic oxide, Hexamethyl phosphoramidate, Triphenylphosphine oxide, α -Picoline, β -Picoline, γ -Picoline] have been synthesized. Molecular adducts are monomeric in benzene and non-electrolyte in acetonitrile. IR spectra and conductance measurement suggest that the complexes are neutral.

Keywords— Adducts, bis (pentafluorophenyl) antimony (III) chloride, characterised, Lewis acidity, monomeric, non-electrolyte, pentafluorophenyl antimony (III) dichloride.

1 INTRODUCTION

Acceptor properties of antimony (III) halide and organo substituted antimony(III) halide have not been studied to considerable extent. Antimony (III) due to presence of three halo group behaves as strong Lewis acid and report on the synthesis of neutral adducts and anionic complexes with enhanced coordination no. up to 4 to 5 are usually encountered and have been reported [1-7]. These reports have mainly been of academic interest and have not been exploited for other organo group substituted antimony (III) halide. Successive replacement of chloride group by phenyl and methyl group still leaves for example; R_nSbCl_{3-n} ($n=1&2$) with considerable Lewis acidity. Phenyl substituted antimony halide are better Lewis acid compared to methyl analogous. However, replacement of methyl group by CF_3 enhances the Lewis acidity of complexes with different Ligands have been prepared [6, 7]. The acceptor properties of $PhSbCl_2$ and Ph_2SbCl have been investigated by Nottingham & workers toward oxygen, nitrogen and sulphur donors. $PhSbCl_2$ forms complexes both 1:1 and 1:2 stoichiometry while Ph_2SbCl form only 1:1 complexes [6].

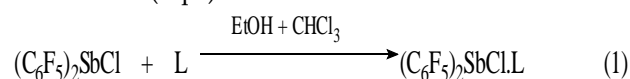
The neutral, anionic and cationic complexes of Ar_2SbCl and $PhSbCl_2$ have been prepared by us but the coordination number of the central metal atom does not exceed beyond five.

As has been mentioned above replacement of methyl group from $MeSbCl_2$ by trifluoromethyl group enhances the Lewis acidity, it was considered worth while to examine whether replacement of an aryl group (C_6H_5 , $p-CH_3C_6H_4$) by pentafluorophenyl group ($R_f = C_6F_5$) will enhance the Lewis acidity to such an extent so as to facilitate the formation of complexes in which coordination number of central metal up to five.

The present work deals with the preparation and isolation of neutral adducts of $(R_f)_2SbCl$ and $(R_f)SbCl_2$ ($R_f=C_6F_5$) with oxygen, nitrogen and sulphur donors. Two series of compounds were obtained in 1:1 and 1:2 stoichiometry. However, $(R_f)_2SbCl$ does not form complexes with 2 moles of ligand. The complexes have been characterised by elemental analysis, molar conductance and molecular weight data. The structure of the complexes has been assigned on the basis of IR and NMR spectra.

2 RESULTS AND DISCUSSION

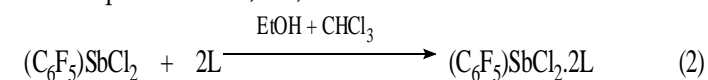
Under anhydrous oxygen free condition neutral adducts of type (I, III, V, VII, IX, XI, XIII, XVI), could be obtained by interaction of bis(pentafluorophenyl) antimony(III) chloride, $(C_6F_5)_2SbCl$ and pentafluorophenyl antimony (III) dichloride with an equivalent of neutral monodentate ligand in ethanol and chloroform (Eq.1).



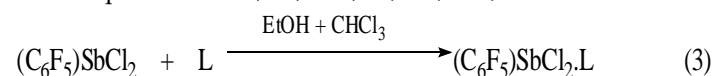
Where L: Pyridine (Py), Picoline (α - C_6H_7N , β - C_6H_7N & γ - C_6H_7N), Triphenylarsenic oxide (Ph_3AsO), Thiourea (TU), Triphenyl phosphine oxide (Ph_3PO), Hexamethyl phosphoramidate (HMPA).

The adducts of type (II, IV, VI, VIII, X, XII, XIV, XV, XVII, XVIII) could be obtained by interaction of pentafluorophenyl antimony(III) dichloride with 1:2 (for II, XV, XVII) or in appropriate stoichiometry of neutral monodentate liquid in ethanol and chloroform (Eq. 2 and 3).

for Compound No. II, XII, XVIII



for Compound No. IV, VI, VIII, IX, XII, XIV, XVII



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Where L : Pyridine (Py), α - Picoline, β - Picoline, γ - Picoline (Pic), Triphenyl phosphine oxide (Ph_3PO), Hexamethyl phosphoramide (HMPA), Thiourea (TU).

All the reactions were found to proceed smoothly under mild condition. The products can be crystallized from petroleum ether (40-60°) or diethyl ether. In general mp of the adducts or complexes are high and few of them were found to decompose without melting. These adducts are readily soluble in polar solvents. These are stable toward atmospheric oxygen and moisture.

These adducts are monomeric in freezing benzene. Conductance measurement value of 10^{-3}M solution of adducts in acetonitrile suggest the absence of ionic species.

2.1 IR Spectroscopy

The IR absorption due to C_6F_5 group attached to antimony are almost identical and do not differ significantly from those observed for pentafluorophenyl (III) compound earlier [8, 9, 10].

2.1.1 IR spectra of the adducts with oxygen donors

The IR absorption characteristic of C_6F_5 group $\nu(\text{Sb}-\text{C})$ and $(\text{Sb}-\text{Cl})$ stretching frequency prepared in present paper resemble well with earlier values [8] and are listed in Table 4.

In case of oxygen donor, Ph_3PO , $\nu(\text{P}-\text{O})$ appearing at 1192cm^{-1} in the free ligand show a negative shift and appear around 1130 ± 5 indicating co-ordination through oxygen atom of ligand [11].

In case of Ph_3AsO complexes, the characteristic $\nu(\text{As}=\text{O})$ [12,13], lying at 880cm^{-1} in the spectra of the free ligand undergoes a distinct negative shift on complexation. The corresponding absorption in the spectra of the adduct appears at $835 \pm 5\text{cm}^{-1}$ suggesting coordination from oxygen atom of the base.

In case of HMPA complexes, the characteristic $\nu(\text{p}=\text{O})$ vibration appearing at 1218cm^{-1} in free ligand is considerably lowered to 1140 ± 2 on complexation indicating coordination through oxygen of base [11].

2.1.2 IR spectra of adducts with nitrogen donor

Infrared absorption for all the isolated compounds associated with the antimony-pentafluorophenyl group and the aromatic donors overlaps and presents a complex picture which makes proper assignment considerably difficult. However bands due to aromatic donors which are characteristic have been identified to a certain extent.

Thus, pyridine out of plane deformation [6] observed at 404cm^{-1} in the free ligand, is shifted to 414 ± 5 in $(\text{C}_6\text{F}_5)\text{SbCl}_2$ and $(\text{C}_6\text{F}_5)_2\text{SbCl}$ complex. Similarly, in plane deformation mode which appear at $604 \pm 2\text{cm}^{-1}$ in the 1:1 and 1:2 complexes. The characteristic $\nu\text{C}=\text{N}$ vibration in the adduct with nitrogen donors (pyridine and Picoline) reported to appear in the range $1568-1575\text{cm}^{-1}$ in free ligand [11] undergoes a positive shift on complexation and appear at $1605 \pm 15\text{cm}^{-1}$ suggesting co-ordination through nitrogen atom of the base.

2.1.3 IR spectra of adducts with sulphur donor

In case of thiourea complexes, $\nu\text{C}=\text{N}$ and $\nu\text{C}=\text{S}$ do not suffer any significant shift compared to free ligand. The positive shift of $\nu(\text{N}-\text{H})$ from 3300cm^{-1} in free thiourea to 3375cm^{-1} in the adducts indicates coordination through sulphur atom of the ligand [11].

As expected, bands associated with antimony-chlorine modes moves to lower energy on complexation e.g. from $340-320\text{cm}^{-1}$ in $(\text{C}_6\text{F}_5)\text{SbCl}_2$ to $315 \pm 5\text{cm}^{-1}$ is shifted to $290 \pm 10\text{cm}^{-1}$ [2, 6].

2.2 ^1H NMR, ^{13}C NMR & ^{19}F NMR spectra

2.2.1 ^1H NMR Spectroscopy

The ^1H NMR spectra of compound no I, II shows similar multiplet for pyridine in range of δ 7.36 ppm to 8.98 ppm in which proton at 4th position shows most downfield peak, are characteristic for aromatic protons attached by pyridine in pyridine complexes. Compound no III, V, VII, IV, VI, VIII exhibits most shielded peak for protons of methyl group ranges from δ 2.31 to 2.53 ppm and a multiplet ranges from δ 7.18 ppm to 8.69 ppm are characteristic for picoline complexes. Compound no IX, X exhibits multiplet for phenyl group attached with arsenic atom in range of δ 7.30 ppm to 7.45 ppm. Compound no XI, XII also shows multiplet for phenyl group attached with phosphorus atom in range of δ 7.45 to 7.47 ppm. Compound no XIII, XIV; XV exhibits two signals at δ 2.42 ppm and δ 2.32 ppm due to $-\text{N}-\text{CH}_3$ protons which is characteristic for HMPA complexes [14]. Compound no XVI, XVII, and XVIII exhibit singlet at δ 9.53 ppm shows that protons at nitrogen atom are some what similar to aldehydic protons which are deshielded and gives downfield peak characteristic for thiourea complex.

All the ^1H NMR spectra of aforesaid compounds are taken in CDCl_3 as solvent and tetramethylsilane as reference material.

2.2.2 ^{13}C NMR Spectroscopy

The ^{13}C NMR or CMR spectra of all the complexes exhibit signal at δ 101 ppm for C_1 , 148 ppm for C_2 , 137.3 ppm for C_3 , C_5 and 143.3 ppm for C_4 atom of pentafluorophenyl group attached with antimony. Compound no I, II exhibit additional peaks at δ 149.9 ppm for C_2 , 124.5 ppm for C_3 , C_5 , and 137.8 ppm for C_4 atom which are characteristic for pyridine complexes. Compound no III, V, VII, IV, VI, VIII exhibit peaks ranges from 18.0 ppm to 23.9 ppm for methyl carbon, 148.6 to 158.0 ppm for C_2 , 120.9 to 133.9 ppm for C_3 , C_5 , 136.0 to 147.0 ppm for C_4 atoms, are characteristic for picoline complexes. Compound no IX, X exhibits peaks at 129 ppm for C_1 , 128.7 ppm for C_3 , C_4 , C_5 atoms of triphenylarsine oxide complexes for their phenyl group attached with arsenic atom. Compound no XI, XII exhibit peaks at 133.1 ppm for C_1 , 132.3 ppm for C_2 , 128.8 ppm for C_3 , C_5 and 134.2 ppm for C_4 atoms are characteristic of triphenylphosphine oxide complexes. Compound no XIII, XIV, XV exhibits peaks at 36.5 ppm characteristics for HMPA complex and in last compound no XVI, XVII, XVIII exhibits peaks at 176.7 ppm characteristic for

thiourea complexes.

All the ^{13}C NMR spectra of aforesaid compounds are taken in tetramethylsilane as reference material.

2.2.2 ^{19}F NMR Spectroscopy

The ^{19}F NMR spectra showed signal at δ -122.40 ppm, -146.20 ppm and -152.06 ppm corresponding to $\text{F}_{2,6}$, F_4 and $\text{F}_{3,5}$ respectively.

2.1 Stereochemistry of neutral molecular adducts

On the basis of elemental analysis, IR, NMR spectra, molecular weight and conductance measurement, the neutral molecular adducts can be assigned tetra coordinated and penta-coordinated structure as shown in figure 1, 2 & 3. Similar structures have earlier been assigned for 1:1 and 1:2 addition products with R_2SbCl and RSbCl_2 respectively [2], [6], [15].

3 Experimental

Bis(pentafluorophenyl)antimony(III) chloride, $(\text{C}_6\text{F}_5)_2\text{SbCl}$ and (pentafluorophenyl)antimony(III) dichloride $(\text{C}_6\text{F}_5)\text{SbCl}_2$ was prepared by reported method [16] through redistribution reaction. All the reagents 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.

Analytical data are given in Table 1 & 2. Conductivity data Table 3 were obtained in acetonitrile with the help of a Philips magic eye type PR 950 Conductivity Bridge using a dip type conductivity cell. Molecular weights were determined cryoscopically in benzene given in Table 3. IR spectra were recorded on a Perkin Elmer 577 spectrophotometer in the range $4000\text{-}200\text{ cm}^{-1}$ Table 4 & 5. Typical experimental details of the reactions are described below. All the complexes were prepared in similar fashion.

3.1 Reaction of $(\text{C}_6\text{F}_5)_2\text{SbCl}$ with Pyridine (I)

A solution of bis(pentafluorophenyl)antimony(III) chloride, $(\text{C}_6\text{F}_5)_2\text{SbCl}$ (0.491 g, 1mmol) in chloroform (30 cm^3) and pyridine (0.079 g, 1mmol) in ethanol (30 cm^3) were stirred together at room temperature for 4 h and then refluxed for 1 h to ensure complete reaction. It was then filtered and the filtrate was distilled off to remove excess of solvent to get viscous solid of bis(pentafluorophenyl)antimony(III) chloride-Pyridine adducts. It was recrystallized from petroleum ether ($40\text{-}60^\circ\text{C}$) to afford bis(pentafluorophenyl)antimony(III) chloride- Pyridine adducts.

3.2 Reaction of $(\text{C}_6\text{F}_5)_2\text{SbCl}$ with Ph_3AsO (IX)

To a solution of bis(pentafluorophenyl)antimony(III) chloride, $(\text{C}_6\text{F}_5)_2\text{SbCl}$ (0.491 g, 1mmol) in chloroform (30 cm^3), triphenylarsine oxide (0.322 g, 1mmol) in methanol (30 cm^3), was added drop wise. The reactants were stirred for 4 h at room temperature under nitrogen and the refluxed further for 24 h. It was then filtered and filtrate on concentration in vacuo yielded a off white solid characterised as bis(pentafluorophenyl)antimony(III) chloride- triphenylarsine oxide adduct was recrystallized from petroleum ether (40-

60°C).

3.3 Reaction of $(\text{C}_6\text{F}_5)\text{SbCl}_2$ with $\text{Ph}_3\text{P}_3\text{O}$ (XII)

A solution of (pentafluorophenyl)antimony(III) dichloride, $(\text{C}_6\text{F}_5)\text{SbCl}_2$ (0.360 g, 1mmol) in chloroform (30 cm^3) and triphenylphosphine oxide (0.278 g, 1mmol) in ethanol (30 cm^3) were stirred together at room temperature for 4 h. It was then filtered and filtrate on concentration in vacuo yielded a light green solid characterized as (pentafluorophenyl)antimony(III) dichloride- triphenylphosphine oxide adduct was recrystallized from petroleum ether ($40\text{-}60^\circ\text{C}$).

3.4 Reaction of $(\text{C}_6\text{F}_5)\text{SbCl}_2$ with HMPA (XV)

A solution of (pentafluorophenyl)antimony(III) dichloride, $(\text{C}_6\text{F}_5)\text{SbCl}_2$ (0.360 g, 1mmol) in chloroform (30 cm^3) and HMPA (0.358 g, 2mmol) in ethanol (30 cm^3) were stirred together at room temperature for 6 h. It was then filtered and filtrate on concentration in vacuo yielded a solid which was recrystallized from petroleum ether ($40\text{-}60^\circ\text{C}$) to afford (pentafluorophenyl)antimony(III) dichloride-HMPA adduct.

4 Figures

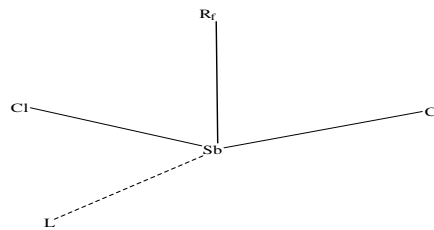


Fig: 1 $\text{R}_f\text{SbCl}_2\cdot\text{L}$

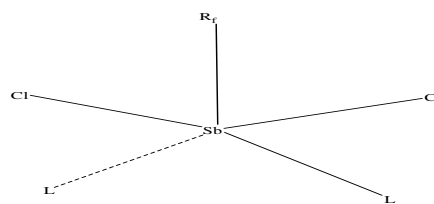


Fig: 2 $\text{R}_f\text{SbCl}_2\cdot\text{L}_2$

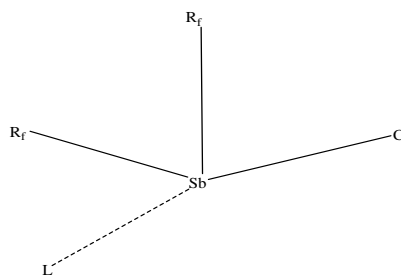


Fig: 3 $(\text{R}_f)_2\text{SbCl}\cdot\text{L}$

5 Tables

Table 1 Analytical data for bis(pentafluorophenyl)antimony(III) chloride neutral adducts.

Compound No.	Adduct/Complexes	Mp (°C)	Yield (%)	Analysis: Found(Calculated:%)		
				C	H	N
				I	(C ₆ F ₅) ₂ SbCl.Py	178
III	(C ₆ F ₅) ₂ SbCl.α-Pic	179	68	36.90(36.99)	1.20(1.21)	2.38(2.40)
V	(C ₆ F ₅) ₂ SbCl.β-Pic	170	57	36.90(36.99)	1.20(1.21)	2.48(2.40)
VII	(C ₆ F ₅) ₂ SbCl.γ-Pic	172	62	36.90(36.99)	1.20(1.21)	2.48(2.40)
IX	(C ₆ F ₅) ₂ SbCl.Ph ₃ AsO	240d	72	44.25(44.29)	1.85(1.86)	----
XI	(C ₆ F ₅) ₂ SbCl.Ph ₃ PO	235	74	46.80(46.82)	1.95(1.96)	----
XIII	(C ₆ F ₅) ₂ SbCl.HMPA	105	67	32.23(32.24)	2.70(2.71)	6.25(6.27)
XVI	(C ₆ F ₅) ₂ SbCl.TU	230d	74	27.50(27.52)	0.70(0.71)	4.92(4.94)

Table 2 Analytical data for (pentafluorophenyl)antimony(III) dichloride neutral adducts.

Compound No.	Adduct/Complexes	mp(°C)	Yield(%)	Analysis: Found (Calculated:%)		
				C	H	N
				II	(C ₆ F ₅)SbCl ₂ .2 Py	175d
IV	(C ₆ F ₅)SbCl ₂ .α Pic	174	67	31.80(31.83)	1.55(1.56)	3.05(3.09)
VI	(C ₆ F ₅)SbCl ₂ .β-Pic	170	69	31.80(31.83)	1.55(1.56)	3.05(3.09)
VIII	(C ₆ F ₅)SbCl ₂ .γ-Pic	175	70	31.80(31.83)	1.55(1.56)	3.05(3.09)
X	(C ₆ F ₅)SbCl ₂ .Ph ₃ AsO	235	69	42.25(42.27)	2.20(2.22)	----
XII	(C ₆ F ₅)SbCl ₂ .Ph ₃ PO	240	72	45.15(45.18)	2.35(2.37)	----
XIV	(C ₆ F ₅)SbCl ₂ .HMPA	180	73	26.73(26.74)	3.35(3.37)	7.78(7.80)
XV	(C ₆ F ₅)SbCl ₂ .2 HMPA	100	69	30.09(30.11)	5.03(5.05)	11.65(11.70)
XVII	(C ₆ F ₅)SbCl ₂ .TU	116	73	19.26(19.29)	0.90(0.93)	6.42(6.43)
XVIII	(C ₆ F ₅)SbCl ₂ .2 TU	152	70	18.75(18.77)	1.55(1.58)	10.90(10.94)

Table 3 Table 3 Molecular weight, conductance measurement of molecular adducts of bis(pentafluorophenyl) antimony(III) chloride and pentafluorophenylantimony(III) dichloride

Compound No.	Molar conductance in acetonitrile (ohm ⁻¹ cm ² mol ⁻¹)	Molecular weight in nitrobenzene found(Calculated)
I	4.6	568.2(570.43)
II	5.8	515.65(517.92)
III	3.2	583.2(584.45)
IV	6	450.65(452.85)
V	5.6	582.2(584.45)
VI	5.8	449.65(452.85)
VII	4.8	581.2(584.45)
VIII	5.9	450.65(452.85)
IX	2.3	812.12(813.56)
X	2.4	679.57(681.95)
XI	3.6	767.2(769.61)
XII	3.6	635.65(638.01)
XIII	4.4	668.2(670.53)
XIV	4.4	536.65(538.92)
XV	3.86	716.65(648.86)
XVI	5.4	568.2(567.45)
XVII	5.6	434.65(435.84)
XVIII	4.6	509.65(511.96)

Table 4 Table 4 IR spectra for (R_n)_nSbCl_{3-n}.mL (cm⁻¹) (n = 2; m = 1, 2

Compound No.	v(Sb-C)	v(Sb-I)/v(Sb-N)	v(C=N)/v(P=O)/(N-H)/(As-O) ligand (complex)
I	357ms	290s	404, 604, 1568
II	460ms	310	404,604,1568(419,618,1585)
V	458ms	289s	419, 621, 1610
IX	444ms	292s	880(840)
XI	445ms	288s	1192(1130)
XII	447ms	316s	1120
XIII	465 ms	292s	1212(1140)
XV	459 ms	315s	1212(1236)
XVI	449 ms	290s	3300(3368)
XVIII	452 ms	310s	3300(3380)

Table 5 Relevant IR frequencies of (pentafluorophenyl)antimony(III) derivatives.

[16] J. W. Dele, H. J. Emeleus, R. N. Haszeldine, J. M. Moss, J. Chem. Soc. (1957) 3708.

R ₂ SbCl	RSbCl ₂	Assignments
220(ms)	221(w)	d, t
290(w)	287(w)	t
341(m)	339(ms)	Sb-Cl
447(w)	451(vw)	γ
560(m)	594(mw)	p
605(m)	607(m)	r
713(m)	715(m)	s
779(m)	780(ms)	v
956(vs)	856(vvs)	q

s = strong; m = medium; w = weak; v = very

6 Conclusions

The replacement of an aryl group (C₆H₅, p-CH₃C₆H₅) by pentafluorophenyl group enhances the Lewis acidity to such an extent as so to facilitate the formation of complexes. These complexes are monomeric and stable to atmospheric moisture and oxygen.

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