

Molecular Adducts of tris(tetrachloropyridyl)antimony(III)chlorides $(C_5Cl_4N)_nSbCl_{3-n}$ with Neutral Monodentate Oxygen, Nitrogen and Sulphur, donors Ligands

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Abstract

Penta & hexa-coordinate neutral adducts $(C_5Cl_4N)_3SbCl.L$ and $(C_5Cl_4N)_3SbCl_2.L$ [L= α , β & γ -picoline, HMPA, Ph_3PO , Ph_3AsO , TU, Py] have been synthesized. Molecular adducts are monomeric in benzene and non-electrolyte in acetonitrile. IR spectra and conductance measurement suggest the presence of co-ordination of Oxygen, Nitrogen, and Sulphur donor ligands in adducts.

Spectroscopic data conform to the requirement of penta coordinate and hexa coordinate configuration for neutral adducts.

Keywords: Tris (Tetrachloropyridyl) Antimony(III) Chloride, Molecular Adducts; Monomeric; Non-Electrolyte; Penta Co-Ordinate and Hexa Co-Ordinate .

Introduction

The Lewis acidity of pentavalent organoantimony compounds, R_nSbX_{3-n} has extensively been investigated in the last two decades by various groups of workers [1]. The studies are not confined to R_2SbCl and $RSbCl_2$ having more chlorine content but has been extended to R_3SbCl_2 derivatives as well. The latter classes of compounds, based on hydrocarbon ligand are not good acceptor, but the introduction of CF_3 and C_6F_5 groups on the metal atom (Sb) considerably enhances the Lewis acidity as evident by the formation of hexaco-ordinate complexes of the type $(CF_3)_2SbCl.L$ and $(C_5Cl_4N)_3SbCl.L$. The synthesis and stereochemistry of penta fluorophenyl antimony(III) dichloride with a number of ligands viz dimethyl formamide, diphenyl formamide, triphenylphosphine oxide, arsine oxide, pyridine, picoline, thiourea has been reported. A tetra and penta-ordinate environment around antimony has tentatively been proposed for such complex. On the basis of analytical and spectroscopic data, it may be noted that except to a single reference on the formation and characterization of $(C_5Cl_4N)_3SbCl.L$ no other study related to the synthesis of molecular adducts has been reported to date [2]. In view of our interest in the chemistry and various aspects of fluoro carbon based organoantimony compounds including their antimicrobial and antitumor activity, developed with the paucity of published data in the field the author considered it worth to synthesis a series of molecular adducts of pentafluorophenyl antimony(III)dichloride triphenyl phosphine oxide, $(C_6F_5)Sb.Ph_3PO$, with oxygen, nitrogen and sulphur donor Lewis bases. A few complexes of $(C_5Cl_4N)_3SbCl$ have also been synthesized for the sake of complexation.

Results and discussion

Under anhydrous oxygen free condition neutral adducts could readily be obtained by the interaction of bis(pentafluorophenyl)antimony (III)chloride obtained by the metathetical reaction of $(C_6H_5)_2SbCl$ and neutral monodentate ligands similar reaction at penta fluorophenyl antimony (III)dichloride with neutral monodentate ligands recrystallized and dried before use, was treated with the desired ligand in equivalent molar ratio in anhydrous ethanol.



Where L = α,β,γ -Picoline, HMPA, triphenylarsenicoxide(Ph_3AsO), triphenylphosphineoxide(Ph_3PO), Thiourea(TU) C_5H_5N (Pyridine; Py)

All the reactions were found to proceed smoothly under mild condition. The completion of the reaction takes place with three hours. In most of the cases products were obtained as solid after evaporation the solvent which were crystallized with petroleum ether (40-60°C) or the mixture of diethyl ether and petroleum ether (60-80°C). 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 repeated crystallization as well as TLC run in polar solvents with a single spot excluded the presence of mixture of reactants. Elemental analysis, conductance and molecular weight data are given in table 2&3 are 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 range between 20-30 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ at room temperature (25°C) which shows the absence of ionic species in solution.

Infra red spectroscopy

All the complexes (listed in table 1) were characterized in the solid state by their infra red spectra in the region $4000\text{-}200\text{cm}^{-1}$. Important IR frequencies for the complexes together with their assignment are listed in table-4. There assignment have been made by comparing the spectra in $4000\text{-}200\text{cm}^{-1}$ region in the solid state of the complexes with these of free ligands.

The IR absorption due to (C_5Cl_4N) group attached to antimony atom are almost identical and do not differ significantly from those observed for pentafluorophenyl (V) compounds earlier [2, 3, 4].

IR spectra of the adducts with Oxygen Donors

An absorption of strong intensity for $\nu(As=O)$ and $\nu(P=O)$ lying at 880 and 1192cm^{-1} respectively, in the spectra of the free ligands undergoes a distinct negative shift on complexation. The corresponding absorption in the spectra of the adducts appears at 835 ± 5 and $1162\pm 5 \text{cm}^{-1}$ suggesting co-ordination from oxygen atom of the bases.

The relative donor abilities of the ligand as apparent from the value of Ph_3AsO/Ph_3PO . On the basis of present and same previous studies a medium strong band in the region $350\text{-}470\text{cm}^{-1}$ is assigned to $\nu(Sb-O)$, stretching frequency.

IR Spectra of adducts with Nitrogen Donors:

The $\nu(CN)$ frequency in $(C_5Cl_4N)_3SbCl_2.Py$ and $(C_5Cl_4N)_3SbCl_2, 3\text{-Pic}$ is seen to decrease significantly to $1610 \pm 5\text{cm}^{-1}$. In addition to this a

bond at $3300 \pm 10 \text{cm}^{-1}$ assignable to $\nu(NH)$ mode in free ligand is shifted to slight lower frequency $3010 \pm 20 \text{cm}^{-1}$ [5]. In the IR spectra of the ligand the assignment of the Sb-N bond is tentatively assigned at about $385 \pm 5 \text{cm}^{-1}$.

IR Spectra of adducts with Sulphur Donors

In sulphur donor ligand (TU) an absorption at 1069cm^{-1} reported to possess equal contribution from $\nu(CN)$ and $\nu(CS)$. This remain unaffected on adduct formation and appears at 1075cm^{-1} . When coordination occurs through sulphur atom, the $\nu(CN)$ suffers a positive shift while the $\nu(CS)$ suffers an almost negative shift. As a consequence to this the resulting absorption remains apparently unchanged [5]. The positive shift of $\nu(NH)$ from 3300cm^{-1} in free ligand to 3375cm^{-1} in its adducts indicates absence of coordination through N atom of the ligand and indirectly suggest $Sb \leftarrow S$ bonding. However on the basis of some previous observation and present studies, the $(Sb \leftarrow S)$ bond is assigned at 380cm^{-1} [5].

As expected, bands associated with antimony chlorine mode move to lower energy on completion e.g. from $340\text{-}320\text{cm}^{-1}$ in $C_6F_5SbCl_2$ to $315\pm 5\text{cm}^{-1}$ is shifted to $290\pm 10 \text{cm}^{-1}$, Sb-C bond appear in the range $450\text{-}470 \text{cm}^{-1}$ [6,7].

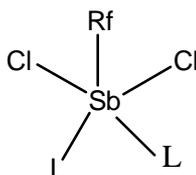
Stereochemistry of neutral molecular adducts $(Rf)_2SbCl.L$ & $(Rf)SbCl_2.2L$

It has been assumed that the addition of Lewis base, L to the central atom in a tetra-coordinate & penta-coordinate molecule takes place in a steric and electrostatic factor play an important role in determining the position of entry of L. It is well established that the more electronegative group goes to the axial position and less electronegative on equatorial positions. Therefore base L should settle in the equatorial position.

In views of the above idea the nucleophilic attack at position between two fluoro groups to produce structure (Fig. 1) appears to be most favorable, since Rf is less electronegative than any halogen atom directly bonded to metal.

Thus analytical, conductance measurement, molecular weight determination and IR data clearly indicates that the newly synthesized complexes have tetra & penta co-ordination environment around antimony with tetrahedral configuration as has been suggested for $R_2SbCl.L$ complexes [5]. It is generally accepted that the tris(tetrachloropyridyl)antimony have a geometry of a tetrahedral.

In adduct formation as indicated, antimony atom increases its coordination number to forth & fifth for penta coordinate complexes. A tentative assignment of tetrahedral structure may be represented as below (Fig. 1).



Experimental

Tris(tetrachloropyridyl)antimony(III)chlorides ($C_5Cl_4N)_3SbCl$ & tris(tetrachloropyridyl)antimony(V)dichloride, $(C_5Cl_4N)_3Sb(Cl)_2$ was prepared by the reported method [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 a Philips magic eye type PR 950 Conductivity Bridge using a dip type conductivity cell. Molecular weight was determined cryoscopically in bromine. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer in the range $4000-200\text{ cm}^{-1}$. 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.

Reaction of $(C_5Cl_4N)_3Sb(Cl)_2$ with DMF Ligand :

In an oxygen free atmosphere a solution of & tris(tetrachloropyridyl)antimony (V) chloride (0.738g, 0.5mmol) in methanol (25cm^3) and DMF (0.0731g, 0.5mmol) in the same solvent (25cm^3) were stirred together at 80°C for 3h. After that it was filtered off. The filtrate on concentration in vacuo yielded a white crystalline solid was recrystallised from petroleum ether ($40^\circ-60^\circ$) to afford & tris(tetrachloropyridyl)antimony (V), dimethyl formamide added $(C_6F_5)_3Sb$ DMF.

Reaction of $(C_5Cl_4N)_3Sb(Cl)_2$ with Ph_3PO Ligand

A solution of tris(tetrachloropyridyl)antimony (V) chloride (0.7388, 0.5 mmol) in methanol (25cm^3) of triphenyl phosphine oxide (0.278g, 0.5mmol) were stirred together at 80°C for three hour under nitrogen. It was filtrate on concentration earlier in vacuo afforded a light brown solid and was recrystallised from solvent ether to give tris(tetrachloropyridyl)antimony (V) triphenyl phosphine oxide adducts.

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Table-1
Preparation, Properties And Elemental Analysis Of Molecular Adducts Of
Tris(Tetrachloropyridyl)Antimony(III)Chlorides

C. No	Adducts/Complexes	Ligand (g) Solvent (ml)	M.P. (°C)	Colours	Found (Calcd)%		
					C	H	N
I	$R_f = (C_5Cl_4N)_3Sb$ $(R_f)_2SbCl.C_5H_5N$	L=Pyridine C_5H_5N (0.079g).EtOH	178	Viscous	35.75(35.78)	0.86(0.88)	2.43(2.46)
II	$(R_f)_2SbCl_2.2.C_5H_5N$	C_5H_5N (0.158g).EtOH	175 ^d	White	37.00(37.09)	1.90(1.93)	5.39(5.41)
III	$(R_f)_2SbCl.\alpha-C_6H_7N$	L=picoline $\alpha-C_6H_7N$ (0.093g).EtOH	179	White	36.95(36.97)	1.18(1.20)	2.37(2.40)
IV	$(R_f)_2SbCl_2.\alpha-C_6H_7N$	$\alpha-C_6H_7N$ (0.093g)EtOH	174	Viscous	31.78(31.81)	1.54(1.55)	3.07(3.09)
V	$(R_f)_2SbCl.\beta-C_6H_7N$	$\beta-C_6H_7N$ (0.093g)EtOH	170	Off White	36.95(36.97)	1.18(1.20)	2.38(2.40)
VI	$(R_f)_2SbCl_2.\beta-C_6H_7N$	$\beta-C_6H_7N$ (0.093g)EtOH	170	Pale Yellow	31.78(31.81)	1.52(1.55)	3.08(3.09)
VII	$(R_f)_2SbCl.\gamma-C_6H_7N$	$\gamma-C_6H_7N$ (0.093g)EtOH	172	White	36.98(36.97)	1.21(1.20)	2.42(2.40)
VIII	$(R_f)_2SbCl_2.\gamma-C_6H_7N$	$\gamma-C_6H_7N$ (0.093g)EtOH	175	White	31.78(31.81)	1.52(1.55)	3.08(3.09)
IX	$(R_f)_2SbCl.Ph_3AsO$	L=Ph₃AsO $(C_6H_5)_3AsO$ (0.322g)EtOH	240 ^d	Off White	44.25(44.27)	1.83(1.84)	-
X	$(R_f)_2SbCl_2.Ph_3AsO$	$(C_6H_5)_3AsO$ (0.322g)EtOH	235	White	42.25(42.26)	2.17(2.20)	-
XI	$(R_f)_2SbCl.Ph_3PO$	L=Ph₃PO $(C_6H_5)_3PO$ (0.278g)EtOH	235	Brown	46.77(46.80)	1.91(1.95)	-
XII	$(R_f)_2SbCl_2.Ph_3PO$	$(C_6H_5)_3PO$ (0.278g)EtOH	240	Light Green	45.15(45.17)	2.33(2.35)	-
XIII	$(R_f)_2SbCl.HMPA$	L=HMPA $[(CH_2N)_3P(O)]$ (0.179g)EtOH	105	Off White	32.20(32.23)	2.67(2.69)	6.24(6.27)
XIV	$(R_f)_2SbCl_2.HMPA$	$[(CH_2N)_3P(O)]$ (0.179g)EtOH	180	White	26.70(26.73)	3.32(3.34)	7.78(7.80)
XV	$(R_f)_2SbCl_2.2HMPA$	$[(CH_2N)_3P(O)]$ (0.358g)EtOH	100	White	30.07(30.09)	5.00(5.02)	11.67(11.70)
XVI	$(R_f)_2SbCl.H_2NCSNH_2$	L=Thiourea.H₂NCSNH₂ H_2NCSNH_2 (0.076g)MeOH	230 ^d	Off White	27.48(27.25)	0.69(0.71)	4.92(4.94)
XVII	$(R_f)_2SbCl_2.H_2NCSNH_2$	H_2NCSNH_2 (0.076g).MeOH	116	White	19.25(19.28)	0.90(0.92)	6.40(6.43)
XIX	$(R_f)_2SbCl_2.2H_2NCSNH_2$	H_2NCSNH_2 (0.152g).MeOH	152	White	18.74(18.76)	1.55(1.56)	10.91(10.94)

Table-2
Molecular Weight, Conductance Measurement And Yield Of Molecular Adducts Of
Tris(Tetrachloropyridyl)Antimony(III)Chlorides

S.No	Adducts /Complexes	Molar conductance (Ohm ⁻¹ cm ² mol ⁻¹) acetonitrile	Molecular weight in nitrobenzene Found (calcd).	Yield	
				g	%
I	(C ₅ Cl ₄ N) ₃ SbCl.C ₅ H ₅ N	4.6	568.2(570.2)	0.339	59
II	(C ₅ Cl ₄ N) ₃ Sb.Cl ₂ .2C ₅ H ₅ N	5.8	515.65 (517.65)	0.321	62
III	(C ₅ Cl ₄ N) ₃ Sb.Cl.α-C ₆ H ₇ N	3.2	583.2(584.2)	0.397	68
IV	(C ₅ Cl ₄ N) ₃ Sb.Cl ₂ .α-C ₆ H ₇ N	6.0	450.65(452.65)	0.303	67
V	(C ₅ Cl ₄ N) ₃ SbCl.β-C ₆ H ₇ N	5.6	582.2(584.2)	0.333	57
VI	(C ₅ Cl ₄ N) ₃ SbCl ₂ .β-C ₆ H ₇ N	5.8	449.65(452.65)	0.312	69
VII	(C ₅ Cl ₄ N) ₃ SbCl ₂ .γ-C ₆ H ₇ N	4.8	581.2(584.2)	0.362	62
VIII	(C ₅ Cl ₄ N) ₃ SbCl ₂ .γ-C ₆ H ₇ N	5.9	450.65(452.65)	0.317	70
IX	(C ₅ Cl ₄ N) ₃ SbCl.(C ₆ H ₅) ₃ AsO	2.3	814.12 (813.12)	0.585	72
X	(C ₅ Cl ₄ N) ₃ SbCl ₂ .(C ₆ H ₅) ₃ AsO	2.4	679.57 (681.57)	0.470	69
XI	(C ₅ Cl ₄ N) ₃ SbCl.Ph ₃ .PO	3.6	767.2(769.2)	0.569	74
XII	(C ₅ Cl ₄ N) ₃ SbCl ₂ .Ph ₃ .PO	3.6	635.65(637.65)	0.259	72
XIII	(C ₅ Cl ₄ N) ₃ SbCl.HMPA	4.4	668.20(670.20)	0.449	67
XIV	(C ₅ Cl ₄ N) ₃ SbCl ₂ .HMPA	4.4	536.65(538.65)	0.392	73
XV	(C ₅ Cl ₄ N) ₃ SbCl ₂ .2HMPA	3.86	716.65(717.65)	0.495	69
XVI	(C ₅ Cl ₄ N) ₃ SbCl.NH ₂ CSNH ₂	5.4	568.20(567.20)	0.420	74
XVII	(C ₅ Cl ₄ N) ₃ SbCl ₂ .NH ₂ CSNH ₂	5.6	434.65(435.65)	0.318	73
XVIII	(C ₅ Cl ₄ N) ₃ SbCl ₂ .2NH ₂ CSNH ₂	4.6	509.65(511.65)	0.358	70

Table-3
INFRARED SPECTRA FOR (Rf)_nSb.Cl_{3-n}. ml.cm⁻¹ [n=1;m=2;n=2;m=1]

Compd. No. (Adduct)	v(Sb-C)	v(Sb-Cl)	v(Sb-I) / (Sb-N)	v(C=N)/v(P-O)/(N-H)/(As-O) ligand (complex)
I	357ms	290ms	370w	404,604,1568
II	460ms	310	381w	404,604,1568 (419,618,1585)
V	458ms	289s	386w	419,621,1610
IX	444ms	292s	390w	880(840)
XI	445ms	288s	419w	1192(1130)
XII	447ms	316s	415w	1120
XIII	465ms	292s	424w	1212(1140)
XV	459ms	315s	432w	1212(1136)
XVI	449ms	290s	-	3300(3368)
XVIII	452ms	310s	-	3300(3380)

w = weak, ms = medium strong, s = strong

References

1. Ashvin Kumar Aggarwal PhD Thesis: Studies on organo-antimony (III) and antimony (V) derivatives, Lucknow University, Lucknow, India (1990).
2. Prem Raj, A.K. Aggarwal, A.K. Saxena, J. Fluorine. Chem. 42(1989) 163-172.
3. A. Otero, P.Royo, J. Organomet. Chem. 154 (1978) 13-19.
4. B.A.Nevett, A.Perry, Spectrochem. Acta.A.31 (1975) 101-106.
5. Prem Raj, N.Mishra, Indian Journal of chemistry 30A(1991) 901-903.
6. M.Hall, D.B.Sowerby, J.Organometallic chemistry, 347 (1988) 59-70; W.S.Sheldrick, C.Matrin, Z.Natureforsch, Teli B46 (1991) 639-646.
7. M.Nunn, M.J.Begley, D.B.Sowerby, Polyhedron 15 (1996) 3167-3174.
8. Prem Raj, A.K.Saxena, K.Singhal, A.Ranjan, Polyhedron 4(1985) 251-258.
9. M.Fild, O.Glemser, G.Christoph, Angew.Chem 76(1964) 953.
10. Ashok Ranjan, PhD Thesis, Synthesis and reactivity of some non-transitional organometallic compounds, Lucknow University, Lucknow.