

On the molecular adducts of tris(pentafluorophenyl)antimony(V) diisothiocyanate with neutral monodentate ligands

Dharmendra K. Srivastava, Ram Nath Prasad Yadav, Prem Raj, Isha Rizvi, Prof. Amarika Singh

Abstract- Hexa-coordinated neutral adducts $(C_6F_5)_3Sb(NCS)_2 \cdot L$ [L = DPF, α -Pic., β -Pic., γ -Pic., DMF, Ph_3AsO , Ph_3PO , DMSO, 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 coordination of O, N and S donor ligands in adduct. Spectroscopic data conform to the requirement of octahedral configuration for these neutral adducts.

Keywords— Molecular adducts, monomeric, metathetical, nonelectrolyte, neutral ligand, octahedral, tris(pentafluorophenyl)antimony(V) diisothiocyanate.

1 INTRODUCTION

The Lewis acidity of pentavalent organoantimony compounds, R_nSbX_{5-n} has extensively been investigated in the last two decades by various groups of workers. The studied 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 latter classes of compounds based on hydrocarbon ligand are not good acceptor but the introduction of CF_3 and C_6F_5 groups on to the metal atom (Sb) considerably enhances the Lewis acidity as evident by the formation of hexacoordinated complexes of the type $(CF_3)_3SbCl_2 \cdot L$ and $(C_6F_5)_3SbCl_2 \cdot L$. The synthesis and stereochemistry of tris(pentafluorophenyl)antimony(V) dichloride with a number of ligands viz. dimethyl formamide(DMF), diphenyl formamide (DPF), picoline (α -Pic., β -Pic., γ -Pic.), triphenylarsine oxide (Ph_3AsO), triphenyl phosphine oxide (Ph_3PO), dimethyl sulphoxide (DMSO), thiourea (TU), pyridine (Py) has been reported [1]. 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 to a single reference on the formation and characterisation of $(C_6F_5)_3SbCl_2 \cdot L$ no other study related to the synthesis of molecular adducts has been reported to date [1]. In view of our interest in the chemistry and various aspect of fluorocarbon based organoantimony compounds including their antimicrobial and antitumor activity, coupled with the paucity of published data in the field, the author considered it worth to synthesize a series of molecular

-adducts of tris (pentafluorophenyl) antimony (V)

-diisothiocyanate, $(C_6F_5)_3Sb(NCS)_2$ with oxygen, nitrogen and sulphur donor Lewis bases. A few complexes of $(C_6F_5)_3SbCl_2$ have also been synthesized for the sake of comparison.

2 RESULTS AND DISCUSSION

Tris(pentafluorophenyl)antimony(V) diisothiocyanate obtained by the metathetical reaction of tris(pentafluorophenyl)antimony(III) dichloride, $(C_6F_5)_3SbCl_2$ and potassium thiocyanate, KNCS, recrystallized and dried before use, was treated with the desired ligand in equimolar ratio in anhydrous methanol. The reactions were carried out under anhydrous oxygen free conditions.

All the reactions were found to proceed smoothly under mild conditions. The completion of reactions takes place within 3h. In most of the cases products were obtained as solid after evaporating 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 solvents 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 reactant.

Elemental analysis, conductance and molecular weight data are given in table 1 and 2 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 10-3M solution in acetonitrile ranges between 20-30 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ at the room temperature (30°C) which shows the absence of ionic species in solution.

3 IR Spectroscopy

The entire complexes (listed in Table 1) were characterized in the solid state by their IR spectra in the region 4000-200 cm^{-1} . Important IR frequencies for the complexes together with their assignment are listed in Table-3. These assignments have been

- Author name is Dharmendra K. Srivastava; he is about to submission of Ph. D. thesis in Organometallic Chemistry at Chemistry Department, Lucknow University, India, E-mail:dharmendra.srivastava007@gmail.com.
- Co-Author name is Isha Rizvi, currently pursuing Ph. D. from Institute of Engineering & Technology, Constituent College of G. B. T. U., Sitapur Road Lucknow, India.

made by comparing the spectra in 4000-200 cm^{-1} region in the solid state of complexes with those of free ligands. The IR absorption due to C_6F_5 group attached to antimony atom are almost identical and do not differ significantly from those observed for pentafluorophenyl (V) compounds earlier [2], [3], [4].

3.1 IR spectra of the adducts with oxygen donors

The $\nu(\text{C}=\text{O})$ modes in various amides bases appearing at 1650 ± 15 cm^{-1} undergo negative shift and are identified at 1608 ± 10 cm^{-1} in the spectra of adducts suggesting weakening of $\text{C}=\text{O}$ bond and coordination through the oxygen atom of the base. On the basis of $-\Delta \nu(\text{CO})$, the DPF was found better donors as compared to DMF [5].

An absorption of strong intensity for $\nu(\text{S}=\text{O})$, $\nu(\text{As}=\text{O})$ and $\nu(\text{P}=\text{O})$ lying at 1045, 880 and 1195 cm^{-1} respectively, in the spectra of free ligands undergoes a distinct negative shift on complexation. The corresponding absorption in the spectra of adduct appear at 940, 835 and 1162 cm^{-1} suggesting coordination from oxygen atom of the base.

The relative donor ability of the ligand as apparent from the values of $-\Delta \nu(\text{C}=\text{O})$, follow the sequence $\text{DMSO} > \text{Ph}_3\text{AsO} > \text{Ph}_3\text{PO}$. On the basis of present and some previous studies a medium strong band in the region 380-410 cm^{-1} is assigned to $\nu(\text{Sb}-\text{O})$ stretching frequency [5].

3.2 IR spectra of the adducts with nitrogen donors

The $\nu(\text{CN})$ frequency in $(\text{C}_6\text{F}_5)_3\text{Sb}(\text{NCS})_2\cdot\text{Py}$ and $(\text{C}_6\text{F}_5)_3\text{Sb}(\text{NCS})_2\cdot\text{Pic}$ is seen to decrease significantly to 1610 ± 5 cm^{-1} . In addition to this a band at 3310 ± 10 cm^{-1} assignable to $\nu(\text{NH})$ mode in free ligand is shifted to slight lower frequency 3310 ± 20 cm^{-1} [5]. In the free IR spectra of ligand the assignment of the $\text{Sb}-\text{N}$ bond is tentatively assigned at about 385 ± 5 cm^{-1} .

3.3 IR spectra of the adducts with sulphur donors

In sulphur donor ligands (TU) absorption at 1069 cm^{-1} reported to possess equal contribution from $\nu(\text{CN})$ and $\nu(\text{CS})$. These remains unaffected on adduct formation and appear at 1075 cm^{-1} . When coordination occurs through sulphur atom, the $\nu(\text{CN})$ suffers a positive shift while $\nu(\text{CS})$ suffers an almost equal negative shift. As a consequence to this resulting absorption remains apparently unchanged [5]. The positive shift of $\nu(\text{NH})$ from 3360 cm^{-1} and 3300 cm^{-1} in free ligand to 3410 and 3370 cm^{-1} in its adducts indicates absence of coordination through N atom of the ligand and indirectly suggest $\text{Sb} \leftarrow \text{S}$ bonding.

However on the basis of some previous observation and present studies, the $\text{Sb} \leftarrow \text{S}$ bond is assigned at 380 cm^{-1} [5]. The diagnostic frequencies due to NCS group bound to antimony appears around at 2080, 840 and 475 cm^{-1} which could be attributed to asymmetric (NCS), symmetric(C-S) and bending modes NCS respectively. The pattern and intensity does not show any significant change reported earlier for $(\text{C}_6\text{F}_5)_3\text{Sb}(\text{NCS})_2$ compounds [8]. $\text{Sb}-\text{C}$ bond appear in the range 445-465 cm^{-1} [6], [7].

3.4 Stereochemistry of neutral molecular adducts $(\text{C}_6\text{F}_5)_3\text{Sb}(\text{NCS})_2\cdot\text{L}$

It has been assumed that the addition of Lewis base L, to the central atom in a trigonal bipyramidal molecule acquire a trigonal plane and steric and electrostatic factor play an im-

portant 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 should settle in the equatorial position. It is also supported by a tentative assignment of $\text{Sb}-\text{N}$ bond at 326 cm^{-1} appearing in all the spectra and attributed to NCS present in axial position. In view of the above idea the nucleophilic attack at the 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 hexacoordination environment around antimony with octahedral configuration as has been suggested for $\text{R}_2\text{SbCl}_3\cdot\text{L}$ complexes [5]. It is generally accepted that the tris(pentafluorophenyl)antimony(V) diisothiocyanate have a geometry of a trigonal bipyramidal with two thiocyanate group occupying axial position. In adduct formation as indicated number to six for hexacoordinated complex. A tentative assignment of octahedral structure may be represented as in figure 1.

4 EXPERIMENTAL

Tris(pentafluorophenyl)antimony(V) dichloride, $(\text{C}_6\text{F}_5)_3\text{SbCl}_2$ and tris(pentafluorophenyl)antimony(V) diisothiocyanate, $(\text{C}_6\text{F}_5)_3\text{Sb}(\text{NCS})_2$ 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.

4.1 Reaction of $(\text{C}_6\text{F}_5)_3\text{Sb}(\text{NCS})_2$ with DMF ligand

In an oxygen free atmosphere a solution of tris(pentafluorophenyl)antimony(V) diisothiocyanate (0.738 g, 0.5 mmol) in methanol (25 cm^3) and DMF (0.0731 g, 0.5 mmol) in the same solvent (25 cm^3) were stirred together at 80°C for 3 h. After that it was filtered off. The filtrate on concentration in vacuo yielded a white crystalline solid was recrystallised from petroleum ether (40-60°C) to afford tris(pentafluorophenyl)antimony(V) diisothiocyanate- dimethyl formamide adduct, $(\text{C}_6\text{F}_5)_3\text{Sb}(\text{NCS})_2\cdot\text{DMF}$.

4.2 Reaction of $(\text{C}_6\text{F}_5)_3\text{Sb}(\text{NCS})_2$ with Ph_3PO ligand

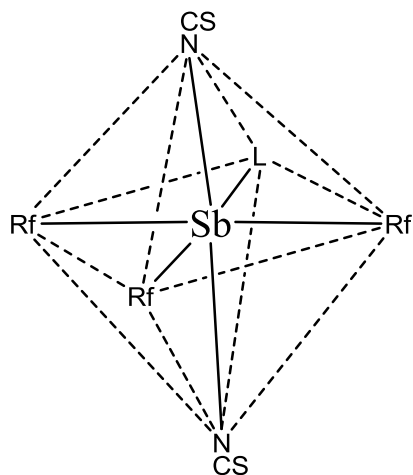
A solution of tris(pentafluorophenyl)antimony(V) diisothiocyanate (0.738 g, 0.5 mmol) in methanol (25 cm^3) and a solution of the same solvent (25 cm^3) of triphenylphosphine oxide (0.278 g, 0.5mmol) were stirred together at 80°C for 3 h under nitrogen. It was filtered off and the filtrate on concentration in

vacuo afforded a light brown solid and was recrystallized from solvent ether to give tris(pentafluorophenyl)antimony(V) diisothiocyanate-triphenylphosphine adduct.

Molecular weight, conductance measurements of molecular adducts of tris(pentafluorophenyl)antimony(V) diisothiocyanate adducts

5 FIGURES & TABLES

Figure 1 showing octahedral disposition of groups around antimony.



Where Rf = $-C_6F_5$, L= Neutral Ligand

TABLE 1

Analytical data for tris(pentafluorophenyl)antimony(V) diisothiocyanate neutral adducts

S.No.	Adducts $R_f=C_6F_5$	mp(°C)	Yield (%)	Analysis: Found (Calculated :%)		
				C	H	N
I	$(R_f)_3Sb(NCS)_2.DPF$	195	64	37.34(37.35)	1.72(1.74)	4.83(4.84)
II	$(R_f)_3Sb(NCS)_2.\alpha Pic$	204	69	37.50(37.52)	0.82(0.85)	5.03(5.05)
III	$(R_f)_3Sb(NCS)_2.\beta Pic$	170	70	37.50(37.52)	0.82(0.85)	5.03(5.05)
IV	$(R_f)_3Sb(NCS)_2.\gamma Pic$	188	71	37.50(37.52)	0.82(0.85)	5.03(5.05)
V	$(R_f)_3Sb(NCS)_2.DMF$	197	66	34.00(34.01)	0.85(0.87)	5.15(5.17)
VI	$(R_f)_3Sb(NCS)_2.Ph_3PO$	200	56	46.25(46.27)	1.50(1.53)	2.82(2.84)
VII	$(R_f)_3Sb(NCS)_2.Ph_3AsO$	165	57	42.85(43.00)	1.40(1.42)	2.62(2.64)
VIII	$(R_f)_3Sb(NCS)_2.DMSO$	180	69	32.30(32.33)	0.73(0.74)	3.40(3.43)
IX	$(R_f)_3Sb(NCS)_2.TU$	183	71	30.92(30.94)	0.45(0.49)	6.85(6.87)
X	$(R_f)_3Sb(NCS)_2.Py$	207	72	36.68(36.70)	0.60(0.62)	5.12(5.14)

TABLE 2

S. No.	Complex(Adducts)	Molar conductance	Molecular weight in nitrobenzene
	$R_f=C_6F_5$	(ohm ⁻¹ cm ² mol ⁻¹)	Found(Calculated)
In acetonitrile			
I	$(R_f)_3Sb(NCS)_2.HCON(C_3H_7)_2$	20.6	865.70(868.29)
II	$(R_f)_3Sb(NCS)_2.\alpha-C_6H_7N$	22.2	825.75(832.22)
III	$(R_f)_3Sb(NCS)_2.\beta-C_6H_7N$	22.3	825.75(832.22)
IV	$(R_f)_3Sb(NCS)_2.\gamma-C_6H_7N$	22.7	825.75(832.22)
V	$(R_f)_3Sb(NCS)_2.HCON(CH_3)_2$	28.9	805.10(812.19)
VI	$(R_f)_3Sb(NCS)_2.(C_6H_5)_3PO$	25.2	1014.75(986.40)
VII	$(R_f)_3Sb(NCS)_2.(C_6H_5)_3AsO$	24.4	1069.60(1061.33)
VIII	$(R_f)_3Sb(NCS)_2.(CH_3)_2SO$	27.6	812.75(817.23)
IX	$(R_f)_3Sb(NCS)_2.NH_2CSNH_2$	30.8	813.75(815.21)
X	$(R_f)_3Sb(NCS)_2.C_5H_5N$	29.9	815(818.19)

TABLE 3 IR spectra for $(R_f)_3Sb(NCS)_2.mL$ (cm⁻¹)

S. No.	$\nu(\text{Sb-C})$	$\nu(\text{Sb-S})/\nu(\text{Sb-O})/\nu(\text{Sb-N})$	$\nu(\text{C=N})/(\text{S=O})/\nu(\text{P-O})/(\text{N-H})/(\text{As-O})$
Ligand complex			
I	458ms	385ms	1660(1612)
II	461ms	382	1615
III	458ms	384w	1612
IV	445ms	320w	1610
V	447ms	395ms	1660(1615)
VI	465ms	405ms	1195(1162)
VII	459ms	390ms	880(835)
VIII	450ms	380ms	1045(940)
IX	455ms	382ms	3300(3368)
X	459ms	381ms	1612

CONCLUSION

The replacement of aryl group (C_6H_5 , $p-CH_3C_6H_5$) from $(C_6H_5)_3SbCl_2$ by pentafluorophenyl group enhances the Lewis acidity to such an extent as so to facilitate the formation of complexes but replacement of chloride by thiocyanate group permit only one ligand to attach with antimony atom due to high electron density & steric factor. These complexes are monomeric and stable to atmospheric moisture and oxygen.

ACKNOWLEDGMENT

The author is thankful to the Head, Chemistry Department, Lucknow University & I. E. T., Constituent college of G. B. T. U. ,Lucknow for providing necessary laboratory facilities, and special thanks to Ram Nath Prasad Yadav who previously done this work but not previously published in any journal, which was further reinvestigated and extended by author.

REFERENCES

- [1] Isha Rizvi, Amarika Singh, N. Singh, Dharmendra K. Srivastava, International Journal of Scientific & Engineering Research, V-3, Issue-5, May-2012.
- [2] Ashvin Kumar Aggarwal Ph. D. Thesis: Studies on organo-antimony(III) and antimony(V) derivatives, Lucknow University, Lucknow, India (1990).
- [3] Prem Raj, A. K. Aggarwal, A. K. Saxena, J. Fluorine. Chem. 42 (1989) 163-172.
- [4] A. Otero, P. Royo, J. Organomet. Chem. 154 (1978) 13-19.
- [5] B. A. Nevett, A. Perry, Spectrochim. Acta. A 31 (1975) 101-106.
- [6] Prem Raj, N. Misra, Ind. J. Chem., 30A (1991) 901-903.
- [7] M. Hall, D. B. Sowerby, J. Organomet. Chem. 347 (1988) 59-70; W. S. Sheldrick, C. Martin, Z. Natureforsch Teli B 46 (1991) 639-646.
- [8] M. Nunn, M. J. Begley, D. B. Sowerby, Polyhedron 15 (1996) 3167-3174.
- [9] Prem Raj, A. K. Saxena, K. Singhal, A. Ranjan Polyhedron 4 (1985) 251-258.
- [10] M. Fild, O. Glemser, G. Christoph, Angew. Chem. 76 (1964) 953.
- [11] Ashok Ranjan, Ph. D. Thesis: Synthesis and reactivity of some non-transitional Organometallic compounds, Lucknow University, Lucknow (1984).