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SYNTHESIS, CHARACTERISATION AND REACTIONS OF CATIONIC COMPLEXES OF ARYLANTIMONY(III) CHLORIDES $\text{Ar}_n\text{SbCl}_{3-n}$ WITH PERCHLORATE AND TETRAFLUOROBORATE ANIONS

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Abstract

Several hitherto unreported cationic complexes of the general formula $[\text{Ar}_2\text{SbL}][\text{Y}]$ and $[\text{ArSbL}_2][\text{Y}]_2$ [ Where, $\text{Ar} = \text{C}_6\text{H}_5$, $\text{L} = \alpha\text{-Picoline, Pyridine, Ph}_3\text{AsO, hexamethyl phosphoramide (HMPA), thiourea (TU) and Y} = \text{ClO}_4^-\text{- BF}_4^-$ ] have been synthesized and characterized by solid state IR, $^1\text{H}$ NMR, elemental analysis, conductance and molecular weight measurements. The physicochemical data, cations $[\text{Ar}_2\text{SbL}]^{+1}$ and $[\text{ArSbL}_2]^{+2}$ are assigned a pyramidal structure.

Key words: Arylantimony(III) chloride, Cationic complex, IR spectra, Elemental analysis, Molecular weight measurement, Perchlorate, Tetrafluoroborate.

Introduction

There has been a considerable interest centered around the chemistry of organoantimony(III) halides over the past two decades. As a result a variety of parent, $\text{SbPh}_n\text{X}_{3-n}$ ($n = 1, 2$) compounds where $\text{X} = \text{halides, imide, heterocyclic species, xanthates, thiophosphate, carboxylate}$ have been synthesized and studied (Premraj et al. 1989a, Premraj et al. 1989b and Pandey 2001). Anionic complexes of pentfluorophenylantimony(III) chloride have been synthesized (Yadav 2012). Lewis acidity of $\text{SbPh}_n\text{X}_{3-n}$ ($\text{X} = \text{halide}$) towards monodentate and bidentate neutral $\text{O, N, and S}$ donors and electronegatively charged donors has been investigated (Hall & Sowerby 1986 and Nunn et al. 1996). Apart from synthetic utility they have aroused interest due to their antitumour activity (Yadav 2012). A perusal of literature reveals that the existence and isolation of solid salts of complex cations of the type $[\text{RSbL}_1]^{+3}$ and $[\text{RSbL}_2]^{+2}$ are well documented (Nishi & Okawara 1972, Jha & Joshi 1984, Saxena et al. 1990, Premraj et al 1992, Singhal et al. 2003 and Singhal et al. 2004).

In the present communication we report the synthesis and reactions of two series of cationic complexes of the type $[\text{Ar}_2\text{SbL}][\text{Y}]$ and $[\text{ArSbL}_2][\text{Y}]_2$ where, $\text{Ar} = \text{Phenyl and L} = \alpha\text{-picoline, pyridine, Ph}_3\text{AsO, HMPA and TU}$. Solid state IR spectra and solution state $^1\text{H}$ NMR spectra added by some other solution phase studies have been carried out to characterize and elucidate the structure of newly synthesized compounds.

Result and Discussion

Under unhydrous oxygen free conditions, arylantimony(III) cationic complexes of the type $[\text{Ar}_n\text{SbL}_{3-n}][\text{Y}]_{3-n}$ can readily be obtained by the intraction of performed solution of arylantimony(III) chlorides, neutral monodentate ligand and silver and sodium salt of the anion in appropriate stoichiometry as shown below:
An infrared spectrum for all the compounds was recorded in the range 4000-400 cm$^{-1}$ and the conductance values are listed in Table-3.

5, 13, 14, 16, 17, 18) reported values of the 1:1 electrolytes in the solution.

The conductance values are listed in Table-3. The consistency in melting points after repeated crystallization as well as mixed melting points rules out the possibility of the presence of unreacted reactants. The analytical data given in table 1–3 correspond well to the proposed formulation of the complexes. Conductance measurements values of 10$^{-2}$ M solutions in acetonitrile for the complexes (1, 2, 5, 13, 14, 16, 17, 18) are in good agreement with the reported values of the 1:1 electrolytes in the solution. The conductance values are listed in Table-3.

**IR spectra**

An infrared spectrum for all the compounds was recorded in the range 4000-400 cm$^{-1}$ in KBr or CsI pellets. The absorption frequencies inherent to phenyl groups are in close proximity reported for Ph$_3$SbCl and PhSbCl$_2$ (Hall & Sowerby 1986, Pandey 2001 and Singhal et al. 2003) and hence not discussed and tabulated. Diagnostic frequencies associated with ligands and characteristic anionic frequencies have been identified and discussed below.

Both pyridine and $\alpha$-picoline exhibit characteristic vibration v(C=N), appearing in the range 1565-1580 cm$^{-1}$ in free ligands, undergoes a positive shift of (1590-1610 cm$^{-1}$) suggesting coordination through nitrogen atom of the base (Premraj & Agarwal 1992 and Premraj et al. 1992).

In the case of TPAO (triphenyl arsenic oxide), the characteristics v(As-O), vibration is lowered in case of each complex as compared to its position in free ligand (880 cm$^{-1}$) and is shifted to 830-845 cm$^{-1}$ (Premraj & Agarwal 1992 and Premraj et al. 1992).

The diagnostic v(P=O) vibration appearing at 1212 cm$^{-1}$ in case of HMPA is considerably lowered 1130-1145 cm$^{-1}$ on complexation. This lowering clearly, suggest coordination through nitrogen atom of the base (Premraj et al. 1989, Premraj & Agarwal 1992, Premraj et al. 1992 and Pandey 2001).

In case of thiourea a band of strong intensity appearing of 1045 ± 24 has been attributed to possess contribution from v(C=N) and v(C=S) modea. After complexation, v(C=N) exhibit a positive shift if the coordination takes place through the sulphur atom, while v(C=S) undergoes almost an equal negative shift. The resulting spectra of the complexes, therefore do not exhibit any peculiar change on coordination through sulphur atom and the resulting absorption remains apparently unchanged. The positive shift of v(N-H) from 3300 cm$^{-1}$ in free thiourea to ~ 3370-3380 cm$^{-1}$ in the complexes is suggestive coordination through nitrogen atom of the ligand (Premraj & Mishra 1991).

The v(Sb-O) was found in the range 415-435 cm$^{-1}$ and is consistent with the earlier made assignment for complex having Sb-O linkage.

Due to the complexity of the spectra as well as limitation below 400 cm$^{-1}$, (Sb-N) stretching could not be assigned with certainty, v(Sb-N) band has reported to appear in the range 350-370 cm$^{-1}$.

The v(Sb-N) stretching corresponding to ‘Y’ mode of the phenyl group appear in the range 445-470 cm$^{-1}$.

The characteristic vibration due to BF$_4^-$ and ClO$_4^-$ do not show any significant shifting as compared to free anions vibration and given in Table – 4.

**$^1$H NMR Spectra**

The $^1$H NMR spectra of two representative compound (13 & 14) showed singlet at 2.46 and 2.58 (due to methyl group) and multiplets for phenyl protons centered at $\delta$ 7.80 ppm, $\delta$ 7.25 ppm and $\delta$ 7.08 ppm of which the former (lower field multiplet) is attributed to ortho and the latter two (high field multiplet) are attributed to meta and para protons of phenyl groups.

Thus on the basis of IR, $^1$H NMR spectra, molar conductance and molecular weight measurement, the newly synthesised complex cation are assigned a pyramidal structure as shown below:

\[
\begin{align*}
\text{Ar}_2\text{SbCl} + \text{AgY}/\text{NaY} & \rightarrow [\text{Ar}_2\text{SbL}][\text{Y}] + \text{AgCl}/\text{NaCl} \\
\text{ArSbCl}_2 + 2\text{L} + 2\text{Na} (\text{or Ag}) \text{Y} & \rightarrow [\text{ArSbL}_2][\text{Y}]_2 + 2\text{NaCl}
\end{align*}
\]

Where, Ar = C$_6$H$_5$; L = $\alpha$-Picoline, Pyridine, Ph$_3$AsO, HMPA, TU; Y = ClO$_4^-$-BF$_4^-$

\[
\begin{align*}
\text{Ar}_2\text{SbCl} + \text{AgY}/\text{NaY} & \rightarrow [\text{Ar}_2\text{SbL}][\text{Y}] + \text{AgCl}/\text{NaCl} \\
\text{ArSbCl}_2 + 2\text{L} + 2\text{Na} (\text{or Ag}) \text{Y} & \rightarrow [\text{ArSbL}_2][\text{Y}]_2 + 2\text{NaCl}
\end{align*}
\]
Experimental

Diarylantimony(III) chloride, \( \text{Ar}_2\text{SbCl} \) and arylantimony(III) chlorides, \( (\text{ArSbCl}_2) \) were prepared by the addition of antimony trichloride to triphenylantimony. Anhydrous silver perchlorate was prepared by the standard procedure. Sodium tetrafluoroborate (Lobacheme) was used as such. All the ligands were of reagent grade and used without further purification. The solvents were purified dried before use. All manipulations were conducted in an atmosphere of nitrogen and stringent precautions were taken to moisture.

The melting points of the compounds were determined on the electrically operated melting point apparatus (M/s Toshniwal and Bros, Mumbai India).

The stoichiometry of the compound was established by elemental analysis. Percentage of C, H, and N the compounds was obtained on a semi-microscale (using elemental analyser Carlo Eaba 1106, Thomas CH analyser and Coleman N analyser). Conductivity data were obtained in nitrobenzene with help of a Philips magic eye type PR 950 conductivity bridge using a dip type conductivity cell. IR spectra were recorded on a Perkin Elmer 577 spectrophotometer in the range 4000-200 \( \text{cm}^{-1} \) in KBr or CsI pellets. \(^1\text{H} \) NMR spectra in CDCl\(_3\) solution were determined on a Varian EM – 360 L spectrometer using TMS as an internal standard. Molecular weights data in benzene and nitrobenzene soluble compounds were determined cryoscopically in freezing benzene or nitrobenzene using a Beckman thermometer of accuracy \( \pm 0.01^\circ \text{C} \). Typical experimental details of the few reactions are described below. Relevant IR assignments, \(^1\text{H} \) NMR spectra, analytical data and molar conductance values are listed in table 1-4.

**Reaction of Dphenylantimony(III) Chloride with \( \alpha \)-picoline and Silver Perchlorate \([\text{Ph}_2\text{Sb}(\alpha\text{-pic})]\text{ClO}_4 \) (1)**

In an oxygen free environment diphenylantimony(III) chloride (0.311 g, 1 mmol) and neutral ligand \( \alpha \)-picoline (0.093 g, 1 mmol) was taken in dry chloroform and silver perchlorate (0.207 g, 1 mmol) in dry methanol was added to this solution. After stirring the mixture for about 6 h; it was refluxed for 2 h and AgCl formed as a white precipitate was filtered off. The filtrate on concentration in \textit{vacuo} afforded a white solid which was crystallized from petroleum ether (40-60 \( ^\circ \text{C} \)). \( \text{M.P.: 160}^\circ \text{C, Yield: 0.290 g, (62%)}. \)

**Reaction of Phenylantimony(III) Dichloride with \( \alpha \)-picoline and Sodium Tetrafluoroborate \([\text{PhSb}(\alpha\text{-pic})][\text{BF}_4]_2 \) (4)**

Phenylandantimony(III) dichloride (0.270 g, 1 mmol) and neutral ligand \( \alpha \)-picoline (0.186 g, 2 mmol) were taken in dry chloroform and sodium tetrafluoroborate (0.220 g, 2 mmol) in dry methanol was added to this solution. After stirring the mixture for about 5 h, it was then refluxed for 3 h and NaCl so formed as precipitate was filtered off. The filtrate on concentration in \textit{vacuo}, afforded a light orange solid which was crystallized from petroleum ether (40-60\( ^\circ \text{C} \)). \( \text{M.P.: 188}^\circ \text{C, Yield: 0.419 g (75%)}. \)
| C. No. | Complexes                  | Ar₂SbCl₃ₓ(α) (g) n=1 & 2 Ag/Na Y (g) (solvent) | Ligand (g) (solvent) | M.P. (°C) | Colour |
|-------|---------------------------|---------------------------------------------|----------------------|-----------|--------|
| 1.    | L=α-picoline              | Ph₂SbCl (0.311g) (CHCl₃)                   | AgClO₄ (0.207g) (MeOH) | α-Picoline (0.093g) (CHCl₃) | 160     | White  |
| 2.    | [Ph₂SbL] [BF₄]           | Ph₂SbCl (0.311g) (CHCl₃)                   | NaBF₄ (0.110g) (MeOH) | α-Picoline (0.093g) (CHCl₃) | 90      | Off white |
| 3.    | [PhSbL₂] [ClO₄]₂         | PhSbCl₂ (0.270g) (CHCl₃)                   | AgClO₄ (0.415g) (MeOH) | α-Picoline (0.186g) (CHCl₃) | 185     | White  |
| 4.    | [PhSbL₂] [BF₄]₂          | PhSbCl₂ (0.270g) (CHCl₃)                   | NaBF₄ (0.220g) (MeOH) | α-Picoline (0.186g) (CHCl₃) | 188     | Light orange |
| 5.    | L=Pyridine                | Ph₂SbCl (0.311g) (CHCl₃)                   | AgClO₄ (0.207 g) (MeOH) | C₅H₅N (0.079 g) (CHCl₃) | 143     | White  |
| 6.    | [Ph₂SbL] [BF₄]           | Ph₂SbCl (0.311g) (CHCl₃)                   | NaBF₄ (0.110g) (MeOH) | C₅H₅N (0.079 g) (CHCl₃) | 189     | Cream  |
| 7.    | [PhSbL₂] [ClO₄]₂         | PhSbCl₂ (0.270g) (CHCl₃)                   | AgClO₄ (0.415 g) (MeOH) | C₅H₅N (0.158 g) (CHCl₃) | 190     | White  |
| 8.    | [PhSbL₂] [BF₄]₂          | PhSbCl₂ (0.311g) (CHCl₃)                   | NaBF₄ (0.220g) (MeOH) | C₅H₅N (0.158 g) (CHCl₃) | 168     | Cream  |
| 9.    | L=Ph₃AsO                  | Ph₂SbCl (0.311g) (CHCl₃)                   | AgClO₄ (0.207 g) (MeOH) | Ph₃AsO (0.322g) (MeOH) | 180     | White  |
| 10.   | [Ph₂SbL] [BF₄]           | Ph₂SbCl (0.311g) (CHCl₃)                   | NaBF₄ (0.110g) (MeOH) | Ph₃AsO (0.322g) (MeOH) | 175     | White  |
| 11.   | [PhSbL₂] [ClO₄]₂         | PhSbCl₂ (0.270g) (CHCl₃)                   | AgClO₄ (0.415 g) (MeOH) | Ph₃AsO (0.644g) (MeOH) | 185     | White  |
| 12.   | [PhSbL₂] [BF₄]₂          | PhSbCl₂ (0.270g)(CHCl₃)                    | NaBF₄ (0.220g) (MeOH) | Ph₃AsO (0.644g) (MeOH) | 190     | White  |
| 13.   | [Ph₂SbL] [ClO₄]           | Ph₂SbCl (0.311g) (CHCl₃)                   | AgClO₄ (0.207 g) (MeOH) | HMPA (0.179 g) (MeOH) | 192     | White  |
| 14.   | [Ph₂SbL] [BF₄]           | Ph₂SbCl (0.311g) (CHCl₃)                   | NaBF₄ (0.110 g) (MeOH) | HMPA (0.179 g) (MeOH) | 95      | White  |
| 15.   | [PhSbL₂] [ClO₄]₂         | PhSbCl₂ (0.270g) (CHCl₃)                   | AgClO₄ (0.415 g) (MeOH) | HMPA (0.358 g) (MeOH) | 182     | White  |
| 16.   | [PhSbL₂] [BF₄]₂          | PhSbCl₂ (0.270g) (CHCl₃)                   | NaBF₄ (0.220g) (MeOH) | HMPA (0.358 g) (MeOH) | 177     | White  |
| 17.   | L=Thiourea                | Ph₂SbCl (0.311g) (CHCl₃)                   | AgClO₄ (0.207 g) (MeOH) | H₂NCSNH₂ (0.076g) (CHCl₃) | 174     | Yellow |
| 18.   | [Ph₂SbL] [BF₄]           | Ph₂SbCl (0.311g) (CHCl₃)                   | NaBF₄ (0.110 g) (MeOH) | H₂NCSNH₂ (0.076g) (CHCl₃) | 170     | White  |
| 19.   | [PhSbL₂] [ClO₄]₂         | PhSbCl₂ (0.270g) (CHCl₃)                   | AgClO₄ (0.415 g) (MeOH) | H₂NCSNH₂ (0.152g) (CHCl₃) | 182     | White  |
| 20.   | [PhSbL₂] [BF₄]₂          | PhSbCl₂ (0.270g) (CHCl₃)                   | NaBF₄ (0.220g) (MeOH) | H₂NCSNH₂ (0.152g) (CHCl₃) | 190     | White  |
Table 2: Elemental analysis of Arylantimony(III) cationic complexes

| No. | Complexes                        | Empirical formula | Found (Calcd) % |
|-----|----------------------------------|-------------------|-----------------|
|     |                                  |                   | C    | H    | N         |
| 1.  | [Ph₂SbL] [ClO₄₂]                 | C₁₈H₁₇NCIO₃Sb     | 44.13 (46.13)  | 2.63 (3.63) | 1.75 (2.09) |
| 2.  | [Ph₂SbL] [BF₄]                   | C₁₈H₁₇NBF₄Sb      | 46.41 (47.41)  | 2.73 (3.73) | 2.97 (3.07) |
| 3.  | [PhSbL₂] [ClO₄₂]                 | C₁₈H₁₉NCIO₄Sb     | 36.0 (37.01)   | 2.26 (3.26) | 3.40 (4.80) |
| 4.  | [PhSbL₂] [BF₄₂]                  | C₁₈H₁₉N₂BF₄Sb     | 36.65 (38.68)  | 2.10 (3.40) | 4.00 (5.01) |
| 5.  | [Ph₂SbL] [ClO₄]                  | C₁₇H₁₂NCIO₄Sb     | 42.91 (44.91)  | 2.20 (3.30) | 2.01 (3.08) |
| 6.  | [Ph₂SbL] [BF₄]                   | C₁₇H₁₃NBF₄Sb      | 45.20 (46.20)  | 2.20 (3.40) | 2.20 (3.17) |
| 7.  | [PhSbL₂] [ClO₄₂]                 | C₁₆H₁₂N₂ClO₄Sb    | 33.55 (34.55)  | 1.70 (2.70) | 4.04 (4.04) |
| 8.  | [PhSbL₂] [BF₄₂]                  | C₁₆H₁₂N₂BF₄Sb     | 35.20 (36.20)  | 1.83 (2.83) | 4.28 (5.28) |
| 9.  | [Ph₂SbL] [ClO₄]                  | C₃₀H₂₃ClO₃AsSb     | 50.60 (5.64)   | 2.40 (3.59) | -          |
| 10. | [Ph₂SbL] [BF₄]                   | C₃₀H₂₃BF₄OAsSb     | 50.59 (5.59)   | 2.65 (3.65) | -          |
| 11. | [PhSbL₂] [ClO₄₂]                 | C₁₈H₁₃ClO₄ₑ₅AsSb  | 26.60 (28.6)   | 3.10 (4.65) | -          |
| 12. | [PhSbL₂] [BF₄₂]                  | C₁₈H₁₃B₂F₂O₃₅As₅Sb| 27.65 (29.66)  | 2.98 (4.81) | -          |
| 13. | [Ph₂SbL] [ClO₄]                  | C₁₈H₁₂N₃ClO₄PSb   | 37.98 (38.98)  | 4.05 (5.05) | 6.58 (7.58) |
| 14. | [Ph₂SbL] [BF₄]                   | C₁₈H₁₂N₃BF₄O₂₅Sb  | 37.88 (38.88)  | 3.17 (5.17) | 5.76 (7.76) |
| 15. | [PhSbL₂] [ClO₄₂]                 | C₁₈H₁₄N₃ClO₄P₂₅Sb| 27.40 (28.58)  | 4.30 (5.43) | 10.12 (11.12)|
| 16. | [PhSbL₂] [BF₄₂]                  | C₁₈H₁₄N₃B₂F₂O₂₅Sb | 28.10 (29.57)  | 4.00 (5.61) | 10.21 (11.50)|
| 17. | [Ph₂SbL] [ClO₄]                  | C₁₈H₁₄N₃ClO₄Sb    | 33.29 (34.57)  | 2.06 (3.10) | 5.02 (6.21) |
| 18. | [Ph₂SbL] [BF₄]                   | C₁₈H₁₄N₃BF₄SSb    | 34.57 (35.57)  | 2.19 (3.19) | 5.38 (6.38) |
| 19. | [PhSbL₂] [ClO₄₂]                 | C₁₈H₁₄N₃ClO₄S₂₅Sb | 16.40 (17.47)  | 1.31 (2.37) | 9.10 (10.19)|
| 20. | [PhSbL₂] [BF₄₂]                  | C₁₈H₁₄N₃B₂F₂S₂₅Sb | 16.31 (18.31)  | 1.00 (2.48) | 9.68 (10.68)|

Reaction of Diphenylantimony(III) Chloride with Pyridine and Sodium Tetrafluoroborate

[Ph₂Sb.Py][BF₄] (6)

In an anhydrous condition, diphenylantimony(III) chloride (0.311 g, 1 mmol) was taken in dry chloroform and sodium tetrafluoroborate (0.110 g, 1 mmol) in dry methanol was added to this solution. After stirring the mixture for about 6 h it was further refluxed for 3 h and NaCl so formed as a precipitate was filtered off. The filtrate on concentration in vacuo afforded a cream colored solid which was crystallized from petroleum ether (40-60°C). M.P.: 189°C, Yield: 0.305 g, (69%).

Reaction of Phenylantimony(III) Dichloride with Triphenylarsine Oxide and Silver Perchlorate

[PhSb₂(Ph₃AsO)] [ClO₄] (11)

In an oxygen free environment, phenylantimony(III) dichloride (0.270 g, 1 mmol) and neutral ligand triphenylarsine oxide (0.644 g, 2 mmol) were taken in dry chloroform and silver perchlorate (0.415 g, 2 mmol) in dry methanol was added to this solution. After stirring the mixture for about 6 h, it was further refluxed for 3 h and AgCl so formed as a precipitate was filtered off. The filtrate on concentration in vacuo afforded a white solid which was crystallized from petroleum ether (40-60°C). M.P.: 185°C, Yield: 0.558 g, (74%).
Table 3: Molar conductance and yield of Arylantimony(III) cationic complexes

| C. No. | Complex               | Molar Conductance in Nitrobenzene (Ohm⁻¹ cm² mol⁻¹) | Yield (g) | Yield (%) |
|--------|-----------------------|----------------------------------------------------|-----------|-----------|
| 1.     | [Ph₂SbL][ClO₄]       | 52.4                                               | 0.290     | 62        |
| 2.     | [Ph₂SbL][BF₄]        | 54.2                                               | 0.305     | 67        |
| 3.     | [PhSbL₂][ClO₄]       | 50.6                                               | 0.409     | 70        |
| 4.     | [PhSbL₂][BF₄]        | 51.7                                               | 0.419     | 75        |
| 5.     | [PhSbL][ClO₄]        | 56.2                                               | 0.359     | 79        |
| 6.     | [PhSbL][BF₄]         | 59.2                                               | 0.305     | 69        |
| 7.     | [PhSbL₂][ClO₄]       | 56.2                                               | 0.411     | 74        |
| 8.     | [PhSbL₂][BF₄]        | 50.7                                               | 0.424     | 80        |
| 9.     | [PhSbL][ClO₄]        | 53.4                                               | 0.411     | 59        |
| 10.    | [PhSbL][BF₄]         | 51.9                                               | 0.411     | 60        |
| 11.    | [PhSbL₂][ClO₄]       | 58.3                                               | 0.558     | 74        |
| 12.    | [PhSbL₂][BF₄]        | 57.6                                               | 0.553     | 76        |
| 13.    | [PhSbL][ClO₄]        | 59.5                                               | 0.300     | 54        |
| 14.    | [PhSbL][BF₄]         | 54.7                                               | 0.379     | 70        |
| 15.    | [PhSbL₂][ClO₄]       | 57.6                                               | 0.544     | 72        |
| 16.    | [PhSbL₂][BF₄]        | 51.5                                               | 0.577     | 79        |
| 17.    | [PhSbL][ClO₄]        | 58.3                                               | 0.343     | 76        |
| 18.    | [PhSbL][BF₄]         | 53.9                                               | 0.290     | 66        |
| 19.    | [PhSbL₂][ClO₄]       | 51.8                                               | 0.379     | 69        |
| 20.    | [PhSbL₂][BF₄]        | 54.2                                               | 0.378     | 72        |

Table 4: IR data of Arylantimony (III) cationic complexes

| Comp. No. | ν(C=N)/ν(N-H) Complex | ν(As-O)/ν(P-O) Free | ∆ν | νSb-C | Anion Frequencies |
|-----------|-----------------------|---------------------|----|-------|------------------|
| 1         | 1590                  | 1575                | 15 | 445   | 1990 vs 620s     |
| 2         | 1600                  | 1575                | 25 | 450   | 1018 vs 520s     |
| 3         | 1595                  | 1575                | 20 | 447   | 1990 vs 620s     |
| 4         | 1600                  | 1575                | 25 | 460   | 1018 vs 520s     |
| 5         | 1598                  | 1575                | 23 | 465   | 1990 vs 620s     |
| 6         | 1602                  | 1575                | 27 | 450   | 1015 vs 520s     |
| 7         | 1590                  | 1575                | 15 | 471   | 1990 vs 620s     |
| 8         | 1611                  | 1575                | 36 | 765   | 1018 vs 520s     |
| 9         | 830                   | 880                 | 50 | 762   | 1920 vs 620s     |
| 10        | 835                   | 880                 | 45 | 745   | 1018 vs 520s     |
| 11        | 840                   | 880                 | 40 | 450   | 1990 vs 620s     |
| 12        | 845                   | 880                 | 35 | 465   | 1018 vs 520s     |
| 13        | 1130                  | 1211                | 81 | 470   | 1990 vs 620s     |
| 14        | 1134                  | 1212                | 78 | 404   | 1018 vs 526s     |
| 15        | 1140                  | 1212                | 72 | 450   | 1990 vs 620s     |
| 16        | 1146                  | 1212                | 66 | 440   | 1018 vs 520s     |
| 17        | 3370                  | 3300                | 70 | 445   | 1990 vs 620s     |
| 18        | 3374                  | 3300                | 74 | 455   | 1018 vs 520s     |
| 19        | 3376                  | 3300                | 76 | 460   | 1990 vs 620s     |
| 20        | 3380                  | 3300                | 80 | 470   | 1018 vs 520s     |

vs = very strong, s = strong.

Reaction of Diphenylantimony(III) Chloride with HMPA and Silver Perchlorate [Ph₂Sb. HMPA][ClO₄] (13)

In an anhydrous condition, diphenylantimony(III) chloride (0.311 g, 1 mmol) and neutral ligand HMPA (0.179 g, 1 mmol) was taken in dry chloroform and silver perchlorate (0.207 g, 1 mmol) in methanol was added to this solution. After stirring the mixture for 7
h, it was refluxed for 2 h and AgCl so formed as a precipitate was filtered off. The filtrate on concentration in vacuo, afforded a white solid which was crystallized from petroleum ether (40-60°C). M.P.: 192°C, Yield: 0.300 g, (54%).

**Reaction of Phenylantimony(III) Dichloride with Thiourea and Sodium Terafluoroborate**

[PhSb(TU)₃][BF₄]₂ (20)

In an oxygen free environment, phenylantimony(III) dichloride (0.270 g, 1 mmol) and neutral ligand thiourea (0.152 g, 2 mmol) were taken in dry chloroform and sodium tetrafluoroborate (0.220 g, 2 mmol) in dry methanol was added to this solution. After stirring the mixture for 7 h, it was refluxed for 2 h and NaCl formed as a precipitate was filtered off. The filtrate on concentration in vacuo, afforded a white solid which was crystallized from benzene. M.P.: 190°C, Yield: 0.378 g, (72%).

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**References**

Hall M and Sowerby DB (1986) Preparation of the crystal structures of [HPy]₃[SbCl₄], [NMe₄]₃[SbBr₃] and [NMe₄]₃[Sb₂Br₃Cl₆]. *J. Chem. Soc. (Dalton Trans.)* 1231-1238.

Jha NK and Joshi DM (1984) Synthesis and configuration of some triorganooantimony(V) chelates of tetradentate Schiff base. *Synth. React. Inorg. Met.-Org. Chem.* 14: 445-465.

Nishi N and Okawara R (1972) Stereoisomerism of dihalodiaryl(acetylacetonato)-antimony(V) compounds. *J. Organomet. Chem.* 38: 335-343.

Premraj, Agarwal AK and Misra N (1989 a) Synthesis and reactions of diarylantimony(III) amides *Polyhedron*, 8: 581-584.

Premraj, Agarwal AK and Saxena AK (1989 b) The preparation of pentafluorophenyl antimony(III) and antimony(V) halides and mixed halides *J Fluorine Chem.,* 42: 163-172.

Premraj and Misra N (1991) Prepration and characterization of molecular adduct of diarylantimony(V) chloride, R₂SbCl₃L. *Ind. J. Chem.* 30: 901-903.

Premraj, Agrawal AK and Singhal K (1992) Synthesis and geometry of complex triorganooantimony(V) cations *Synth. React. Inorg. Met. Org. Chem.* 22: 1471-1494

Premraj and Agrawal AK (1992) Synthesis and characterization of complex triorganooantimony(V) cations, R₂Sb(L-L)²⁺ *Synth. React. Inorg. Met-Org. Chem.* 22: 543-557.

Saxena AK, Premraj and Dixit SK (1990) Preparation and structure of some substituted tertiaryarylantimony(V) complexes of tetradentate Schiff bases *Synth. React. Inorg. Met- Org. Chem.* 20: 199-208.

Singhal K, Yadav RNP, Premraj and Agarwal AK (2003) On the Lewis acidity of tris(pentafluorophenyl)antimony(V) dichloride towards neutral monodentate O, N and S donor ligands *J. Fluorine Chem.* 121: 131-134.

Singhal K, Kant R, Yadav RNP, Pandey PC and Premraj (2004) Synthesis and structures of complex diorganooantimony(V) cations of the type [R₂SbL₃]⁺ *Synth. React. Inorg. Met-Org. Chem.* 34: 459-468.

Yadav RNP (2012) Synthesis and characterization of anionic complexes of pentafluorophenylantimony(III) chloride, (R₃)₅SbCl₃₈ *Nep. J. Integrated Sci.* 2: 14-19.

Yadav RNP (2012) Metals in oncology: An overview *Academic Voices* 2: 54-58.