



GLOBAL JOURNAL OF SCIENCE FRONTIER RESEARCH: B  
CHEMISTRY

Volume 15 Issue 3 Version 1.0 Year 2015

Type : Double Blind Peer Reviewed International Research Journal

Publisher: Global Journals Inc. (USA)

Online ISSN: 2249-4626 & Print ISSN: 0975-5896

# Triarylantimony(V) Dicarboxylates: Synthesis, Characterisation and Reactions

By Ram Nath Prasad Yadav

*Tribhuvan University, Nepal*

**Abstract-** A series of new triarylantimony(V) dicarboxylates of the general formula  $\text{Ar}_3\text{SbL}_2$  (where  $\text{Ar} = \text{C}_6\text{H}_5$  and  $\text{L} = \text{C}_6\text{H}_5\text{CONHCH}_2\text{COO}^-$ ,  $\text{C}_6\text{H}_2(\text{OH})_3\text{COO}^-$ ,  $\text{C}_6\text{H}_5\text{COO}^-$ ,  $\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{COO}^-$ ,  $\text{C}_6\text{H}_4(\text{OH})\text{COO}^-$ ,  $(\text{C}_6\text{H}_5)_2(\text{OH})\text{C.COO}^-$ ) have been prepared by the reaction of triarylantimony(V) dichloride and a carboxylic acid in the presence of triethylamine as well as the metathesis of sodium or silver salt of the carboxylic acid and triarylantimony(V) dichloride. The newly synthesized compounds have been characterized by conventional methods. A tentative trigonalbipyramidal structure is suggested in which (OCOR) group occupy axial position and the three organic groups are situated at the equatorial position. The melting points of compounds did not change even after prolong stirring with water at room temperature for several hours indicating their hydrolytic stability.

**Keywords:** Triarylantimony, Dicarboxylates, Hydrolytic stability, IR spectra, NMR spectra, Metathesis, Chelate.

**GJSFR-B Classification :** FOR Code: 259999



*Strictly as per the compliance and regulations of :*



# Triarylantimony(V) Dicarboxylates: Synthesis, Characterisation and Reactions

Ram Nath Prasad Yadav

**Abstract-** A series of new triarylantimony(V) dicarboxylates of the general formula  $\text{Ar}_3\text{SbL}_2$  (where  $\text{Ar} = \text{C}_6\text{H}_5$  and  $\text{L} = \text{C}_6\text{H}_5\text{CONHCH}_2\text{COO}^-$ ,  $\text{C}_6\text{H}_2(\text{OH})_3\text{COO}^-$ ,  $\text{C}_6\text{H}_5\text{COO}^-$ ,  $\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{COO}^-$ ,  $\text{C}_6\text{H}_4(\text{OH})\text{COO}^-$ ,  $(\text{C}_6\text{H}_5)_2(\text{OH})\text{C.COO}^-$ ) have been prepared by the reaction of triarylantimony(V) dichloride and a carboxylic acid in the presence of triethylamine as well as the metathesis of sodium or silver salt of the carboxylic acid and triarylantimony(V) dichloride. The newly synthesized compounds have been characterized by conventional methods. A tentative trigonalbipyramidal structure is suggested in which (OCOR) group occupy axial position and the three organic groups are situated at the equatorial position. The melting points of compounds did not change even after prolong stirring with water at room temperature for several hours indicating their hydrolytic stability.

**Keywords:** triarylantimony, dicarboxylates, hydrolytic stability, ir spectra, nmr spectra, metathesis, chelate.

## I. INTRODUCTION

Voluminous amount of work done on the chemistry of organic derivatives of antimony(III) and antimony(V) (Yadav 2012<sup>a</sup>, Yadav 2013<sup>a</sup>, Yadav 2014<sup>a</sup> and Yadav 2014<sup>b</sup>). As a result a variety of carboxylate derivatives, particularly organoantimony(V) were synthesized and characterized by various group of workers. The carboxylate derivatives were obtained by different routes, e.g. by oxidation of tertiary antimony(III), the anionic exchange or by salt precipitation reactions (Doak *et al.* 1965).

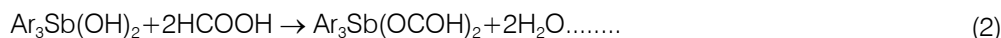
The use of lead tetraacetate as oxidizing agents towards triorganoantimony(III) derivatives resulted in the formation of triorganoantimony(V) dicarboxylates.



Where, R = Me, Pr, or Bu

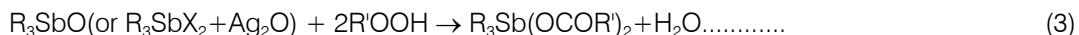
Interaction of triarylantimonydihydroxide with carboxylic acids, viz; formic acid could lead to the

formation of triarylantimony(V) dicarboxylates (Chang *et al.* 1975, Goal & Ridley 1972 and Hevyanek *et al.* 1978).



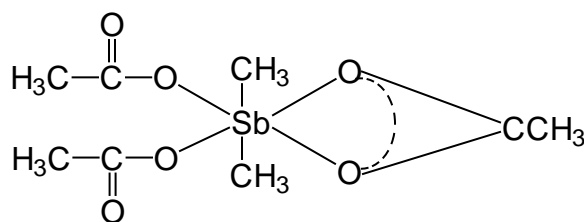
A series of triorganoantimony(V) dicarboxylates has been obtained by the reaction of triorganoantimony oxides with a number of carboxylic acids. Antimony

oxides used in this reaction were preformed by the reaction of triorganoantimonydihalides with silver halides (Chang *et al.* 1975).



The above reaction does not go well with all the acids and it has been reported that the reactions with terphthalic acid, succinic acid and sebacic acids, however, result in the formation of polymeric products (Doak *et al.* 1974). Goel and Ridley (Goel & Ridley 1972) were the first to make a systematic and comprehensive study on the physico-chemical parameters of trimethylantimony(V) derivatives of fluoro, chloro, bromo and cyano-acetic acid.

A few organoantimony(V) carboxylates of the type  $\text{R}_2\text{Sb}(\text{OCOR}')_3$  and  $\text{R}_4\text{SbOCOR}'$  have also been prepared. Based on the infrared and Raman data, an octahedral structure with two mono dentate and one chelating acetate groups has been proposed for  $(\text{CH}_3)_2\text{Sb}(\text{OCOCH}_3)_3$  (Meinema & Noltes 1972).



has been reported by Kiran *et al.* (Singhal *et al.* 1987). Based on spectroscopic and some solution phase studies a trigonalbipyramidal structure has been suggested for tetraaryl antimony(V) carboxylate derivatives by Raj and co-workers as has been reported in case of tetraphenylformate (Premraj *et al.* 1984).

Kumar Swami (Kumara *et al.* 1999) synthesized mixed halo acetate derivatives of the general formula  $R_2SbCl(OAc)_2$ . The crystal structure study revealed that both the acetate group act as bidentate ligand leading to hepta coordination around antimony. This is in sharp contrast to  $Me_2Sb(OAc)_3$  where coordination number of antimony does not go beyond six and only one carboxylate group act as bidentate moiety (Geol & Ridley 1972). It may partly be ascribed due to steric hindrance of three acetate group preventing hepta coordination.

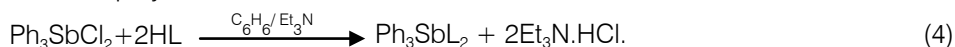
The main objective of this work was to ascertain the mode of bonding of COOH group to antimony atom, to investigate chemical behavior and constitution of triarylantimony(V) carboxylates linear or polymeric and

change in the nature of triarylantimony(V) carboxylates on changing the organic group bound to antimony or change of carboxylic group and to investigate the antimicrobial and antiproliferative activity (Yadav 2012<sup>b</sup> and Yadav 2013<sup>b</sup>) generally associated with organometal carboxylates.

With the above aim in the mind, we have synthesized a few new triarylantimony(V) dicarboxylates. The results of these studies are reported in this paper.

## II. RESULTS AND DISCUSSION

Under anhydrous oxygen free atmosphere triarylantimony(V) dicarboxylates have been prepared either by the interaction of triarylantimony(V) dichloride with a carboxylic acid in 1:2 molar ratio in presence of triethylamine using benzene as the solvent or by simple metathesis of triarylantimony(V) dichloride with the sodium or silver salt of the corresponding carboxylic acid using methanol as the solvent.



[M = Na or Ag; L =  $C_6H_5CONHCH_2COO^-$ ,  $C_6H_2(OH)_3COO^-$ ,  $C_6H_5COO^-$ ,  $C_6H_5C_2H_2COO^-$ ,  $C_6H_4(OH)COO^-$ ,  $(C_6H_5)_2(OH)C.COO^-$ ]

The reactions were carried out in dried benzene/methanol at room temperature with constant stirring for about 2-3 h. The contents were also refluxed at the reflux temperature of the respective solvent to ensure completion of the reaction. The yields of the products were nearly quantitative except for the losses during the workup process. The complexes are moderately soluble in chloroform and acetonitrile. They are off-white crystalline solids with sharp melting points. The complexes remain unaffected by air and atmospheric moisture. In the representative cases the melting points of compounds did not change even after prolong stirring with water at room temperature for several hours indicating their hydrolytic stability.

The molecular weight measurement in freezing benzene suggests that these carboxylate derivatives have monomeric constitution. The molar conductance of  $10^{-3}$  M solution of all the complexes at room temperature are in the range between 20-30  $\Omega^{-1} cm^2 mol^{-1}$  in acetonitrile which shows the absence of ionic species in solution.

## III. INFRARED SPECTRA

As has been discussed above, organoantimony carboxylates display a variety of structures. The coordination number of the central metal atom and the mode of bonding of the ligand are largely affected by the physical state, the numbers of organic groups bound to antimony and nature of ligand. Thus, in  $Ar_2SbOAc$  the ligand is bridging giving infinite chain

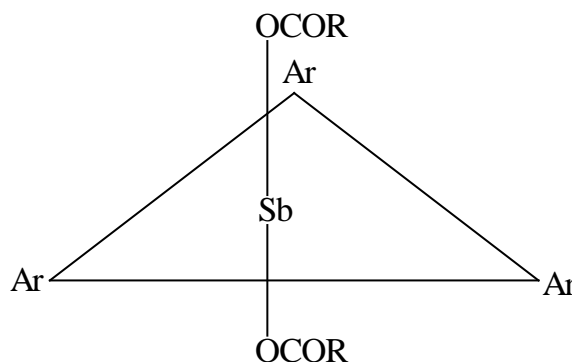
structure in solid state while in chloroform, it assumes a bipyramidal geometry. On the other hand, in  $R_3Sb(OAc)_2$  and  $R_4SbOAc$  the carboxylate moiety is strictly unidentate imparting pentacoordination around antimony. In  $SbO(Ac)_3$ . One of the acetate groups is simultaneously chelating and bridging and two of the ligands are chelating. In case of dimethyl triacetate the presence of both monodentate and bidentate has been reported. Carboxylate groups have been observed in tetramethylstibonium acetate, formate, trichloroacetates, propionates bivalate and benzoates, carboxylate group behaving as a monodentate ligand in solution imparting penta coordination around antimony. On the other hand in solid state, carboxylate group behaves as a bidentate ligand in which antimony is hexacoordinated.

Thus, carboxylate group is capable of behaving as a monodentate as well as bidentate group. It can readily be distinguished with the aid of infrared spectra through a comparison with data previously given for the solid state in similar type compounds as well as for other organoantimony(V) carboxylates for example  $R_4SbOAc$  and  $R_2SbOAc_3$  ( $R = CH_3C_6H_4$  and  $C_6F_5$ ) the difference in the position of asymmetric  $\nu(CO)$  and symmetric  $\nu(CO)$  is an important key factor in deciding the nature of carboxylate group. The appearance of medium strong band around  $1680 cm^{-1}$  can readily be assigned to the  $\nu(CO)$  mode of the monodentate 'ester like' carboxylate group. The absence of any band around  $1500 cm^{-1}$  ruled out the possibility of the presence of a bidentate carboxylate group. The

difference between  $\nu_{\text{asy}}(\text{CO})$  and  $\nu_{\text{sym}}(\text{CO})$  is more than  $200\text{ cm}^{-1}$  ruling out polymeric nature of the carboxylate group. This is also supported by the fact the newly synthesized compound are soluble in chloroform, acetonitrile, methanol etc. Thus the infrared data, molecular weight and molar conductance measurement indicate that the carboxylate derivatives exhibit pentacoordination around antimony. The Sb-C bond corresponding to Y mode was observed between  $440\text{--}460\text{ cm}^{-1}$ . A medium band appearing in the range  $415\text{--}422$  can tentatively assigned Sb-O bond.

#### a) $^1\text{H}$ NMR spectra

$^1\text{H}$  NMR spectra of a representative compound triphenylantimonydisalicylate or  $[(\text{C}_6\text{H}_5)_3\text{Sb}(\text{O}_2\text{CC}_6\text{H}_4\text{OH})_2]$



$\text{Ar} = \text{C}_6\text{H}_5$  and  $\text{OCOR} = \text{C}_6\text{H}_5\text{CONHCH}_2\text{COO}^-$ ,  $\text{C}_6\text{H}_3(\text{OH})_3\text{COO}^-$ ,  $\text{C}_6\text{H}_5\text{COO}^-$ ,  $\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{COO}^-$ ,  $\text{C}_6\text{H}_4(\text{OH})\text{COO}^-$ ,  $(\text{C}_6\text{H}_5)_2(\text{OH})\text{C}\cdot\text{COO}^-$

Figure : Suggested structure of  $\text{Ar}_3\text{SbL}_2$ .

## IV. EXPERIMENTAL

### a) Materials and Methods

Triarylantimony(V) dichloride was prepared by slowly passing chlorine for 30 min through a solution of triphenylantimony in pet-ether. Carboxylic acids used in the reactions were purified before use. Sodium/silver salts of the organic moieties were freshly prepared and dried *in vacuo* before use. All solvents were purified, dried and distilled before use as per the literature methods (Vogel 1989) and reactions were carried out under nitrogen atmosphere.

IR spectra were recorded in the range  $4000\text{--}200\text{ cm}^{-1}$  using KBr/CsI pellets on a Perkin-Elmer 577

spectrophotometer.  $^1\text{H}$  NMR spectra were recorded on an EM 360L Varian spectrometer in  $\text{CDCl}_3$  containing TMS as an external standard at room temperature. The molar conductance of  $10^{-3}\text{ M}$  solutions was determined at  $25^\circ\text{C}$  with a PR-9500 Phillips conductivity assembly. Molecular weights were determined cryoscopically in benzene using a Beckmann thermometer of  $\pm 0.01^\circ\text{C}$  accuracy.

### b) Preparation of the Antimony(V) Derivatives

Details of the typical experiments are described below. Relevant IR assignments, analytical data and molar conductance values are listed in Table 1-4.

Table 1: Preparation and Properties for Triarylantimony (V) Dicarboxylates

S. No.	Complex $\text{Ar}_3\text{SbL}_2$	Ligand (g) Solvent (ml)	$\text{Ar}_3\text{SbCl}_2(\text{g})$ Solvent (ml)	Molar ratio	M.P. ( $^\circ\text{C}$ )	Colour	Recrystallisation Solvent
1.	$\text{Ar} = \text{C}_6\text{H}_5$ $\text{Ar}_3\text{Sb}(\text{OCOCH}_2\cdot\text{NHCOC}_6\text{H}_5)_2$	$\text{C}_6\text{H}_5\text{CONHCH}_2\text{COOH}$ (0.358) $\text{C}_6\text{H}_6$ (30)	0.424 $\text{C}_6\text{H}_6$ (30)	1:2	218	White	Hexane
2.	$\text{Ar}_3\text{Sb}(\text{OCO}(\text{OH})_3\text{C}_6\text{H}_2)_2$	$\text{C}_6\text{H}_2(\text{OH})_3\text{COOAg}$ (0.554) $\text{C}_6\text{H}_6$ (30)	0.424 $\text{C}_6\text{H}_6$ (30)	1:2	118	Off white	Petroleum ether ( $40\text{--}60^\circ\text{C}$ )

3.	$\text{Ar}_3\text{Sb}(\text{OCOC}_6\text{H}_5)_2$	$\text{C}_6\text{H}_5\text{COOH}$ (0.244) $\text{C}_6\text{H}_6$ (30)	0.424 $\text{C}_6\text{H}_6$ (30)	1:2	160	Light brown	Petroleum ether (40-60°C)
4.	$\text{Ar}_3\text{Sb}(\text{OCOC}_2\text{H}_2\text{C}_6\text{H}_5)_2$	$\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{COOH}$ (0.296) $\text{C}_6\text{H}_6$ (30)	0.424 $\text{C}_6\text{H}_6$ (30)	1:2	197	Light pink	Hexane-petroleum ether (40-60°C)
5.	$\text{Ar}_3\text{Sb}(\text{OCO}(\text{OH})\text{C}_6\text{H}_4)_2$	$\text{C}_6\text{H}_4(\text{OH})\text{COONa}$ (0.320) $\text{C}_6\text{H}_6$ (30)	0.424 $\text{C}_6\text{H}_6$ (30)	1:2	142	White	Petroleum ether (40-60°C)
6.	$\text{Ar}_3\text{Sb}(\text{OCO.C}(\text{OH})(\text{C}_6\text{H}_5)_2)_2$	$(\text{C}_6\text{H}_5)_2(\text{OH})\text{CCOOH}$ (0.456) $\text{C}_6\text{H}_6$ (30)	0.424 $\text{C}_6\text{H}_6$ (30)	1:2	205	Light brown	Hexane

Table 2 : Elemental Analysis of Triarylantimony (V) Dicarboxylates

S. No.	Complex $\text{Ar}_3\text{SbL}_2$	Empirical formula	Found (Calcd.) %		
			C	H	N
	Ar = $\text{C}_6\text{H}_5$				
1.	$\text{Ar}_3\text{Sb}(\text{OCOCH}_2\text{NHCOC}_6\text{H}_5)_2$	$\text{C}_{36}\text{H}_{31}\text{O}_6\text{N}_2\text{Sb}$	59.92 (60.95)	3.97 (4.37)	3.62 (3.95)
2.	$\text{Ar}_3\text{Sb}(\text{OCO}(\text{OH})_3\text{C}_6\text{H}_2)_2$	$\text{C}_{32}\text{H}_{25}\text{O}_{10}\text{Sb}$	54.99 (55.59)	2.75 (3.62)	-
3.	$\text{Ar}_3\text{Sb}(\text{OCOC}_6\text{H}_5)_2$	$\text{C}_{32}\text{H}_{25}\text{O}_4\text{Sb}$	63.76 (64.56)	4.00 (4.20)	-
4.	$\text{Ar}_3\text{Sb}(\text{OCOC}_2\text{H}_2\text{C}_6\text{H}_5)_2$	$\text{C}_{40}\text{H}_{29}\text{O}_4\text{Sb}$	68.66 (69.09)	3.97 (4.17)	-
5.	$\text{Ar}_3\text{Sb}(\text{OCO}(\text{OH})\text{C}_6\text{H}_4)_2$	$\text{C}_{32}\text{H}_{25}\text{O}_6\text{Sb}$	60.27 (61.27)	3.02 (3.99)	-
6.	$\text{Ar}_3\text{Sb}(\text{OCO.C}(\text{OH})(\text{C}_6\text{H}_5)_2)_2$	$\text{C}_{46}\text{H}_{37}\text{O}_6\text{Sb}$	67.92 (68.42)	3.29 (4.59)	-

Table 3 : Molar Conductance and Yield of Triarylantimony (V) Dicarboxylates

C. No.	Molar conductance ( $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ )	Yield	
		(g)	(%)
1.	19	0.469	66
2.	22	0.477	69
3.	23	0.398	67
4.	26	0.486	70
5.	25	0.426	68
6.	22.2	0.573	71

 Table 4 : IR Data for the Triarylantimony (V) Carboxylates ( $\text{Cm}^{-1}$ )

C. No.	$\nu_{\text{assy}}(\text{COO})$	$\nu_{\text{sym}}(\text{COO})$
1.	1620	1340
2.	1625	1315
3.	1635	1320
4.	1630	1310
5.	1650	1290
6.	1665	1295

i *Reactions of Triarylantimony(V) Dichloride with Hippuric Acid (1)*

A solution of triphenylantimony(V) dichloride (0.424 g, 1 mmol) in benzene (~40 ml) and silver salt of hippuric acid (0.358 g, 2 mmol) in benzene (~30 ml) was stirred together in dark conditions. A white precipitate of AgCl was formed which was filtered off. The filtrate on concentration yielded a white solid of triphenylantimony(V) dihippurate which was recrystallised by hexane. M.P.: 218°C; Yield: 0.468 g, (66%).

ii *Reaction of Triarylantimony(V) Dichloride with Silver Salt of Gallic Acid (2)*

In an oxygen free atmosphere, a solution of triphenylantimony(V) dichloride (0.424 g, 1 mmol) in benzene (~30 ml) and gallic acid (0.554 g, 2 mmol) in the same solvent (~30 ml) were stirred together in the presence of triethylamine at room temperature for 6 h.  $\text{Et}_3\text{N} \cdot \text{HCl}$  was formed and filtered off. The filtrate on concentration in *vacuo* yielded a off white crystalline solid which was recrystallized from petroleum ether (40°-



60°C) to afford triphenylantimony(V) gallate. M.P.: 118°C; Yield: 0.477 g, (69%).

iii *Reaction of Triarylantimony(V) Dichloride with Sodium Salt of Salicylic Acid (5)*

A solution of triphenylantimony(V) dichloride (0.424g, 1mmol) in benzene (~30 ml) and sodium salt of salicylic acid (0.320 g, 2 mmol) in benzene (~30 ml) was refluxed for 6 h. The solution was cooled and after filtration, concentrated *in vacuo* to yield white solid, identified triphenylantimony(V) salicylate and recrystallised from petroleum ether (40°-60°C). M.P.: 142°C; Yield: 0.426 g, (68%).

## V. ACKNOWLEDGEMENT

The author is thankful to the Head, Department of chemistry, Lucknow University for providing necessary laboratory facilities; the Director, Regional Sophisticated Instrumentation Centre, CDRI, Lucknow for microanalysis and spectral data. Thanks are also due to Dr. Premraj, Professor of Chemistry, Lucknow University, Lucknow India for his valuable suggestions.

## REFERENCES RÉFÉRENCES REFERENCIAS

- Chang M.M.Y., Su K. and Musher J.I. (1974). Some new organoantimony(V) compounds. *Isht. J. Chem.*, 12(5), 967-970.
- Doak G.O., Long G.G. and Freedman L.D. (1965). The Infrared spectra of some phenyl substituted pentavalent antimony compounds. *J. Organomet. Chem.*, 4(1), 82-91.
- Doak G.O., Long G.G. and Freedman L.D. (1974). Antimony: Annual survey covering the year 1975. *J. Organomet. Chem.*, 130, 365-404.
- Goel R.G. and Ridley D.R. (1972). Studies on trimethyl and triphenylantimony(V) derivatives of haloacetic acids. *J. Organomet. Chem.*, 38, 83-91.
- Hevyanek J., Mleziva J. and Lycka L. (1978). Triphenylantimonydiester preparation. *J. Organomet. Chem.*, 157(2), 163-166.
- Meinema H.A. and Noltes J.G. (1972). Investigations on organoantimony compounds: VI. Preparation and properties of thermally stable dialkylantimony(V) compounds of the types  $R_2Sb(OR)_3$ ,  $R_2Sb(OAc)_3$  and  $R_2Sb(O)OH$ . *J. Organomet. Chem.*, 36, 313-322.
- Premraj, Ranjan A., Singhal K. and Rastogi R. (1984). Synthesis and characterization of tetraarylstibonium amides, oximates and carboxylates. *Synth. React. Inorg. Met-Org. Chem.*, 14(2), 269-282.
- Singhal K., Rastogi R. and Premraj. (1987). Synthesis and biological evaluation of some substituted tetraarylantimony(V) derivatives. *Ind. J. Chem.*, 26A, 146-150.
- Swamy K.C. Kumara, Said Musa A. and Netaji M. (1999). A heptacoordinate mononuclear diphenylantimonycarboxylate. *J. Chem. Crystallography*, 29(10), 1103-1106.
- Vogel A.I. (1989). *Practical Organic Chemistry*, 5<sup>th</sup>edn., Longmans, London.
- Yadav R.N.P. (2014<sup>a</sup>). Synthesis, characterization and reactions of some pentafluorophenylantimony (III) diamides. *International Journal of Advanced Research in Biological Sciences*, 1(2), 108-114.
- Yadav R.N.P. (2014<sup>b</sup>). Preparation, characterization and reactions of stable adducts of tris(pentafluorophenyl) antimony (V) diisothiocyanates. *Global J. of Science Frontier Research:B. (Chemistry)*. 14(3), 5-9.
- Yadav R.N.P. (2013<sup>a</sup>). Synthesis, characterization and reactions of cationic complexes of arylantimony(III) chlorides  $Ar_nSbCl_{3-n}$  with perchlorate and tetrafluoroborate anions. *Int. J. Appl. Sci. Biotechnol.* 1(2), 42-48.
- Yadav R.N.P. (2013<sup>b</sup>). Insecticidal and antimicrobial activity of triarylantimony(V) derivatives. *Academic Voices*. 3(1), 40-45.
- Yadav R.N.P. (2012<sup>a</sup>). Synthesis and characterization of anionic complexes of pentafluorophenylantimony(III) chloride,  $(R_F)_nSbCl_{3-n}$ . *Nep. J. of Integrated Sciences*. 2(1), 14-19.
- Yadav R.N.P. (2012<sup>b</sup>). Metals in oncology: An overview. *Academic Voices*. 2(1), 54-58.

This page is intentionally left blank