

Synthesis and Characterisation of Some New Organoantimony (V) Aryloxyacetates

Kiran Singhal, Dharmendra K. Srivastava, Prem Raj, A. Pandey

Abstract— A series of new tri and tetra-organoantimony (V) aryloxyacetates of the general formula $R_3Sb(OCOCH_2OR')_2$; and $R_4Sb(OCOCH_2OR')$ [where $R = p-OCH_3C_6H_4-$, C_6H_5- & $R' = p-CH_3C_6H_4-$, $m-CH_3C_6H_4-$, $o-CH_3C_6H_4-$, $\beta-C_{10}H_7-$, $o-ClC_6H_4-$], have been synthesised and characterised. These complexes are monomeric in benzene and non-electrolyte in acetonitrile. IR, NMR spectral data suggest the hepta-coordination with weak secondary interaction in between antimony and carbonyl oxygen of aryloxyacetate ligands.

Keywords— Tri and tetra-organoantimony (V) aryloxyacetates, IR, 1H NMR, $^{13}CNMR$ spectra, monomeric, non ionic, secondary interaction.

1 INTRODUCTION

The great variety of structural possibilities offered by organo-metal carboxylates perhaps is the main factor for the continued interest in this class of compounds [27-34]. Despite a considerable interest in organometallic carboxylates and the variety of metals for which such derivatives have been synthesized, corresponding aryl oxyacetates are mainly confined to tin. The etheral oxygen may or may not involve in coordination with metal atom and thus play an important role in changing the geometry of the complex. Studies on organotin complexes of aryloxy acetic acids indicate intramolecular O-Sn coordination particularly in case of alkyl tin derivatives with monomeric constitution in solid state. In sharp contrast to this triphenyltin derivatives having pentacoordination around tin were found to be polymeric with bridging carbonyl group. A perusal of literature reveals that the role of pentacoordination, particularly in case of group 14 and group 15 elements in reaction mechanism is potentially one of the best method to explore the possibility of conformation extended from the ideal trigonal bipyramidal to the square or rectangular bipyramidal geometry and the compounds of pentacoordinated phosphorus, arsenic and antimony are probably the most interesting [1-10].

In case of thioacetate secondary bonding takes place through chelation [2, 6, 7]. Another important group of ligand which has not attracted much attention, but closely resembles to carboxylates, is aryl oxy acetates. However unlike acetate or thioacetate, aryl oxy acetates has one extra donor site i.e.; $Ar-O-$, in addition to the $-C=O$ functionality.

It is note worthy that despite such a great variety of structural possibility, as discussed above, exhibit by organom

et. al carboxylates and the variety of metals for which such derivatives have been synthesized corresponding aryloxyacetates are mainly confined to transition metal derivatives [11] with an occasional reference to organotin¹² and organo antimony [12, 13] derivatives. It has been found that etheral oxygen of aryloxyacetates group may or may not involve in coordination with metal atom and thus play a great role in shaping the geometry of the complex.

A perusal of the literature further reveals that the complexes of aryloxyacetic acids in case of organotin possess intermolecular $O \rightarrow Sn$ co-ordination, particularly for alkyltin derivatives and the compounds are monomeric in solid state. In sharp contrast to this triaryltin derivative having penta coordination around the tin were found to be polymer with bridging carboxylic group [12]. Although the aryloxy acetate of organophosphorous and little known but the compound containing P-O, Sb-O, As-O have been studied to an appreciable extent [14, 15]. On the basis of ultraviolet and infrared spectra it has been concluded that aryloxyacetate behave as monodentate ligand toward antimony (V) but slight decrease in IR frequencies for carbonyl group indicate toward secondary interaction.

A comparison of spectral data of the organoantimony acetate with those of free ligands both in solid state and in solution rules out the likelihood of co-ordination of antimony through etheral oxygen of the aryloxy group [9]. However, there seems to be no systematic and comparative study of aryloxyacetate derivative of antimony in +5 oxidation state as yet. In conclusion, in the solid state it indicates that sterically disfavored conformations of TBPY antimony (V) complexes may be stabilized by secondary bonding interaction involving diaxially coordinated ester ligands. The complex geometry accompanied by the expansion of the co-ordination sphere from five to seven [23].

Continuing our interest in the carboxylate derivatives of group 15 elements [16, 20], a series of aryloxyacetate derivatives of the general formula $Ph_3Sb(OCOCH_2OR)_2$ and $(p-MeO-C_6H_4)_3Sb(OCOCH_2OR)_2$ and $Ph_4Sb(OCOCH_2OR)$ [where $R =$ substituted aryl group; $p-CH_3C_6H_4-$, $m-CH_3C_6H_4-$, $o-CH_3C_6H_4-$, $\beta-C_{10}H_7-$, $o-Cl-C_6H_4$] has been synthesized and characterized.

The main objectives of this work were aimed at:

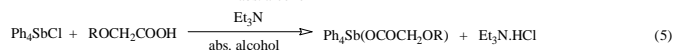
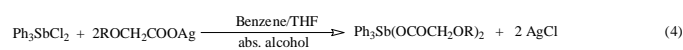
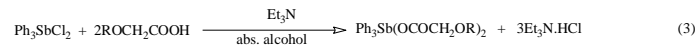
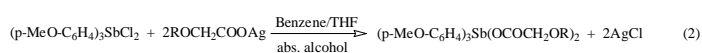
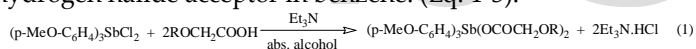
- Corresponding author is Dr. (Mrs.) Kiran Singhal, Associate Professor, Chemistry Department, University of Lucknow, Lucknow and is the thesis supervisor of Mr. Dharmendra K. Srivastava.
- Email: singhal.kiran@gmail.com Ph: +91-9415159894
- Contract Grant Sponsor: University Grants Commission, New Delhi, India Vide Letter No. 37-429/2009 SR.
- Dr. Prem Raj is Senior Professor Chemistry Department, Lucknow University, Lucknow, U. P., India.

1. To synthesise and isolate hitherto unreported organo antimony (V) aryloxyacetate derivatives.
2. To investigate the role of etheral oxygen of aryloxyacetate group, i.e., whether it participates in bonding or not and of carbonyl oxygen and thus raising the co-ordination number of antimony (V) beyond five.
3. To ascertain the mode of bonding of aryloxyacetate group toward antimony i.e., whether the acetate group (s) act as monodentate or bidentate group or as a both.

2 RESULTS AND DISCUSSION

The dual behaviour of an acetate group as a monodentate or bidentate ligand has been well established in case of phenyl antimony (V) tetra acetate and dimethyl antimony (V) triacetate, where one acetate group is bidentate and the remaining act as a monodentate [15, 16]. Similarly, antimony in tetramethyl and -tetra phenyl antimony (V) acetate has been found to possess trigonal bipyramidal geometry in solution with the acetate group acting as bidentate ligand. Thus it appears that it is the physical state and the nature and the number of organic groups attached to the antimony atom.

Under anhydrous oxygen-free conditions, with absolute methanol as solvent, the reaction of tri (p-methoxy) antimony dichloride, triphenyl antimony dichloride or tetraphenyl antimony chloride with silver salts of aryloxyacetic acids gave tri- and tetra-organo antimony (V) aryloxy acetates. The reactions with organoantimony (V) halides with aryloxyacetic acids were also carried out in presence of triethyl amine as hydrogen halide acceptor in benzene. (Eq. 1-3).



[where R = p-CH₃C₆H₄-, m-CH₃C₆H₄-, C₁₀H₇-, o-ClC₆H₄-, o-CH₃C₆H₄-, Ph = C₆H₅-]

All the reactions were performed under an atmosphere of dry nitrogen. Tetrahydrofuran (THF) was distilled under an atmosphere of nitrogen from sodium benzophenone. Silver salts of carboxylic acids were prepared from the corresponding sodium salt by reaction with AgNO₃. The products were recrystallized from petroleum ether (40^o – 60^oC) or benzene. The complexes are off white to light brown solid and are generally obtained as a sticky mass which on treatment with sodium dried benzene. Solidified and subsequently crystallized with benzene/pet-ether. The complexes are fairly stable to air and moisture and have sharp melting point. There is no regular trend of the melting point of the complexes and they melt without decomposition. Complexes are soluble in chloroform and acetonitrile. They can be stored at room temperature without decomposition for several weeks. The constancy in

melting points after repeated crystallization as well as TLC run in chloroform – hexane mixture (1:1) with the observation of a single spot excluded the presence of mixture of reactants. The molar conductance of 10⁻³ M solution were recorded in methanol and were in the range of 15–25 ohm⁻¹, mole⁻¹ cm² indicating the absence of ionic species in solution [21]. The complexes were found to be monomeric in nitro benzene.

2.1 INFRARED SPECTRA

As expected infrared absorptions inherent to phenyl group (substituted i.e. p-tolyl) bound to antimony do not differ appreciably from those values reported from parent (p-tolyl)₃Sb compounds, and hence not discussed here [22]. Infrared absorptions of diagnostic value for Phenyl antimony and p-tolyl antimony aryloxyacetates, related to the ligands have been identified which on preliminary stage indicate mode of bonding of aryloxy ligand. The data are presented in Table 3. The Characteristic ν(OH) absorption bond of ligands which appeared around 3400 cm⁻¹ in the free acid, was found missing in the newly synthesised complexes. A medium strong intensity bond appearing at 1580-1690 cm⁻¹ can confidently be assigned to ν_{asy} (OCO) mode whilst the comparatively weaker bond in the range 1360-1390 cm⁻¹ can be attributed to ν_{sym} (OCO) bond. The deformation mode as a medium intensity bond was found in the range 770 – 800 cm⁻¹. The absorption associated with the antimony – oxygen appears in the range between 400 – 440 cm⁻¹ and the absorption due to antimony carbon corresponding to γ-mode occurs in the range 450-470 cm⁻¹. These values clearly indicate the formation of phenyl; p-methoxyphenyl antimony (V) aryloxyacetates.

The comparison of IR spectra of the compounds with those of respective ligand in solid and solution shows a very slight shift in ν_{asy} (C = O), ν_{sym} (C – O) and ν(C – O – C) deformation band which in turn showed the lack of co-ordination antimony through – C = O center of the ligands but it represents a slight presence of secondary interaction which indirectly provides strength to the sterically congested TBPY geometry. Further it has been reported earlier that separation between [ν(ν_{asy}(OCO) – ν_{sym}(OCO))] is smaller, around 150 cm⁻¹ in the case of linear polymeric moieties and is considerably larger (around 250 – 350 cm⁻¹) for monomeric compounds [16 – 20]. Since the separation observed in the present compounds is fairly large (2300 cm⁻¹), monomolecular constitution seems to be most plausible where antimony would be having a co-ordination number five. This observation is in sharp contrast to organo tin complexes of aryloxyacetates which have been found to be polymeric involving carboxylic bridges [12].

2.2 ¹H NMR SPECTRA

¹H NMR spectra (Table 5) of the compounds were recorded in CDCl₃ using TMS as an internal reference. The disappearance of –OH proton signal (δ 9.2 ppm) present in the ligand indicate the formation of aryloxy acetate derivative. The appearance of singlet for –CH₂– protons in compounds at δ 4.80–4.8: ppm showed that both the ligands are equivalent and seemed to be in one plane. The protons of phenyl group directly attached with antimony appears as multiplet in the range δ7.70 – 7.30 ppm, protons of o-tolyl group directly attached with antimony

also appears as multiplet in the range δ 7.35 – 7.00 ppm and of CH_3 – group attached to oxygen atom of methoxy group appears to shielded at δ 3.85 ppm. Protons of β -naphthyl group also appears as multiplet in the range δ 8.00 – 7.20 ppm and $-\text{CH}_2-$ group of acetate moiety appears at δ 5.14 ppm. Protons of ortho, Meta and para-cresol appears as multiplet in the range δ 2.10 – 7.25 ppm and of $-\text{CH}_2-$ appears at δ 5.10 ppm. Protons of Ortho – Chlorophenoxy acetate appears as multiplet in the range δ 6.90 – 7.55 ppm and of $-\text{CH}_2-$ at δ 5.12 ppm.

2.3 ^{13}C NMR SPECTRA

The ^{13}C NMR (Table 6) of all the compounds were recorded in CDCl_3 at 75 MHz on 300 MHz FT NMR (Bruker DRX – 300) instrument and the data are summarized in Table. In every case i – c (δ 139.5 – 135.5) ppm of phenyl ring and i – c (δ 129.5 – 135.5) ppm of p-MeO – phenyl ring (i.e. Sb – C) was found to be more deshielded than O – C; δ (135.5 – 137.5) ppm; m – C, δ (110.5 – 129.5) ppm; and p – c, δ (157.6 – 128.7) ppm. The methyl carbon of methoxy group of p-tolyl moiety directly attached to antimony appeared at δ (55.8 – 56.0) ppm. The β -naphthol aryloxy acetate moiety appears at δ (105.9 – 156.5) ppm. The ortho, meta, para cresol moiety of aryloxy acetate group appears in the range δ (110.5 – 160.5) ppm and CH_3 – group appears at δ (15.5 – 22.5) ppm, in both cases the $-\text{CH}_2-$ group of aryloxy acetate moiety appears in the range of δ (68.5 – 69.0) ppm.

3 EXPERIMENTAL

Triphenyl antimony (V) dichloride Ph_3SbCl_2 , tri (p-tolyl) antimony (V) dichloride $(\text{p-MeO-C}_6\text{H}_4)_3\text{SbCl}_2$ were prepared by Grignard reaction followed by oxidative addition of chlorine and tetraphenyl stibonium (V) chloride was prepared by Quarternisation reaction as follow:

3.1 Tri (p-tolyl) antimony

A solution of antimony trichloride (22.8g, 0.1mol) and 4-bromo anisole (47.1g, 0.1mol) in benzene (200 ml) was added drop wise to a boiling suspension of sodium (13.8g, 0.6mol) in the same solvent (300 ml). The reaction mixture was refluxed for 4h with occasional shaking and then filtered hot. The residue was extracted twice with hot benzene. The solvent was extracted twice with hot benzene. The solvent was completely distilled and the remaining residue was recrystallised from alcohol-petroleum ether (60-80°C) mixture.

M.P.: 120°C Lit.: 120-121°C [25]

3.2 Tris (p-tolyl) antimony (V) dichloride

It was prepared by slowly passing freshly prepared chlorine for 30 minute through a solution of tris (p-tolyl) antimony (4.43g, 0.01mol) in carbon tetrachloride. Filtration and recrystallization from the same solvent gave tris (p-tolyl) antimony (V) dichloride; $(\text{p-CH}_3\text{O-C}_6\text{H}_4)_3\text{Sb}$.

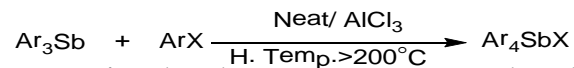
M.P.: 156-157°C Lit.: 157°C [26]

3.3 Quarternisation Reaction

Tetraphenyl stibonium (V) chloride

Tetraaryl stibonium halide, Ar_4SbX , was conveniently prepared by Quarternisation reaction of triaryl stibine, Ar_3Sb , with aryl halide, ArX , in the presence of Lewis acid catalyst

anhydrous aluminium (III) chloride.



A mixture of triphenyl antimony (7.0g, 0.02mol), anhydrous aluminium (III) chloride (7.0g, 0.05mol) and chlorobenzene (2.86g, 0.02mol) was taken in a dry round bottom flask with an air condenser. The reaction mixture was heated gradually on an oil bath up to 225-230°C in half an hour, and this temperature was maintained for further 2h. The black oily mass was poured in one liter capacity beaker containing water (600ml) and boiled on wire gauge till complete black mass was disappeared in to water leaving only little residue. Solution was filtered and the filtrate was concentrated to 1/4th of the original volume. Solution was cooled and then added KCl (5g, 0.04mol) to obtain white crystalline Tetraphenylstibonium chloride, which was dried between pads and recrystallised from absolute alcohol.

M.P.: 215°C

Lit.: 208-218°C [24]

Typical experimental details of the reactions are described below. Relevant IR and UV, NMR assignments and analytical data are summarized in Table 1-6.

3.4 Reaction of Tri (p-tolyl) antimony (v) dichloride or Tris (4-methoxyphenyl) antimony (v) dichloride with O – cresol phenoxy acetate or (2 – (O – tolyl oxy) acetoxy) silver (1)

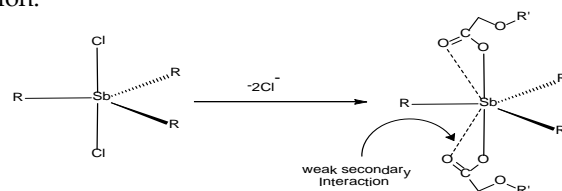
To a stirring solution of tris (4-methoxyphenyl) antimony (v) dichloride (0.514 g; 1 mmol) was added (2 – (O – tolyl – oxy) acetoxy) silver (0.546g; 2 mmol) in presence of benzene as solvent was stirred in anhydrous. Oxygen free conditions for 6h, followed by refluxing for 2h to ensure completion of the reaction. A flocculent white ppt. of AgCl was formed which was filtered off. The filtrate on concentration gave a light brown solid which was recrystallized by petroleum ether (40° – 60° C).

3.5 Reaction of tris (4-methoxyphenyl) antimony (v) dichloride with (2-(2-chlorophenoxy) acetoxy) silver (5)

To a stirring solution of tris (4-methoxyphenyl) antimony (v) dichloride (0.514g; 1.0 mmol) in benzene was being added (2 – (2 – chlorophenoxy) acetoxy) silver (0.586g; 0.2 mmol) in benzene and was stirred in anhydrous oxygen free conditions for 6h. It was later refluxed for 2h to ensure completion of the reaction. An off white precipitate of AgCl was formed which was filtered off. The filtrate on concentration gave a light brown solid which was crystallized from hexane and petroleum ether (40° – 60°C) mixture.

4 FIGURES

Figure 1 Showing Trigonal Bipyramidal arrangement of antimony (V) aryloxyacetates with possible weak secondary interaction:



5 TABLES

Table - 1: Preparation and Properties of Organoantimony (V) aryloxyacetates

S.No.	Complex	Recrystallization solvent	M.P. (°C)	Colour
1	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-O) ₂	Hexane + Pet. ether (40 ⁰ - 60 ⁰ C)	132	Light Brown
2	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-m) ₂	Hexane + Pet. ether (40 ⁰ - 60 ⁰ C)	128	Light Brown
3	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-p) ₂	Benzene	110	Light Brown
4	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₁₀ H ₇ -β) ₂	Pet. Ether (40 ⁰ -60 ⁰ C)	125	Dirty White
5	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (Cl)-O) ₂	Hexane - Benzene	140	White
6	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₁₀ H ₇ -β) ₂	Benzene	135	Dirty White
7	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ Cl - O) ₂	Benzene	88	White
8	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃) - O) ₂	Benzene	148	White
9	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃) - p) ₂	Hexane	145	White
10	(C ₆ H ₅) ₂ Sb(OCOCH ₂ O C ₆ H ₄ (Cl) - O) ₂	Pet. Ether (40 ⁰ - 60 ⁰)	90	Light Brown
11	(C ₆ H ₅) ₂ Sb(OCO CH ₂ O C ₆ H ₄ (CH ₃) - O) ₂	Pet. Ether (40 ⁰ - 60 ⁰ C) - Hexane	126	Light Brown
12	(C ₆ H ₅) ₂ Sb(OCO CH ₂ O C ₆ H ₄ (CH ₃) - p) ₂	Benzene	200	Light Brown

Table 2 Elemental Analysis data

S.No.	Complex	Molar Conductance (in MeOH) (Ohm ⁻¹ mole ⁻¹ cm ²)	Molecular Weight Found (Calcd.)
1	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-o) ₂	15.01	772.51 (773.48)
2	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-m) ₂	16.5	771.51 (773.48)
3	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-p) ₂	17.5	772.51 (773.48)
4	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₁₀ H ₇ -β) ₂	21.02	844.30 (845.55)
5	(p-CH ₃ O - C ₆ H ₄) ₂ Sb(OCOCH ₂ O C ₆ H ₄ (Cl) - o) ₂	23.05	809.85 (814.32)
6	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₁₀ H ₇ -β) ₂	17.05	745.40 (755.47)
7	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ Cl - o) ₂	16.01	714.25 (724.24)
8	(C ₆ H ₅) ₂ Sb(OCOCH ₂ O C ₆ H ₄ (CH ₃) - p) ₂	20.15	682.89 (683.40)
9	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃) - p) ₂	20.19	682.75 (683.40)
10	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (Cl) - o) ₂	17.61	612.78 (615.76)
11	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃) - o) ₂	16.07	590.89 (595.34)
12	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃) - p) ₂	20.14	594.38 (595.34)

Table 3 Elemental Analysis data of Organoantimony (v) Aryloxyacetates

S.No.	Complex	Empirical Formula	Found (Calcd.)%	
			C	H
1	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-o) ₂	C ₃₉ H ₃₉ O ₆ Sb	60.51(60.56)	4.05 (5)
2	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-m) ₂	C ₃₉ H ₃₉ O ₆ Sb	60.01 (60.56)	4.15 (5)
3	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-p) ₂	C ₃₉ H ₃₉ O ₆ Sb	59.80 (60.56)	4.98 (5)
4	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₁₀ H ₇ -β) ₂	C ₄₅ H ₃₉ O ₆ Sb	62.87 (63.92)	3.95 (4)
5	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (Cl)-o) ₂	C ₃₇ H ₃₃ Cl ₂ O ₆ Sb	53.12 (54.57)	4.00 (4)
6	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₁₀ H ₇ -β) ₂	C ₄₂ H ₃₃ O ₆ Sb	66.11 (66.77)	4.15 (4)
7	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ Cl - o) ₂	C ₃₄ H ₂₇ Cl ₂ O ₆ Sb	55.19 (56.39)	3.61 (3)
8	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃) - o) ₂	C ₃₆ H ₃₃ O ₆ Sb	61.89 (63.27)	3.98 (4)
9	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃) - p) ₂	C ₃₆ H ₃₃ O ₆ Sb	61.89 (63.27)	3.98 (4)
10	(C ₆ H ₅) ₂ Sb(OCOCH ₂ O C ₆ H ₄ (Cl) - o) ₂	C ₃₃ H ₂₆ ClO ₆ Sb	60.85 (62.42)	4.10 (4)
11	(C ₆ H ₅) ₂ Sb(OCO CH ₂ O C ₆ H ₄ (CH ₃) - o) ₂	C ₃₃ H ₂₉ O ₆ Sb	65.51 (66.58)	3.98 (4)
12	(C ₆ H ₅) ₂ Sb(OCO CH ₂ O C ₆ H ₄ (CH ₃) - p) ₂	C ₃₃ H ₂₉ O ₆ Sb	65.01 (66.58)	4.01 (4)

Table 4 IR Absorption frequencies of Organoantimony (V) aryloxy acetates

S.No.	Complex	ν _{max} (C=O)	ν _{max} (C-Sb)	ν(Sb - O)	ν(Sb - C)
1	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-o) ₂	1680	1383	420	452
2	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-m) ₂	1685	1386	425	451
3	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-p) ₂	1675	1386	425	456
4	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₁₀ H ₇ -β) ₂	1695	1389	425	470
5	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (Cl)-o) ₂	1698	1389	430	470
6	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₁₀ H ₇ -β) ₂	1685	1390	419	469
7	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ Cl - o) ₂	1703	1395	411	455
8	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃) - o) ₂	1675	1360	415	458
9	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃) - p) ₂	1694	1360	417	451
10	(C ₆ H ₅) ₂ Sb(OCOCH ₂ O C ₆ H ₄ (Cl) - o) ₂	1693	1367	415	461
11	(C ₆ H ₅) ₂ Sb(OCO CH ₂ O C ₆ H ₄ (CH ₃) - o) ₂	1655	1375	411	465
12	(C ₆ H ₅) ₂ Sb(OCO CH ₂ O C ₆ H ₄ (CH ₃) - p) ₂	1664	1360	417	467

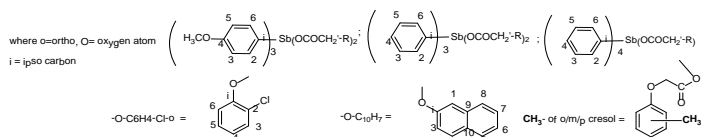
Table 5 ¹H NMR Spectra of Representative Organoantimony (V) Aryloxy Acetates In δppm

Comp. No.	CH ₃ O-	-O-C ₆ H ₄	C ₆ H ₅	-CH ₂ '-	CH ₃ -	-O-C ₆ H ₄ -	-O-C ₁₀ H ₇ -	-C-
	C2/C6	C3/C5	C2/C6 C3/C4/C5			C2/C6 C3/C5		
1	3.80-3.85 (S)	6.80-7.45 (m)	6.90-7.01 (m)	-	4.90-5.10 (s)	6.80-7.00 (m)	7.10-7.55 (m)	-
4	3.75-3.90 (s)	6.75-7.35 (m)	6.90-7.00 (m)	-	4.90-5.15 (s)	-	7.20-7.99 (m)	-
5	3.80-3.89 (s)	6.70-7.50 (m)	6.89-7.12 (m)	-	4.19-5.25 (s)	6.70-7.15 (m)	7.10-7.85 (m)	7.1
6	-	-	7.44-7.50 (m)	-	4.94-5.25 (s)	-	7.15-8.10 (m)	-
7	-	-	7.30-7.55 (m)	-	4.91-5.05 (s)	6.77-7.17 (m)	6.10-7.77 (m)	7.1
8	-	-	7.45-7.55 (m)	-	4.90-5.85 (s)	2.10-2.55 (m)	6.00-7.15 (m)	-
11	-	-	7.35-7.55 (m)	-	4.85-5.25 (s)	2.10-2.75 (m)	6.85-7.01 (m)	-

Where, S = singlet, d = doublet, t = triplet, q = quatret and m = multiplet

Table - 6 ¹³C NMR Spectra of Representative Organoantimony (V) Aryloxy Acetates

Comp. No.	R-Sb					Ligands				
	CH ₃ O-	-O-C ₆ H ₄	C ₆ H ₅	-CH ₂ '-	CH ₃ -	-O-C ₆ H ₄ -	-O-C ₁₀ H ₇ -			
	i-C	C2/C6	C3/C5	i-C	C2/C6 C3/C4/C5	C2/C6 C3/C5	i-C	C3/C5		
1	54.8	130.5	136.5	112.5	-	65.5	15.8	112.5	155.5	130.5
4	55.6	132.5	136.8	118.5	-	67.5	-	-	-	155.8
5	54.9	133.5	138.5	115.8	-	60.8	-	110.5	156.5	139.5
6	-	-	-	135.5	136.5	128.5	70.1	-	-	158.9
7	-	-	-	139.5	140.5	130.5	69.5	-	114.5	158.5
8	-	-	-	140.5	132.5	125.9	68.5	18.5	120.5	160.5
11	-	-	-	138.5	135.5	130.1	68.7	16.10	118.5	162.5



6 CONCLUSION

Based on IR, UV and NMR spectral data enumerated above, it may tentatively be concluded that aryl oxyacetate under the present study behave as monodentate ligand having character of weak secondary interaction towards antimony in +5 oxidation state. Conductance measurement and molecular weight data showed that these aryloxyacetates have monomeric constitution and are nonconducting.

ACKNOWLEDGMENT

The authors are thankful to Head, Department of Chemistry, University of Lucknow, Lucknow for providing necessary laboratory facility and University Grant Commission, New Delhi, India for providing financial assistance through a Major Research Project vide letter No. 37-429/2009/ SR.

REFERENCES

- [1] R.C. Mehrotra and R. Bohra, Metal Carboxylates, *Academic Press, London*, 1983 and references there in.
- [2] S.P. Bone and D.B. Sowerby, *J. Organo met. Chem.*, 184, 181, 1980.
- [3] M. Wieber, I. Fetzer-kremling, H. Reith and Burschka, *Z. Natuforrch. Teil B*, 42, 815, 1987.
- [4] R.G. Goel, *Can. J. Chem.*, 47, 4607, 1969.
- [5] V.H. Schmidbouer, R.H. Mitschke and S. Weidlein, *Z.. Anorg. Allg. Chem.*, 386, 146, 1971.
- [6] M. Hall, D.B. Sowerby and C.P. Falshaw, *J. Organo met. Chem.* 315, 321. 1986.
- [7] H.J. Frohn and H. Maurer, *J. Fluorine Chem.*, 343, 129, 1986.
- [8] G.S. Harris, A. Khan and I. Lennon, *J. Fluorine Chem.*, 37, 247, 1987.
- [9] A.K. Saxena, A. Ranjan and P.S. Venkataramani, *J. Fluorine Chem.*, 64, 107, 1993.
- [10] H.A. Meinema and J.G. Noltes, *J. organome chem.*, 313, 1972.
- [11] G. Smith, E.J. O' Reilly, C.H.L. Kennard, K. stadnaka & B Oloeksyn, *Inorg. Chim. Acta*, 47, 11, 1981.
- [12] T.K. Chattopadhyay, A.K. Kumar, B. Majee, *Ind. J. Chem.*, 33A , 948, 1994.
- [13] N. Sharma, B.S. Golen, R.K. Mahajan, S.C. Chaudhri, *Polyhedron*, 10, 789, 1991; V.K. Jain, R. Bohra and R.C. Mehrotra, *Struct. Bond*, 52, 147, 1982.
- [14] Ashok Ranjan, A.K. Saxena, P.S. Venkataramani, *Ind. J. Chem.*, 33A, 948, 1994.
- [15] Ajita Pandey, "Studies on Organoarsenic (v) and organo-antimony (v) derivatives", Ph.D. Thesis, Lucknow University, Lucknow, 1998; R.R. Holmes "Penta co-ordinated Phosphorous structure and spectroscopy" vol.1, ACS manager, Washington D.C. 1980.
- [16] Prem Raj, A.K. Aggarwal, Kiran Singhal, *Synth. React. Inorg. Met. Org. Chem.*, 22(5), 509, 1992.
- [17] Prem Raj, A.K. Saxena, Kiran Singhal, A.Ranjan, *Polyhedron*, 4(2), 251, 1985.
- [18] Kiran Singhal, Rajiv Rastogi, P.Raj, *Ind. J. Chem.*, 26A, 146, 1987.
- [19] Prem Raj, Ashok Ranjan, Kiran Singhal, Rajiv Rastogi, *Synth. React. Inorg. Met. Org. Chem.*, 14(2), 269, 1984.
- [20] Prem Raj, K. Singhal, S. Agnihotri, *Synth React Inorg, met. org. chem.* 2001.
- [21] W.J. Geary, *Coord. Chem. Rev.*, 7, 81, 1971.
- [22] E. Maslowsky (Jr.) *Organomet. chem.*, 70, 153, 1974.

- [23] Hubert Baruki, Simon J. coles, J.F. Costello, T. Gelbrich and M.B. Hursthouse, *DALTON*, (2000).
- [24] J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1, 192, (1940).
- [25] S. P. Olifirenko, *Chem. Abstr.*, 63, 8401, (1965).
- [26] J. Chatt and F. G. Mann, *J. Chem., Soc.*, 1182, (1940).
- [27] K. Singhal, R. Rastogi, P. Raj, *India Journal of Chemistry*, v- 26A, pp. 146-150, 1987.
- [28] K.I. Singhal, P. Raj, *Synth. React. Inorg. Met-Org. Chem.*, 23(6), pp. 1011-1020, 1993.
- [29] F. Jee, A. K. Aggarwal, P. Raj, *Proc. Indian natn. Sci. Acad*, 59, A, 3, pp 309-313, 1993.
- [30] G. B. Deacon, W. Roy, J. and J. M. Pfeiffer, *Aust. J. Chem.*, 37, pp 527-535, 1984.
- [31] T. Hasan, P. K. Singh, R. Mishra, P. Raj, N. Misra, *Pramana Journal of Physics*, v-68, 5, pp. 875-880, 2007.
- [32] Th. Klapotke, *Journal of Organometallic Chemistry*, 331, pp. 299-307, 1987.
- [33] S. Agnihotri, P. Raj, K. Singhal, *Synth. React. Inorg. Met-Org. Chem.*, 32 (3), pp. 449-464, 2002.
- [34] P. Raj, S. Agnihotri, K. Singhal, *Synth. React. Inorg. Met-Org. Chem.*, 32 (3), pp. 569-581, 2002.

Table - 1: Preparation and Properties of Organoantimony (V) aryloxyacetates

S.No.	Complex	Recrystallization solvent	M.P. (°C)	Colour
1	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-O) ₂	Hexane + Pet. ether (40° - 60°C)	132	Light Brown
2	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-m) ₂	Hexane + Pet. ether(40° - 60°C)	128	Light Brown
3	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-p) ₂	Benzene	110	Light Brown
4	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₁₀ H ₇ -β) ₂	Pet. Ether (40°-60°C)	125	Dirty White
5	(p-CH ₃ OC ₆ H ₄) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (Cl)-O) ₂	Hexane - Benzene	140	White
6	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₁₀ H ₇ -β) ₂	Benzene	135	Dirty White
7	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ Cl - O) ₂	Benzene	88	White
8	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-O) ₂	Benzene	148	White
9	(C ₆ H ₅) ₂ Sb(OCOCH ₂ OC ₆ H ₄ (CH ₃)-p) ₂	Hexane	145	White
10	(C ₆ H ₅) ₂ Sb(OCOCH ₂ O C ₆ H ₄ (Cl)-O)	Pet. Ether (40° - 60°)	90	Light Brown
11	(C ₆ H ₅) ₂ Sb(OCO CH ₂ O C ₆ H ₄ (CH ₃)-O)	Pet. Ether (40° - 60°C) - Hexane	126	Light Brown
12	(C ₆ H ₅) ₂ Sb(OCO CH ₂ O C ₆ H ₄ (CH ₃)-p)	Benzene	200	Light Brown