

## Synthesis and Spectroscopic Characterization of Bis and Mono Halide (Antimony(III) *O,O'*-Ditolyldithiophosphate) Compounds

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Received 19 September 2013 / Accepted 6 October 2013

**Abstract:** Antimony complexes of the type  $[Sb\{S_2P(OR)_2\}_nCl_{3-n}]$  (where R = *o*-, *m*-, *p*-C<sub>6</sub>H<sub>4</sub>Me; n =1-2) have been obtained by the reaction of antimony(III) chloride with ammonium salts of *O,O'*-di(*o*-, *m*-, *p*-tolyl) dithiophosphates in 1:2 and 1:1 molar ratio by stirring followed by refluxing in benzene. All these complexes have been characterized by elemental analysis and IR, <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. On the basis of experimental and spectroscopic studies distorted trigonal bipyramidal geometry (tbp) around antimony having a lone pair of electron, at axial position may be proposed for the complexes corresponded to [*o*-, *m*- or *p*-MeC<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>SbCl<sub>2</sub>] while an octahedral geometry with a lone pair of electrons may be suggested for the complexes [*o*-,*m*- or *p*-MeC<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>]<sub>2</sub>SbCl].

**Keywords:** Anisobidentate complexes, Ditolyl dithiophosphates, <sup>1</sup>H NMR, <sup>31</sup>P NMR

### Introduction

Arsenic, antimony and bismuth halides function as very weak Lewis acids towards thio ethers<sup>1</sup> and has great affinity for anionic dithiolato ligands<sup>2-14</sup>. These complexes exhibit remarkable diversity in their coordination patterns because as coordination centre, these complexes exhibit unpredictable structural behaviour due to the presence of lone pair of electrons on the metal, small ligand bite and molecular associations. The dithiolato ligands can behave as monodentate<sup>8-9</sup>, bidentate<sup>6-10</sup> and bridging<sup>14</sup>. The bidentate and bridging coordination patterns are comparatively more stable than monodentate probably due to inorganic ring formation. The -PS<sub>2</sub> group of the dithiophosphate ligand can coordinate as isobidentate and anisobidentate. A number of antimony(III) complexes with these ligands have been described and some of them have also been characterized by single crystal x-ray structural analysis<sup>4-7</sup>.

Huidac and co workers have investigated anticancer activity of  $Ph_2Sb[S_2P\{O(i-Pr)\}_2]$ <sup>15,16</sup>.  $Sb[S_2P(OEt)_2]_3$ <sup>7</sup> was reported in lubrication engineering as passivating agents for decontaminant metals in the catalytic cracking of petroleum for treating petroleum heavy oil. The group 15 chalcogenide materials obtained from pyrolysis of such derivatives (e.g. 1.7(Sb)) and their ternary compounds (e.g. CuSbS<sub>2</sub>) have been used in solar cells, photolithography, holographic recording, optical memory devices, photoconductors and as thermoelectric generators and coolers<sup>17,18</sup>.

Keeping in mind the preceding interesting facets of dithiophosphate chemistry and in continuation of our earlier work with group 15 elements<sup>6</sup> we report herein the synthesis and characterization of some novel complexes of antimony(III) with *O,O'*-ditolyl dithiophosphate ligands by using antimony trichloride and ditolyldithiophosphate ligands in 1:2 and 1:1 molar ratio.

## Experimental

Owing to extremely hydrolysable nature of the starting materials as well as the newly synthesized compounds, stringent precautions were taken to exclude atmospheric moisture throughout all the experimental manipulations.  $P_2S_5$  and  $SbCl_3$  were purchased from E. Merk and used as received without further purification. *o*-, *m*-, *p*- Cresols, solvents (benzene, *n*-hexane) (E. Merk) were distilled prior to use. Literature methods were used for the preparation of *O,O'*-ditolyl dithiophosphoric acids<sup>18-20</sup>. Ammonium salts of the dithiophosphoric acids were prepared by reaction of parent acid with an equimolar amount of ammonia in benzene.

Sulphur was estimated gravimetrically as barium sulphate (Messenger's method)<sup>21</sup> and antimony(III) was estimated iodometrically<sup>21</sup>. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer in KBR pellets in the range 350-4000  $cm^{-1}$ .  $^1H$  NMR and  $^{31}P$  NMR spectra were recorded on a Bruker DRX-300 spectrometer in  $CDCl_3$  solutions using TMS as an internal standard and  $H_3PO_4$  as an external standard respectively.

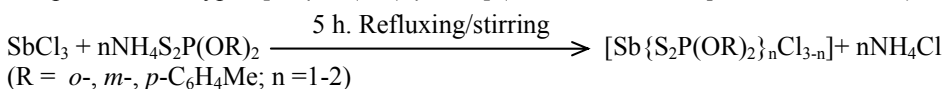
### *Synthesis of $[Sb\{S_2P(OR)_2\}_nCl_{3-n}]$ ( $R = o$ -, $m$ -, $p$ - $C_6H_4Me$ ) complexes*

The benzene solution of (10 mL) antimony(III) chloride (0.25 g, 1.09 mmol) was added drop wise with constant stirring to benzene suspension of ammonium salt of di-(*m*-tolyl)dithiophosphoric acid (0.71 g, 2.18 mmol). The colour of the reaction mixture was changed to yellow which was then refluxed for ~5 h. Now the contents were brought to room temperature and ammonium chloride was separated by filtration under anhydrous conditions and excess solvent was removed from the filtrate in *vacuum* yielding a pale yellow viscous oily liquid.

Yield: 0.80g, 94%; *Anal.* Calc. for  $C_{28}H_{28}O_4S_4P_2ClSb$ : Sb, 15.69; S, 16.53. Found: Sb, 15.20; S, 16.22%. Other complexes of antimony(III) trichloride with ammonium salts of *O,O'*-di(*o*-, *m*-, *p*-tolyl) dithiophosphates in 1:2 and 1:1 molar ratio were synthesized in the same manner.

## Results and Discussion

Antimony complexes of the type  $[Sb\{S_2P(OR)_2\}_nCl_{3-n}]$  ( $R = o$ -,  $m$ -,  $p$ - $C_6H_4Me$ ) have been obtained by the reaction of antimony(III) chloride with ammonium salts of *O,O'*-di(*o*-, *m*-, *p*-tolyl) dithiophosphates in 1:2 and 1:1 molar ratio by refluxing in benzene yielded complexes of the type,  $[Sb\{S_2P(OR)_2\}_nCl_{3-n}]$  (where  $R = o$ -,  $m$ -,  $p$ - $C_6H_4Me$ ;  $n=1-2$ ).



These complexes were soluble in common organic solvents such as benzene, dichloromethane, toluene, acetone and chloroform *etc.* and conversely insoluble in the non polar organic solvents as carbon tetrachloride and hexane. It was not possible to obtain the crystals of the compounds either by cooling or by slow evaporation of the solution of these complexes after many efforts. The products were characterized by elemental analysis, IR,  $^1H$  and  $^{31}P\{^1H\}$  NMR spectroscopy. The elemental analyses were found consistent to the molecular formula of the complexes.

### IR spectra

The IR spectra of antimony(III) (*O,O'*-ditolyl dithiophosphate) complexes (Table 1) have been measured in the range 4000-350  $\text{cm}^{-1}$  and assignments have been made by comparisons with spectra of salts of *O,O'*-di(*o*-, *m*- or *p*-tolyl) dithiophosphoric acids<sup>18-20</sup> and analogous antimony(III) *O,O'*-dialkyl/ditolyl dithiophosphates<sup>6,22</sup>. Two strong intensity bands present in the region 1173-1133 and 931-722  $\text{cm}^{-1}$  have been assigned to  $\nu[(\text{P})\text{-O-C}]$  and  $\nu[\text{P-O-(C)}]$  stretching vibrations, respectively, in complexes **1-6**. The bands of medium intensity present in the region 660-650 and 563-517  $\text{cm}^{-1}$  may be ascribed to  $\nu(\text{P}=\text{S})$  and  $\nu(\text{P-S})$ . These bands are remarkably shifted to lower frequency as compared to their free ammonium salts of di(*o*-, *m*- or *p*-tolyl) dithiophosphoric acids, consistent with coordination of sulfur of  $\text{P}=\text{S}$  to the antimony.

**Table 1.** Selected IR spectroscopic data ( $\text{cm}^{-1}$ ) for the antimony(III) (*O,O'*-ditolyl dithiophosphate) Complexes in KBr pellets in the range (4000-350)  $\text{cm}^{-1}$

S.No	Compound	$\nu [(\text{P})\text{-O-C}]$	$\nu [\text{P-O-(C)}]$	$\nu(\text{P}=\text{S})$	$\nu(\text{P-S})$
1	$[\text{Sb}\{\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{Me-}o)_2\}_2\text{Cl}]$	1173s	766s	660m	536m
2	$[\text{Sb}\{\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{Me-}o)_2\}_2\text{Cl}_2]$	1169m	762s	655s	534s
3	$[\text{Sb}\{\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{Me-}m)_2\}_2\text{Cl}]$	1133m	779s	652m	547m
4	$[\text{Sb}\{\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{Me-}m)_2\}_2\text{Cl}_2]$	1142s	786s	657m	550s
5	$[\text{Sb}\{\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{Me-}p)_2\}_2\text{Cl}]$	1169s	722m	650s	517s
6	$[\text{Sb}\{\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{Me-}p)_2\}_2\text{Cl}_2]$	1170s	931m	652m	563w

Key: *s* = strong, *m* = medium, *w* = weak

### <sup>1</sup>H NMR spectra

The spectra for the complexes **1-6** were recorded in  $\text{CDCl}_3$  at room temperature. The <sup>1</sup>H NMR spectroscopic data (Table 2) of antimony(III) (*O,O'*-ditolyl dithiophosphate) complexes are similar to those of the corresponding salts of dithiophosphoric acids probably due to the large separation between antimony and the hydrogen atoms. A sharp singlet is observed for methyl protons of tolyl group in the region 2.26-2.32 ppm displaying negligible shift as compared to the corresponding salts of *O,O'*-di(*o*-, *m*- or *p*-tolyl) dithiophosphoric acids. The phenyl protons appear in the expected range 6.60-7.38 ppm in these complexes undergoing a negligible shift as compared to free ligand signify coordination of the ligand to metal centre. An integral of these shifts also supports the formation of 1:2 and 1:1 complexes between antimony trichloride and the dithiophosphate ligands.

### <sup>31</sup>P{<sup>1</sup>H} NMR spectra

The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of these complexes were recorded in  $\text{CDCl}_3$  (Table 2). A sharp singlet in the region 83.95-88.39 ppm for each complex indicates the anisobidentate coordination of the dithiophosphate group to the metal centre in the molecules<sup>23</sup>. Presence of only one signal indicates equivalent nature of phosphorus nuclei as well as symmetrical nature of molecule and purity of the compound. The <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts for these complexes **1-6** are shifted 17-20 ppm towards low frequency from those of the corresponding salts of *o*-, *m*- and *p*-ditolyl dithiophosphoric acids might be due the anisobidentate nature of the ditolyl dithiophosphate moieties.

**Table 2.** Selected  $^1\text{H}$  NMR and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopic data for antimony(III) (*O,O'*-ditolyl dithiophosphate) complexes

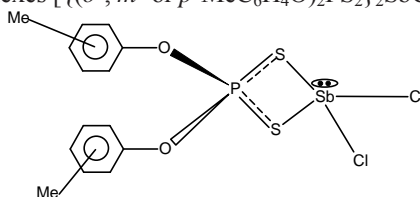
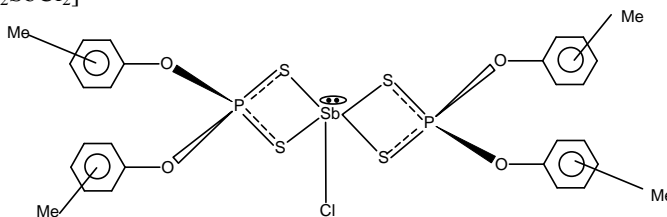
S.No	Compound	$^1\text{H}$ NMR, $\delta$ ppm*	$^{31}\text{P}\{^1\text{H}\}$ NMR $\delta$ ppm*
1	$[\text{Sb}\{\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{Me-}o)_2\}_2\text{Cl}]$	2.26(s,[12H],Me), 7.08-7.34(m,[16H],OC <sub>6</sub> H <sub>4</sub> )	83.95
2	$[\text{Sb}\{\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{Me-}o)_2\}_2\text{Cl}_2]$	2.28 (s,[6H],Me), 7.11-7.38 (m,[8H],OC <sub>6</sub> H <sub>4</sub> )	88.31
3	$[\text{Sb}\{\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{Me-}m)_2\}_2\text{Cl}]$	2.32(s,[12H],Me), 6.60-7.22(m,[16H],OC <sub>6</sub> H <sub>4</sub> )	85.58
4	$[\text{Sb}\{\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{Me-}m)_2\}_2\text{Cl}_2]$	2.30(s, [6H],Me), 7.02-7.24 (m,[8H],OC <sub>6</sub> H <sub>4</sub> )	88.39
5	$[\text{Sb}\{\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{Me-}p)_2\}_2\text{Cl}]$	2.32(s,[12H],Me), 7.05-7.13(m,[16H],OC <sub>6</sub> H <sub>4</sub> )	85.47
6	$[\text{Sb}\{\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{Me-}p)_2\}_2\text{Cl}_2]$	2.29(s, [6H],Me), 6.99-7.25 (m, [8H],OC <sub>6</sub> H <sub>4</sub> )	84.64

Keys: *s* = singlet, *m* = multiplet

\* $^1\text{H}$  NMR and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker DRX-300(300MHz) spectrometer in  $\text{CDCl}_3$  solutions using tetramethylsilane as an internal standard and 85%  $\text{H}_3\text{PO}_4$  as an external standard respectively.

## Conclusion

On the basis of the above spectroscopic data and comparison of relevant data with the literature, a plausible geometry with anisobidentate coordination of the ligands to the antimony atom may be proposed for these complexes. In addition anisobidentate mode of the *O,O'*-di(*o*-, *m*- or *p*-tolyl) dithiophosphoric acid ligands towards the antimony atom has already been established by our research group through single crystal x-ray diffraction<sup>6</sup>. It would be appropriate to suggest distorted trigonal bipyramidal geometry (tbp) around antimony having a lone pair of electron, perhaps, at axial position for the complexes corresponded to  $[(o\text{-}, m\text{-} \text{ or } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2\text{SbCl}_2]$  (Figure 1) while an octahedral geometry with a lone pair electrons may be suggested for the complexes  $[\{(o\text{-}, m\text{-} \text{ or } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2\}_2\text{SbCl}]$  (Figure 2).

**Figure 1.** Proposed trigonal bipyramidal geometry of the complexes  $[(o\text{-}, m\text{-} \text{ or } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2\text{SbCl}_2]$ **Figure 2.** Proposed octahedral geometry of the complexes  $[\{(o\text{-}, m\text{-} \text{ or } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2\}_2\text{SbCl}]$

### Acknowledgment

We are thankful to SAIF, Punjab and CDRI, Lucknow for the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectral analyses.

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