Synthesis and Characterization of Some Triphenylantimony(V) Derivatives of N, O and S Containing Monofunctional Bidentate Ligands

Pankaj K. Sharma, Rajendra K. Sharma, A.K. Rai and Y.P. Singh*

Department of Chemistry, University of Rajasthan, Jaipur - 302 004, India
e-mail : yp_singh07@yahoo.co.in

ABSTRACT

Triphenylantimony(V)isopropoxide, $Ph_3Sb(OPr^i)_2$, reacts with monofunctional bidentate benzothiazoline ligands of the type $HNC_6H_4SC(R)CH_2C(O)R'$ [where R = CH_3, R′=CH_3(**1**); R=CH_3, R′=C_6H_5(**2**); R=CH_3,R′=4-$CH_3C_6H_4$(**3**); R=CH_3,R′=4-ClC_6H_4(**4**); and R=CF_3,R′=C_6H_5(**5**)] in 1:1 molar ratio in refluxing benzene solution to give corresponding triphenylantimony(V) derivatives, $Ph_3Sb(OPr^i)[SC_6H_4N:C(R)CH_2C(O)R']$. These newly synthesized compounds have been characterized by elemental analyses, molecular weight measurements and IR as well as NMR (^1H and ^{13}C) spectral studies. These studies show the bidentate nature of the ligands and a hexa-coordination around the central antimony atom in these complexes.

INTRODUCTION

The compounds of organoantimony are well known for their applications in chemotherapy as antimony compounds exhibit antiparasitic /1/, antitumor /2/, and antifertility /3/ activity. Interest in the chemistry of higher co-ordinated organoantimony(V) derivatives has increased in the last two decades, with special interest in their molecular structure, as antimony may attain a co-ordination number of 5,6 and even 7 in some special cases /4-10/. A number of $R_3Sb(V)$ (R=alkyl or aryl group) derivatives of multidentate ligands have been synthesized and characterized /4-10/ and in some cases it has been observed that the co-ordination number of antimony is seven /4,5/.

Benzothiazolines constitute an important class of multidentate ligands and some Al /11/, Ga and In /12/ derivatives of benzothiazolines have been reported, in which these ligands have been reported to behave as bifunctional tridentate ligands. In view of the reported bifunctional tridentate behaviour of these benzothiazolines, it was thought that organoantimony(V) derivatives of these ligands would have a higher coordination number, but in the present case the nature of these ligands is found to be mono-functional bidentate and thus resulted organoantimony(V) derivatives have hexa-coordination around the central antimony atom. In view of this we report in this communication the synthesis and characterisation of triphenylantimony(V) derivatives of these ligands.

EXPERIMENTAL

Materials and Methods

All the experiments were carried out under moisture-free conditions. All the chemicals used were of reagent grade. Solvents (E. Merck) were dried by standard methods before use. Ph_3SbBr_2 was prepared by literature method /13/. The benzothiazoline ligands, $\overline{HNC_6H_4SC}(R)CH_2C(O)R'$ [where $R=CH_3$, $R'=CH_3(L^1H)$; $R = CH_3$, $R'=C_6H_5(L^2H)$; $R=CH_3, R'=4\text{-}CH_3C_6H_4(L^3H)$; $R=CH_3$, $R'=4\text{-}ClC_6H_4(L^4H)$; and $R=CF_3$, $R'=C_6H_5(L^5H)$] were prepared /14/ by the equimolar condensation reactions of β-diketones and 2-aminothiophenol in benzene solution and were purified by distillation under reduced pressure before use. Triphenylantimony(V)isopropoxide was prepared by the interaction of Ph_3SbBr_2 with sodium isopropoxide /15/. Antimony was determined iodometrically /16/. Nitrogen and sulphur were estimated by Kjeldahl's and Messenger's methods respectively /16/. Isopropoxide was determined by the chromate oxidimetric method /17/. Molecular weights of these complexes were determined ebullioscopically using Beckmann's thermometer. IR spectra were recorded on a Nicolet DX FTIR spectrophotometer in the range 4000-200 cm^{-1} on a CsI cell. ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 solution on a JEOL-FX-90Q (90MHz) or Brucker DPX-300 MHz NMR spectrometer, using TMS as an internal and external reference respectively.

Since all these organoantimony(V) compounds have been synthesized by a similar method, therefore, for the sake of convenience, the synthesis of one representative compound is given in detail. The synthetic and analytical data of the other analogous complexes have been summarized in Table-1.

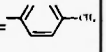
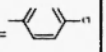
Preparation of $Ph_3Sb(OPr^i)[SC_6H_4N{:}C(CH_3)CH_2C(O)CH_3]$

A weighed amount of sodium metal (0.32 g, 13.92 mM) was added to ~20ml of well dried isopropanol and the mixture was stirred for ~1 hour. A benzene solution of Ph_3SbBr_2 (3.57 g, 6.96 mM) was added to it. The reaction mixture was refluxed for about four hours. The NaBr thus precipitated was filtered off. A benzene solution of the ligand, $\overline{HNC_6H_4SC}(R)CH_2C(O)R'$ (1.44 g, 6.95 mM) was mixed to the filtrate solution of $Ph_3Sb(OPr^i)_2$ and the reaction mixture was refluxed for ~5 hours under a fractionating column. The progress as well as the completion of the reaction was checked by estimating the liberated isopropanol in the azeotrope. After the completion of the reaction, the excess solvent was distilled off and traces of solvent were removed under reduced pressure to give a viscous product. For purification, this viscous compound was dissolved in a small amount of benzene and then petroleum ether (40-60°C) was added to it till the compound began to separate. This solution was kept overnight at -10°C. After decanting off the solvent, the compound was dried under vacuum [yield 86%, (3.69 g)].

Table I

Analytical Data and Physical Properties of the Complexes

$Ph_3Sb(OPr^i)$ $[SC_6H_4N:C(R)CH_2C(O)R']$

Complex	Reactants gm (mM)			Molecular Formula, Color, Physical State and % Yield	Pr^iOH(gm) Found (Calc.)	Elemental Analysis (%) Found (Calc.)			(OPr^i)(%) Found (Calc.)	Molecular Weight Found (Calc.)
	Na	Ph_3SbBr_2	Ligand			Sb	N	S		
R=CH_3 R'=CH_3	0.32 (13.92)	3.57 (6.96)	1.44 (6.95)	$C_{32}H_{34}NO_2SSb$, Light Brown, Viscous, 86	0.40 (0.42)	19.60 (19.69)	2.21 (2.26)	5.02 (5.18)	9.47 (9.55)	611 (618.44)
R=CH_3 R'= 	0.29 (12.61)	3.23 (6.30)	1.70 (6.31)	$C_{37}H_{36}NO_2SSb$, Dark Brown, Viscous, 85	(0.35) (0.38)	17.77 (17.89)	2.00 (2.06)	4.68 (4.71)	8.56 (8.68)	668 (680.51)
R=CH_3 R'= 	0.30 (13.05)	3.35 (6.53)	1.85 (6.53)	$C_{38}H_{38}NO_2SSb$, Light Brown, Viscous, 87	0.37 (0.39)	17.65 (17.53)	1.96 (2.02)	4.53 (4.62)	8.43 (8.51)	686 (694.54)
R=CH_3 R'= 	0.28 (12.18)	3.12 (6.08)	1.85 (6.09)	$C_{37}H_{35}ClNO_2SSb$, Dark Brown, Viscous, 81	0.33 (0.36)	16.89 (17.03)	1.89 (1.96)	4.29 (4.48)	8.24 (8.26)	703 (714.96)
R=CF_3 R'= 	0.27 (11.74)	3.01 (5.87)	1.90 (5.88)	$C_{37}H_{33}F_3NO_2SSb$, Dark Brown, Viscous, 88	0.32 (0.35)	16.48 (16.58)	1.59 (1.91)	4.21 (4.37)	7.99 (8.04)	725 (734.48)

RESULTS AND DISCUSSION

Reactions of $Ph_3Sb(OPr^i)_2$, prepared by the reaction of Ph_3SbBr_2 and $NaOPr^i$ in 1:2 molar ratio, with corresponding monofunctional bidentate ligands in 1:1 molar ratio in refluxing benzene, result in the formation of organoantimony(V) derivatives.

(i) $2Pr^iOH + 2Na \longrightarrow 2NaOPr^i + H_2\uparrow$

(ii) $2NaOPr^i + Ph3SbBr_2 \xrightarrow[\text{Reflux}]{C_6H_6} Ph_3Sb(OPr^i)_2 + 2NaBr\downarrow$

(iii) $Ph_3Sb\left(OPr^i\right)_2 + H\overline{NC_6H_4SC}(R)CH_2C(O)R' \xrightarrow[\text{Reflux}]{C_6H_6}$

$Ph_3Sb\left(OPr^i\right)[SC_6H_4N:C(R)CH_2C(O)R'] + Pr^iOH$

where R = CH_3, R' = CH_3(**1**); R=CH_3, R'=C_6H_5(**2**); R=CH_3,R'=4-$CH_3C_6H_4$(**3**); R=CH_3, R' = 4-ClC_6H_4(**4**) and R = CF_3,R'=C_6H_5(**5**)

These colored, viscous compounds are soluble in common organic solvents. Ebullio-scopic molecular weight measurements reveal their monomeric nature in benzene solution. Physico-chemical and spectral data of these compounds show that in these derivatives, the ligands behave as monofunctional moiety rather than bifunctional as reported earlier /11,12/.

Spectral Studies

Infra-red spectra

The presence of νNH (3225-3335 cm^{-1}) and the absence of νSH mode in the spectra of free ligands reveal the presence of benzothiazoline ring in these ligands. The absence of νNH band and presence of a band due to ν>C=N group at 1619-1625 cm^{-1} (in ligand at 1602-1609 cm^{-1}) indicate the rearrangement of the benzothiazoline ring on complex formation. This rearrangement of the benzothiazoline ring is also supported by the appearance of two new bands at 425-432 cm^{-1} and at 370 - 385 cm^{-1} due, to νSb←N [18] and νSb–S [19] vibrations respectively. The absorption band due to >C=O group is observed at 1720-1730 cm^{-1}. No shift has been observed in its position on complexation, indicating that this group does not participate in bonding. The Sb-Ph vibrations (Y-mode) have been observed in the range 450-473 cm^{-1} /20/.

^{1}H NMR spectra

The ^{1}H NMR spectral data (Table-II) show the presence of expected number of signals corresponding to the number of chemically different types of protons present in these derivatives. A broad signal observed for the -NH proton in the spectra of benzothiazolines at δ4.53-6.46ppm is found to be absent in the spectra of corresponding organoantimony(V) derivatives, indicating the deprotonation of this group and the formation of Sb←N and Sb–S bonds by rearrangement of the benzothiazoline ring.

Table-II

^{1}H NMR Spectral Data (δ ppm) of the Complexes $Ph_3Sb(OPr^i)[SC_6H_4N{:}C(R)CH_2C(O)R']$

Complex	R	R′	$-CH_2-$	CH (Opr^i)	$(CH_3)(Opr^i)$	$-NC_6H_4S-$	Ph-Sb
$R=CH_3$ $R'=CH_3$	2.03 (s)	1.66(s)	2.79(s)	3.77 (sept)	1.05 (d)	6.50-7.17 (m)	7.52-8.40 (m)
$R=CH_3$ R′= 	2.33(s)	6.49-7.40 (m)	2.62 (s)	3.65 (sept)	1.16 (d)	6.49-7.40 (m)	7.74-8.09 (m)
$R=CH_3$ *R′= 	2.39 (s)	6.33-7.27(m)	2.63(s)	3.68 (sept)	0.94 (d)	6.33-7.27 (m)	7.70-8.16 (m)
$R=CH_3$ R′= 	2.36 (s)	6.42-7.44 (m)	2.56(s)	3.71 (sept)	1.05 (d)	6.42-7.44 (m)	7.56-8.20 (m)
$R=CF_3$ R′= 	-	6.30-7.62 (m)	2.49(s)	3.59 (sept)	1.05 (d)	6.30-7.62 (m)	7.70-8.11 (m)

(s) = Singlet; (d) = Doublet; (m) = Multiplet; (sept) = Septet

*A singlet for CH_3 protons has been observed at δ2.16 ppm.

The signal for methylene protons is observed as a sharp singlet at δ 2.49 - 2.79 ppm. The presence of CH_2 signal and the absence of =CH as well as –C–OH signal, in the spectra of ligands as well as complexes, indicate the absence of enolization of >C=O group in these ligands; hence they do not behave as bifunctional ligands with the enolization of >C=O group into –C–OH group. Various R and R' protons are observed at their expected positions with small downfield shifts as compared to their positions in the corresponding ligands. The protons of phenyl groups attached to antimony atom appear as a complex pattern in the range δ 7.52 - 8.40 ppm.

^{13}C NMR Spectra

A comparative study of ^{13}CNMR spectra of these triphenylantimony(V) complexes (**1-5**) (Table-III) with the spectra of free benzothiazoline ligands (**L^1H-L^5H**) provides some useful informations about the mode of bonding in these derivatives. The signal observed for >C=N group carbon at δ 161.39 - 165.74 ppm in the spectra of free ligands shows a downfield shift of ~5 ppm and is observed at δ167.95 - 168.55 ppm in the spectra of the complexes. This downfield shifting in the position of >C=N group signal supports the participation of this group in bonding with rearrangement of the benzothiazoline ring on complexation, followed by the formation of Sb←N and Sb-S bonds. A small shift has also been observed in the position of R, R' and CH_2 signals on complexation as compared to their positions in free ligands.

It is interesting to note that these ligands do not show enolization as -CH_2 signal is observed instead of =CH signal. Appearance of >C=O signal at δ192.95 - 194.02 ppm further rules out the possibility of the enolization of these ligands. The >C=O signal is observed without any shift in the spectra of complexes, indicating that this group does not participate in the bonding. Presence of >CH (OPr^i) and (CH_3)(OPr^i) signals at δ 68.01 - 69.01 and 25.42 - 26.25 ppm, respectively, indicates the monofunctional behaviour of these ligands. It is clear from the above facts that these ligands behave as monofunctional bidentate moiety. This is in contrast to the earlier reports on Al /11/, Ga and In /12/ etc. derivatives of these ligands, in which these ligands have been reported as bifunctional tridentate moiety. The phenyl carbons attached to antimony atom appear in the region δ 127.76 - 154.62 ppm.

In view of the monomeric nature of these complexes and the monofunctional bidentate nature of the ligand moiety, as evidenced by the analytical and spectral data, the following structure (Fig.-1), in which central antimony atom acquires an octahedral geometry, may be assigned to these organoantimony(V) derivatives.

Table III

^{13}C NMR Spectral data (δ ppm) of the complexes $Ph_3Sb(OPr^i)[NC_6H_4S:C(R)CH_2C(O)R']$

Complex	R	R′	CH_2	-CH(OPr^i)	CH_3(Opr^i)	>C=O	>C=N		Sb-Ph
R=CH_3 R′=CH_3	28.16	21.61	62.10	68.25	26.01	192.95	167.95	152.55, 136.18 134.50,128.76 124.25,121.82	153.55 (i) 136.51 (o) 128.64 (m) 128.01 (p)
R=CH_3  R′–	29.06	134.64 130.28 126.40 129.05	61.94	68.01	25.42	193.90	168.55	153.00,135.83 134.90,128.91 124.68,121.89	154.02 (i) 136.85 (o) 128.55 (m) 127.99 (p)
R=CH_3  *R′=	28.96	130.16 126.50 129.11 127.17	62.25	68.69	25.62	193.30	168.20	153.11,135.62 134.76,128.80 124.30,121.81	154.1 (i) 136.92 (o) 128.65 (m) 127.66 (p)
R=CH_3  R′–	29.01	135.02 129.97 126.45 129.21	62.45	69.01	26.25	194.02	167.99	152.99,135.42 134.80,128.86 124.11,121.76	153.95 (i) 136.78 (o) 128.82 (m) 127.86 (p)
R=CH_3  R′=	110.21	134.99 129.65 126.75 129.33	61.99	68.75	25.42	193.89	168.42	153.42,135.20 134.70,128.76 124.21,121.86	154.15 (i) 136.98 (o) 128.55 (m) 128.07 (p)

*^{13}C signal for CH_3 group has been observed at δ26.80 ppm.

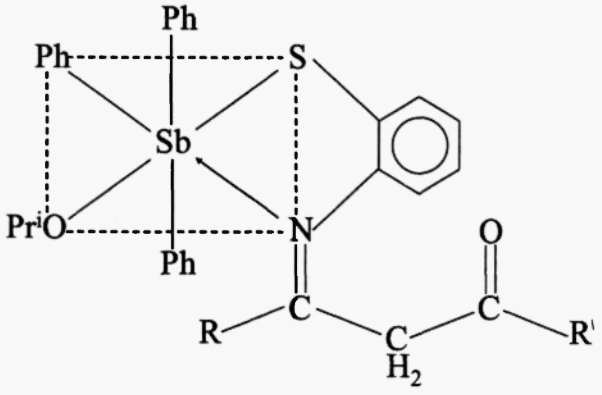


Fig.1: Proposed Structure of the Complexes $Ph_3Sb(OPr^i)$ $[SC_6H_4N:C(R)CH_2C(O)R']$

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