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SYNTHESIS AND CHARACTERIZATION OF SOME NEW MONOPHENYLANTIMONY(III) DERIVATIVES OF BIFUNCTIONAL TETRADENTATE LIGANDS

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ABSTRACT

Monophenylantimony(III) derivatives of bifunctional tetradentate ligands having the general formula $PhSb[RC(NC_6H_4S)CH_2(NC_6H_4S)CR^1]$ where $R{=}CH_3$, $R'{=}CH_3,C_6H_5$ and $4\text{-}CH_3C_6H_4$; $R{=}CF_3$, $R^1{=}CF_3$ and $-C{=}CH{-}CH{=}CHS$ have been prepared by the reactions of triphenylantimony(III) and the corresponding ligands. These compounds have been characterised by elemental analyses, molecular weight determinations, IR, ^1H, ^{13}C and ^{19}F NMR spectral studies.

INTRODUCTION

During the last one and a half decades, the chemistry of organoantimony(III) derivatives with N and S donor ligands has been extensively perused in view of the

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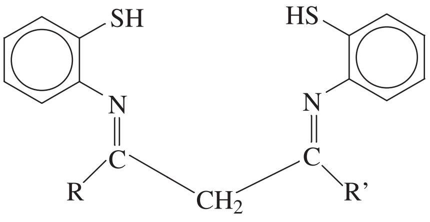


R = CH_3, R^1 = CH_3(**1**), C_6H_5 (**2**) and 4-$CH_3C_6H_4$ (**3**);

R = CF_3, R^1 = CF_3 (**4**) and —C═CH—CH═CHS (**5**)

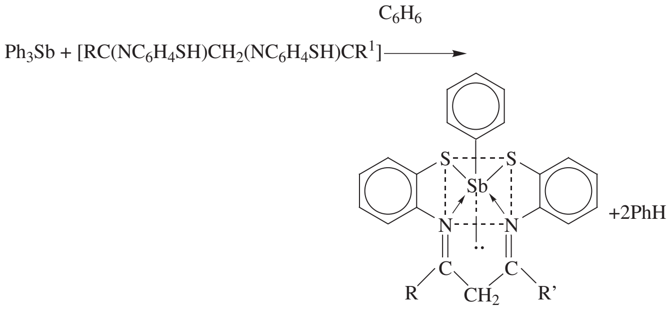
Figure 1. Structure of the bifunctional tetradentate ligands.

potential fungicidal (1), bactericidal (2) and chemotherapeutic (3) applications as well as stereochemical aspects (4–6) of such compounds.

A perusal of the literature (7) reveals that most of the work on organoantimony(III) complexes is confined to monofunctional bidentate ligands and almost no work has been reported with bifunctional tetradentate ligands. In view of this, it has been considered worthwhile to synthesise and characterise some organoantimony(III) complexes using bifunctional tetradentate ligands containing S and N donor atoms (Fig. 1).

RESULTS AND DISCUSSION

Reactions of triphenylantimony(III) with the ligands [$RC(NC_6H_4SH)–CH_2(NC_6H_4SH)CR^1$] in 1:1molar ratio proceed with the cleavage of the antimony carbon bond of Ph_3Sb and yield the monosubstituted derivatives as given below:



$$Ph_3Sb + [RC(NC_6H_4SH)CH_2(NC_6H_4SH)CR^1] \xrightarrow{C_6H_6}$$

R = CH_3, R' = CH_3,C_6H_5 and 4-$CH_3C_6H_4$; R = CF_3, R^1= CF_3 and —C═CH—CH═CHS

After removing the solvent under reduced pressure, light yellow coloured semi-solid compounds were obtained which were found to be sparingly soluble in CH_2Cl_2, $CHCl_3$ and CCl_4 but highly soluble in benzene. Osmometric molecular weight measurements reveal their monomeric nature in benzene solution. These compounds could not be distilled even under reduced pressure as they are thermally unstable and decomposed on heating above 130°C.

IR Spectra

The disappearance of the ν(SH) absorption band in the spectra of these monophenylantimony(III) complexes, which has been observed at 2499–2603 cm^{-1} in the spectra of the ligands, indicates the deprotonation of the SH group of the ligand and the formation of a Sb-S bond. The formation of the Sb-S bond has been further confirmed by the appearance of a new band at 372–395 cm^{-1} which has been assigned to ν(Sb-S) (8). Another new band appearing at 430–435 cm^{-1} in the spectra of complexes has been assigned to ν(Sb-N) (9). The formations of a $Sb \leftarrow N$ bond is further supported by the lowering of the $\nu(C{=}N)$ frequency by 12–18 cm^{-1} on complexation (complexes: 1607–1614 cm^{-1}; ligands: 1619–1632 cm^{-1}). The ν(Sb-C) (8–10) band has been observed at 434–453 cm^{-1} in these derivatives.

^{1}H NMR Spectra

A comparative study of the ^{1}H NMR spectra of these derivatives (Table I) with those of the corresponding free ligands shows the disappearance of the SH signal which was observed as a broad signal in the range of δ 2.44–4.40 ppm in the spectra of the free ligands. The methylene protons are observed as a singlet in the range of δ 2.82–4.49 ppm and a small shift is observed in the complexes as compared to their position in the free ligands. The protons of the various R and R^1 groups have been observed in the range δ 2.59–2.78 ppm. Phenyl and thiophene protons of the ligand moieties are found to be merged with the signals of the phenyl protons attached to the antimony atom and observed as multiplet in the range δ 6.46–8.37 ppm.

^{13}C NMR Spectra

A comparison of the ^{13}C NMR spectra of the monophenylantimony(III) complexes with those of the ligands provides very useful information about the mode of bonding. The spectra of the ligand show one set of signals for the carbons of R and R^1 groups as well as CH_2 carbons. However, two sets of signals

Table I. ^{1}H NMR Spectral Data[a] of Bifunctional Tetradentate Ligands (a) and Their Corresponding Monophenylantinony(III) Derivatives (b)

Ligand(a)/Complex(b)	R	$-CH_2-$	R^1	$-NC_6H_4S-$	$-SH$	C_6H_5-Sb
(a) $R{=}CH_3$, $R^1{=}CH_3$	2.53 (s, 3H)	2.80 (s, 2H)	2.53 (s, 3H)	6.39–8.03 (m, 8H)	2.44 (bs, 2H)	–
(b) $R{=}CH_3$, $R^1{=}CH_3$	2.78 (s, 3H)	2.82 (s, 2H)	2.78 (s, 3H)	6.49–8.08 (m, 8H)	–	6.49–8.08 (m, 5H)
(a) $R{=}CH_3$, $R^1{=}C_6H_5$	2.59 (s, 3H)	2.81 (s, 2H)	6.42–8.12 (m, 5H)	6.42–8.12 (m, 8H)	3.64 (bs, 2H)	–
(b) $R{=}CH_3$, $R^1{=}C_6H_5$	2.60 (s, 3H)	2.85 (s, 2H)	6.53–8.21 (m, 5H)	6.53–8.21 (m, 8H)	–	6.53–8.21 (m, 5H)
(a) $R{=}CH_3$, $R^1{=}4\text{-}CH_3C_6H_4$[b]	2.57 (s, 3H)	2.83 (s, 2H)	6.63–8.14 (m, 4H)	6.63–8.14 (m, 8H)	3.86 (bs, 2H)	–
(b) $R{=}CH_3$, $R^1{=}4\text{-}CH_3C_6H_4$[b]	2.59 (s, 3H)	2.85 (s, 2H)	6.64–8.37 (m, 4H)	6.64–8.37 (m, 8H)	–	6.64–8.37 (m, 5H)
(a) $R{=}CF_3$, $R^1{=}CF_3$	–	4.43 (bs, 2H)	–	6.53–8.11 (m, 8H)	4.27 (bs, 2H)	–
(b) $R{=}CF_3$, $R^1{=}CF_3$	–	4.59 (bs, 2H)	–	6.59–8.27 (m, 8H)	–	6.59–8.27 (m, 5H)
(a) $R{=}CF_3$, $R^1{=}C_4H_3S$	–	4.32 (bs, 2H)	6.42–8.12 (m, 3H)	6.42–8.12 (m, 8H)	4.40 (bs, 2H)	–
(b) $R{=}CF_3$, $R^1{=}C_4H_3S$	–	4.36 (bs, 2H)	6.46–8.15 (m, 3H)	6.46–8.15 (m, 8H)	–	6.46–8.15 (m, 5H)

[a] s = singlet; m = multiplet; bs = broad singlet.

[b] protons of CH_3 group ($4\text{-}CH_3C_6H_4$) were observed at δ 2.38 and 2.44 ppm as singlets in the ligand and complex, respectively.

have been observed for the carbons of >C=N and the substituted phenyl rings. The appearance of the two sets of signals may be due to the presence of two magnetically non-equivalent phenyl rings. This may be explained by considering two -NC_6H_4SH rings in two different planes due to the steric hindrance of the -NC_6H_4SH groups.

In the spectra of the complexes, the signals for R and R^1 carbons show a small shift but the signal for the >C=N carbon shows a down field shift of 2–3 ppm in comparison to their positions in the parent ligands. This indicates the involvement of the nitrogen atom of the ligand moiety in the bonding. A new set of four signals for phenyl carbons attached to antimony appears in the spectra of the complexes in the range δ 126–154.9 ppm. The corrected chemical shift values δ^1 defined (11–12) as $\delta^1 = \delta$ C(p)-δ C(m) (where δ C(p) and δ C(m) are the chemical shift values of *para* and *meta* carbon atoms of the phenyl group) are found in the range -2.77 to -0.86 in these complexes. This negative value of δ^1 indicates the release of electrons from antimony atom to the phenyl ring through $d\pi$-$p\pi$ conjugation. σR° values (13) (calculated by the relation $\sigma R^\circ = \delta^1/22.06$) of these complexes are also found to have negative values. A small value of σR° indicates the poor donor capability of the antimony atom.

^{19}F NMR Spectra

The ^{19}F NMR spectrum of the complex $PhSb[CF_3C(NC_6H_4S)CH_2(NC_6H_4S)CCF_3]$ exhibits only one signal at -82.47 ppm for both CF_3 groups. This indicates that both CF_3 groups are in same environment. This observation is in close agreement with the ^{13}C NMR data of the complex.

In view of the monomeric nature of these derivatives and the tetradentate behaviour of the ligands in the complexes as well as the IR and NMR spectral data observed, the following structure (Fig. 2) in which the central antimony atom acquires an octahedral geometry with phenyl group and lone pair occupying trans positions appear to be highly plausible.

EXPERIMENTAL

Moisture was carefully excluded throughout the experiments. The chemicals used were of reagent grade. Triphenylantimony (Aldrich) was used as such without further purification. The ligands have been synthesised by the condensation reaction of β-diketones and 2-aminothiophenol (Merck) in 1:2 molar ratio. Antimony was determined iodometrically. Nitrogen and sulfur were determined by Kjeldhal's and Messenger's methods, respectively (14). Molecular weights

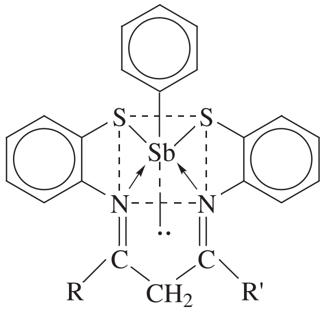
Table II. ^{13}C NMR Spectral Data of Bifunctional Tetradentate Ligands (a) and Their Corresponding Monohenylantinony(III) Derivatives (b) (in δ ppm)

Ligand (a)/Complex (b)	R	$-CH_2$	R^1	$>C=N$	$-NC_6H_4S-$	Sb-Ph[a]	$\delta^1 = Cp\text{-}Cm(\sigma R^{\circ})$	^{19}F
(a) $R=CH_3$, $R^1=CH_3$	19.58	31.46	19.58	1.66.85 162.25	115.01, 117.93,118.48 120.64, 121.18, 122.11 124.49, 124.81, 130.24 130.94, 133.65, 134.05	–	–	–
(b) $R=CH_3$, $R^1=CH_3$	19.61	31.47	19.61	167.70 163.02	115.06, 117.93, 118.69 121.40, 122.92, 124.70 127.19, 127.87, 130.45 131.64, 136.51, 137.16	154.7 135.86 128.77 126.00	–2.77 (–0.12)	–
(a) $R=CH_3$, $R^1=C_6H_5$	19.55	31.52	127.84 129.85 130.66 131.37	166.50 162.06	115.07, 118.00, 121.45 122.92, 124.46, 126.06 127.25, 129.04, 130.17 131.64, 134.36, 135.75	–	–	–
(b) $R=CH_3$, $R^1=C_6H_5$	19.72	31.6	127.47 129.09 130.01 131.17	167.70 162.32	115.11, 118.04, 121.72 123.73, 125.30, 126.44 127.03, 127.42, 130.88 131.64, 136.57, 137.22	154.90 137.22 129.69 127.79	–1.90 (–0.08)	–
(a) $R=CH_3$, $R^1=4-CH_3C_6H_4$[b]	19.66	31.40	127.84 129.09 130.07 131.69	166.23 162.05	115.54, 118.69, 121.45, 122.81, 124.43, 126.0, 127.09, 127.84, 130.50, 132.56, 133.56, 134.76	–	–	–
(b) $R=CH_3$, $R^1=4-CH_3C_6H_4$[b]	19.71	31.47	127.84 129.20	166.42 162.11	118.74, 120.75, 121.51 122.92, 124.76, 126.82	154.17 138.84	–0.86	

			130.28 131.75		127.47, 127.95, 130.93 133.80, 136.57, 137.16	128.82 127.96	(–0.04)	–
(a) R=CF_3, R^1=CF_3	110.05(q)	31.37	110.05(q)	166.58 161.76	115.01, 117.18, 121.35 122.86, 124.92, 126.06 127.25, 128.72, 130.72 131.32, 133.75, 134.98	–	–	–81.26
(b) R=CF_3, R^1=CF_3	110.13(q)	32.39	110.13(q)	168.25 162.05	115.19, 118.04, 121.72 123.73, 125.30, 126.44 129.74, 130.39, 130.88 131.64, 134.18, 136.57	154.9 137.22 129.42 127.90	–1.52 (–0.06)	–82.47
(a) R=CF_3, R^1=C_4H_3S	110.24(q)	32.22	126.82 127.14 128.04 128.98	167.66 162.92	116.14, 118.02, 120.12 121.34, 123.70, 125.24 126.54, 127.34, 129.31 129.90, 131.75, 133.25	–	–	(–74.50)
(b) R=CF_3, R^1=C_4H_3S	110.67	32.91	126.82 127.19 128.06 129.15	168.25 163.32	121.51, 123.35, 125.24 126.71, 127.63, 127.9 129.36, 129.80, 130.07 130.28, 136.51, 137.43	154.39 138.84 128.77 126.54	–2.23 (–0.10)	–78.62

[a] Antimonyphenyl carbons are given in the order C(i), C(o), C(m) and C(p), respectively.

[b] Signal for CH_3 group carbon (4-$CH_3C_6H_4$) were obseved at δ 25.95 and 26.21 ppm in ligand and complex, respectively.



R= CH_3, R^1 = CH_3 (**1**), C_6H_5 (**2**) and 4-$CH_3C_6H_4$ (**3**);

R= CF_3, R^1 = CF_3 (**4**) and $-\overline{\mathrm{C{=}CH{-}CH{=}CHS}}$ (**5**)

Figure 2. Proposed structure of the monophenylantimony(lll) complexes of bifunctional tetradentate ligands.

were measured on a Knauer vapour pressure osmometer in benzene solution. IR spectra have been recorded in a Csl cell on a Nicolet DXFT IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Jeol-FX-90Q (90 MHz) NMR spectrometer in $CDCl_3$ and C_6H_6 solutions, respectively, using TMS as internal reference. ^{19}F NMR spectra were recorded in $CDCl_3$ solution using trifluoroacetic acid as external reference.

Since all of the complexes have been synthesised by the same method, for the sake of brevity, the synthesis of one representative compound is being given in detail.

Synthesis of $PhSb[CH_3C(NC_6N_4S)CH_2(NC_6H_4S)CCH_3]$

About 25 mL of a benzene solution of Ph_3Sb (1.529 g, 4.33 mmol) was added to a benzene suspension (−15 mL) of the ligand $[CH_3C(NC_6H_4SH)CH_2(NC_6H_4SH)CCH_3]$ (1.362 g, 4.33 mmol) and the solution was refluxed for 5–6 hours. After the completion of the reaction, the excess solvent was removed under reduced pressure. For purification, this compound was dissolved in a small amount of benzene (∼15 mL) and then petroleum ether(bp. 40–60°C) was added slowly till a viscous compound began to seperate. The solution was kept overnight at about −10°C. The viscous compound left after decanting off the solvent, was dried under reduced pressure. Yield, 1.75 g (86%).

Table III. Synthetic and Analytical Data of Bifunctional Tetradentate Ligands(a) and Their Corresponding Monohenylantinony(III) Derivatives (b)

Ligand (a) Complex (b)	Reactants[a]		Molecular Formula (Yield%)	State, Color and B.p.(11 mm/Hg)/M.p.	Analysis			M.W. Found (Calc.)
	x	y			%Sb Found (Calc.)	%S Found (Calc.)	%N Found (Calc.)	
(a) R=CH_3, R^1=CH_3			$C_{17}H_{18}N_2S_2$ (87)	Liq., Orange, 127°C (B.p.)	–	20.32 (20.35)	8.82 (8.91)	–
(b) R=CH_3, R^1=CH_3	1.362	1.529	$C_{23}H_{21}N_2S_2Sb$ (86)	Semi solid, Yellow	23.54 (23.83)	12.10 (12.55)	5.22 (5.48)	486 (511.5)
(a) R=CH_3 R^1=C_6H_5			$C_{22}H_{20}N_2S_2$ (91)	Liq., brown, 134°C (B.p.)	–	16.95 (16.99)	7.38 (7.43)	–
(b) R=$CH_3$$R^1$=$C_6H_5$	1.810	1.697	$C_{28}H_{23}N_2S_2Sb$ (82)	semisolid, light yellow	20.12 (20.22)	10.15 (10.45)	4.62 (4.88)	560 (573.8)
(a) R=CH_3, R^1=4-$CH_3C_6H_4$			$C_{23}H_{22}N_2S_2$ (89)	Liq., orange, 136°C (B.p.)	–	16.32 (16.38)	7.10 (7.16)	–
(b) R=CH_3,R^1=4-$CH_3C_6H_4$	1.394	1.260	$C_{29}H_{25}N_2S_2Sb$ (77)	Semisolid, brown	20.31 (20.39)	10.72 (10.91)	4.48 (4.76)	601 (587.7)
(a) R=CF_3, R^1=CF_3			$C_{17}H_{12}F_6N_2S_2$ (84)	Solid, black, 145°C (B.p.); 73-74° (M.p.)	–	15.12 (15.15)	6.58 (6.62)	–
(b) R=CF_3, R^1=CF_3	1.518	1.268	$C_{23}H_{15}F_6N_2S_2Sb$ (78)	viscous, greenish	19.50 (19.65)	10.33 (10.35)	4.50 (4.51)	602 (619.5)
(a) R=CF_3, R^1=C_4H_3S			$C_{20}H_{15}N_2S_3F_3$ (87)	Liq., greenish black, 147°C (B.p.)	–	–	6.38 (6.42)	–
(b) R=CF_3, R^1=C_4H_3S	2.222	1.979	$C_{26}H_{18}S_3N_2F_3Sb$ (79)	viscous, greenish black	19.0 (19.21)	15.14 (15.16)	4.32 (4.42)	620 (633.3)

[a] Reactants for (b), x = Ligand, y = Ph_3Sb.

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