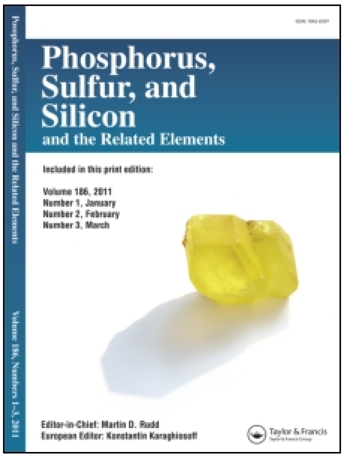

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Synthesis and Characterization of Some New Organoantimony(III) Derivatives of N,S Donor Bifunctional Tetradentate Schiff Bases

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SYNTHESIS AND CHARACTERIZATION OF SOME NEW ORGANOANTIMONY(III) DERIVATIVES OF N,S DONOR BIFUNCTIONAL TETRADENTATE SCHIFF BASES

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Reactions of triphenylantimony(III) with the corresponding Schiff bases in equimolar ratios yield the phenylantimony(III) derivatives, $PhSb[RC(NC_6H_4S)CH_2(NC_6H_4S)CCOOCH_3]$ *(R =* C_6H_5, *4-*ClC_6H_4*, 4-*BrC_6H_4*, and 4-*$CH_3C_6H_4$*). These derivatives have been characterized by elemental analyses, molecular weight measurements, and IR as well as NMR (*^1H *and* ^{13}C*) spectral studies which reveal a five coordination around the central antimony atom.*

Keywords: Five coordinated antimony(III); Schiff bases; triphenylantimony(III)

INTRODUCTION

The chemistry of organoantimony(III) compounds continues to attract the attention due to their significant biological activities[1] and chemotherapeutic applications.[2] Phenylantimony(III) derivatives of the ligands derived by the condensation of acetylacetone and hexafluoroacetyl acetone with 2-aminothiophenol are found to have antifertility activity.[3]

In continuation to our work on organoantimony(III) derivatives of the tetradentate Schiff bases derived by the condensation of 2-aminothiophenol with β-diketones,[4] we report the synthesis and characterization of some phenylantimony(III) derivatives of Schiff bases derived from the condensation of 2-aminothiophenol and aroyl pyruvates.

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RESULTS AND DISCUSSION

The Sb—C bond of Ph_3Sb can be easily cleaved by protic ligands because of the polar nature of Sb—C bond and therefore Ph_3Sb has been used for the preparation of the phenylantimony(III) complexes. Thus the reactions of Ph_3Sb with the Schiff bases $RC(NC_6H_4SH)CH_2(NC_6H_4SH)CCOOCH_3$ in 1:1 molar ratios in benzene yield the corresponding phenylantimony(III) derivatives-

$$Ph_3Sb + RC(NC_6H_4SH)CH_2(NC_6H_4SH)CCOOCH_3$$
$$\xrightarrow{C_6H_6} PhSb[RC(NC_6H_4S)CH_2(NC_6H_4S)CCOOCH_3] + 2PhH$$

where

$$R = C_6H_5,\ 4\text{-}ClC_6H_4,\ 4\text{-}BrC_6H_4 \text{ and } 4\text{-}CH_3C_6H_4$$

These colored semisolid compounds are soluble in benzene but sparingly soluble in CH_2Cl_2, $CHCl_3$, and CCl_4. Osmometric molecular weight determination reveal their monomeric nature in benzene solution at 45°C.

IR SPECTRA

A medium intensity band due to ν_{SH} observed in the region 2573–2629 cm^{-1} in the spectra of Schiff bases is found to be absent in their organoantimony(III) derivatives indicating the formation of a Sb—S bond. Appearance of a new band at 362–372 cm^{-1} which may be assigned to $\nu_{Sb–S}$ modes[5] in the spectra of complexes further supports the formation of Sb—S bond. The >C=N group band is found to be shifted toward lower wave number on complex formation (ligands: 1620–1631; complexes 1607–1617 cm^{-1}) which indicates the involvement of >C=N group in bonding and formation of a Sb←N bond. Formation of Sb←N bond may be supported by the appearance of $\nu_{Sb\leftarrow N}$ vibrations[6] at 435–445 cm^{-1}.

An intense band due to >C=O (ester) group has been observed in the region 1736–1759 cm^{-1}. No appreciable shift has been observed in the position of this band as compared to its position in the spectra of Schiff bases. This indicates that >C=O group does not participate in bonding. The $\nu_{Sb–C}$ vibrations[7,8] have been observed in the region 445–455 cm^{-1}.

^{1}H NMR SPECTRA

A singlet observed for the —SH proton in the spectra of the Schiff bases at δ 3.98–4.15 ppm is not observed in the corresponding organoantimony(III) derivatives indicating the removal of SH proton and the

TABLE I ^{1}H NMR Spectral Data of $PhSb[RC(NC_6H_4S)CH_2(NC_6H_4S)$-$CCOOCH_3]$ (in δ ppm)

S. No.	Complex	R^a	CH_2	$-OCH_3$	$-NC_6H_4S$	Ph—Sb
1	$R = C_6H_5$	7.60–7.89 (o,p)	2.56	3.85	6.49–7.29	7.92–8.24
2	$R = 4\text{-}ClC_6H_4$	7.58–7.98 (o)	2.63	3.91	6.52–7.32	7.99–8.30
3	$R = 4\text{-}BrC_6H_4$	7.64–8.02 (o)	2.56	3.89	6.59–7.38	8.12–8.39
4	$R = 4\text{-}CH_3C_6H_4$^{b}	7.56–7.95 (o)	2.62	3.88	6.68–7.42	7.99–8.28

[a] Meta protons of these groups are observed alongwith $-NC_6H_4S-$ protons in the range δ 6.49–7.42 ppm.

[b] CH_3 protons of $4\text{-}CH_3C_6H_4$ group are observed as a singlet at δ 2.37 ppm.

formation of a Sb—S bond. The sharp singlets observed at δ 2.56–2.63 and 3.85–3.91 ppm have been assigned to CH_2 and OCH_3 group protons respectively (Table I). The ortho and para protons of various R groups ($R = C_6H_5$, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, and $4\text{-}CH_3C_6H_4$) are observed at δ 7.56–8.02 ppm. The meta protons of these groups are found to be merged with the $-NC_6H_4S$ group protons and are observed in the range δ 6.49–7.42 ppm. The protons of aromatic ring attached to antimony atom appear as a complex pattern at δ 7.92–8.39 ppm in these derivatives.

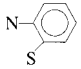
^{13}C NMR SPECTRA

In ^{13}C NMR spectra two sets of signals have been observed for $>C{=}N$ group in these derivatives. This signal shows a considerable shift in its position as compared to its position in corresponding free Schiff bases indicating the involvement of $>C{=}N$ group in bonding. The substituted phenyl rings ($-NC_6H_4S-$) also exhibit two sets of signals. It is interesting to note that the group R, CH_2, and $COOCH_3$ carbon reveal only one set of signal at their expected positions (Table II).

Appearance of two sets of signals for $>C{=}N$ carbon and substituted phenyl ring carbons indicates dissymmetry in these complexes. This may be due to the steric hindrance between two bulky phenylene rings of ligand moiety due to which these two rings do not exist in same plane. As a result distortion in the basal plane of the complexes takes place and two set of signals are observed. Appearance of only one set of signal for various R and CH_2 as well as $COOCH_3$ group carbons indicates that the distortion is limited to the basal plane of the complexes only.

A new set of four signals observed in the spectra of complexes in the range δ 126.82–154.01 ppm has been assigned to the phenyl carbons attached to antimony atom. In view of the possibility of $d\pi - p\pi$ conjugation between phenyl ring and the antimony atom, the corrected chemical shift value of this phenyl ring has been calculated by the

TABLE II ^{13}C NMR Spectral Data of Monophenylantimony(III) Derivatives of the Type PhSb[RC(NC$_6$H$_4$S)-CH$_2$(NC$_6$H$_4$S)CCOOCH$_3$] (in δ ppm)

S. No.	Complex	R	CH$_2$	OCH$_3$	>C=O	>C=N		Sb–Ph[a]	δ^1 (σR°)
1	R = C$_6$H$_5$	127.52 128.70 130.21 131.75	28.75	53.55	189.15	168.65 161.75	121.22, 122.37, 123.74, 124.98, 125.50, 126.35, 127.98, 128.64, 129.55, 130.45, 131.25, 132.75	153.73 136.74 128.72 126.95	−1.77 (−0.08)
2	R = 4-ClC$_6$H$_4$	127.92 128.72 130.94 132.33	28.53	53.61	192.11	167.98 161.95	121.35, 122.53, 124.47, 125.47, 126.73, 127.88, 129.55, 130.44, 131.92, 132.43, 132.98, 133.45	154.01 136.54 128.09 126.85	−1.24 (−0.06)
3	R = 4-BrC$_6$H$_4$	127.86 128.69 129.91 132.89	28.65	53.62	192.41	167.55 161.45	121.37, 123.21, 124.59, 125.43, 126.07, 126.79, 127.23, 128.67, 129.22, 130.79, 131.92, 133.08	153.48 136.64 128.29 126.97	−1.32 (−0.06)
4	R = 4-CH$_3$C$_6$H$_4$[b]	127.78 128.64 129.45 131.29	29.04	53.55	190.45	168.02 161.15	121.03, 121.82, 122.80, 123.98, 124.75, 125.98, 126.17, 127.28, 128.89, 129.85, 131.89, 132.50	153.69 136.50 128.45 126.86	−1.59 (−0.07)

[a] Antimony phenyl carbons values are given in order C(i), C(o), C(m), and C(p) respectively.

[b] Signal for CH$_3$ group carbon of 4-CH$_3$C$_6$H$_4$ has been observed at δ 27.06 ppm.

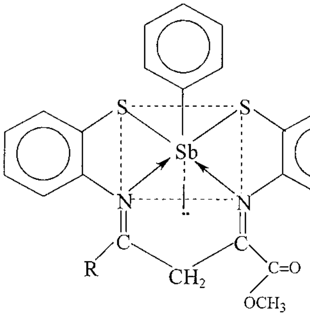


FIGURE 1 Proposed structure of the complexes $PhSb[RC(NC_6H_4S)CH_2(NC_6H_4S)CCOOCH_3]$.

relation $\delta^1 = \delta C_p - \delta C_m$[9] (where δC_p and δC_m are the chemical shift values of para and meta carbons of the ring). The δ^1 values are found to be negative (−1.77 to −1.24 ppm) which indicate the shift of electron density from antimony atom toward phenyl ring through $d\pi - p\pi$ conjugation. Hammet Taft Constant[10] (calculated by the relation $\sigma R^\circ = \delta^1/22.06$) of these complexes are also found to be negative (0.06 to −0.08) indicating the poor donor capability of antimony atom.

Disappearance of the signal/band for SH groups and a shift in the position of band/signal >C=N group indicates the bifunctional tetradentate nature of these Schiff bases. This is supported by the appearance of two new bands for Sb—S and Sb←N in the IR spectra of these complexes. In view of the presence of one phenyl group, one bifunctional tetradentate ligand moiety, and a lone pair of electrons on the central antimony atom, a pseudo-octahedral geometry (Figure 1) may be proposed for these derivatives in which N and S atoms form a basal plane and the phenyl group and a lone pair of electrons occupy trans position to each other.

EXPERIMENTAL

Aroyl pyruvates used for the synthesis of the Schiff bases have been prepared by literature method.[11] The Schiff bases have been synthesized by the condensation reactions of 2-aminothiophenol with some substituted aroyl pyruvates in 2:1 molar ratio. These Schiff bases have been characterized by elemental analysis and spectral [IR, NMR (^1H and ^{13}C)] studies. Ph_3Sb (Aldrich) was used as such without further purification. Sulphur was estimated gravimetrically[12] (Messenger's method) as $BaSO_4$. Nitrogen and antimony were estimated by Kjeldahl's method and iodometrically respectively.[12] Molecular weights were determined

TABLE III Synthetic and Analytical Data of PhSb[RC(NC_6H_4S)CH_2(NC_6H_4S)$CCOOCH_3$]

		Reactants			% Elemental analysis found (calc.)			
S. No.	Complex	Schiff base g (mM)	Ph_3Sb g (mM)	Molecular formula (yield %)	Sb	S	N	Molecular weight found (calc.)
1.	R = C_6H_5	1.002 (2.38)	0.842 (2.38)	$C_{29}H_{23}N_2S_2O_2Sb$ (81)	19.67 (19.70)	10.35 (10.38)	4.49 (4.54)	595 (618)
2.	R = 4-ClC_6H_4	2.458 (5.40)	1.907 (5.40)	$C_{29}H_{22}N_2S_2O_2ClSb$ (83)	18.64 (18.67)	9.82 (9.83)	4.25 (4.29)	640 (652)
3.	R = 4-BrC_6H_4	1.026 (2.05)	0.725 (2.05)	$C_{29}H_{22}N_2S_2O_2BrSb$ (86)	17.45 (17.47)	9.15 (9.20)	3.99 (4.01)	680 (696)
4.	R = 4-$CH_3C_6H_4$	1.637 (3.76)	1.321 (3.75)	$C_{30}H_{25}N_2S_2O_2Sb$ (81)	19.26 (19.27)	10.11 (10.15)	4.42 (4.43)	610 (631)

on a Knauer vapour pressure osmometer using benzene solution. IR spectra were recorded on a Nicolet DX FTIR Spectrophotometer in the range 4000–200 cm^{-1} on a CsI cell. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 300 MHz Spectrometer in $CDCl_3$ solution using TMS as an internal and external reference respectively.

Since similar routes have been adopted for the synthesis of Schiff bases and their organo antimony(III) derivatives therefore, the experimental detail of one representative Shiff base and one organoantimony (III) derivative is being described in detail. The synthetic and analytical data of the remaining complexes are summarized in Table III.

Synthesis of Schiff Base $C_6H_5C(NC_6H_4SH)$-$CH_2(NC_6H_4\ SH)CCOOCH_3$

A weighed amount of methyl 4-phenyl 2,4-dioxo butanoate (1.20 g, 5.42 mM) was mixed to the benzene solution of 2-aminothiophenol (1.36 g, 10.84 mM) in a 100 ml round bottom flask. The reaction mixture was refluxed for 6–7 h under a fractionating column. The water liberated during the course of condensation reaction was removed azeotropically. The volatile fraction was removed under reduced pressure. The Schiff base was further purified by recystallistion from pet. ether (40–60°) and benzene mixture. This Shiff base was analysed to give N = 8.87%, S = 20.33%; Calc. N = 8.90%, S = 20.35%. The analytical data of the other Schiff bases are found to be statisfactory with in ±0.5% range.

Synthesis of $PhSb[C_6H_5C(NC_6H_4S)CH_2(NC_6H_4S)CCOOCH_3]$

A benzene solution of the schiff base $C_6H_5C(NC_6H_4SH)CH_2$-$(NC_6H_4SH)CCOOCH_3$ (1.27 g, 2.38 mM) was added to the benzene solution of Ph_3Sb (0.84 g, 2.38 mM). The reaction mixture was refluxed for about 4 h. After the completion of the reaction, the excess solvent was removed under reduced pressure to give the viscous product. For the purification, this viscous compound was dissolved in a small amount of benzene and then pet. 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.

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