Synthesis and characterisation of phenylantimony(III) derivatives of 2-(2-hydroxyphenyl) benzothiazolines

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Equimolar reactions of $PhSb(OMe)_2$ (prepared *in situ*) and 2-(2-hydroxyphenyl)benzothiazolines LH_2 yield the addition products $PhSb(OMe)_2LH_2$, while equimolar reactions of $PhSbCl_2$ with Na_2L yield Schiff's base derivatives PhSbL, with rearrangement of the benzothiazoline ring. All these derivatives have been characterised by elemental analyses and plausible structures established

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Benzothiazolines constitute an important class of multidentate ligands. The ring opening is induced by metal ions with the formation of Schiff's base chelates.[1,2] However the benzothiazoline ring does not open with some metal chlorides like $AsCl_3$,[3] $SbCl_3$[3] and $BiCl_3$,[3] and addition products are formed. In the case of $Me_3Sn(OH)$ and $Me_3Sn(OEt)$,[4] substitution products are formed with opening of the benzothiazoline ring.

Recently, we have investigated[5] the reactions of $PhAsCl_2$ with NaOMe and 2-(2-hydroxy phenyl benzothiazolines) (LH_2) by two different routes. The reactions of $PhAs(OMe)_2$ with ligand yield addition products, whereas the reactions of $PhAsCl_2$ with the sodium salts of ligands yield the substitution products.

These interesting results prompted us to extend these reactions to the analogous antimony compounds. The results are described and discussed below.

Result and discussion

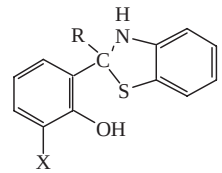
The reactions of $PhSb(OMe)_2$ (prepared *in situ* by the reaction of $PhSbCl_2$ and NaOMe in 1:2 molar ratio) have been carried out with the benzothiazolines LH_2 in equimolar ratio, yielding 1:1 addition products.

$$PhSbCl_2 + 2NaOMe \xrightarrow[\text{Reflux}]{\text{Benzene}} PhSb(OMe)_2 + 2NaCl\downarrow$$

$$PhSb(OMe)_2 + LH_2 \xrightarrow[\text{Reflux}]{\text{Benzene}} PhSb(OMe)_2LH_2$$

1a–c

Where LH_2 =



	LH_2	R	X
a	L^1H_2	H	H
b	L^2H_2	Me	H
c	L^3H_2	H	OMe

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However, equimolar reactions of $PhSbCl_2$ with the sodium salts of the benzothiazolines, Na_2L, in benzene solution proceed with rearrange ment of the benzothiazoline ring and the formation of Sb–S and Sb–O bonds yielding the substituted products.

$$LH_2 + 2NaOMe \xrightarrow[\text{Reflux}]{\text{Benzene}} Na_2L + 2MeOH$$

$$PhSbCl_2 + Na_2L \xrightarrow[\text{Reflux}]{\text{Benzene}} PhSbL + 2NaCl\downarrow$$

2a–c

After removing the solvent under reduced pressure, coloured viscous complexes, soluble in common organic solvents like benzene, chloroform *etc*., are obtained. These complexes are found to be monomeric in benzene solution. Their solubility decreases on ageing.

Spectroscopic studies

Absence of an SH stretching mode (~2450 cm^{-1}) and the presence of an NH stretching mode in the range 3260–3390 cm^{-1} in the IR spectra of the ligands indicates the presence of the benzothiazoline ring in the ligands. In the spectra of complexes (**1a–c**) the value of νNH is lowered by 25–30 cm^{-1}, as compared to its value in the corresponding ligand (complexes: 3235 cm^{-1}, ligand 3260–3390 cm^{-1}). This indicates the participation of the NH group in bonding. This is further confirmed by the appearance of a new band in the region (428–432 cm^{-1}), which has been assigned to the Sb←N[6] stretching vibration. The phenolic –OH band does not show any shift from its position in the free ligand. This indicates that the -OH group of the ligand moiety does not participate in bonding.

The spectra of derivatives **2a–c** show the disappearance of –NH and –OH stretching bands which were observed at 3260–3390 cm^{-1} and 3251–3427 cm^{-1} respectively in the free ligands. This is further supported by the appearance of some new bands at 1621–1647 cm^{-1}, 432–436 cm^{-1}, 375–390 cm^{-1} and 312–328 cm^{-1}, which have been assigned to νC=N, νSb←N,[6] νSb–S,[7] and νSb–O[8] respectively. This indicates the rearrangement of the benzothiazoline ring, leading to the formation of Schiff base complexes. The Sb–C stretching absorbtion[9,10] has been observed at 440–451 cm^{-1}.

The ^1H NMR spectra (Table 1) of the complexes **Ia–c** show down field shifting of the NH signal. This supports the formation of the Sb←N bond during the complexation. I the ligand, the phenolic –OH signal has been observed in the range δ12.23–12.85 ppm. No significant shift has been observed in the position of the phenolic –OH signal on complexation,

Table 1 ^{1}H NMR spectral data (δ ppm) of $PhSb(OMe)_2LH_2$ and PhSbL

Complex	R	OMe	Aromatic	OH	NH	Ph–Sb
1a	8.73	3.40	6.98–7.49	12.71	8.32	7.87–8.22
1b	2.35	3.42	6.38–7.78	12.23	4.21	7.91–8.32
1c	8.09	3.45	6.79–7.89	12.82	7.99	7.95–8.41
2a	8.79	–	6.95–7.45	–	–	7.91–8.22
2b	2.39	–	6.48–7.98	–	–	7.89–8.32
2c	8.19	–	6.85–7.95	–	–	7.72–8.40

indicating that this group does not participate in bonding in complexes **1a–c**.

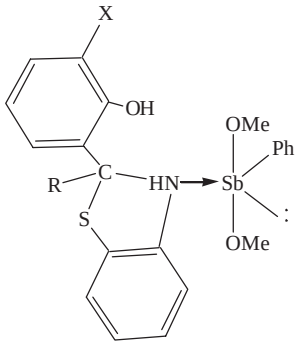
However, the ^{1}H NMR spectra of organoantimony(III) derivatives (**2a–c**) show disappearance of –NH, as well as –OH signals observed as broad signals in the range δ3.72–8.34 ppm and δ12.20–12.82 ppm in the spectra of the ligands. This indicates deprotonation of both groups on complexation. This also supports the opening of benzothiazoline ring and formation of Sb–S and Sb–O bonds.

A comparison of ^{13}C NMR spectra of monophenyl antimony(III) derivatives **1a–c** with the spectra of corresponding ligands shows a small shift in the position of the >C(R)–N signal as compared to its position in the free ligands. This indicates the involvement of the nitrogen atom of the benzothiazoline in bonding. No appreciable shift has been observed in the position of the C-OH group carbon on complexation. This shows that this group does not participate in the bonding.

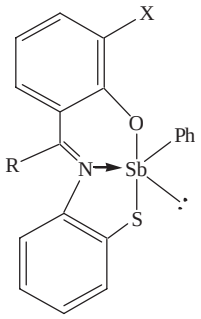
However, ^{13}C NMR spectra of the derivatives (**2a–c**) show a down field shift in the position of the C–N carbon signal. This confirms the formation of a >C=N→Sb bond by rearrangement of the benzothiazoline ring during the complexation. A downfield shift in the position of the C–OH group carbon on complexation indicates deprotonation of the phenolic –OH group and the formation of an Sb–O bond. The substituted phenylene ring carbons are observed in the range δ121.07–171.91 ppm. The $–NC_6H_4S–$ group carbons are observed in the range δ123.07–149.99 ppm. A new set of four signals observed in the range δ126.72–153.01 ppm (**1a–c**) and δ126.66–154.96 ppm (**2a–c**) have been assigned to phenyl ring carbons attached to antimony atom.

In view of the possibility of dπ–pπ conjugation between Sb–Ph, the corrected chemical shift values[11] δ' have been calculated by the relation δ'=δCp–δCm (where δCp and δCm are the chemical shift values of *para* and *meta* carbons of the ring). The δ' values are found to be negative in the range –1.38 to –1.92 ppm. The Hammet-Taft constant[12] [$\sigma R^o = \delta'/22.06$] is also found to be negative in these complexes, indicating the poor donor capability of the antimony atom.

In view of the monomeric nature of these derivatives ebullioscopically and monodentate (**1a–c**) and bifunctional tridentate (**2a–c**) behaviour of ligand moieties in the complexes as evident from observed IR and NMR spectral data, the following structures, in which the central antimony atom acquires trigonal bipyramidal geometry, appear to the highly plausible.



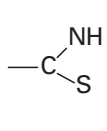
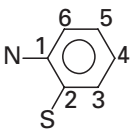
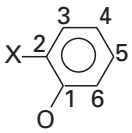
1a–c



2a–c

In view of presence of the methoxy group, the possibility could not be ruled out of dimerisation through the OMe bridge or through hydrogen bonding in compounds (**1a–c**). To check this possibility, cryoscopic molecular weight

Table 2 ^{13}C NMR Spectral data (δppm) of $PhSb(OMe)_2LH_2$ and PhSbL

Complex	CH3	OMe	>C=N				Sb–Ph*	δ'(σR°)
1a	–	49.99	–	161.99	149.0 (1) 138.01 (2) 134.91 (3) 128.96 (4) 124.98 (5) 123.07 (6)	169.22 (1) 125.06 (2) 133.99 (3) 119.96 (4) 134.33 (5) 121.07 (6)	152.71 135.36 128.80 126.22	–1.88 (–0.08)
1b	25.88	51.07	–	162.06	149.88 (1) 139.07 (2) 135.11 (3) 129.01 (4) 125.71 (5) 123.71 (6)	169.52 (1) 128.37 (2) 134.76 (3) 120.06 (4) 134.12 (5) 121.98 (6)	153.01 136.02 128.10 126.72	–1.38 (–0.06)
1c	–	50.92	–	162.71	149.99 (1) 139.92 (2) 134.57 (3) 129.77 (4) 125.79 (5) 123.71 (6)	168.99 (1) 127.27 (2) 135.06 (3) 121.01 (4) 134.52 (5) 122.12 (6)	152.81 135.26 128.29 126.95	–1.34 (–0.06)
2a	–	–	167.71	–	149.78 (1) 139.99 (2) 135.07 (3) 128.98 (4) 125.99 (5) 123.07 (6)	171.71 (1) 128.15 (2) 135.08 (3) 121.92 (4) 135.17 (5) 122.22 (6)	154.91 136.09 128.77 126.98	–1.79 (–0.08)
2b	26.01	–	166.92	–	149.91 (1) 139.95 (2) 134.69 (3) 128.66 (4) 125.71 (5) 123.24 (6)	171.91 (1) 128.92 (2) 136.07 (3) 121.92 (4) 135.17 (5) 122.22 (6)	154.11 136.96 128.45 126.66	–1.79 (–0.08)
2c	–	–	167.07	–	149.33 (1) 138.78 (2) 134.97 (3) 128.17 (4) 126.07 (5) 124.07 (6)	170.12 (1) 129.02 (2) 135.81 (3) 122.01 (4) 136.01 (5) 122.43 (6)	154.96 136.02 128.75 126.83	–1.92 (–0.09)

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

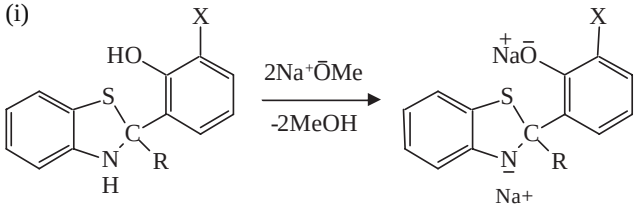
determination of representative compound (**1a**) has been carried out, and this indicates that the compound is monomeric even at lower temperature, which may be due to the steric factor of the benzothiazoline ligand moiety. However, in the substituted product (**2a–c**) the possibility of dimerisation may be ruled out as there is no site available for dimerisation in these compounds.

It is important to note that the reaction of ligand with $PhSb(OMe)_2$ gives the addition product. However, reactions of $PhSbCl_2$ with the sodium salts of ligands give the substitution products. The formation of substitution and addition products may be explained by considering the following mechanism.

(1) Substitution products

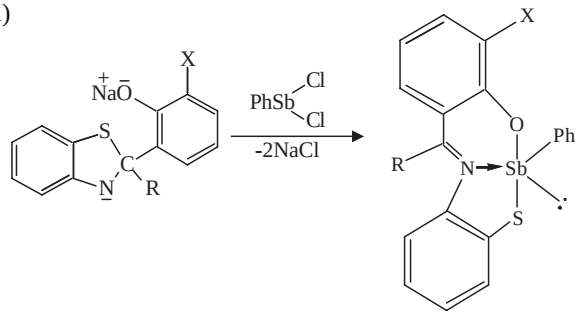
The reaction of NaOMe with ligand lead to the formation of a sodium salt with abstraction of acidic (labile) hydrogens from N–H and O–H groups.

(i)



In the second step addition of $PhSbCl_2$, which has two polar Sb–Cl bonds, results in the formation of the substituted product.

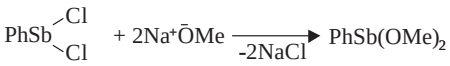
(ii)



Substitution product

(II) Addition products

In the case of addition product, first $PhSbCl_2$ is treated with NaOMe which results in the formation of $PhSb(OMe)_2$.



$PhSb(OMe)_2$ is not able to abstract the acidic hydrogen from the NH and OH groups so the only possibility is Sb←N bond formation and thus only addition products are obtained.

Experimental

All the reactions were carried out under anhydrous conditions. The chemicals used were of reagent grade. Solvents (E. Merck) were purified and dried by standard procedures.[13] Monophenylantimony(III) dichloride was prepared by the literature method.[14] The benzothiazolines[4] LH_2were prepared by the equimolar condensation reaction of 2-aminothiophenol and $HOC_6H_3XC(R)=O$. Antimony was estimated iodometrically[15] and sulphur was estimated by Messenger's method.[15] Molecular weights of these complexes were determined ebullioscopically as well as cryoscopically (only one representative compound **1a**) in benzene solution, using a Beckmann thermometer. C, H and N analyses were carried out on a Carlo Erba 1108 elemental analyzer. IR spectra were recorded on a Nicolet DX FT IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on JEOL-FX - 90Q (90 MHz) and Bruker DPX (300 Hz) instruments in $CDCl_3$, using TMS as an internal reference.

Synthetic details of one representative compound of **1a–c** and **2a–c** are given below. Synthetic and analytical data of the other compounds are summarised in Table 3.

Synthesis of **1a**: A weighed amount of sodium metal (0.34g, 14.76 mM) was treated with ~ 15 ml dried methanol and this mixture was stirred for 30 min. A benzene suspension of $PhSbCl_2$ (1.99g, 7.38 mM) was added and the mixture was refluxed for 30 min. After cooling, a benzene solution of the benzothiazoline $[HOC_6H_4C(H)N(H)C_6H_4S]$ (1.69 g, 7.37 mM) was added. The reaction mixture was again refluxed for ~ 4 h. The NaCl precipitated was filtered off and the excess of solvent from the filtrate was removed under reduced pressure. The resultant viscous compound was then purified by dissolving it in a small amount of $CHCl_3$ (~20 ml) followed by addition of *n*-hexane till a viscous compound began to separate. This solution was kept overnight at – 10°C. After decanting off the solvent, the compound was finally dried under vacuum.

Synthesis of **1b**: A weighed amount of sodium metal (0.22g, 9.56 mM) was added to ~ 15 ml of dried methanol with constant stirring for 30 min. A benzene solution of the benzothiazoline $HOC_6H_4C(H)N(H)C_6H_4S$, (1.10g, 4.79 mM) was added and the mixture was refluxed for 45 min. This solution was then treated with a benzene suspension of $PhSbCl_2$ [1.29g, 4.78 mM. This reaction mixture was further refluxed for ~ 3 h. The NaCl formed during the course of reaction was filtered off and the excess of solvent was removed under reduced pressure. The viscous compound thus obtained was purified from a mixture of $CHCl_3$ and *n*-hexane.

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Table 3 Synthetic and analytical data of **1a–c** and **2a–c**

Complex	Reactants, g/mM			Molecular formula yield/%	% Elemental analysis			Found (Calc.)		Mol. wt Found (Calc.)
	Na	Ligand	$PhSbCl_2$		Sb	S	C	H	N	
1a	0.34 (14.76)	1.69 (7.37)	1.99 (7.38)	$C_{21}H_{22}NO_3SSb$ 82	24.80 (24.82)	6.49 (6.52)	51.28 (51.43)	4.21 (4.32)	2.82 (2.85)	479 502.6* (490.4)
1b	0.30 (13.04)	1.59 (6.53)	1.76 (6.52)	$C_{22}H_{24}NO_3SSb$ 86	24.12 (24.13)	6.32 (6.34)	52.19 (52.39)	4.28 (4.39)	2.74 (2.77)	490 (504.4)
1c	0.24 (10.42)	1.35 (5.21)	1.41 (5.22)	$C_{22}H_{24}NO_4SSb$ 83	23.35 (23.39)	6.13 (6.15)	50.55 (50.78)	4.09 (4.26)	2.66 (2.69)	499 (520.4)
2a	0.22 (9.56)	1.10 (4.79)	1.29 (4.78)	$C_{19}H_{14}NOSSb$ 85	28.52 (28.56)	7.46 (7.50)	53.49 (53.53)	4.32 (4.49)	3.24 (3.28)	415 (426.3)
2b	0.24 (10.44)	1.27 (5.22)	1.41 (5.22)	$C_{20}H_{16}NOSSb$ 86	27.62 (27.64)	7.24 (7.26)	54.45 (54.55)	4.44 (4.58)	3.16 (3.18)	419 (440.4)
2c	0.21 (9.13)	1.18 (4.55)	1.23 (4.56)	$C_{20}H_{16}NO_2SSb$ 84	26.65 (26.68)	6.98 (7.01)	52.39 (52.63)	4.36 (4.42)	3.02 (3.06)	445 (456.4)

*Value of molecular wt. by cryscopically method.

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