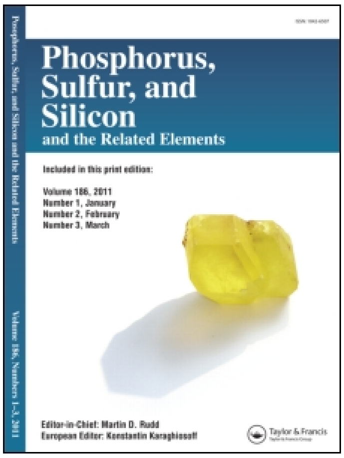

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ORGANOBISMUTH(III) DERIVATIVES OF STERICALLY HINDERED BIFUNCTIONAL TETRADENTATE SCHIFF BASES: SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION

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The equimolar reactions of Ph_3Bi with the bifunctional tetradentate Schiff bases proceed with cleavage of two Bi—C bond of Ph_3Bi and result in the formation of phenylbismuth(III) derivatives $PhBi[RC(NC_6H_4S)CH_2(NC_6H_4S)CCOOCH_3]$ where $R = C_6H_5$, $4\text{-}ClC_6H_4$,$4\text{-}BrC_6H_4$, and $4\text{-}CH_3C_6H_4$. Physico-chemical, IR, and NMR (^1H and ^{13}C) spectral studies have been carried out to investigate the structural aspect of these derivatives which reveal a penta coordination around the central Bi atom.

Keywords: Bifunctional tetradentate ligands; octahedral geometry; spectral study

The chemistry of organobismuth compounds continue to attract attention due to their antitumor activity,[1] pharmacology,[2] catalytical activity, and applications as the precursor for super conducting materials.[4–6] In addition to the applications, the stereochemistry of organobismuth compounds is also very interesting and steric factor appears to play very important role in the determination of the geometry of these compounds. For example $PhBi(S_2CNEt_2)_2$ has tetrahedral geometry[7] whereas $MeBi(S_2CNEt_2)_2$ is dimeric with pentagonal geometry.[8] In this article we report the synthesis and characterization of organobismuth(III) derivatives of sterically hindered bifunctional tetradentate Schiff base ligands.

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RESULTS AND DISCUSSION

The reactions of Ph_3Bi have been carried out with corresponding Schiff bases in 1:1 molar ratios in refluxing benzene to yield the organobismuth(III) derivatives, $PhBi[RC(NC_6H_4S)CH_2(NC_6H_4S)CCOOCH_3]$

$$Ph_3Bi + RC(NC_6H_4SH)CH_2(NC_6H_4SH)CCOOCH_3$$
$$\xrightarrow{C_6H_6} PhBi[RC(NC_6H_4S)CH_2(NC_6H_4S)CCOOCH_3] + 2\ PhH$$

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 compounds are found to be solid in nature and have a poor solubility in common organic solvents. These compounds are thermally unstable as they decompose on heating above 158°C.

IR SPECTRA

A comparison of IR spectra of these derivatives with the corresponding Schiff bases shows the disappearance of SH band (observed as a weak band in the region 2573–2629 cm^{-1} in the spectra of free Schiff bases) and appearance of a new band at 260–271 cm^{-1} which may be assigned to the νBi—S mode of vibrations.[9] This indicates the deprotonation of SH group and the formation of a Bi—S bond. The absorption band due to >C=N group is found to be shifted toward lower wave number on complexation (Schiff bases: 1620–1631 cm^{-1}, complexes 1605–1615 cm^{-1}) indicating the involvement of >C=N group in bonding and formation of a Bi—N bond. Formation of Bi—N bond is further supported by the appearance of a new band at 320–335 cm^{-1} (νBi—N) in the spectra of complexes.[10] A shrap band due to the >C=O (ester) group has been observed in the region 1736–1750 cm^{-1}. No appreciable shift has been observed in the position of this band on complexation indicating that the >C=O (ester) group does not participate in bonding. The Bi—C stretching vibrations have been observed in the range 385–395 cm^{-1} in these derivatives.[9]

^{1}H NMR SPECTRA

The signal observed at δ 3.98–4.15 ppm due to SH proton in the spectra of free Schiff bases is found to be absent in the corresponding organobismuth(III) derivatives. This indicates the formation of a Bi—S bond. A

TABLE I ^{1}H NMR Spectral Data of Phenylbismuth(III) Derivatives $PhBi[RC(NC_6H_4S)CH_2(NC_6H_4S)\text{-}CCOOCH_3]$ (in δ ppm)

S. No.	Complex	R	$-CH_2-$	$-OCH_3$	$-NC_6H_4S-$	Bi—Ph
1	$R = C_6H_5$	7.59–7.94	2.64	3.83	6.53–7.51	8.04–8.61
2	$R = 4\text{-}ClC_6H_4$	7.56–7.97	2.73	3.84	6.52–7.53	8.03–8.62
3	$R = 4\text{-}BrC_6H_4$	7.61–8.01	2.86	3.95	6.55–7.56	8.07–8.65
4	$R = 4\text{-}CH_3C_6H_4$[a]	7.53–7.95	2.72	3.89	6.49–7.45	8.11–8.61

[a] CH_3 group protons of $4\text{-}CH_3C_6H_4$ group are observed as a singlet at δ 2.25 ppm.

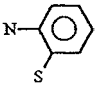
sharp singlet observed at δ 3.83–3.95 ppm has been assigned to CH_3 protons of $COOCH_3$ group. The ortho and para protons of the groups R ($R = C_6H_5$, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, and $4\text{-}CH_3C_6H_4$) have been observed in the range δ 7.53–8.01 ppm. The meta proton of these groups are observed alongwith $-NC_6H_4S-$ group protons in the range δ 6.49–7.56 ppm. The phenyl ring (attached to bismuth atom) protons have been observed as a complex pattern in the range δ 8.03–8.65 ppm (Table I).

^{13}C NMR SPECTRA

^{13}C NMR spectra of these compounds have been recorded in DMSO-d_6 solution using TMS as an external reference (Table II). Steric hindrance between two bulky $-NC_6H_4S$-groups plays an important role in deciding the geometry of these derivatives. Two set of signals have been observed for >C=N as well as $-NC_6H_4S$ group carbons. However, only one set of signal has been observed for R, CH_2 and $COOCH_3$ group carbons. Appearance of two set of signals for >C=N and $-NC_6H_4S$-group carbons may be explained by considering the steric hindrance between two bulky $>C{=}N{-}C_6H_4S$-groups. Due to this steric hindrance, two bulky groups which seems to be chemically equivalent are not found to be magnetically equivalent as they do not exist in the same plane and result two set of signals.

A downfield shift (~2–3 ppm) has been observed in the position of >C=N group signal on complexation indicating the participation of >C=N group in bonding. Phenyl group (attached to Bi atom) carbons have been observed in the range δ 128.13–154.67 ppm. In view of the possibility of dπ-pπ conjugation between Ph—Bi, corrected chemical shift values (δ') for phenyl carbons have been calculated[11] by the relation $\delta^1 = \delta Cp - \delta Cm$ (where δCp and δCm are the chemical shift values of para and meta carbons of the phenyl ring). The δ^1 values are found to be negative in the range -1.45 to -1.02 ppm indicating the dπ -pπ conjugation in these derivatives. The Hammet-Taft constant[12]

TABLE II ^{13}C NMR Spectral Data of Phenylbismuth(III) Derivatives $PhBi[RC(NC_6H_4S)CH_2(NC_6H_4S)\ CCOOCH_3]$ (δ ppm)

Complex	R	CH_2	OCH_3	>C=O	>C=N		Bi—Ph[a]	$\delta^1(\sigma R^\circ)$
$R = C_6H_5$	127.89	28.63	53.72	189.26	171.34	119.28, 121.07, 123.17	154.02	−1.02
	128.77				162.98	124.02, 126.12, 127.79	136.79	(−0.04)
	129.92					129.06, 130.01, 131.72	129.33	
	131.52					132.33, 133.02, 134.06	128.31	
$R = 4\text{-}ClC_6H_4$	127.59	28.77	53.60	192.65	170.12	119.65, 121.85, 123.28	154.30	−1.45
	128.84				163.66	124.16, 125.67, 127.92	137.03	(−0.06)
	130.69					128.89, 130.97, 132.49	130.17	
	131.17					133.02, 134.01, 134.92	128.72	
$R = 4\text{-}BrC_6H_4$	127.52	28.61	53.60	192.47	169.28	119.44, 121.72, 122.23	154.67	−1.24
	128.69				163.25	123.26, 124.01, 124.96	138.94	(−0.05)
	129.35					125.56, 126.22, 127.85	129.04	
	13.189					129.84, 130.97, 132.49	127.80	
$4\text{-}CH_3C_6H_4$[b]	127.53	28.10	53.52	190.47	170.74	119.16, 121.25, 123.16	153.90	−1.25
	128.69				163.12	124.19, 125.20, 126.09	138.64	(0.05)
	129.68					127.59, 128.37, 129.38	129.80	
	131.23					130.86, 131.12, 132.06	128.13	

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

[b] Singal for CH_3 group carbon of $4\text{-}CH_3C_6H_4$ has been observed at δ 25.73 ppm.

σ R° (calculated by the equation $\sigma R^\circ = \delta^1/22.06$) is also found to be negative which show the poor dπ-pπ conjugation in these derivatives.

Disappearance of —SH band/signal, shift in the position of >C=N band/signal and appearance of the new bands for Bi←N as well as Bi—S support the bifunctional tetradentate behavior of ligand moiety. In view

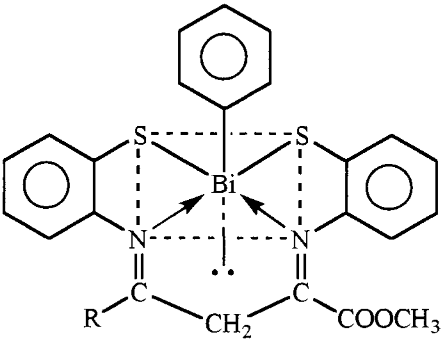


FIGURE 1 Structure of the complexes $PhBi[RC(NC_6H_4S)CH_2(NC_6H_4S)CCOOCH_3]$.

of the presence of one phenyl group, alone pair of electrons and bifunctional tetradentate ligand moiety attached to bismuth atom a pseudo-octahedral geometry may be assigned to these derivatives (Figure 1).

EXPERIMENTAL

Moisture was carefully excluded through out the experimental manupulation. Ph_3Bi was prepared by literature method.[13] The Schiff bases were prepared by the condensation of 2-aminothiophenol with some aroyl pyruvates. Bi was estimated complexometrically.[14] Nitrogen and sulphur was estimated by Kjeldahl's and Messanger's method respectively.[14] IR spectra of these derivatives were recorded on a Nicolet DX FT IR spectrophotometer in the range 4000–200 cm^{-1} using CsI cell. ^1H and ^{13}C NMR spectra were recorded on Brucker DPX 300 MHz spectrometer in $CDCl_3$ and DMSO-d_6 solution using TMS as an internal and external reference respectively. Since same method has been used to synthesize all these complexes therefore, for the sake of convenience, the synthesis of one representative complex is given in detail. The synthetic and analytical data of the other analogous complexes have been summarised in Table III.

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

A benzene solution (~20 ml) of Ph_3Bi (1.93 g, 4.38 mM) was added to the refluxing benzene solution of the Schiff base $C_6H_5C(NC_6H_4SH)CH_2(NC_6H_4SH)COOCH_3$ (1.48 g, 4.38 mM) and the reactions mixture was refluxed for ~4 h. After the completion of the reaction, the compound was filtered off and dried under vacuum.

TABLE III Synthetic and Analytical Data of Phenylbismuth(III) Derivatives $PhBi[RC(NC_6H_4S)CH_2(NC_6H_4S)\text{-}CCOOCH_3]$

	Reactants g (mM)			% Elemental analysis found (calc.)		
Complex	Schiff base	Ph_3Bi	Molecular formula (% Yield)	Bi	S	N
$R = C_6H_5$	1.48	1.93	$C_{29}H_{23}N_2S_2O_2Bi$	29.65	9.09	3.94
	(4.38)	(4.38)	(85)	(29.67)	(9.10)	(3.97)
$R = 4\text{-}ClC_6H_4$	1.96	1.90	$C_{29}H_{22}N_2S_2O_2ClBi$	28.26	8.54	3.74
	(4.31)	(4.31)	(86)	(28.28)	(8.58)	(3.78)
$R = 4\text{-}BrC_6H_4$	1.94	1.71	$C_{29}H_{22}N_2S_2O_2BrBi$	26.67	8.15	3.55
	(3.87)	(3.87)	(81)	(26.68)	(8.18)	(3.57)
$R = 4\text{-}CH_3C_6H_4$	1.53	1.54	$C_{30}H_{25}H_2S_2O_2Bi$	28.97	8.86	3.82
	(3.52)	(3.52)	(79)	(29.0)	(8.89)	(3.88)

The compounds were recrystallized from hot benzene-hexane mixture in 85% yield.

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