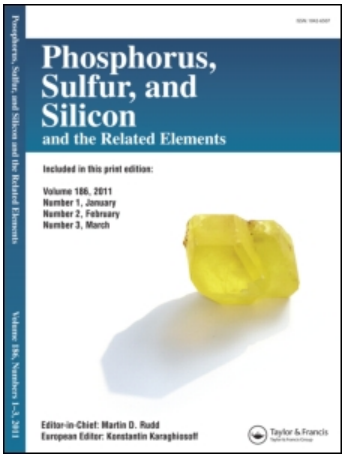

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SYNTHESIS AND CHARACTERIZATION OF SOME NEW MONOPHENYLBISMUTH(III) DERIVATIVES OF N, O, AND S CONTAINING SCHIFF BASES

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Some new monophenylbismuth(III) complexes of the type $PhBi[SC_6H_4N{:}C(R)CH_2C(O)R']_2$ *[where* $R = CH_3$, $R' = CH_3$ *(1);* $R = CH_3$, $R' = C_6H_5$ *(2);* $R = CF_3$, $R' = -C{=}CH{-}CH{=}CHS$ *(3);* $R = CF_3$, $R' = C_6H_5$ *(4)] have been synthesized by the reactions of* Ph_3Bi *with corresponding benzothiazoline ligands,* $HNC_6H_4SC(R)CH_2C(O)R'$ *in 1:2 molar ratios in benzene solution. All these derivatives have been characterized by the elemental analyses, molecular weight measurements, and their probable structure has been proposed on the basis of IR and NMR (*^1H *and* ^{13}C*) spectral studies.*

Keywords: Benzothiazolines; corrected chemical shift vlaue; Hammet Taft constant; monophenylbismuth(III) derivatives; octahedral geometry

The chemistry of organobismuth compounds continue to attract attention due to their biological activity[1] and wide pharmacological[2] and industrial applications[3] including their use as precursor in material science.[4–7] However, most of the work on organobismuth(III) compound is limited to monofunctional bidentate[8–11] ligands and the work on multidentate ligand is limited to a few compounds only.[12]

In view of above, we report the synthesis and characterization of some new organic derivatives of monophenylbismuth(III) with benzothiazolines derived from β-diketones and 2-aminothiophenol which have been reported to behave as bifunctional tridentate in case of aluminium,[13] gallium,[14] and indium derivatives.[14]

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RESULTS AND DISCUSSION

Reactions of Ph_3Bi with corresponding benzothiazoline ligands [$HNC_6H_4SC(R)CH_2C(O)R'$] in 1:2 molar ratios in refluxing benzene proceed with rearrangement of benzothiazoline ring and yield the Schiff base monophenylbismuth(III) derivatives, $PhBi[SC_6H_4N{:}C(R)CH_2C(O)R']_2$.

$$Ph_3Bi + 2[HNC_6H_4SC(R)CH_2C(O)R'] \xrightarrow[\text{Reflux}]{\text{Benzene}} PhBi[SC_6H_4N{:}C(R)CH_2C(O)R']_2 + 2PhH$$

where R = CH_3, R′ = CH_3 (1); R = CH_3, R′ = C_6H_5 (2); R = CF_3, R′ = –C=CH–CH=CHS (3); R = CH_3, R′ = C_6H_5 (4).

During these reactions cleavage of two Ph-Bi bonds takes place. These monomeric, coloured, semi solid compounds are sparingly soluble in common organic solvents.

SPECTROSCOPIC STUDIES

IR Spectra

Absence of νSH mode ($\sim$2540 cm^{-1}) and presence of νNH mode (3230–3340 cm^{-1}) in the spectra of free ligands indicates the presence of benzothiazoline ring in the ligand. Spectra of monophenylbismuth(III) compounds (**1–4**) show disappearance of νNH band and appearance of two new bands in the region 248–265 cm^{-1} and 317–328 cm^{-1} that have been assigned to νBi-S[15] and νBi←N[16] vibration modes respectively. This may be explained by assuming the deprotonation of NH group and rearrangement of benzothiazoline ring during the complex formation. The formation of Bi←N bonds is further supported by a shift of $\sim$15 cm^{-1} toward higher wave number in the position of νC=N which appear at 1602–1615 cm^{-1} in the spectra of complexes. The spectra of ligands as well as complexes (**1–4**) show a band in the range (1682–1702 cm^{-1}) due to the presence of >C=O group. Absence of any shift in its position indicates that >C=O group does not take part in the bonding i.e. the ligand behave as monofunctional bidentate moiety. The Bi-C stretching vibrations[15] have been observed in the range 385–398 cm^{-1} in these derivatives.

^{1}H NMR Spectra

Deprotonation of NH group has been supported by the disappearance of NH proton signal (observed as broad signal in the range δ

TABLE I ^{1}H NMR Spectral Data of PhBi[SC_6H_4N:C(R)CH_2C(O)R′]$_2$ (in δ ppm)

Complex	R	R′	CH_2	$-NC_6H_4S-$	C_6H_5-Bi
1	2.79	2.12	2.79	6.50–7.41	7.78–8.40
2	2.51	7.48–7.89	2.86	6.49–7.46	7.89–8.68
3	—	6.59–7.65	3.70	6.49–7.63	7.90–8.43
4	—	7.43–7.92	3.42	6.49–7.55	7.86–8.59

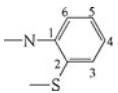
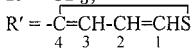
4.53–6.46 ppm in the spectra of ligands) from the spectra of these complexes (Table I). The methylene protons are observed as a singlet in the range of δ 2.79–3.70 ppm and a small shift has been observed in the complexes as compared to their position in the free ligands. Presence of CH_2 signal and absence of —CH signal in the spectra of ligands as well as complexes indicates that these ligands do not behave as bifunctional moieties as the enolisation of >C=O group requires conversion of CH_2 group into =CH group. Alkyl protons are observed in the range δ 2.12–2.79 ppm. Phenyl ring protons attached to the bismuth atom are observed as a complex pattern in the range δ 7.78–8.69 ppm.

^{13}C NMR Spectra

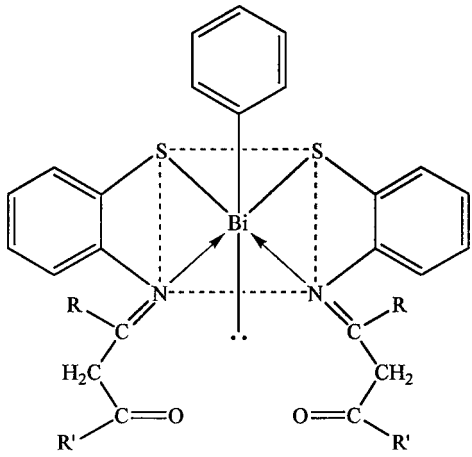
A comparision of ^{13}C NMR spectra of the monophenyl bismuth(III) complexes (Table II) with those of the ligands provides very useful information about the mode of bonding. Signal for >C=N carbon appears at δ 167.46–167.83 ppm. This signal was present in the spectra of ligand at δ 161.39–165.74 ppm. A downfield shift of ~2–6 ppm confirms the rearrangement of benzothiazoline ring during the complexation. The signals for R, R′, and CH_2 carbons show a small shift in comparision to their position in the free ligand in the spectra of these complexes. A signal for >C=O group carbon has been observed in the range δ 183.27–193.85 ppm without any appreciable shift, indicating that this group does not participate in bonding during the complexation. A new set of four signals for phenyl carbons attached to bismuth appears in the spectra of the complexes in the range δ 127.14–154.48 ppm.

In view of the possibility of dπ-pπ conjugation between Ph-Bi, corrected chemical shift values (δ') for phenyl carbons have been calculated[17] by relation $\delta' = \delta$Cp-δCm (where δCp and δCm are the chemical shift values of para and meta carbons of the phenyl ring). The δ' values are found to be negative in the range -1.18 to -0.84 ppm indicating the dπ-pπ conjugation in these derivatives. The values of Hammet-Taft Constant[18] σR° (calculated by the equation

TABLE II ^{13}C NMR Spectral Data of $PhBi[SC_6H_4N{:}C(R)CH_2C(O)R']_2$ (in δ ppm)

Complex	R	R′	CH_2	>C=O	>C=N		Bi-Ph[a]	δ' (σR°)
$R = CH_3$, $R' = CH_3$	28.99	23.09	57.96	190.28	167.46	154.69 (1), 137.81 (2), 134.05 (3), 128.21 (4), 124.81 (5), 122.21 (6)	153.56 147.47 129.08 127.98	−1.10 (−0.05)
$R = CH_3$, 	26.67	133.08 (1) 130.64 (2) 126.32 (3) 128.49 (4)	66.22	193.85	167.52	157.35 (1), 137.66 (2), 133.52 (3), 127.29 (4), 125.06 (5), 122.28 (6)	153.32 142.02 129.02 127.84	−1.18 (0.05)
$R = CF_3$, 	109.26 (q)	130.77 (1) 127.87 (2) 126.71 (3) 130.29 (4)	70.14	183.27	167.83	156.95 (1), 137.95 (2), 134.24 (3), 126.71 (4), 125.48 (5), 121.77 (6)	153.10 145.16 129.59 128.69	−0.9 (−0.04)
$R = CF_3$, 	106.32 (q)	133.02 (1) 131.44 (2) 126.92 (3) 129.63 (4)	69.63	183.70	167.69	156.96 (1), 137.48 (2), 135.66 (3), 127.40 (40), 125.81 (5), 122.51 (6)	153.74 149.90 129.63 128.79	−0.84 (−0.04)

[a]Bismuthphenyl carbon values are given in order C(i), C(o), C(m), C(p) respectively.



R = CH_3, R′ = CH_3 (1); R = CH_3, R′ = C_6H_5 (2); R = CF_3, R′ = -C=CH-CH=CHS (3); R = CF_3 and R′ = C_6H_5 (4).

FIGURE 1 Proposed structure of the compounds (**1–4**).

$\sigma R^{\circ} = \delta'/22.06$) also are found to be negative which show the poor dπ-pπ conjugation in these derivatives.

On the basis of above discussion it may be concluded that these ligands behave as monofunctional bidentate moiety which is in contrast to the earlier reports in which these ligands are reported to behave as bifunctional tridentate moiety.[13,14] In view of the monomeric nature of these derivatives and the monofunctional bidentate behavior of the ligands in these complexes, following structure (Figure 1) with pseudo-octahedral geometry around bismuth atom may be proposed for these derivatives.

EXPERIMENTAL

All reactions were carried out under anhydrous conditions. Solvents (E. merck) have been dried by standard procedures.[19] Ph_3Bi was prepared by the literature method.[20] The benzothiazoline ligands,[21] HNC$_6$H$_4$SC(R)CH$_2$C(O)R′(LH) (where LH = L^1H, R = CH_3, R′ = CH_3; L^2H, R = CH_3, R′ = C_6H_5; L^3H, R = CF_3, R′ = –C=CH–CH=CHS; L^4H, R = CF_3 and R′ = C_6H_5) have been prepared by the condensation reactions of β-diketones and 2-aminothiophenol in 1:1 molar ratio in benzene solution and were purified by distillation under reduced pressure

TABLE III Synthetic and Analytical Data of $PhBi[SC_6H_4N{:}C(R)CH_2C(O)R']_2$

Reactants		Molecular formula yield (%)	Elemental analysis found (calc)			M. wt. found (calc)
Ph_3Bi g (mM)	Ligand g (mM)		%Bi	%S	%N	
0.87 (1.98)	L^1H	$C_{28}H_{29}N_2O_2S_2Bi$	29.89	9.02	3.98	694
	0.82 (3.95)	81 (1)	(29.91)	(9.18)	(4.01)	(698.7)
0.93 (2.11)	L^2H	$C_{38}H_{33}N_2O_2S_2Bi$	25.32	7.69	3.31	820
	1.14 (4.22)	79 (2)	(25.40)	(7.79)	(3.40)	(822.8)
0.67 (1.52)	L^3H	$C_{34}H_{19}F_6N_2O_2S_4Bi$	22.09	13.52	2.82	939
	1.00 (3.04)	78 (3)	(22.17)	(13.60)	(2.97)	(942.8)
0.44 (1.00)	L^4H	$C_{38}H_{27}F_6N_2O_2S_2Bi$	19.11	5.81	2.49	1083
	0.64 (1.99)	80 (4)	(19.22)	(5.90)	(2.58)	(1086.9)

before use. Bismuth was estimated complexometrically.[21] Sulphur and nitrogen were estimated by Messenger[22] and Kjeldahl[22] methods respectively. Molecular weights of these complexes were determined ebullioscopically using Beckmann's thermometer. IR spectra were recorded on a Nicolet DX FT IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (90 MHz) and Brucker DPX-300 MHz NMR spectrometer in $CDCl_3$ or DMSO-d_6 using TMS as an internal reference.

Since a similar method has been used for the synthesis of all the compounds, synthesis of one representative compound is being given here in detail and the synthetic and analytical data of other analogous compounds have been summarized in Table III.

Synthesis of Compound (1)

Benzene solution (~20 ml) of Ph_3Bi (0.87 g, 1.98 mM) was added to benzene solution (~20 ml) of $HNC_6H_4SC(CH_3)CH_2C(O)CH_3$ (0.82 g, 3.95 mM) and the reaction mixture was refluxed for ~8 h. After the completion of reaction, the excess of solvent was removed under reduced pressure. For the purification, this compound was dissolved in small amount of benzene ~15 ml and then the petroleum ether (40–60°C) was added slowly until a viscous compound begins to separate out. The solution was kept overnight at about −10°C. After decanting off the solvent, the viscous compound left was dried under reduced pressure. Yield, 81% (1.12 g).

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