Preparation and Spectroscopic Characterization of Heteronuclear Complexes of Bismuth-Containing Schiff Base Ligands

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ABSTRACT

Heteronuclear derivatives of bismuth with Schiff base having the composition $Na(\mu\text{–}OPr^i)_2Bi[SC_6H_4NC(R)CHC(O)COOCH_3]$ have been synthesised by equimolar reaction of $NaBi(OPr^i)_4$ with benzothiazoline ligands, $HNC_6H_4SC(R)CHC(OH)COOCH_3$ [where R = $C_6H_5(L^1H_2)$, 4-$BrC_6H_4(L^2H_2)$, 4-$ClC_6H_4(L^3H_2)$, 4-$CH_3OC_6H_4(L^4H_2)$, 4-$CH_3C_6H_4(L^5H_2)$] in refluxing benzene. The reaction proceeds with the rearrangement of benzothiazoline ring. All the complexes have been characterised by elemental analysis, conductivity and molecular weight measurements and spectral (IR and NMR) studies.

INTRODUCTION

Metal alkoxides have been studied intensely during the past decades because of their uses as potential precursors for sol-gel and chemical vapour deposition process /1-8/. Bismuth oxide plays a significant role in the preparation of superconducting materials /9/, oxide ion conduction /10/ and oxidation catalyst /11/ etc. A survey of literature reveals that there has been significant development in the chemistry of heterometallic alkoxides of bismuth /12-14/. However, less attention has been paid to heterometallic alkoxide complexes of bismuth with organic ligands /13,15-17/. We, therefore, report the synthesis and characterization of heteronuclear alkoxide derivatives of bismuth-containing Schiff base ligands.

EXPERIMENTAL

Materials and Methods

Moisture was carefully excluded throughout the experimental work. All the chemicals used were of reagent grade. $NaBi(OPr^i)_4$ /18/ and benzothiazoline ligands /19/ have been synthesised by reported methods.

Solvents were dried by literature methods /20/. Nitrogen, sulphur and bismuth were estimated by Kjeldhal's /21/, Messenger /21/ and complexometric /21/ methods respectively. Isopropanol and isopropoxy groups were estimated oxidimetrically using IN $K_2Cr_2O_7$ in 25% sulphuric acid /22/. Molecular weights of these derivatives have been determined ebullioscopically in benzene solution, using Beckman's thermometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a JEOL FT AL 300 MHz spectrometer. Chemical shift values of ^1H and ^{13}C NMR have been expressed in ppm relative to TMS as an internal (^1H) and external (^{13}C) reference. IR spectra were recorded on FT IR spectrophotometer model 8400 S Schimadzu as nujol mull on KBr optics in the range 4000-400 cm^{-1}.

Since a similar method has been used for the synthesis of all these complexes, for the sake of brevity the synthesis of one representative complex is given in detail. The synthetic and analytical data of other analogue complexes have been summarised in Table 1.

Synthesis of $Na(\mu\text{–}OPr^i)_2Bi[\overline{SC_6H_4NC(R)CHC(O)COOCH_3}]$

A benzene solution (~25ml) of $NaBi(OPr^i)_4$ (1.42g, 3.03 mmol) was mixed with a benzene solution (~25 ml) of ligand (L^1H_2) (0.95g, 3.03 mmol) and the mixture was refluxed on a fractionating column for about five hours. The isopropanol liberated was periodically fractionated off azeotropically with benzene. Isopropanol was estimated to check the progress and completion of reaction. After completion of the reaction, the volatile components were removed under reduced pressure to yield a yellow coloured solid compound in 90% yield. The compound was purified by dissolving it in benzene and then adding n-hexane till the precipitate began to separate. The precipitate was redissolved by heating and the mixture was kept overnight at low temperature (0-5°C). The compound was obtained as yellow solid compound, the solvent was removed by decantation and the compound was finally dried under reduced pressure.

RESULTS AND DISCUSSION

The reactions of $NaBi(OPr^i)_4$ have been carried out with corresponding benzothiazoline ligands in 1:1 molar ratio in refluxing benzene to yield the heteronuclear Schiff base derivatives.

$$NaBi(OPr^i)_4 + H\overline{NC_6H_4S}C(R)CHC(OH)COOCH_3 \rightarrow Na(\mu\text{-}OPr^i)_2Bi\,\overline{[SC_6H_4NC(R)CHC(O)COOCH_3]} + 2\,Pr^iOH$$

(where, R = C_6H_5, 4-BrC_6H_4, 4-ClC_6H_4, 4-$CH_3OC_6H_4$, 4-$CH_3C_6H_4$)

Isopropanol liberated in the reaction was fractionated off azeotropically with benzene and the progress and completion of reaction was checked by estimating the amount of liberated isopropanol in the azeotrope. After removing volatile components under reduced pressure at room temperature, coloured solid compounds are obtained. These compounds are found to be monomeric in nature by ebullioscopic molecular weight measurements in benzene solution.

Table 1

Synthetic and analytical data of the complexes, $Na(\mu\text{–}OPr^i)_2Bi[SC_6H_4NC(R)CHC(O)COOCH_3]$

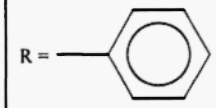
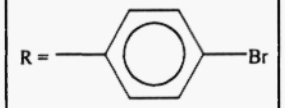
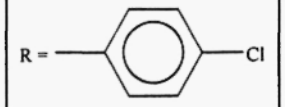
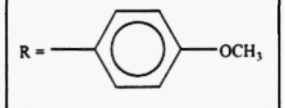
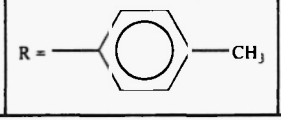
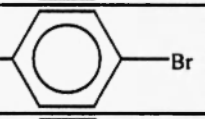
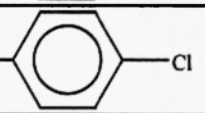
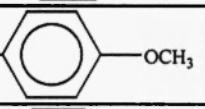
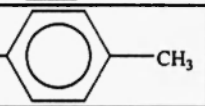
S. No.	Complexes	Reagents g(mmol)		Molecular formula, Colour, Physical state, Yield (%)	Pr^iOH Found (Calc.)	Analysis % Found (Calc.)				Molecular weight Found (Calc.)
		$NaBi(OPr^i)_4$	Ligands			Bi	N	S	$-OPr^i$	
1.	R = 	1.42 (3.03)	0.95 (3.03)	$C_{23}H_{27}NO_5SNaBi$ Yellow solid 90	0.35 (0.36)	31.45 (31.59)	2.10 (2.12)	4.81 (4.85)	17.81 (17.86)	651.51 (661.50)
2.	R = 	1.35 (2.88)	1.13 (2.88)	$C_{23}H_{26}NO_5SBrNaBi$ Dark yellow solid 92	0.33 (0.35)	28.09 (28.22)	1.85 (1.89)	4.31 (4.33)	15.89 (15.96)	738.48 (740.40)
3.	R = 	1.40 (2.99)	1.04 (2.99)	$C_{23}H_{26}NO_5SClNaBi$ Yellow solid 86	0.34 (0.36)	29.95 (30.03)	2.00 (2.01)	4.55 (4.61)	16.91 (16.98)	682.71 (695.94)
4.	R = 	1.51 (3.22)	1.11 (3.23)	$C_{24}H_{29}NO_6SNaBi$ Brown solid 88	0.37 (0.39)	30.11 (30.22)	1.99 (2.02)	4.62 (4.64)	17.02 (17.09)	680.47 (691.52)
5.	R = 	1.57 (3.35)	1.10 (3.36)	$C_{24}H_{29}NO_5SNaBi$ Yellow solid 89	0.39 (0.40)	30.81 (30.94)	2.04 (2.07)	4.71 (4.75)	17.40 (17.49)	681.52 (675.52)

Table 2

^{1}H NMR spectral data (δ ppm) of the complexes, $Na(\overline{\mu\text{–}OPr^i)_2Bi[SC_6H_4NC(R)CHC(O)COOCH_3]}$

S.No.	Complexes	R	–NC_6H_4S	=CH	OCH_3(ester)	$CH(OPr^i)$	$CH_3(OPr^i)$
1.	R = 	7.36–7.48 (m, 5H)	7.50–8.27 (m, 4H)	9.11 (s, 1H)	2.72 (s, 3H)	5.01 (m, 2H)	1.62 (d, 12H)
2.	R = 	7.24–7.36 (m, 4H)	7.46–8.16 (m, 4H)	9.02 (s, 1H)	2.59 (s, 3H)	4.85 (m, 2H)	1.47 (d, 12H)
3.	R = 	7.24–7.36 (m, 4H)	7.42–8.17 (m, 4H)	9.01 (s, 1H)	2.60 (s, 3H)	4.90 (m, 2H)	1.48 (d, 12H)
4.	R* = 	6.87–7.26 (m, 4H)	7.28–8.14 (m, 4H)	9.03 (s, 1H)	2.56 (s, 3H)	4.86 (m, 2H)	1.48 (d, 12H)
5.	R* = 	6.91–7.30 (m, 4H)	7.33–8.17 (m, 4H)	9.01 (s, 1H)	2.59 (s, 3H)	4.87 (m, 2H)	1.49 (d, 12H)

*–OCH_3 and –CH_3 group signals are observed as signglets at δ 3.81 and 2.35 ppm respectively.

Abbr. s = singlet, d = doublet, m = multiplet

Table 3

^{13}C NMR spectral data (δ ppm) of the complexes, $Na(\mu\text{–}OPr^i)_2Bi[SC_6H_4NC(R)CHC(O)COOCH_3]$

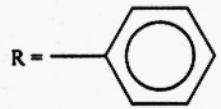
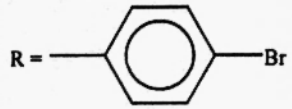
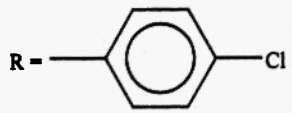
S.No.	Complexes	R	–CH_6H_4S-	CN	C–O	=CH	$CH(OPr^i)$	$CH_3(OPr^i)$	C=O	CH_3(ester)
1.	R = 	137.50 128 65 127.24 126 44	156.00 140.10 133.14 129.47 125.25 122.99	162.50	167.20	96.80	68.01	26.90	196.90	25.91
2.	R = 	132 25 130 65 127.12 126.84	155.88 144.96 131.58 127.44 125.80 122.56	164.50	167.35	97.50	67.26	26.54	197.00	25.64
3.	R = 	132 50 130.71 127.22 126.52	156.01 143.98 131.14 127.25 125.47 122.65	163.97	167.21	97.35	67.58	26.14	197.12	25.39

Table 3 (continued)

4.	R* =	133.50 129.86 126.39 130.22	156.01 139.39 130.44 129.41 125.43 122.46	163.07	168.10	97.00	67.58	26.35	196.27	25.93
5.	R* =	135.36 128.47 127.66 126.16	156.03 140.00 138.10 129.19 125.21 122.48	163.40	167.25	97.90	67.87	26.58	197.10	25.97

*–OCH_3 and –CH_3 group signals are observed at δ 55.48 ppm and 28.50 ppm respectively.

Conductometric measurements reveal their nonelectrolylic nature. These compounds have further been characterized by IR and NMR (^1H and ^{13}C) spectral studies.

SPECTROSCOPIC STUDIES

Infra-Red Spectra

A comparison of IR spectra of these derivatives with corresponding benzothiazoline ligands shows disappearance of the νOH band observed as a broad band in the region 3638-3417 cm^{-1} in the free ligands and appearance of a new band at 435-425 cm^{-1}, which may be assigned to the νBi-O mode of vibrations /23/. This indicates deprotonation of the OH group and formation of a Bi–O bond. A broad band observed at 3325-3225 cm^{-1} in the spectra of free ligands (due to νNH modes) is found to be absent in the spectra of complexes and new bands at 1640-1630 cm^{-1}, 482-475 cm^{-1} and 404-401 cm^{-1} are observed, which have been assigned to νC=N, νBi←N /24/ and νBi–S /24/ mode of vibrations, respectively. Deprotonation of NH group and formation of C=N, Bi←N and Bi–S bonds indicate rearrangement of the benzothiazoline ring and subsequent formation of these bonds. New bands appearing at 1202-1200 cm^{-1} and 1150-1135 cm^{-1} have been assigned to (-OPr^i) groups /25/. In addition to these, bands observed at 1080-1070 cm^{-1} and 450-442 cm^{-1} were assigned to νC–O /25/ and νBi–O /25/ mode of vibrations, respectively.

^1H NMR Spectra

In the ^1H NMR spectra of the complexes, disappearance of the signals observed in the spectra of free ligands at δ 15.10-15.35 ppm and δ 3.90-4.40 ppm, due to –OH and –NH protons respectively, indicate the deprotonation of –OH and –NH groups during complexation. In the spectra of the complexes, the bridging isopropoxy groups appeared as multiplet (–OCH) and doublet ($–CH_3$) at δ 4.85-5.01 ppm and δ 1.47-1.62 ppm respectively. In the spectra of $NaBi(OPr^i)_4$ these signals were present at δ 4.02 ppm and δ 1.21 ppm respectively. The singlets observed at δ 9.01-9.11 ppm and δ 2.56-2.72 ppm have been assigned to =CH and $–OCH_3$(ester) protons. Phenylene protons appeared at δ 6.87-8.27 ppm as multiplet.

^{13}C NMR Spectra

In the ^{13}C NMR spectrum of $NaBi(OPr^i)_4$ the signals observed at δ 67.02 ppm and δ 22.93 ppm have been assigned to –OCH and $–CH_3$ carbons of (–OPr^i) groups. These signals are shifted in the spectra of coresponding bismuth complexes on complexation. The signals observed at δ 158.68-160.07 ppm and δ 161.88-163.10 ppm, which have been assigned to CN and C–OH groups respectively in the spectra of ligands, show a downfield shift in the spectra of complexes as compared to their positions in the spectra of ligands. This indicates rearrangement of the benzothiazoline ring and participation of >C–O group in bonding on complexation. These are further supported by the downfield shift of =CH group carbon as compared to the free ligands. The >C=O (ester) and $–NC_6H_4S–$ group carbons were observed at δ 196.27-197.12 ppm and δ

122.46-156.03 ppm respectively.

In view of the tridentate bifunctional nature of the ligands and presence of bridging isopropoxy groups, a bismuth atom appears to have pentacoordinated structure. Sodium and bismuth appear to have been bridged through isopropoxy groups, which is supported by the nonelectrolytic nature of these complexes.

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