

## Synthesis and characterization of some new homodinuclear alkoxo derivatives of bismuth(III) containing dialkyldithiophosphate ligands

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Reactions of sodium tetraisopropoxobismuthate(III),  $\text{NaBi}(\text{OPr}^i)_4$  (prepared *in situ*) with chlorobis (dialkyldithiophosphato)bismuth(III) compounds,  $[(\text{RO})_2\text{P}(\text{S})\text{S}]_2\text{BiCl}$  in 1:1 molar ratio in refluxing benzene solution yield a new series of homodinuclear alkoxide derivatives of bismuth(III) of the type  $[(\text{RO})_2\text{P}(\text{S})\text{S}]_2\text{Bi}(\mu\text{-OPr}^i)_2\text{Bi}(\text{OPr}^i)_2$  [where, R = Me(**1**); Et(**2**); Pr(**3**); Pr<sup>n</sup>(**4**); and Bu<sup>n</sup>(**5**)]. All the derivatives in this series are non-volatile, moisture-sensitive, dark-brown colored, viscous liquids, which are soluble in common organic solvents. The compounds have been characterized by elemental analyses and molecular weight measurements. Probable structure for the derivatives is proposed on the basis of IR and NMR (<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P) spectral studies.

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Alkoxy groups are unique ligands amongst the oxygen containing ones as these have remarkable flexible bridging tendency between similar as well as dissimilar metal atoms, and adjust themselves according to the extent of the ramification<sup>1-5</sup> of the alkyl groups and the atomic sizes of different metal atoms bridged by them. There has been a renewed interest in bismuth alkoxides as potential precursors for sol-gel and chemical vapor deposition preparations of bismuth containing superconductors<sup>6,7</sup> and ferroelectrics<sup>8-10</sup>. Although during the last two decades, there has been significant development in the chemistry of heterobimetallic alkoxides of bismuth<sup>11-16</sup>, there is a dearth of studies on corresponding homodinuclear alkoxides. Also, dinuclear alkoxides of bismuth containing deprotonated dithiophosphates and isopropoxometallate group have not been reported so far, though a number of dialkyldithiophosphate derivatives of bismuth are known<sup>17-25</sup>. Keeping that in view, it was considered worthwhile to synthesize the first series of homodi-

nuclear alkoxide derivatives of bismuth(III) involving deprotonated dithiophosphates and investigate their physicochemical properties.

### Experimental

All reactions were carried out under anhydrous conditions. Solvents (E. Merck) were carefully dried by standard methods before use. Mixed chlorobis(dialkyldithiophosphato)bismuth(III)<sup>17</sup>  $[(\text{RO})_2\text{P}(\text{S})\text{S}]_2\text{BiCl}$  and sodium tetraisopropoxobismuthate(III)<sup>26</sup>,  $\text{Na}[\text{Bi}(\text{OPr}^i)_4]$  were prepared by known methods. Bismuth<sup>27</sup> and sulphur<sup>27</sup> were determined by complexometric and Messenger's methods, respectively.

Elemental analyses (C and H) were carried out on a Perkin Elmer series II 2400 C,H,N analyzer. Molecular weights were determined cryoscopically in freezing benzene solution using a Beckmann's thermometer. IR spectra were recorded on 8400 S Shimadzu FT IR spectrophotometer as liquid films on a KBr cell in the range 4000–400  $\text{cm}^{-1}$ . Multinuclei NMR spectra were recorded in  $\text{CDCl}_3$  solution on a JEOL FT AL 300 MHz spectrometer; chemical shift values of <sup>1</sup>H and <sup>13</sup>C NMR were expressed in ppm relative to TMS as an internal reference and that of <sup>31</sup>P NMR in ppm relative to  $\text{H}_3\text{PO}_4$  as external reference, respectively. The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. *m*-Nitrobenzyl alcohol (NBA) was used as the matrix.

### Synthesis of homodinuclear alkoxide derivative (1)

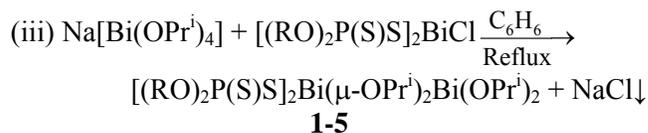
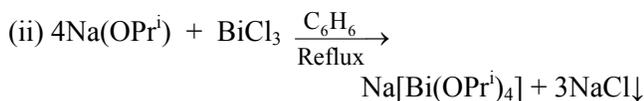
A weighed amount of sodium metal (0.21 g, 9.13 mmol) was added to 15 mL of well dried isopropanol and the mixture was stirred for 1 h. When the reaction between Na and Pr<sup>i</sup>OH is complete, a benzene solution (~20 mL) of  $\text{BiCl}_3$  (0.72 g, 2.28 mmol) was added to it and the reaction mixture was refluxed for ~3 h on a magnetic stirrer hot plate. After cooling to room temperature, a ~25 mL benzene solution of  $[(\text{MeO})_2\text{P}(\text{S})\text{S}]_2\text{BiCl}$  (1.28 g, 2.29 mmol) was added to it. After stirring for ~2 h, this reaction mixture was finally refluxed gently for ~1 h to ensure the completion of reaction. The precipitated NaCl (0.53 g) was removed by filtration. Removal of volatile components from filtrate under reduced pressure yielded

1.95 g (88.37%) of derivative (**1**) as liquid compound. For purification, this compound was dissolved in a small amount of benzene and then *n*-hexane was added to it till the compound began to separate. This mixture was kept overnight at 0°C. After decanting off the solvent, the compound was dried under vacuum [yield 84.56% (1.87 g)].

Similar procedure was adopted for the syntheses of all other new homodinuclear derivatives, **2-5**. The physical and analytical data of these derivatives are summarized in Table 1. Amounts of the reactants actually used and the NaCl precipitated are shown below in brackets: (**2**) Na (0.19 g, 8.26 mmol), BiCl<sub>3</sub> (0.65 g 2.06 mmol) and [(EtO)<sub>2</sub>P(S)S]<sub>2</sub>BiCl (1.27g, 2.06 mmol); NaCl (0.48 g); (**3**) Na (0.22g, 9.57 mmol), BiCl<sub>3</sub> (0.75 g, 2.38 mmol) and [(Pr<sup>n</sup>O)<sub>2</sub>P(S)S]<sub>2</sub>BiCl (1.60 g, 2.38 mmol); NaCl (0.56 g); (**4**) Na (0.18g, 7.88 mmol), BiCl<sub>3</sub> (0.62 g, 1.97 mmol) and [(Pr<sup>n</sup>O)<sub>2</sub>P(S)S]<sub>2</sub>BiCl (1.31 g, 1.95 mmol); NaCl (0.45 g); (**5**) Na (0.17 g, 7.39 mmol), BiCl<sub>3</sub> (0.58 g, 1.84 mmol) and [(Bu<sup>n</sup>O)<sub>2</sub>P(S)S]<sub>2</sub>BiCl (1.34 g, 1.84 mmol); NaCl (0.43 g).

## Results and discussion

New alkoxo derivatives, **1-5** have been synthesized by the reactions of mixed chlorobis(dialkyldithiophosphato)bismuth(III) compounds, [(RO)<sub>2</sub>P(S)S]<sub>2</sub>BiCl with sodium tetraisopropoxobismuthate(III), Na[Bi(OPr<sup>i</sup>)<sub>4</sub>] (prepared *in situ* by the reaction of sodium isopropoxide and bismuth trichloride, BiCl<sub>3</sub> in 4:1 molar ratio) in 1:1 molar ratio in refluxing benzene solution for ~4 h :



These reactions are quite facile and quantitative. All the newly synthesized derivatives (**1-5**) are dark-brown coloured, moisture-sensitive, non-volatile, viscous-liquids, which are soluble in common organic solvents. Molecular weight measurements reveal their monomeric nature in freezing benzene solution.

## Infra-red spectra

IR data cannot distinguish between the various structural possibilities of dialkyldithiophosphate ligands since it is difficult to assign P=S and P-S stretching frequencies with certainty<sup>28,29</sup> as these are present in the finger print region. The tentative assignments of the important characteristic bands in the IR spectra of these new alkoxo derivatives have been made by comparing them with the IR spectral data reported earlier<sup>17,29-32</sup>.

A shift of ~35 cm<sup>-1</sup> in the position of strong band due to (P=S) stretching vibrations in the spectra of these homodinuclear alkoxide derivatives, **1-5** (observed at 655-680 cm<sup>-1</sup>) as compared to its position (640-690 cm<sup>-1</sup>) in the IR spectra<sup>17,29</sup> of free dialkyldithiophosphoric acids or their sodium salts, may be attributed to the strong bidentate chelation of dithiophosphate moieties with central bismuth atom in these derivatives. Medium intensity bands present in the regions 500-530 cm<sup>-1</sup> and 615-630 cm<sup>-1</sup> may be due to  $\nu_{sym}$  (PS<sub>2</sub>) and  $\nu_{asym}$  (PS<sub>2</sub>) stretching vibrations<sup>30,31</sup>, respectively. The medium intensity broad bands in the regions 780-825 and 960-1000 cm<sup>-1</sup> have been assigned to [P-O-(C)] and [(P)-O-C] stretching modes, respectively<sup>29</sup>. These derivatives, **1-5** also

Table 1— Physical and analytical data of new homodinuclear derivatives, [(RO)<sub>2</sub>P(S)S]<sub>2</sub>Bi(μ-OPr<sup>i</sup>)<sub>2</sub>Bi(OPr<sup>i</sup>)<sub>2</sub>, **1-5**

Compound	Colour/ Physical State	Empirical formula Yield (%)	Mol. wt. Found (Calc.)	Found (Calc.%)			
				Bi	S	C	H
<b>1</b>	Dark brown/ Viscous liquid	C <sub>16</sub> H <sub>40</sub> O <sub>8</sub> P <sub>2</sub> S <sub>4</sub> Bi <sub>2</sub> (85)	966 (968.65)	43.02 (43.15)	13.17 (13.24)	19.80 (19.84)	4.14 (4.17)
<b>2</b>	Dark brown/ Viscous liquid	C <sub>20</sub> H <sub>48</sub> O <sub>8</sub> P <sub>2</sub> S <sub>4</sub> Bi <sub>2</sub> (84)	1022 (1024.76)	40.67 (40.79)	12.46 (12.52)	23.40 (23.44)	4.68 (4.73)
<b>3</b>	Dark brown/ Viscous liquid	C <sub>24</sub> H <sub>56</sub> O <sub>8</sub> P <sub>2</sub> S <sub>4</sub> Bi <sub>2</sub> (87)	1080 (1080.86)	38.55 (38.67)	11.80 (11.87)	26.65 (26.67)	5.18 (5.23)
<b>4</b>	Dark brown/ Viscous liquid	C <sub>24</sub> H <sub>56</sub> O <sub>8</sub> P <sub>2</sub> S <sub>4</sub> Bi <sub>2</sub> (81)	1078 (1080.86)	38.62 (38.67)	11.82 (11.87)	26.61 (26.67)	5.20 (5.23)
<b>5</b>	Dark brown/ Viscous liquid	C <sub>28</sub> H <sub>64</sub> O <sub>8</sub> P <sub>2</sub> S <sub>4</sub> Bi <sub>2</sub> (83)	1133 (1136.96)	36.71 (36.76)	11.24 (11.28)	29.54 (29.58)	5.62 (5.68)

show additional bands in the regions 420-445 and 995-1050  $\text{cm}^{-1}$  due to Bi-O and BiO-C stretching vibrations<sup>32</sup>, respectively.

#### <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectra (Table 2) of all the new compounds exhibit two sets of signals for terminal and bridging isopropoxy groups in the regions 1.21 – 1.32, 1.32 – 1.39 ppm (doublets) {CH(CH<sub>3</sub>)<sub>2</sub>} and 4.10 – 4.61, 4.53 – 4.85 ppm (multiplets) {CH(CH<sub>3</sub>)<sub>2</sub>}, respectively. All alkyl protons of the (RO) group attached to P atom have been observed at their expected positions. Splitting due to coupling between  $\alpha$ -protons and phosphorus nuclei has been observed in the signals of the alkyl groups attached to OP(S)S group.

#### <sup>13</sup>C NMR spectra

A comparative study of <sup>13</sup>C NMR spectra (Table 2) of these new derivatives, **1-5** with the spectra of par-

ent chlorobis(dialkyldithiophosphato)bismuth(III) compounds provides useful information about the mode of bonding in these derivatives. In the <sup>13</sup>C NMR spectra of these homodinuclear derivatives (**1-5**), an upfield shift (~4-6 ppm) has been observed in the positions of the signals of different alkyl group carbons of the dialkyldithiophosphate moieties as compared to their positions in corresponding mixed chlorobis(dialkyldithiophosphato)bismuth(III) compounds. This upfield shift may be due to the fact that the coordination number of bismuth has increased from five to six in going from the parent compounds to these derivatives. Two sets of signals due to terminal and bridging isopropoxy groups have been observed in the spectra of all these new derivatives, **1-5** in the range 22.15 – 23.84, 24.82 – 28.86 ppm {CH(CH<sub>3</sub>)<sub>2</sub>} and 63.74 – 71.53, 72.32 – 73.67 ppm {CH(CH<sub>3</sub>)<sub>2</sub>}, respectively.

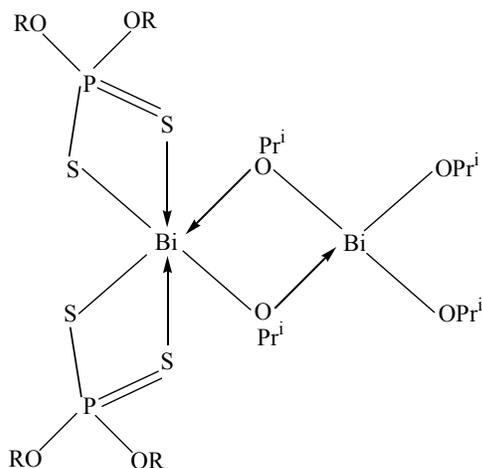
Table 2 — <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectral data ( $\delta$  ppm) of new homodinuclear derivatives, [(RO)<sub>2</sub>P(S)S]<sub>2</sub>Bi( $\mu$ -OPri)<sub>2</sub>Bi(OPr)<sub>2</sub>, **1-5**

Comp.	<sup>1</sup> H NMR chemical shift ( $\delta$ ppm) and coupling constant (J, Hz)	<sup>13</sup> C NMR chemical shift ( $\delta$ ppm)*	<sup>31</sup> P NMR chemical shift ( $\delta$ ppm)
<b>1</b>	1.32, d, 12H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 1.37, d, 12H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ; 3.73, d, 12H, (OCH <sub>3</sub> ) <sub>dtp</sub> ; <sup>3</sup> J <sub>(POCH)</sub> = 13.58 4.61, m, 2H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 4.80, m, 2H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ;	22.15 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 25.06 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ; 52.76 (OCH <sub>3</sub> ) <sub>dtp</sub> ; 71.53 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 73.55 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ;	90.93
<b>2</b>	1.21, d, 12H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 1.32, t, 12H, (CH <sub>3</sub> ) <sub>dtp</sub> ; <sup>3</sup> J <sub>(HCCH)</sub> = 6.97 1.39, d, 12H (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ; 3.70, dq, 8H, (OCH <sub>2</sub> ) <sub>dtp</sub> ; <sup>3</sup> J <sub>(POCH)</sub> = 10.80, <sup>3</sup> J <sub>(HCCH)</sub> = 6.97 4.10, m, 2H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 4.53, m, 2H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ;	16.12 (CH <sub>2</sub> CH <sub>3</sub> ) <sub>dtp</sub> ; 23.84 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 25.34 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ; 63.47 (OCH <sub>2</sub> ) <sub>dtp</sub> ; 67.03 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 73.67 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ;	95.19
<b>3</b>	1.21, d, 12H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 1.32, d, 12H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ; 1.40, d, 24H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>dtp</sub> ; <sup>3</sup> J <sub>(HCCH)</sub> = 6.97 4.33, m, 2H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 4.64, m, 2H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ;	23.44 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 24.82 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ; 25.36 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>dtp</sub> ; 63.74 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 72.90 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ;	92.92
<b>4</b>	4.92, m, 4H, (OCH) <sub>dtp</sub> ; <sup>3</sup> J <sub>(POCH)</sub> = 11.43, <sup>3</sup> J <sub>(HCCH)</sub> = 6.97 0.97, t, 12H, (CH <sub>3</sub> ) <sub>dtp</sub> ; <sup>3</sup> J <sub>(HOCH)</sub> = 7.33 1.23, d, 12H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 1.33, d, 12H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ; 1.74, m, 8H, (CH <sub>2</sub> CH <sub>3</sub> ) <sub>dtp</sub> ; <sup>3</sup> J <sub>(HCCH)</sub> = 7.33 4.02, dt, 8H, (OCH <sub>2</sub> ) <sub>dtp</sub> ; <sup>3</sup> J <sub>(POCH)</sub> = 9.34, <sup>3</sup> J <sub>(HCCH)</sub> = 7.33 4.58, m, 2H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 4.80, m, 2H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ;	73.28 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>dtp</sub> ; 10.20 (CH <sub>3</sub> ) <sub>dtp</sub> ; 23.49 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 25.38 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ; 29.53 (CH <sub>2</sub> CH <sub>3</sub> ) <sub>dtp</sub> ; 64.45 (OCH <sub>2</sub> ) <sub>dtp</sub> ; 69.65 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 72.61 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ;	94.67
<b>5</b>	0.93, t, 12H, (CH <sub>3</sub> ) <sub>dtp</sub> ; <sup>3</sup> J <sub>(HCCH)</sub> = 7.33 1.21, d, 12H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 1.34, d, 12H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ; 1.42, m, 8H, (CH <sub>2</sub> CH <sub>3</sub> ) <sub>dtp</sub> ; <sup>3</sup> J <sub>(HCCH)</sub> = 7.33 1.65, m, 8H, (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>dtp</sub> ; <sup>3</sup> J <sub>(HCCH)</sub> = 7.33 2.88, dt, 8H (OCH <sub>2</sub> ) <sub>dtp</sub> ; <sup>3</sup> J <sub>(POCH)</sub> = 9.34, <sup>3</sup> J <sub>(HCCH)</sub> = 7.33 4.50, m, 2H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 4.85, m, 2H, (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ;	11.65 (CH <sub>3</sub> ) <sub>dtp</sub> ; 18.76 (CH <sub>2</sub> CH <sub>3</sub> ) <sub>dtp</sub> ; 22.17 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 28.86 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ; 34.12 (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>dtp</sub> ; 65.48 (OCH <sub>2</sub> ) <sub>dtp</sub> ; 70.91 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>T</sub> ; 72.32 (CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>B</sub> ;	92.26

T = terminal, B = bridging, dtp = dialkyldithiophosphate, d = doublet, m = multiplet, sep = septet, t = triplet, dq = doublet of quartets, dt = doublet of triplets.

Table 3 — Mass spectral data of the new homodinuclear derivative, (3),  $[\{(CH_3)_2CHO\}_2P(S)_2Bi\{\mu-OCH(CH_3)_2\}_2Bi\{OCH(CH_3)_2\}_2]$ 

No.	Mass no.	Rel. abundance	Assignment
1	1081		$[\{(CH_3)_2CHO\}_2P(S)_2Bi\{\mu-OCH(CH_3)_2\}_2Bi\{OCH(CH_3)_2\}_2]^+$
2	1039	41.7	$[\{(CH_3)_2CHO\}_2P(S)_2Bi\{\mu-OCH(CH_3)_2\}_2Bi(OH)\{OCH(CH_3)_2\}_2]^+$
3	997	8.3	$[\{(CH_3)_2CHO\}_2P(S)_2Bi\{\mu-OCH(CH_3)_2\}_2Bi(OH)_2]^+$
4	981	8.3	$[\{(CH_3)_2CHO\}_2P(S)_2Bi\{\mu-OCH(CH_3)_2\}\{\mu-OCH(CH_3)\}Bi(O)(OH)]^+$
5	965 ?	—	$[\{(CH_3)_2CHO\}_2P(S)_2Bi\{\mu-OCH(CH_3)_2\}\{\mu-OC\}Bi(O)(OH)]^+$
6	937	5.6	$[\{(CH_3)_2CHO\}_2P(S)_2Bi\{\mu-OCH(CH_3)_2\}Bi(O)(OH)]^+$
7	695	5.6	$[\{(CH_3)_2CHO\}_2P(S)_2Bi\{\mu-OCH(CH_3)_2\}_2]^+$
8	637	100.0	$[\{(CH_3)_2CHO\}_2P(S)_2BiH]^+$
9	595	25	$[\{(CH_3)_2CHO\}_2P(S)_2BiH\{(CH_3)_2CHO\}(OH)P(S)]^+$
10	553	30.5	$[\{(CH_3)_2CHO\}_2P(S)_2BiH[(OH)_2P(S)]^+$
11	511	34.7	$[\{(CH_3)_2CHO\}(OH)P(S)_2BiH[(OH)_2P(S)]^+$
12	469	50	$[(OH)_2P(S)_2BiH[(OH)_2P(S)]^+$
13	452	16.7	$[(OH)P(S)_2BiH[(OH)_2P(S)]^+$
14	372	27.8	$(HS)Bi[(OH)_2P(S)]^+$
15	339	52.8	$Bi[(OH)_2P(S)]^{2+}$
16	208	8.3	$Bi^{3+}$

Fig. 1 — Proposed structure of the homodinuclear alkoxide derivatives, 1-5, where [R = Me(1); Et(2); Pr<sup>i</sup>(3); Pr<sup>n</sup>(4); and Bu<sup>n</sup>(5)].

### <sup>31</sup>P NMR spectra

Information about the complexation behaviour of dialkyldithiophosphate ligands with central bismuth atom and the geometry of these new homodinuclear alkoxide derivatives have been obtained from <sup>31</sup>P NMR spectral data (Table 2). The proton decoupled <sup>31</sup>P NMR spectra exhibit only one signal for each new derivative in the range 90.93 – 95.19 ppm. The presence of <sup>31</sup>P NMR signals in this range has been interpreted in terms of bidentate nature of the dialkyldithiophosphate ligands<sup>29</sup> in these derivatives, 1-5.

### FAB mass spectra

The FAB Mass spectrum, recorded for one representative compound (3), provides evidence for its discrete molecular nature in the gas phase as there are not any fragments of higher mass than the monomeric

species should give. The highest mass fragment observed arises from the loss of one alkene (propene) from the isopropoxy groups. The preferable fragmentation pattern for this derivative (3) has been summarized in Table 3.

### Structure elucidation

In view of the monomeric nature of all these new derivatives, the presence of two bidentate dialkyldithiophosphate ligands around central bismuth atom and presence of two types (terminal and bridging) of isopropoxy groups, hexacoordination around the central bismuth atom and tetracoordination around second bismuth atom, following structure (Fig. 1) may be tentatively proposed for these new homodinuclear alkoxide derivatives, 1-5.

It is quite difficult to authenticate the molecular structure of these new derivatives in solid state in the absence of suitable crystals for X-ray crystal structure analysis of at least one of the compounds.

### Acknowledgement

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