APPLIED ORGANOMETALLIC CHEMISTRY
*Appl. Organometal. Chem.* 2006; **20**: 411–415

(www.interscience.wiley.com) DOI:10.1002/aoc.1068

# Synthesis and characterization of some methylbismuth(III) *O,O*-alkylenedithiophosphates: convenient transformation of [MeBi{$S_2PO$-$(CH_2)_4$-O}$_2$] and [MeBi{$S_2POCH(CH_3)CH_2C(O)(CH_3)_2$}$_2$] to pure $Bi_2S_3$

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Received 29 December 2005; Revised 23 January 2006; Accepted 25 February 2006

**A series of methylbismuth(III)*O,O*-alkylenedithiophosphates of the type [MeBi{$S_2P$(O-G-O)}$_2$] [where G = $CH_2CH(CH_3)$ (1), $(CH_2)_4$ (2), $CH_2CH_2CH(CH_3)$ (3), $CH(CH_3)CH(CH_3)$ (4), $CH_2CHCH_2CH_3$ (5), $CH(CH_3)CH_2C(CH_3)_2$ (6) and $C(CH_3)_2C(CH_3)_2$ (7)] have been isolated by the reaction of methylbismuth(III) dichloride with potassium salt of *O,O*-alkylenedithiophosphoric acids in 1 : 2 molar ratio in anhydrous benzene. These newly synthesized derivatives were characterized by elemental analyses, FT IR and multinuclear NMR ($^1$H, $^{13}$C and $^{31}$P) spectral studies. Thermogravimetric analysis of 6 has shown a single-step decomposition of complex to $Bi_2S_3$ at 154.3 °C. Transformation of 2 and 6 to pure $Bi_2S_3$ was carried out successfully at refluxing xylene temperature (142 °C) as revealed by XRD and SEM analyses. Copyright © 2006 John Wiley & Sons, Ltd.**

**KEYWORDS:** methylbismuth(III)*O,O*-alkylenedithiophosphates; $Bi_2S_3$; XRD; SEM; TGA

## INTRODUCTION

We have recently reported the synthesis and characterization of some methylbismuth(III) derivatives containing dithioligands like xanthates, dithiocarbamates and dialkyldithiophosphates. The crystal and molecular structure of some these derivatives exhibit interesting structural variations.[1]

It has been observed that some of these derivatives behave as good precursors for the preparation of pure bismuthinite, $Bi_2S_3$ at low temperature[1,2] as compared with the traditional high-temperature synthetic routes.

In continuation with our search for better single source molecular precursors for the preparation of pure $Bi_2S_3$ led us to synthesize and characterize some unique methylbismuth(III) derivatives with *O,O*-alkylenedithiophosphoric acids. Thermolysis of two representative complexes yields pure $Bi_2S_3$ at refluxing xylene (142 °C) temperature.

## RESULTS AND DISCUSSION

Methylbismuth(III) *O,O*-alkylenedithiophosphates of the type [MeBi{$S_2P$(O-G-O)}$_2$] [where G = $CH_2CH(CH_3)$ (**1**), $(CH_2)_4$ (**2**), $CH_2CH_2CH(CH_3)$ (**3**), $CH(CH_3)CH(CH_3)$ (**4**), $CH_2CHCH_2CH_3$ (**5**), $CH(CH_3)CH_2C(CH_3)_2$ (**6**) and $C(CH_3)_2C(CH_3)_2$ (**7**)] have been synthesized by the reaction of methylbismuth(III) dichloride with potassium *O,O*-alkylenedithiophosphates in 1 : 2 molar ratio in anhydrous benzene as depicted below:

$$MeBiCl_2 + 2KS(S)P(O\text{-}G\text{-}O) \xrightarrow[\text{Stirring}]{\text{Benzene}} MeBi\{S_2PO\text{-}G\text{-}O\}_2 + 2KCl$$

where G = $CH_2CH(CH_3)$ (**1**), $(CH_2)_4$ (**2**), $CH_2CH_2CH(CH_3)$ (**3**), $CH(CH_3)CH(CH_3)$ (**4**), $CH_2CHCH_2CH_3$ (**5**), $CH(CH_3)CH_2C(CH_3)_2$ (**6**) and $C(CH_3)_2C(CH_3)_2$ (**7**).

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**Table 1.** Synthetic and analytical data of methylbismuth(III)*O*,*O*-alkylenedithiophosphates

| Sample no. | Compounds | Yield (%), m.p.(°C) | Color and physical state | Elemental analysis (%), found (calcd) C | H | S | Bi |
|---|---|---|---|---|---|---|---|
| **1** | $MeBi\{S(S)POCH_2CH(O)CH_3\}_2$ | 73<br>— | Brown sticky solid | 14.7 (14.9) | 2.67 (2.69) | 22.6 (22.8) | 37.0 (37.2) |
| **2** | $MeBi\{S(S)PO(CH_2)_4O\}_2$ | 92<br>140[a] | Yellow solid | 18.0 (18.3) | 3.21 (3.24) | 21.4 (21.7) | 35.0 (35.4) |
| **3** | $MeBi\{S(S)POCH_2CH_2CH(O)CH_3\}_2$ | 98<br>— | Brown sticky solid | 18.1 (18.3) | 3.22 (3.24) | 21.6 (21.7) | 35.2 (35.4) |
| **4** | $MeBi\{S(S)POCH(CH_3)CH(O)CH_3\}_2$ | 98<br>— | Brown sticky solid | 18.0 (18.3) | 3.21 (3.24) | 21.5 (21.7) | 35.1 (35.4) |
| **5** | $MeBi\{S(S)POCH_2CH(O)CH_2CH_3\}_2$ | 91<br>— | Brown sticky solid | 18.1 (18.3) | 3.20 (3.24) | 21.4 (21.7) | 35.3 (35.4) |
| **6** | $MeBi\{S(S)POCH(CH_3)CH_2C(O)(CH_3)_2\}_2$ | 96<br>125 | Yellow solid | 24.0 (24.2) | 4.20 (4.21) | 19.6 (19.8) | 32.0 (32.3) |
| **7** | $MeBi\{S(S)POC(CH_3)_2C(O)(CH_3)_2\}_2$ | 90<br>98[a] | Orange solid | 24.1 (24.2) | 4.19 (4.21) | 19.5 (19.8) | 32.1 (32.3) |

[a] Decompose temperature.

**Table 2.** Some relevant IR spectral data (in cm$^{-1}$) of methylbismuth(III)*O*,*O* -alkylenedithiophosphates

| Sample no. | Compounds | $\nu$(Bi–S) | $\nu$(Bi–C) | $\nu$(P=S) | $\nu$(P–S) | $\nu$(P)–O–C | $\nu$P–O–(C) | Ring vibration |
|---|---|---|---|---|---|---|---|---|
| **1** | $MeBi\{S(S)POCH_2CH(O)CH_3\}_2$ | 245 m | 493 m | 649 s | 591 s | 1039 s | 881 s | 951 s |
| **2** | $MeBi\{S(S)PO(CH_2)_4O\}_2$ | 257 m | 492 m | 652 s | 563 s | 1033 s | 853 s | 936 s |
| **3** | $MeBi\{S(S)POCH_2CH_2CH(O)CH_3\}_2$ | 227 m | 492 m | 657 s | 597 s | 1039 s | 887 s | 958 s |
| **4** | $MeBi\{S(S)POCH(CH_3)CH(O)CH_3\}_2$ | 248 m | 468 m | 652 s | 588 s | 1033 s | 885 s | 933 s |
| **5** | $MeBi\{S(S)POCH_2CH(O)CH_2CH_3\}_2$ | 252 m | 462 s | 648 s | 566 s | 1028 s | 868 s | 962 s |
| **6** | $MeBi\{S(S)POCH(CH_3)CH_2C(O)(CH_3)_2\}_2$ | 227 m | 492 m | 657 s | 591 s | 1039 s | 881 s | 948 s |
| **7** | $MeBi\{S(S)POC(CH_3)_2C(O)(CH_3)_2\}_2$ | 251 m | 460 s | 648 s | 565 s | 1017 s | 867 s | 957 s |

s = strong, m = medium.

All these reactions are quite facile and quantitative. These can be completed at room temperature by constant stirring the mixture in benzene for 6 h. These compounds are yellow, orange or brown colored solids/sticky solids (Table 1). Solubility appears to increase with the polarity of solvents.

The solids were re-crystallized from dichloromethane-*n*-hexane mixture. All the above derivatives were stored at low temperature (5 °C) as they are thermally unstable at room temperature.

## IR spectra

Interpretation of IR spectra of these newly synthesized methylbismuth(III) *O*,*O*-alkylenedithiophosphates has been carried out by comparison with the spectrum of $MeBiCl_2$ and other related complexes. The important bands are summarized in Table 2. A medium-intensity absorption band in the region 227–257 cm$^{-1}$ has been assigned[3] to Bi–S, while a medium to strong intensity band in the region 460–493 cm$^{-1}$ has been assigned[3] to Bi–C. A strong band present in the region 648–657 cm$^{-1}$ can be ascribed to $\nu$P=S″ stretching vibrations,[4,5] which are shifted to lower wave number in comparison to the free ligand. This shifting suggests that the *O*,*O*-alkylenedithiophosphates behave as a bidentate mode of attachment in all these derivatives. A strong intensity band present in the region 563–597 cm$^{-1}$ may be attributed to $\nu$P–S symmetric and asymmetric vibrations.[6] The bands present in the region 1017–1039

DOI: 10.1002/aoc

**Table 3.** NMR ($^1$H, $^{13}$C and $^{31}$P) NMR spectral data of methylbismuth(III)*O*,*O*-alkylenedithiophosphates

| Compounds | $^1$H NMR in $\delta$ ppm | $^{13}$C NMR in $\delta$ ppm | $^{31}$P NMR in $\delta$ ppm |
|---|---|---|---|
| $MeBi\{S(S)POCH_2CH(O)CH_3\}_2$ | 4.75 (d, 6.02 Hz, $OC\underline{H}_2$); 4.36–4.46 (m, $OC\underline{H}$); 2.33 (s, Me–Bi); 1.44 (d, 6.30 Hz, $C\underline{H}_3$) | 76.0 ($O\underline{C}H_2$); 72.0 ($O\underline{C}H$); 54.4 (Me–Bi); 23.3($\underline{C}H_3$) | 120.3 |
| $MeBi\{S(S)PO(CH_2)_4O\}_2$ | 4.14 (t, 10.5 Hz, $OC\underline{H}_2$); 2.15 (s, Me–Bi); 1.56–1.87 (m, $OCH_2C\underline{H}_2$) | 66.1 ($O\underline{C}H_2$); 56.7 (Me–Bi); 28.1 ($OCH_2\underline{C}H_2$) | 95.0 |
| $MeBi\{S(S)POCH_2CH_2CH(O)CH_3\}_2$ | 4.69 (t, 9.30 Hz, $OC\underline{H}_2$); 4.17–4.32 (m, $OC\underline{H}$); 2.33 (s, Me–Bi); 1.91–2.11 (m, $OCHC\underline{H}_2$); 1.34 (d, 7.20 Hz, $C\underline{H}_3$) | 74.8 ($O\underline{C}H_2$); 66.0 ($O\underline{C}H$); 54.8 (Me–Bi); 33.2 ($OCH\underline{C}H_2$); 22.0 ($\underline{C}H_3$) | — |
| $MeBi\{S(S)POCH(CH_3)CH(O)CH_3\}_2$ | 4.78–4.87 (m, $OC\underline{H}$); 2.24 (s, Me–Bi); 1.32 (d, 6.00 Hz, $C\underline{H}_3$) | 73.4 ($O\underline{C}H$); 60.8 (Me–Bi); 23.1 ($\underline{C}H_3$) | 105.7 |
| $MeBi\{S(S)POCH_2CH(O)CH_2CH_3\}_2$ | 4.58 (d, 6.30 Hz, $OC\underline{H}_2$); 4.36–4.47 (m, $OC\underline{H}$); 2.37 (s, Me–Bi); 1.64–1.86 (m, $OCHC\underline{H}_2$); 0.97 (t, 7.20 Hz, $C\underline{H}_3$) | 80.9 ($O\underline{C}H_2$); 70.5 ($O\underline{C}H$); 52.6 (Me–Bi); 26.0 ($OCH\underline{C}H_2$); 9.1 ($\underline{C}H_3$) | 120.0 |
| $MeBi\{S(S)POCH(CH_3)CH_2C(O)(CH_3)_2\}_2$ | 4.89–4.96 (m, $OC\underline{H}$); 2.37 (s, Me–Bi); 1.70 (d, 9.00 Hz, $OCC\underline{H}_2$); 1.45 (d, 6.00 Hz, $OCHC\underline{H}_3$); 1.42 (s, $OCC\underline{H}_3$) | 85.2 ($O\underline{C}H$); 71.5 ($O\underline{C}$); 53.3 (Me–Bi); 44.5 ($OC\underline{C}H_2$); 32.0 ($OCH\underline{C}H_3$); 28.0 ($OC\underline{C}H_3$) | 93.0 |
| $MeBi\{S(S)POC(CH_3)_2C(O)(CH_3)_2\}_2$ | 2.26 (s, Me–Bi); 1.47 (s, $C\underline{H}_3$) | 88.9 ($O\underline{C}$); 58.7 (Me–Bi); 24.4 ($\underline{C}H_3$) | 112.5 |

s = singlet, d = doublet, t = triplet, m = multiplet.

and 853–887 cm$^{-1}$ have been assigned to (P)–O–C and P–O–(C) stretching vibrations, respectively. A strong band in the region 933–962 cm$^{-1}$ is most probably due to the dioxaphospholane and dioxaphosphorinane rings.[7]

## NMR spectra

The NMR spectra were recorded in $CDCl_3$ and the data are summarized in Table 3. In the $^1$H NMR spectra, the Me–Bi protons appeared as a singlet in the region $\delta$ 2.15–2.37 ppm, which are shifted to lower field relative to $MeBiCl_2$ ($\delta$ 1.57 ppm) on complexation. The protons due to heterocyclic ring of the ligands appeared at their appropriate positions with expected multiplicities in the $^1$H NMR spectra of these complexes.

In the $^{13}C\{^1H\}$ NMR spectra, the Me–Bi carbon signals appeared at higher field ($\delta$ 52.6–60.8) relative to $MeBiCl_2$. In addition, all these derivatives also exhibited expected signals due to ring carbon atoms.

$^{31}$P NMR spectra of all these derivatives displayed a singlet in a region usually attributed to the chelated *O*,*O*-alkylenedithiophosphate ligands. $^{31}$P NMR chemical shift values appear to be dependent on the size of the heterocyclic ring. In the spectra of dioxaphospholanes (where the ring is five membered) the chemical shift values are between $\delta$ 105.7 and 120.3 ppm in methylbismuth(III) derivatives, while in the corresponding dioxaphosphorinane derivatives (where the ring is six-membered) the chemical shift values were observed at $\delta$ 93.0 ppm.

## XRD patterns

The thermal behavior of two representative compounds (**2** and **6**) has also been studied for the preparation of pure $Bi_2S_3$. These complexes, when refluxed separately for 2 h in xylene under inert media, both yielded blackish gray powders, which were identified as pure $Bi_2S_3$ from microanalysis, XRD patterns[8] (Fig. 1) and IR spectra. The scanning electron micrograph of these products (Fig. 2) taken at different resolutions showed large aggregates of microcrystals.

## Thermogravimetric analysis

The thermogravimetric (TG) curve (Fig. 3) of complex **6** showed a single-step decomposition at 154.3 °C finally leading to the formation of pure bismuthinite, $Bi_2S_3$, from weight loss 33.6 mass %.

# EXPERIMENTAL

All manipulations were carried out under strictly anhydrous and inert conditions. *O*,*O*-alkylenedithiophosphoric acids[6] and methylbismuth(III) dichloride[9] were prepared according to the literature methods. IR spectra were recorded as nujol mulls between CsI plates in a Boman MB–102 FT IR spectrometer. The $^1$H, $^{13}C\{^1H\}$ and $^{31}$P NMR spectra were recorded in 5 mm NMR tubes, on a Bruker DPX-300 spectrometer operating at 300, 75.47 and 121.49 MHz, respectively. Chemical shifts are relative to internal chloroform $\delta$ 7.26 ppm for $^1$H, $\delta$ 77.0 ppm for $^{13}$C and external 85% $H_3PO_4$ for $^{31}$P.

DOI: 10.1002/aoc

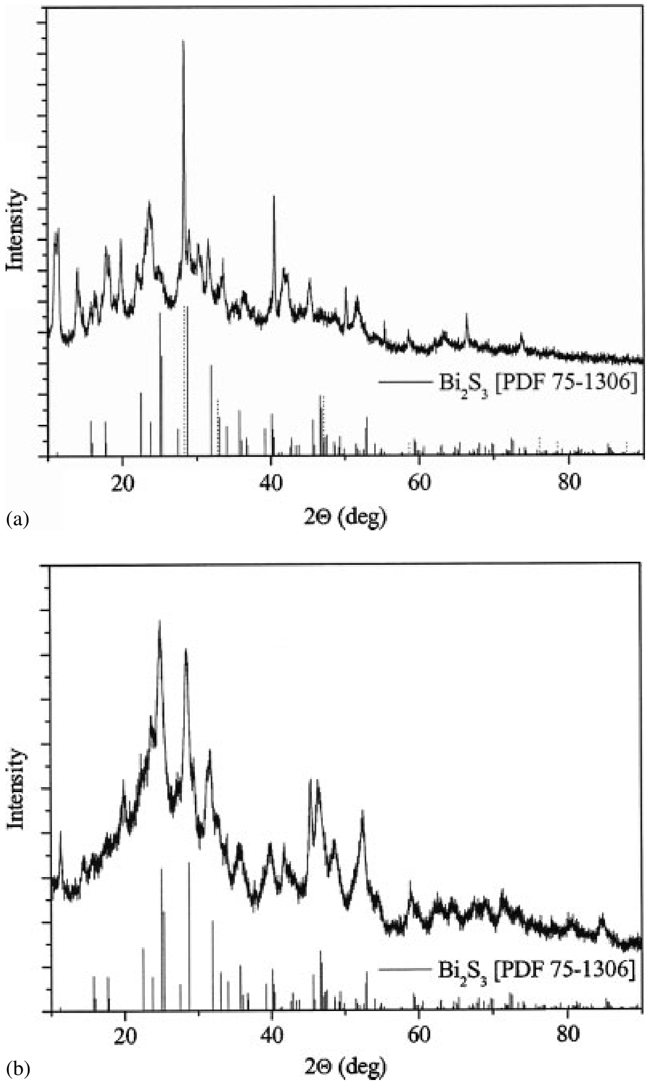

**Figure 1.** XRD patterns of $Bi_2S_3$ obtained from (a) $[MeBi\{S_2\overline{PO\text{-}(CH_2)_4\text{-}O}\}_2]$ and (b) $[MeBi\{S_2\overline{POCH(CH_3)CH_2C(O)}(CH_3)_2\}_2]$ by refluxing in xylene.

Microanalysis was carried out on a Heraeus Carlo Erba 1108 analyzer.

## Preparation of $[MeBi\{S_2\overline{PO\text{-}(CH_2)_4\text{-}O}\}_2]$ (2)

Solid $KS(S)\overline{PO\text{-}(CH_2)_4\text{-}O}$ (1.90 g, 8.55 mmol) was added to a stirred benzene suspension (~40 ml) of $MeBiCl_2$ (1.26 g, 4.27 mmol). The reactants were stirred for 6 h. The solvent was evaporated *in vacuo* and the residue was extracted with chloroform and filtered through a G-3 filtration unit. The solvent was stripped off under vacuum to give a yellow solid (92%), which was re-crystallized from dichloromethane-*n*-hexane mixture. Similarly, other methylbismuth(III) derivatives with *O,O*-alkylenedithiophosphoric acids were prepared (Table 1).

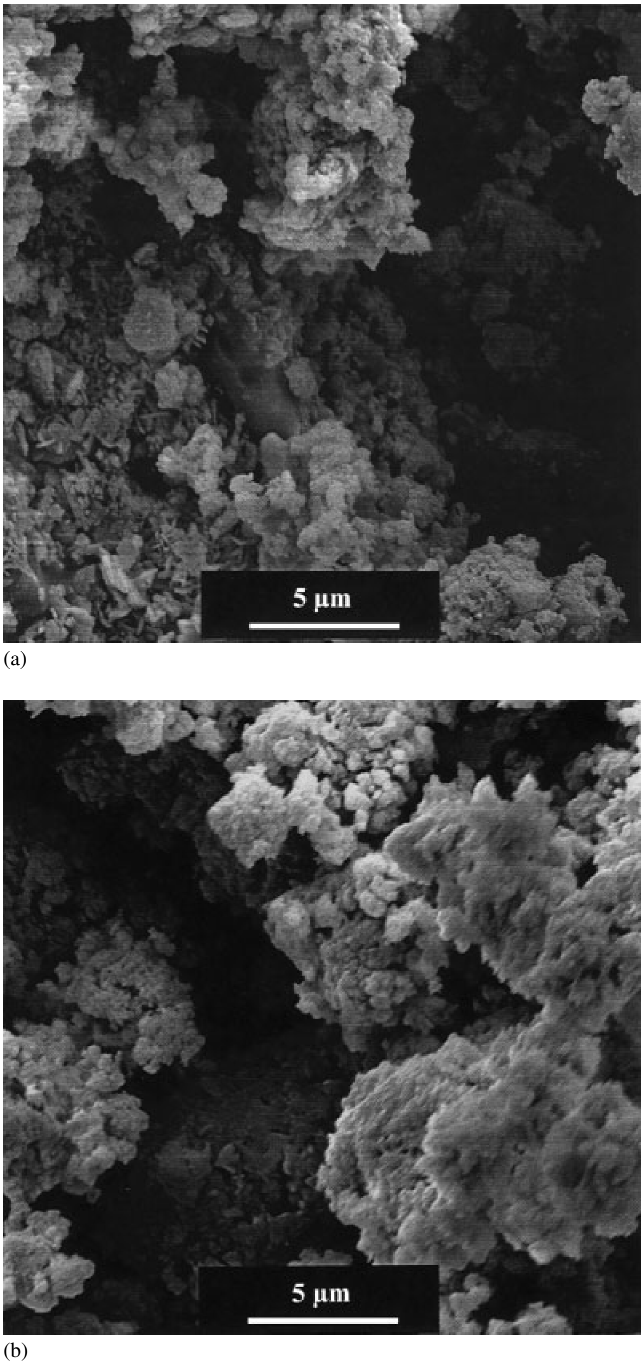

**Figure 2.** SEM images of $Bi_2S_3$ obtained from (a) $[MeBi\{S_2\overline{PO\text{-}(CH_2)_4\text{-}O}\}_2]$ and (b) $[MeBi\{S_2\overline{POCH(CH_3)CH_2C(O)}(CH_3)_2\}_2]$ by refluxing in xylene.

## Pyrolysis of $[MeBi\{S_2\overline{PO\text{-}(CH_2)_4\text{-}O}\}_2]$ (2)

A xylene solution of the complex (**2**) was refluxed for 2 h under $N_2$ atmosphere whereupon a blackish gray material was formed. After cooling to room temperature, the supernatant was decanted and the residue was washed with chloroform

DOI: 10.1002/aoc

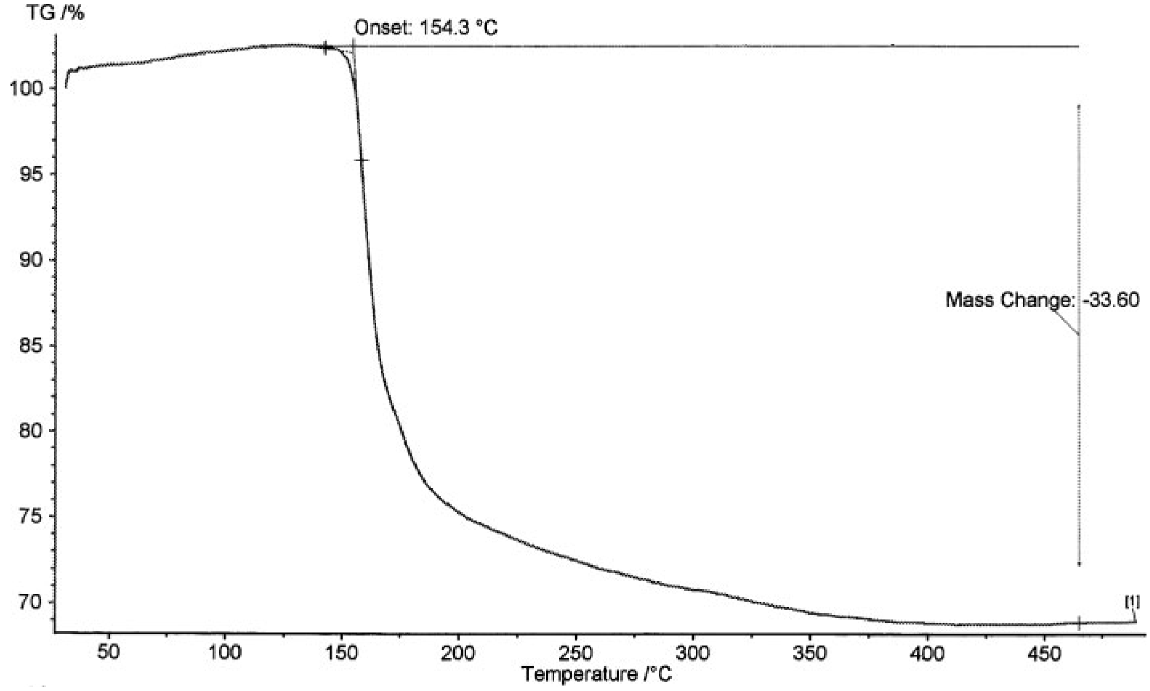

**Figure 3.** TGA curve of $[MeBi\{S_2POCH(CH_3)CH_2C(O)(CH_3)_2\}_2]$.

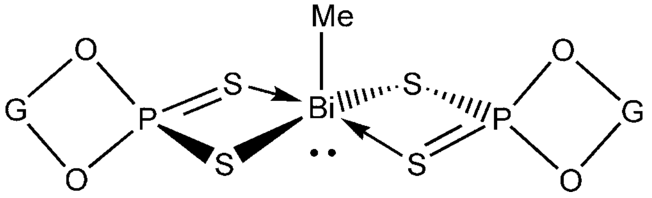

**Figure 4.** Proposed structure for $[MeBi\{S_2P(O\text{-}G\text{-}O)\}_2]$ [where $G = CH_2CH(CH_3)$, $(CH_2)_4$, $CH_2CH_2CH(CH_3)$, $CH(CH_3)CH(CH_3)$, $CH_2CHCH_2CH_3$, $CH(CH_3)CH_2C(CH_3)_2$ and $C(CH_3)_2C(CH_3)_2$].

(2 × 10 ml) and further with *n*-hexane (2 × 10 ml). Finally, it was dried under reduced pressure and identified as pure $Bi_2S_3$ from its XRD pattern (Fig. 1). Analysis: C, 0.8%; H, 0.5%; S, 18.3; Bi, 80.6. A similar procedure was used for the pyrolysis of complex (**6**).

## CONCLUSION

The synthesis and characterization of methylbismuth(III) derivatives with *O*,*O*-alkylenedithiophosphoric acids have been carried out. On the basis of spectral studies, it is reasonable to conclude that all these ligands behave as a bidentate mode of attachment to the metal and the following tentative structure may be proposed for these types of derivatives (Fig. 4). Thermolysis of the two representative derivatives indicates that these are efficient precursors for the preparation of pure bismuthinite, $Bi_2S_3$ at low temperature.

### Acknowledgment

One of the authors (A.K. Jain) is grateful to DST, New Delhi for the award of SRF. Financial support by DST and UGC, New Delhi is highly appreciated.

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DOI: 10.1002/aoc