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# Synthesis and characterization of methylbismuth(III) complexes containing dithio ligands: crystal and molecular structure of [MeBi{$S_2COMe$}$_2$] and transformation of [MeBi{$S_2CO^iPr$}$_2$] to $Bi_2S_3$

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## Abstract

Reactions of sodium/potassium salts of xanthates, dithiocarbamates and dialkyldithiophosphates with methylbismuth dichloride have been carried out in 1:2 stiochiometric ratio in anhydrous benzene and products of the type [MeBi($S_2COR$)$_2$] (R = Me, Et, $Pr^i$), [MeBi($S_2CNR_2$)$_2$] (R = Me, Et, 1/2$C_4H_8N$) and [MeBi{$S_2P(OR)_2$}$_2$] (R = Me, Et, $Pr^i$) have been isolated. All of these complexes were characterized by elemental analyses and by IR and NMR ($^1H$, $^{13}C$ and $^{31}P$) spectra. The X-ray structure of [MeBi($S_2COMe$)$_2$] indicates that the immediate environment around the central bismuth atom is distorted square pyramidal. However, inclusion of a significant Bi···S intermolecular bond results in pentagonal pyramidal geometry. Thermolysis of [MeBi($S_2CO^iPr$)$_2$] in xylene indicates that it is a good precursor for preparation of $Bi_2S_3$ at low temperature.

*Keywords:* Sodium/potassium salts; Crystal and molecular structures; Bismuth

## 1. Introduction

The chemistry of arsenic, antimony and bismuth compounds derived from xanthates, dithiocarbamates and phosphorus based acids have been an active area of research for more than four decades [1–7]. The sustained interest in these compounds is associated with their tendancy to show great structural diversity, ranging from monomeric to polymeric supramolecular assemblies, along with their extensive applications as catalysts, lubricants and biocides [7,8].

Group V chalcogenide materials, including binary and ternary compounds such as $Bi_2Te_3$ and $CuSbS_2$, have attracted considerable attention due to their good photovoltaic properties and high thermoelectric power. Thus they are used in solar cells, photolithiography, holographic recording, optical memory devices, photoconductors and as thermoelectric generators and coolers [9,10]; $Bi_2Te_3$ being the best room temperature thermoelectric material [9]. Although several metal xanthates, dithiocarbamates and dithiophosphates have been used as molecular precursors for metal sulphides in CVD studies [11], the use of group V organometallic derivatives along with these ligands for the preparation of $M_2S_3$ compounds has conspicuously remained unexplored.

In view of above and persuance of our recent work on main group organometallic compounds [12–15], here, we report the synthesis and characterization of methylbismuth(III) complexes containing dithioligands and X-ray crystal structure of [MeBi{$S_2COMe$}$_2$]. Interestingly, the thermolysis of [MeBi{$S_2CO^iPr$}$_2$] in xylene gives pure $Bi_2S_3$ at low temperature.

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## 2. Results and discussion

The reactions of $MeBiCl_2$ with the sodium/potassium salts of xanthates, dithiocarbamates and dialkyldithiophosphates in 1:2 stoichiometry in benzene afford $[MeBi(S_2COR)_2]$ (R = Me, Et, $^i$Pr), $[MeBi(S_2CNR_2)_2]$ (R = Me, Et, $C_4H_8N$) and $[MeBi\{S_2P(OR)_2\}_2]$ (R = Me, Et, $^i$Pr), respectively, in excellent yields (eq. 1). The xanthate complexes were isolated previously in rather poor yields (38–43%) by the reaction of $MeBi(OR)_2$ with $CS_2$ [16] whereas the dithiocarbamate derivatives were isolated in moderate to fair yields [17].

All these complexes are yellow to brown solids or pastes and are soluble in common organic solvents. The assignment of IR bands was made by comparison to the literature and the spectrum of starting material, $MeBiCl_2$. A medium to strong band in the region 457–472 $cm^{-1}$ has been assigned to $\nu$Bi–C [18] while a weak to medium intensity band in the region 246–259 $cm^{-1}$ has been assigned to $\nu$Bi–S [18].

The NMR spectra, which exhibit the expected peak multiplicities and integration, are summarized in Table 4. The Me–Bi protons appeared as a singlet in the region $\delta$ 2.07–2.31 ppm. The signal is deshielded on complexation relative to $MeBiCl_2$ ($\delta$ 1.57 ppm). However, the Me–Bi carbon signal appears at higher field ($\delta$ 40.2–54.2 ppm) relative to $MeBiCl_2$ ($\delta$ 73.1 ppm). The following chemical shift trend is evident from Table 2: xanthates < dithiocarbamate < dialkyldithiophosphate. The $^{31}$P-NMR spectra of dithiophosphate derivatives displayed a singlet in a region usually attributed to the chelated dithio ligand [19]. Arsenic, antimony and bismuth compounds with dithioligands exhibit a single set of NMR resonances in solution even for the molecules show aggregation (inter-molecular interactions) in the solid state [7]. The magnitude of these secondary interactions increases with increasing the size of the metal and also with increasing the number of ligand moieties on the metal center $[M(SS)_3 > RM(SS)_2 > R_2M(SS)]$. The complex $[MeBi(S_2CNEt_2)_2]$ is monomeric in benzene solution [17] and as expected display only one set of $^1$H and $^{13}$C resonances in the NMR spectra. However, the X-ray structural analysis revealed a dimeric structure formed by intermolecular Bi–S interactions. The bismuth atom adopts a slightly distorted pentagonal pyramidal configuration [20].

To throw some light on the solid state structures, $^{13}$C-CPMAS spectra of a few representative complexes $\{[MeBi(S_2COMe)_2]$ $^{13}$C $\delta$: 43.4 (br hump, Bi–Me); 63.8, 64.3 (OMe); 226.0 (br, $S_2C$), $[MeBi(S_2CNMe_2)_2]$ $^{13}$C $\delta$: 45.0 (br, Bi–Me); 62.0, 64.1 ($NMe_2$); 225.4, 227.5 ($S_2C$); $[MeBi(S_2CNEt_2)_2]$ $^{13}$C $\delta$: 11.1, 13.4, 15.5 ($CH_2Me$); 40.5 (Bi–Me); 49.2 (br, $-CH_2-$); 195.8, 198.9 ($S_2C$)$\}$(Fig. 1) have been recorded. The Bi–Me resonance in $[MeBi(S_2COMe)_2]$ and $[MeBi(S_2CNMe_2)_2]$ appear as an unresolved broad signal, however in $[MeBi(S_2CNEt_2)_2]$ only one signal at $\delta$ 40.5 appeared. Two sets of resonances for $CS_2$ and ER (ER = OMe, $NMe_2$, $NEt_2$) carbon of the dithio-ligands are observed. These data suggest that there are two different type of ligands in the solid state, which is further substantiated by the X-ray structure of $[MeBi\{S_2COMe\}_2]$. The complex $[MeBi(S_2CNEt_2)_2]$ [20] showed three signals for $NCH_2CH_3$. The resonances at 11.1 and 13.4 ppm of nearly equal intensity may be attributed to the bridging dithio ligand. The $CH_3$ of ethyl group are anisochronous, the third resonance at 15.5 ppm can be assigned to the chelating bidentate dithio ligand.

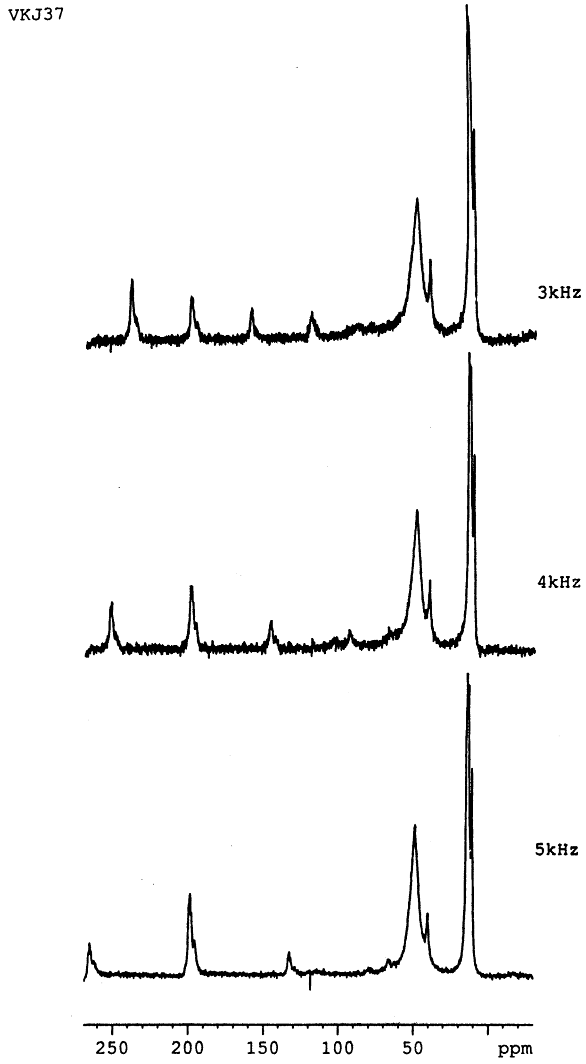
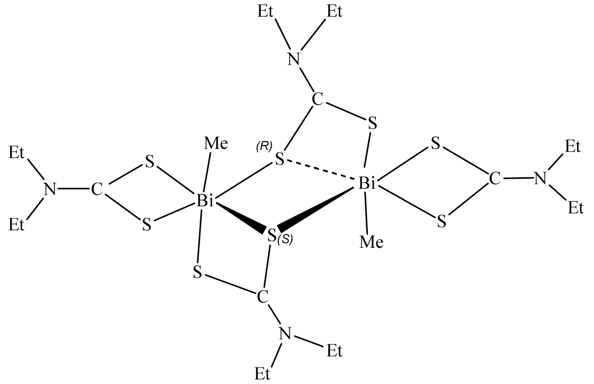


Fig. 1. $^{13}$C{$^1$H} CP-MASS NMR Spectrum of $[MeBi(S_2CNEt_2)_2]$.

$$MeBiCl_2 + 2\,M(\overset{\frown}{S\;\;S}) \longrightarrow [MeBi(\overset{\frown}{S\;\;S})_2] + 2\,MCl$$

$(\overset{\frown}{S\;\;S} = S_2COR,\ S_2CNR_2,\ S_2P(OR)_2;\ M = Na\ or\ K)$



To assess whether these complexes can serve as molecular precursors for the preparation of $Bi_2S_3$ either by spray or aerosol assisted CVD methods, thermal behaviour of a few representative complexes have been studied. $[MeBi(S_2CO^iPr)_2]$ when refluxed in xylene gave blackish grey powder which has been identified as $Bi_2S_3$ from XRD pattern [21] and IR spectral data (288m, 241m, 212s) [22] (Fig. 2). The scanning electron micrographs (Fig. 3) of this powder taken at different resolutions showed large aggregates of microcrystals.

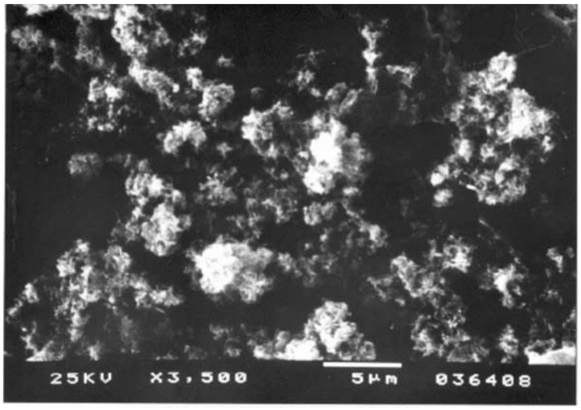


Fig. 2.

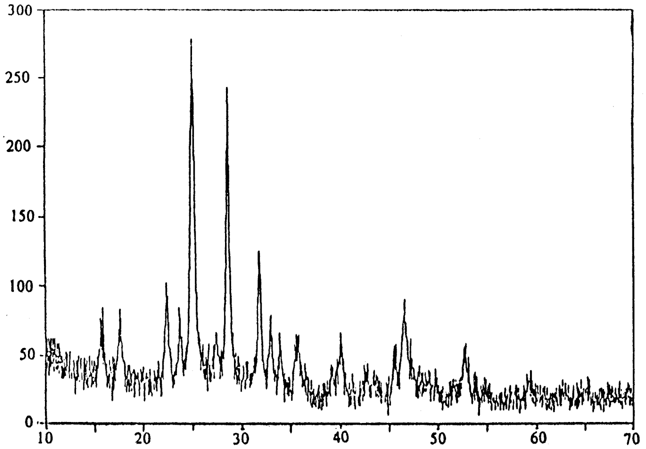


Fig. 3.

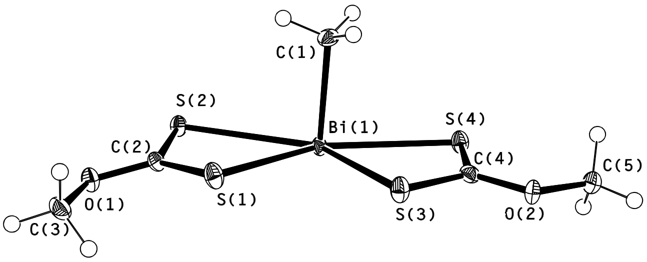


Fig. 4. ORTEP plot showing the immediate environment around bismuth in $MeBi(S_2COMe)_2$

## 2.1. X-ray crystal structure of $MeBi(S_2COMe)_2$ (1)

The immediate environment around bismuth in $MeBi(S_2COMe)_2$ (**1**) is distorted square pyramidal (see Fig. 4). The two bidentate xanthate ligands in the plane each have one shorter (Bi(1)–S(1), 2.784(1) and Bi(1)–S(3), 2.711(1) Å) and one longer bond (Bi(1)–S(2), 2.992(1) and Bi(1)–S(4), 2.844(1) Å). All of these bonds are longer than the sum of the covalent radii of Bi and S of 2.63 Å. By contrast the bond to the methyl group in the vertical position is short, Bi(1)–C(1) 2.234(5) Å, relative to the sum of the covalent radii of Bi and C of 2.37 Å. The Bi–C–S angles range from 86.8(2) to 92.0(2)° and average 90(2)°. The bite angles for the ligand are similar (S(1)–Bi(1)–S(2), 62.06(4) and S(3)–Bi(1)–S(4), 64.70(4)°, as expected, but the angle between the shorter bond of each ligand is considerably smaller than that between the longer (S(1)–Bi(1)–S(3), 79.62(4) and S(2)–Bi(1)–S(4), 153.62(4)°) although their essential co-planarity is clear from the sum of the four angles being 361°. The space between S(2) and S(4) is occupied by an adjacent sulfur atom to give an intermolecular bond, Bi(1)–S(2)′, whose length of 3.253(1) Å is much closer to that of the longest ligand bond than to the sum of the van der Waal radii of Bi and S of ca. 4.0 Å. The S(2)–Bi(1)···S(2)′ and S(4)–Bi(1)···S(2)′ angles are 71.35(4) and 82.82(4)°, respectively, which sum to 153.63°; the angle for S(2)–Bi(1)–S(4). Thus, the environment around Bi can be considered to be a distorted pentagonal pyramid in the solid state to give an extended polymeric structure with the sulfur of the longest Bi–S bond acting as a bridge with a Bi(2)–S(2)–Bi(1)′ angle of 140.46(3)° (see Fig. 5). However, the stereochemically active lone pair on Bi(III) may be present trans to the methyl group would lead to pentagonal bipyramidal confuguration.

## 3. Experimental

Dithiocarbamates, xanthates [23], dialkyldithiophosphates [24] and $MeBiCl_2$ [25] were prepared according to literature methods. Reactions were carried out under

Table 1
Physical and analytical data of methylbismuth(III) complexes derived from dithioligands

| Complexes | Recrystallization solvent (% yield) | M.p. (°C) | % Analysis found (Calc.) | | | | |
|---|---|---|---|---|---|---|---|
| | | | C | H | N | S | Bi |
| [MeBi($S_2COMe$)$_2$] | Benzene–hexane<br>(90) | 112 | 13.6<br>(13.7) | 2.2<br>(2.1) | – | 28.7<br>(29.3) | 47.4<br>(47.7) |
| [MeBi($S_2COEt$)$_2$] | Benzene–hexane<br>(94) | 100 | 17.8<br>(18.0) | 2.7<br>(2.8) | – | 27.4<br>(27.5) | 44.5<br>(44.8) |
| [MeBi($S_2CO^iPr$)$_2$] | Benzene–hexane<br>(99) | 118 | 21.4<br>(21.8) | 3.4<br>(3.5) | –<br>– | 25.9<br>(25.9) | 41.6<br>(42.2) |
| [MeBi($S_2CNMe_2$)$_2$] | Benzene–hexane<br>(98) | 134 | 18.3<br>(18.1) | 3.3<br>(3.3) | 5.6<br>(6.0) | 27.5<br>(27.6) | 44.8<br>(45.0) |
| [MeBi($S_2CNEt_2$)$_2$] | Benzene–hexane<br>(78) | 106 | 25.2<br>(25.4) | 4.0<br>(4.4) | 5.2<br>(5.4) | 24.5<br>(24.6) | 40.8<br>(40.2) |
| [MeBi($S_2CNC_4H_8$)$_2$] | Benzene–hexane<br>(98) | 193 | 25.4<br>(25.6) | 3.5<br>(3.7) | 5.6<br>(5.4) | 24.6<br>(24.8) | 40.3<br>(40.5) |
| [MeBi{$S_2P(OMe)_2$}$_2$] [a] | (99) | | 11.0<br>(11.2) | 2.5<br>(2.8) | – | 23.7<br>(23.8) | 38.7<br>(38.8) |
| [MeBi{$S_2P(OEt)_2$}$_2$] [a] | (95) | – | 18.0<br>(18.2) | 3.6<br>(3.9) | – | 21.3<br>(21.6) | 35.3<br>(35.2) |
| [MeBi{$S_2P(OPr^i)_2$}$_2$] [a] | (94) | – | 24.2<br>(24.0) | 4.4<br>(4.8) | – | 19.6<br>(19.7) | 31.9<br>(32.1) |

[a] Dark yellow coloured viscous liquid.

Table 2
Crystal data and structure refinement for $MeBi(S_2COMe)_2$

| | |
|---|---|
| Empirical formula | $C_5H_9BiO_2S_4$ |
| Formula weight | 438.34 |
| Temperature (K) | 120 |
| Wavelength (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| Unit cell dimensions | |
| $a$ (Å) | 11.5667(4) |
| $b$ (Å) | 6.1223(2) |
| $c$ (Å) | 15.7992(7) |
| $\beta$ (°) | 98.711(1) |
| $V$ (Å$^3$) | 1105.91(7) |
| $Z$ | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 2.633 |
| Absorption coefficient (mm$^{-1}$) | 16.658 |
| $F(000)$ | 808 |
| Crystal size (mm$^3$) | $0.25 \times 0.20 \times 0.08$ |
| $\theta$ Range for data collection (°) | 3.56–27.54 |
| Index ranges | $-14 \leq h \leq 15$, $-7 \leq k \leq 7$, $-20 \leq l \leq 20$ |
| Reflections collected | 4488 |
| Independent reflections | 2514 [$R_{int} = 0.0275$] |
| Max. and min. transmission | 0.3492 and 0.1031 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 2514/0/113 |
| Goodness-of-fit on $F^2$ | 1.074 |
| Final $R$ indices [$F^2 > 4\sigma(F^2)$] | $R_1 = 0.0307$, $wR_2 = 0.0746$ |
| $R$ indices (all data) | $R_1 = 0.0348$, $wR_2 = 0.0769$ |
| Extinction coefficient | 0.0023(2) |
| Largest difference peak and hole (e Å$^{-3}$) | 2.300 and −3.218 |

Table 3
Bond lengths (Å) and bond angles (°) for $MeBi(S_2COMe)_2$

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Bi(1)–C(1) | 2.234(5) | Bi(1)– –S(2)′ | 3.253(1) |
| Bi(1)–S(1) | 2.783(1) | Bi(1)–S(3) | 2.711(1) |
| Bi(1)–S(2) | 2.992(1) | Bi(1)–S(4) | 2.844(1) |
| S(1)–C(2) | 1.692(5) | S(3)–C(4) | 1.708(6) |
| S(2)–C(2) | 1.694(6) | S(4)–C(4) | 1.674(5) |
| O(1)–C(2) | 1.325(7) | O(2)–C(4) | 1.324(6) |
| O(1)–C(3) | 1.451(6) | O(2)–C(5) | 1.443(7) |
| *Bond angles* | | | |
| C(1)–Bi(1)–S(1) | 91.6(2) | C(1)–Bi(1)–S(3) | 89.5(2) |
| C(1)–Bi(1)–S(2) | 92.0(2) | C(1)–Bi(1)–S(4) | 86.8(2) |
| S(1)–Bi(1)–S(2) | 62.06(4) | S(3)–Bi(1)–S(4) | 64.70(4) |
| S(1)–Bi(1)–S(3) | 79.62(4) | S(2)–Bi(1)–S(4) | 153.62(4) |
| S(1)–Bi(1)–S(4) | 144.29(4) | S(2)–Bi(1)–S(3) | 141.68(4) |
| Bi(1)–S(1)–C(2) | 90.03(19) | Bi(1)–S(3)–C(4) | 87.90(18) |
| Bi(1)–S(2)–C(2) | 83.14(18) | Bi(1)–S(4)–C(4) | 84.21(19) |
| S(1)–C(2)–S(2) | 123.4(3) | S(3)–C(4)–S(4) | 123.2(3) |
| S(1)–C(2)–O(1) | 121.5(4) | S(3)–C(4)–O(2) | 114.1(4) |
| S(2)–C(2)–O(1) | 115.1(4) | S(4)–C(4)–O(2) | 122.7(4) |
| C(2)–O(1)–C(3) | 119.7(4) | C(4)–O(2)–C(5) | 118.5(4) |
| C(1)–Bi(1)···S(2)= | 88.9(2) | S(1)–Bi(1)– –S(2)′ | 133.40(4) |
| S(2)–Bi(1)···S(2)= | 71.35(4) | S(3)–Bi(1)– –S(2)′ | 146.97(4) |
| S(4)–Bi(1)···S(2) | 82.28(4) | Bi(1)– –S(2)′–Bi(1)′ | 140.46(3) |

Equivalent position $(1/2-x)$, $(1/2+y)$, $(1/2-z)$ given by a prime.

anhydrous conditions. IR spectra were recorded as nujol mulls between CsI plates in a Bomen MB-102 FT IR spectrometer. The $^1H$-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectra were recorded in 5 mm NMR tubes as freshly prepared $CDCl_3$ solution, 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 $^1H$, ($\delta$ 77.0) for $^{13}C$ and external 85% $H_3PO_4$ for $^{31}P$. Carbon-13 CPMAS-NMR

Table 4
$^{1}H$-, $^{13}C\{^{1}H\}$- and $^{31}P\{^{1}H\}$-NMR dat for methylbismuth(III) complexes with dithio ligands in $CDCl_3$

| Complexes | $^{13}C\{^{1}H\}$-NMR in $\delta$ ppm | $^{1}H$-NMR in$\delta$ ppm | $^{31}P\{^{1}H\}$-NMR in $\delta$ ppm |
|---|---|---|---|
| $MeBiCl_2$ [a] | 73.1 (Bi–Me) | 1.57 (s, Bi–Me) | – |
| $[MeBi(S_2COMe)_2]$ | 41.0 (Bi–Me); 60.2 (OMe); 226.7 ($CS_2$) | 2.23 (s, Bi–Me); 4.20 s, OMe) | – |
| $[MeBi(S_2COEt)_2]$ | 13.8 ($OCH_2Me$); 41.0 (Bi–Me); 70.1 (O–$CH_2$); 225.3 ($CS_2$) | 1.48 (t, 7 Hz, $OCH_2Me$); 2.20 (s, Bi–Me); 4.65 (q, 7 Hz, $CH_2$) | – |
| $[MeBi(S_2CO^{i}Pr)_2]$ | 21.4 ($OCHMe_2$); 40.5 (Bi–Me); 78.8 (OCH); 224.4 ($CS_2$) | 1.45 (d, 6.1 Hz, $OCHMe_2$); 2.20 (s, Bi–Me); 5.68 (sep, 4.5 Hz, OCH) | – |
| $[MeBi(S_2CNMe_2)_2]$ | 40.2 (Bi–Me); 59.8 ($NMe_2$); 226.3 ($CS_2$) | 2.20 (s, Bi–Me); 4.19 (s, $NMe_2$) | – |
| $[MeBi(S_2CNEt_2)_2]$ | 12.1 ($NCH_2Me$); 44.0 (Bi–Me); 47.7 ($NCH_2$); 200.5 ($CS_2$) | 1.23 (t, 7 Hz, $NCH_2Me$); 2.15 (s, Bi–Me); 3.74 (q, 7 Hz, N–$CH_2$) | – |
| $[MeBi(S_2CNC_4H_8)_2]$ | 25.2 ($NCH_2CH_2$); 42.4 (Bi–Me); 53.0($NCH_2$); 198.0($CS_2$) | 1.99 (t, 6.7 Hz, $NCH_2CH_2$); 2.07 (s, Bi–Me); 3.79 (t, 6.7 Hz, $NCH_2$) | – |
| $[MeBi\{S_2P(OMe)_2\}_2]$ | 52.7 (s, Bi–Me); 53.6 (s, OMe) | 2.31 (s, Bi–Me); 3.77 (d, $^{3}J$(P–H) 15 Hz, OMe) | 103.5 |
| $[MeBi\{S_2P(OEt)_2\}_2]$ | 15.7 (d, 7.5 Hz, $OCH_2Me$); 51.4 (Bi–Me); 63.4 (d, 6 Hz, $OCH_2$) | 1.33 (t, 7 Hz, $OCH_2Me$); 2.27 (s, Bi–Me); 4.10 (m, $OCH_2$) | 98.2 |
| $[MeBi\{S_2P(OPr^{i})_2\}_2]$ | 23.7 (d, 4.7 Hz, $OCHMe_2$); 54.2 (Bi–Me); 73.3 (d, 6.5 Hz, OCH) | 1.35 (d, 6.2 Hz, $OCHMe_2$); 2.28 (s, Bi–Me); 4.81 (sep, 6.2 Hz, OCH) | 95.04 |

[a] In DMSO-$d_6$.

spectra were recorded on a Bruker DPX-300 MHz spectrometer operating at 75.47 MHz using magic angle sample spinning. Adamantane was used as an external standard. Signals were identified from spinning side bands by recording the spectra at 2, 3 and 5 kHz spin rates. Microanalysis of the samples was carried out on a Perkin Elmer C, H, N and S II series 2400 analyzer.

### 3.1. Preparation of $[MeBi(S_2COMe)_2]$

Solid $KS_2COMe$ (700 mg, 4.78 mmol) was added to a stirred benzene suspension (30 ml) of $MeBiCl_2$ (703 mg, 2.38 mmol). The reaction mixture was stirred for 5 h and filtered through a G-3 sintered funnel. The filtrate was concentrated in vacuo to give a yellow paste, which was recyrstallised from benzene–hexane as yellow crystals (943 mg, 90%). Other xanthate complexes were prepared in a similar manner.

### 3.2. Preparation of $[MeBi(S_2CNEt_2)_2]$

Solid $NaS_2CNEt_2$ (1.14 g, 6.66 mmol) was added to a stirred benzene suspension (30 ml) of $MeBiCl_2$ (982 mg, 3.33 mmol), and the mixture was stirred for 6 h before filtration through a G-3 filtering unit. The solvent was stripped off in vacuo to afford yellow paste which was then recrystallised from a benzene–hexane mixture (1.35 g, 78%, m.p. 106 °C). Similarly other dithiocarbamate derivatives were prepared.

### 3.3. Preparation of $[MeBi\{S_2P(O^{i}Pr)_2\}_2]$

A methanolic solution of sodium salt of diisopropyldithiophosphate [prepared from sodium metal (102 mg, 4.44 mmol) dissolved in methanol (10 ml) and diisopropyldithiophosphate (949 mg, 4.43 mmol)] was added to a stirred benzene suspension (25 ml) of $MeBiCl_2$ (650 mg, 2.20 mmol). The reaction mixture was stirred for about 6 h before precipitated NaCl was filtered through a G-3 sintered disc. The solvent was removed under vacuum to give a yellow coloured liquid (1.34 g, 94%), which slowly crystallized when left for several days. Similarly all other dithiophosphate derivatives were prepared.

Corresponding data of all these complexes are summarized in Table 1.

### 3.4. Pyrolysis of $[MeBi(S_2CO^{i}Pr)_2]$

A xylene solution (25 ml) of $MeBi(S_2CO^{i}Pr)_2$ (133 mg) was refluxed with stirring under $N_2$ for 30 min whereupon a blackish grey material formed. After cooling, the contents were centrifuged, the supernatant liquid decanted and the residue was washed with hexane (2 × 10 ml) and then air dried (yield 51 mg). The residue was identified as $Bi_2S_3$ from its XRD pattern. Analysis Found: C, 1.0%; H, 0.2%.

### 3.5. X-ray diffraction analysis

A colourless, plate crystal of $MeBi(S_2COMe)_2$ was mounted on a glass fibre. Data was collected on an Enraf Nonius κCCD area detector diffractometer, with $\varphi$ and $\omega$ scans chosen to give a complete asymmetric unit. Cell refinement [26] gave cell constants corresponding to a monoclinic cell whose dimensions are given in Table 2 along with other experimental parameters. An absorption correction was applied [27]. The structure was solved by direct methods [28] and the structure was refined using the WINGX version [16,29] of SHELX-97

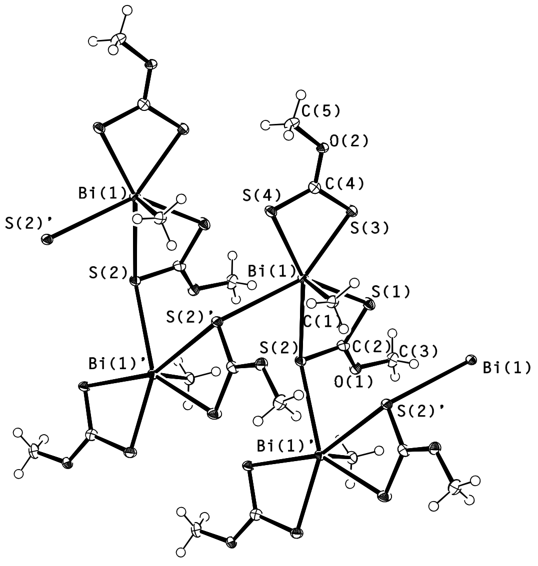


Fig. 5. ORTEP plot showing extended polymeric structure of MeBi($S_2$-COMe)$_2$

[30]. All of the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinement was based on 2514 observed reflections (2301 for $F^2 > 4\sigma(F^2)$) and 113 variable parameters and converged (largest parameter shift was 0.001 times its e.s.d.).

Distances and bond angles are given in Table 3 and the molecule is displayed in the ORTEP diagram in Fig. 4. Additional material available from the Cambridge Crystallographic Data Centre comprises the final atomic coordinates and thermal parameters for all atoms.

## 4. Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 189012 for MeBi($S_2$COMe)$_2$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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