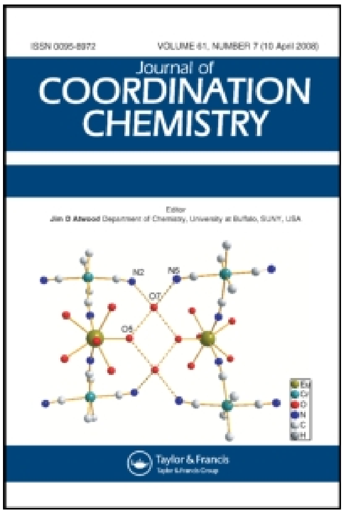

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Homodinuclear glycolate derivatives of bismuth(V) and arsenic(III): synthesis and spectroscopic studies

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Homodinuclear glycolate derivatives of bismuth(V) and arsenic(III): synthesis and spectroscopic studies

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Ligand bridged homodinuclear derivatives of bismuth(V) of the type, $\mathrm{Ph_3B\overline{i{-}O{-}BiPh_3[ORO}]}$ (**1a**–**1d**) [where $\mathrm{R = {-}C(CH_3)_2CH_2CH(CH_3){-}}$ (**1a**), $\mathrm{{-}CH(CH_2CH_3)CH_2{-}}$ (**1b**), $\mathrm{{-}CH(CH_3)CH(CH_3){-}}$ (**1c**), $\mathrm{{-}CH(CH_3)CH_2{-}}$ (**1d**)] have been synthesized by reactions of equimolar oxobis(triphenylbismuth)dichloride, $\mathrm{\{[Ph_3Bi]_2O\}Cl_2}$ with glycols, HOROH in the presence of NaOMe. Reactions of sodiumtetraisopropoxoarsonate, $\mathrm{NaAs(OPr^i)_4}$ with $\mathrm{[\overline{ORO]A}sCl}$ in 1 : 1 molar ratio yielded homodinuclear alkoxo derivatives of arsenic(III) containing glycols, $\mathrm{[\overline{ORO]As}(\mu\text{-}OPr^i)_2As(OPr^i)_2}$ (**2a**–**2d**). All compounds were characterized by elemental analysis, molecular weight determinations, IR and NMR (^{1}H and ^{13}C) spectral studies.

Keywords: Bismuth; Arsenic; Sodiumtetraisopropoxoarsonate; Glycols

1. Introduction

Interest in organobismuth compounds exists due to their antitumor [1], pharmacology [2], catalytic activity [3] and application as a precursor for superconducting materials [4]. In addition to applications, the structural chemistry of organobismuth compounds is also very interesting [5]. Information on the chemistry of organobismuth(V) complexes is still very limited compared to those of arsenic and antimony [5–7]. The glycolate derivatives of various metals and metalloids have been extensively studied [8, 9]. However, homodinuclear glycolate derivatives of bismuth(V) and arsenic(III) have not been reported, though mixed ligand glycolate derivatives of arsenic(III) [10, 11] and bismuth(III) [12] and homodinuclear thioglycolate compound of bismuth(III) [13] have been reported.

We report here some new homodinuclear glycolate complexes of bismuth(V) and arsenic(III).

2. Experimental

All reactions have been carried out under anhydrous conditions. The chemicals used were reagent grade. The solvents were dried by standard methods [19]. $\mathrm{\{[Ph_3Bi]_2O\}Cl_2}$ [15],

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$NaAs(OPr^i)_2$ [9] and [ORO]AsCl [10, 20] have been prepared by literature methods. Arsenic and bismuth have been estimated by iodometric [21] and complexometric [21] methods, respectively. Isopropoxy group was estimated oxidimetrically using 1N $K_2Cr_2O_7$ solution in 25% H_2SO_4 [22]. Molecular weights of these complexes were determined ebullioscopically in benzene solution using Beckman's thermometer.

IR spectra were recorded on a 8400 S Shimadzu Model FT IR spectrophotometer as liquid film or nujol mull on KBr optics from 4000–400 cm^{-1}. NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solution on a JEOL FT AL 300 MHz spectrometer using TMS as an external (^{13}C) and internal (^1H) reference.

Similar methods have been used for the synthesis of derivatives of each series (**1a**–**1d** and **2a**–**2d**). Hence the synthetic detail of only one representative compound of each series is given. Synthetic and analytical data of analogous compounds are summarized in table 1.

2.1. *Synthesis of* $Ph_3Bi{-}O{-}Bi[OC(CH_3)_2CH_2CH(CH_3)O]$ *(1a)*

A weighed amount of sodium (0.09 g, 3.91 mmol) was added to a small amount (~10 mL) of methanol and this mixture was stirred until the sodium reacted with methanol completely. To this clear solution a benzene solution of glycol, $(HOC(CH_3)_2CH_2CH(CH_3)OH)$ (0.23 g, 1.95 mmol) was added and stirred for about two hours at 55–60°C. After cooling the solution, a benzene solution of $\{Ph_3Bi]_2O\}Cl_2$ (1.89 g, 1.95 mmol) was added and again stirred and heated for two hours at 55–60°C. NaCl thus precipitated during the reaction was filtered off. The solvent from the filtrate was removed under vaccum and a yellow viscous liquid obtained. This compound was purified by dissolving in benzene and to this clear solution *n*-hexane was added until the precipitate began to separate. This mixture was stored overnight at 0°C. The solvent was decanted and the compound finally dried under reduced pressure.

2.2. *Synthesis of* $[OC(CH_3)_2CH_2CH(CH_3)O]As(\mu\text{-}OPr^i)_2As(OPr^i)_2$

A benzene solution (~25 mL) of $NaAs(OPr^i)_4$ (0.76 g, 3.35 mmol) was added to a benzene solution (~25 mL) of $[OC(CH_3)_2CH_2CH(CH_3)O]AsCl$ (1.12 g, 3.35 mmol). This mixture was stirred and gently warmed at 55–60°C for abour four hours. The precipitated sodium chloride was filtered off. Removal of excess solvent from the filtrate under reduced pressure yielded a colorless viscous liquid. For purification, this compound was dissolved in benzene and *n*-hexane added until the oily layer began to separate. Then the solution was stored overnight, when an oily layer of compound separated out. After decanting off the solvent, the compound was dried under reduced pressure.

3. Results and discussion

Reactions of $\{[Ph_3Bi]_2O\}Cl_2$ with sodium salt of glycols (prepared by reaction of glycols with sodium methoxide in 1 : 2 molar ratio) yielded new homodinuclear glycolate

Table 1. Synthetic, analytical and physical data of **1a**–**1d** and **2a–2d**.

Complexes	Reagents g (mmol)			NaCl Found (Calcd)	Color & Physical state	Empirical formula & yield g (%)	Analysis found (Calcd)		Molecular weight Found (Calcd)
	Na	Glycols/ NaAs(OPr^i)$_4$	{[Ph$_3$Bi]$_2$O}Cl$_2$/ [ORO]AsCl				As/Bi	–OPr^i	
1a	0.09 (3.91)	0.23 (1.95)	1.89 (1.95)	0.21 (0.23)	Colorless Viscous liquid	$C_{42}H_{42}O_3Bi_2$ 1.72 (87)	41.96 (41.27)	–	1002 (1013)
1b	0.19 (8.26)	0.37 (4.13)	4.00 (4.11)	0.45 (0.48)	Colorless Viscous liquid	$C_{40}H_{38}O_3Bi_2$ 3.48 (85)	43.02 (42.44)	–	969 (985)
1c	0.21 (9.13)	0.41 (4.57)	4.42 (4.55)	0.52 (0.53)	Colorless Viscous liquid	$C_{40}H_{38}O_3Bi_2$ 3.69 (82)	42.09 (42.44)	–	968 (985)
1d	0.16 (6.96)	0.26 (3.47)	3.36 (3.42)	0.39 (0.41)	Colorless Viscous liquid	$C_{39}H_{36}O_3Bi_2$ 3.04 (90)	42.57 (43.06)	–	960 (971)
2a	–	0.76 (3.35)	1.12 (3.35)	0.19 (0.20)	Yellow Sticky semi solid	$C_{18}H_{40}O_6As_2$ 0.91 (93)	29.32 (29.83)	46.11 (47.05)	492 (502)
2b	–	0.69 (3.48)	1.16 (3.47)	0.18 (0.20)	Light yellow Sticky semi solid	$C_{16}H_{36}O_6As_2$ 0.78 (92)	32.01 (31.59)	50.01 (49.83)	459 (474)
2c	–	0.60 (3.02)	1.01 (3.02)	0.19 (0.20)	Yellow Sticky semi solid	$C_{16}H_{36}O_6As_2$ 0.78 (92)	31.22 (31.59)	48.52 (49.83)	462 (474)
2d	–	0.79 (4.28)	1.43 (4.28)	0.23 (0.25)	Yellow Sticky semi solid	$C_{15}H_{34}O_6As_2$ 0.99 (91)	32.19 (32.55)	51.86 (51.35)	447 (460)

derivatives of bismuth(V) (**1a**–**1d**). These colored solid compounds are soluble in common organic solvents.

$$\mathrm{HOROH + 2NaOMe \longrightarrow 2Na^{+}[ORO]^{2-} + 2MeOH}$$

$$\mathrm{\{[Ph_3Bi]_2O\}Cl_2 + 2Na^{+}\,[ORO]^{2-} \longrightarrow Ph_3Bi{-}O{-}BiPh_3[ORO]}$$

where R = $-\mathrm{C(CH_3)_2CH_2CH(CH_3)}-$ (**1a**), $-\mathrm{CH(CH_2CH_3)CH_2}-$ (**1b**), $-\mathrm{CH(CH_3)CH(CH_3)}-$ (**1c**), $-\mathrm{CH\ (CH_3)CH_2}-$ (**1d**).

The homodinuclear alkoxo derivatives of arsenic(III) (**2a**–**2d**) have been synthesized by equimolar reactions of $\mathrm{NaAs(OPr^i)_4}$ with $\mathrm{[ORO]AsCl}$ in warm benzene solution.

$$\mathrm{[ORO]AsCl + NaAs(OPr^i)_4 \longrightarrow [ORO]As(\mu\text{-}OPr^i)_2As(OPr^i)_2 + NaCl}$$

where R = $-\mathrm{C(CH_3)_2CH_2CH(CH_3)}-$ (**2a**), $-\mathrm{CH(CH_2CH_3)CH_2}-$ (**2b**), $-\mathrm{CH(CH_3)CH(CH_3)}-$ (**2c**), $-\mathrm{CH\ (CH_3)CH_2}-$ (**2d**).

These compounds are soluble in common organic solvents like benzene, isopropanol, methanol and chloroform and insoluble in *n*-hexane and petroleum ether. Molecular weight determinations reveal their monomeric nature. Due to moisture sensitivity, these compounds are handled under a moisture-free environment. These compounds are not light sensitive.

These derivatives have been characterized by IR and NMR (^{1}H and ^{13}C) spectral studies.

3.1. *Infrared spectra*

In the spectra of **1a**–**1d**, the disappearance of the band for –OH of glycols and appearance of Bi–O at 435–425 cm^{-1} [14] indicate deprotonation of –OH groups and subsequent formation of Bi–O bonds during complexation. It is further supported by the shift in the position of absorption band for νBi–O–Bi mode observed at 730–720 cm^{-1}. This band was present at 632 cm^{-1} in the spectra of $\mathrm{\{[Ph_3Bi]_2O\}Cl_2}$ [15].

The spectra of **2a**–**2d** also show disappearance of the band for –OH of glycols. An absorption at 440–430 cm^{-1} has been assigned to νAs–OC [16]. The absorption bands observed at 1110–1100 cm^{-1}, 955–945 cm^{-1} and 665–655 cm^{-1} in the spectra of these complexes have been assigned to νC–O (symmetric stretching terminal –OPr$^{\mathrm{i}}$ [17], νC–O (symmetric stretching bridging –OPr$^{\mathrm{i}}$) [17] and νAs–O [18] modes, respectively.

3.2. *^{1}H NMR spectra*

The ^{1}H NMR spectra of **1a**–**1d** and **2a**–**2d** show disappearance of the signal for –OH groups of glycols, indicating deprotonation during complex formation. The signals for various group protons of glycolic moiety are observed in the spectra of these complexes (tables 2 and 3). The phenyl group attached to bismuth is a multiplet in the region δ 7.09–8.44 ppm for **1a**–**1d**.

The bridging isopropoxy group proton signals are observed as multiplet (δ 3.73–4.33 ppm, –OCH) and doublet (δ 0.98–1.23 ppm, $-\mathrm{CH_3}$) in the spectra

Table 2. ^1H and ^{13}C NMR data (in δ ppm) of $Ph_3\overline{Bi{-}O{-}BiPh_3[ORO}]$.

Complexes	^1H NMR (J in Hz)	^{13}C NMR
R = $-C(CH_3)_2CH_2CH(CH_3)-$ (**1a**)	$CH_3C - 1.06_{(s,6H)}$ $CH_2 - 2.00_{(d,2H)}$ (5.49) $CH - 4.15_{(m,1H)}$ $CH_3CH - 1.23_{(d,3H)}$ (7.14) Ph–Bi – 7.15 – 8.41$_{(m,30H)}$	$CH_3C - 27.58$ C-O – 71.59 $CH_2 - 49.38$ CH – 65.65 $CH_3CH - 31.97$ Ph–Bi – 127.08 – 137.47
R = $-CH(CH_2CH_3)CH_2-$ (**1b**)	$CH_3 - 1.09_{(t,\ 3H)}$ (6.00) $CH_2 - 2.51_{(m,2H)}$ $CH - 3.49_{(m,1H)}$ $CH_2O - 4.45_{(d,2H)}$ (3.9) Ph–Bi – 7.28 – 8.42$_{(m,30H)}$	$CH_3 - 28.27$ $CH_2 - 33.96$ CH – 68.36 $CH_2O - 73.64$ Ph–Bi – 125.28 – 149.47
R = $-CH(CH_3)CH(CH_3)-$ (**1c**)	$CH_3 - 2.43_{(d,6H)}$ (3.6) $CH - 3.37_{(m,2H)}$ Ph–Bi – 7.21 – 8.25$_{(m,30H)}$	$CH_3 - 66.07$ CH – 35.80 Ph–Bi – 123.59 – 137.34
R = $-CH(CH_3)CH_2-$ (**1d**)	$CH_3 - 1.17_{(d,3H)}$ (5.69) $CH - 3.25_{(m,1H)}$ $CH_2 - 3.70_{(d,2H)}$ (6.07) Ph–Bi – 7.09 – 8.44$_{(m,30H)}$	$CH_3 - 22.45$ CH – 63.10 $CH_2 - 67.50$ Ph–Bi – 127.50 – 137.44

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

Table 3. ^1H and ^{13}C NMR data (in δ ppm) of $[\overline{ORO]As}(\mu\text{-}OPr^i)_2As(OPr^i)_2$.

Complexes	^1H NMR (J in Hz)	^{13}C NMR
R = $-C(CH_3)_2CH_2CH(CH_3)-$ (**2a**)	$CH_3C - 1.27_{(s,6H)}$ $CH_2 - 1.63_{(d,2H)}$ (11.1) $CH - 4.60_{(m,1H)}$ $\mathbf{CH_3}CH - 1.47_{(d,3H)}$ (13.8) $CH_{OPr}i_{(Bridging)} - 4.29_{(m,2H)}$ $CH_{OPr}i_{(Terminal)} - 4.16_{(m,2H)}$ $CH_{3OPr}i_{(Bridging)} - 1.18_{(d,12H)}$ (6.00) $CH_{3OPr}i_{(Terminal)} - 1.14_{(d,12H)}$ (6.30)	$CH_3C - 29.25$ C–O – 75.12 $CH_2 - 47.96$ CH – 67.15 $CH_3 - 33.80$ $CH_{OPr}i_{(Bridging)} - 65.68$ $CH_{OPr}i_{(Terminal)} - 63.04$ $CH_{3OPr}i_{(Bridging)} - 25.63$ $CH_{3OPr}i_{(Terminal)} - 24.10$
R = $-CH(CH_2CH_3)CH_2-$ (**2b**)	$CH_3 - 1.12_{(t,3H)}$ (5.1) $CH_2 - 1.45_{(m,2H)}$ $CH - 3.82_{(m,1H)}$ $CH_2O - 4.55_{(d,2H)}$ (9.6) $CH_{OPr}i_{(Bridging)} - 4.33_{(m,2H)}$ $CH_{OPr}i_{(Terminal)} - 4.19_{(m,2H)}$ $CH_{3OPr}i_{(Bridging)} - 1.23_{(d,12H)}$ (6.3) $CH_{3OPr}i_{(Terminal)} - 1.18_{(d,12H)}$ (6.0)	$CH_3 - 23.96$ $CH_2 - 37.69$ CH – 61.80 $CH_2O - 76.58$ $CH_{OPr}i_{(Bridging)} - 66.75$ $CH_{OPr}i_{(Terminal)} - 64.11$ $CH_{3OPr}i_{(Bridging)} - 25.59$ $CH_{3OPr}i_{(Terminal)} - 24.09$
R = $-CH(CH_3)CH(CH_3)-$ (**2c**)	$CH_3 - 1.07_{(d,6H)}$ (4.8) $CH - 4.28_{(m,2H)}$ $CH_{OPr}i_{(Bridging)} - 3.73_{(m,2H)}$ $CH_{OPr}i_{(Terminal)} - 3.36_{(m,2H)}$ $CH_{3OPr}i_{(Bridging)} - 0.98_{(d,12H)}$ (6.3) $CH_{3OPr}i_{(Terminal)} - 0.77_{(d,12H)}$(6.0)	$CH_3 - 25.45$ CH – 70.72 $CH_{OPr}i_{(Bridging)} - 65.56$ $CH_{OPr}i_{(Terminal)} - 62.07$ $CH_{3OPr}i_{(Bridging)} - 19.12$ $CH_{3OPr}i_{(Terminal)} - 16.29$
R = $-CH(CH_3)CH_2-$ (**2d**)	$CH_3 - 1.16_{(d,3H)}$ (3.9) $CH - 4.14_{(m,1H)}$ $CH_2 - 4.47_{(d,2H)}$ (4.2) $CH_{OPr}i_{(Bridging)} - 4.30_{(m,2H)}$ $CH_{OPr}i_{(Terminal)} - 3.95_{(m,2H)}$ $CH_{3OPr}i_{(Bridging)} - 1.18_{(d,12H)}$ (6.0) $CH_{3OPr}i_{(Terminal)} - 1.14_{(d,12H)}$ (6.3)	$CH_3 - 25.30$ CH – 65.73 $CH_2 - 75.73$ $CH_{OPr}i_{(Bridging)} - 66.49$ $CH_{OPr}i_{(Terminal)} - 64.26$ $CH_{3OPr}i_{(Bridging)} - 25.65$ $CH_{3OPr}i\ _{(Terminal)} - 18.78$

of **2a–2d**. Moreover, the –OCH and –CH_3 groups of terminal isopropoxy groups were observed in the range δ 3.36–4.19 ppm (multiplet) and δ 0.77–1.18 ppm (doublet), respectively.

3.3. ^{13}C NMR spectra

In the spectra, signals for C–O groups of glycol of the complexes show downfield shifts compared to their position in corresponding free glycols, indicating involvement of these –CO groups in bonding during complexation. In the spectra of the bismuth complexes, a new set of signals in the range δ 123.59–149.47 have been assigned to phenyl groups attached to bismuth. The signals for various carbons of glycol of **1a**–**1d** and **2a**–**2d** have been observed at their expected positions in the spectra, summarized in tables 2 and 3.

Two sets of signals observed at δ 62.07–66.55 ppm, δ 62.07–64.26 ppm and δ 19.12–25.65 ppm, δ 16.29–24.10 ppm, are assigned to –OCH and –CH_3 carbons of bridging and terminal isopropoxy groups of **2a**–**2d**.

4. Conclusion

On the basis of the above spectral evidences, it is clear that both bismuths are bridged by glycolate and oxygen in **1a**–**1d**. In **2a**–**2d**, the arsenics are bridged by isopropoxy groups. Following plausible structures for these complexes may tentatively be proposed (figures 1 and 2).

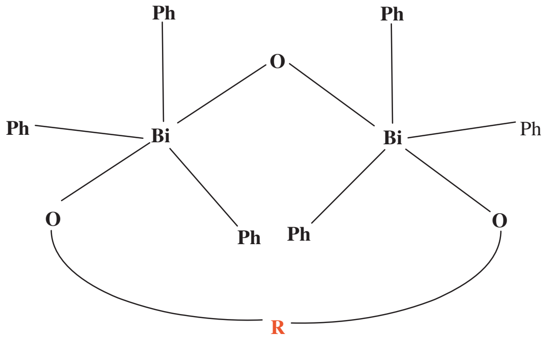

Figure 1. Proposed structure of **1a–1d**.

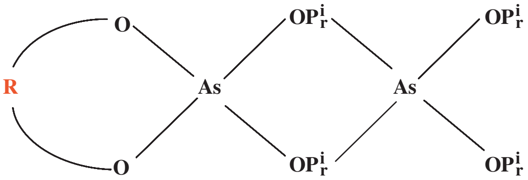

Figure 2. Proposed structure of **2a–2d**.

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