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Bismuth(III) Dimethyldithioarsinate, Bi(S_2AsMe$_2$)$_3$: A New Dimer Formed through Bi . . . S Secondary Bonding

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ABSTRACT

The crystal and molecular structures of bismuth(III) dimethyldithioarsinate, Bi(S_2AsMe$_2$)$_2$, were investigated by X-ray diffraction. The compound is a centrosymmetric dimer in which pentagonal-bipyramidal monomeric units are associated through secondary Bi–S interactions. The structure is compared with that of the analogous dithiophosphinate, Bi(S_2PMe$_2$)$_2$. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

In (organo)metal dithiophosph(in)ato complexes, $R_nM(S_2PR'_2)_m$, ($n = 0, 1, 2, 3$; R′ = alkyl, aryl, alkoxo, aryloxo) the ligands are known to display a broad variety of coordination patterns [1,2], and small changes in the peripheral groups may produce dramatic structural changes in analogous compounds of the same general formula, in which only R′ is different [3,4]. In view of this, it seems of interest to see what effects the replacement of phosphorus for arsenic in the ligand would have and therefore to compare the structures of (organo)metal dithiophosph(in)ates with those of related dithioarsinato complexes $R_nM(S_2AsR'_2)_m$. Such comparisons are limited by the small number of dithioarsinato complexes investigated by X-ray diffraction. Thus, so far, only the crystal structures of $Me_2AsS_2AsMe_2$ [5], $Zn_4S(S_2AsMe_2)_6$ [6], $Me_2Sn(S_2AsMe_2)_2$ [7], $Ph_2Sb(S_2AsPh_2)$ [8], and $Me_3PtS_2AsMe_2$ [9] are available. When direct comparisons are possible, for example, between $Me_2Sn(S_2PMe_2)_2$ [10] and $Me_2Sn(S_2AsMe_2)_2$ [7] or between dimeric $Ph_2Sb(S_2PPh_2)$ and $Ph_2Sb(S_2AsPh_2)$ [8], the molecular structures are very similar. However, the dithioarsinate is a weaker ligand than the dithiophosphinate [11], and significant structural differences between analogous phosphorus- and arsenic-containing ligands cannot be *a priori* ruled out. Thus, Ph_2Sb-S_2PMe_2 is a quasi-cyclic dimer [12], while Ph_2Sb-S_2AsMe_2 is a helical polymer [13], both associated through Sb . . . S secondary bonds. With these considerations in mind, we initiated a program of syntheses and structural investigations of dithioarsinato (organo)metal complexes, aiming at comparing the structures of compounds of general formula $R_nM(S_2ER'_2)_m$ with E = P and As. In fact, we have previously prepared and spectroscopically characterized some main group (organo)metal dithioarsinates [14–16], and we intend to determine the

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solid-state molecular structures of as many as possible such compounds.

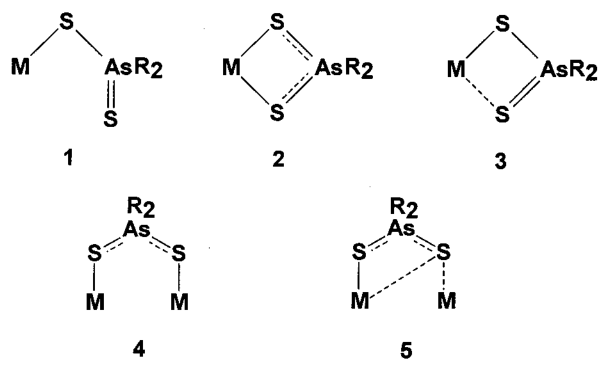
We report here the solid-state molecular structure of $\mathrm{Bi(S_2AsMe_2)_3}$, which can be compared with that of the previously investigated $\mathrm{Bi(S_2PMe_2)_3}$ [17]. Curiously, there are two types of bismuth(III) dithiophosph(in)ates: monomeric, six-coordinate $\mathrm{Bi(S_2PR_2)_3}$ with R = Et [18], OEt [19], and OPr^i [20], and dimeric $\mathrm{[Bi(S_2PR_2)_3]_2}$ with R = Me [17], OMe[21], and Ph[22]. The dimers are associated through secondary Bi . . . S bonds and contain seven-coordinate bismuth(III). The reason for this structural difference [3,4] is not obvious.

The two compounds compared here, $\mathrm{Bi(S_2ER_2)_3}$ (E = P and As), are isostructural, with remarkably similar features. This suggests that coordination patterns analogous to those identified for dithiophosph(in)ates [1,2], that is, monometallic monoconnective [monodentate (**1**)], monometallic biconnective [isobidentate (**2**) or anisobidentate (**3**)], bimetallic biconnective (**4**), or bimetallic triconnective (**5**), can also be expected for dithioarsinates. Dimeric bismuth(III) dithioarsinate $\mathrm{Bi(S_2AsMe_2)_3}$ displays the first authenticated (by X-ray diffraction) example of the bimetallic triconnective coordination pattern (**5**) (Scheme 1).

RESULTS AND DISCUSSION

The molecular structure of the monomeric unit $\mathrm{Bi(S_2AsMe_2)_3}$ is shown in Figure 1, with the atom-numbering scheme. The dimeric crystal structure, which can be described as consisting of two centrosymmetrically related monomeric units joined by secondary Bi . . . S interactions, is shown in Figure 2. Relevant interatomic distances and bond angles are listed in Table 1. The second column in this table gives the corresponding data for the analogous bismuth(III) dimethyldithiophosphinate, as published in Ref. [17]. Please note that the atom-numbering scheme used in Ref. [1] was maintained, and S1 and S2 notations are interchanged in the two structures.

In the monomeric unit, the central bismuth atom is six-coordinate and displays a pentagonal pyramidal geometry, with atoms S1, S2, S4, S5, and S6 in the basal plane (to form the equatorial Bi–S bonds), and S3 in the apical position (to form the axial Bi–S bond). The unit contains three nonequivalent $\mathrm{BiS_2As}$ chelate rings; thus, in the equatorial plane, the chelate ring Bi1SiS2As1 is symmetrical, with basically isobidentate ligands (coordination pattern **2**), as shown by the interatomic distances



SCHEME 1

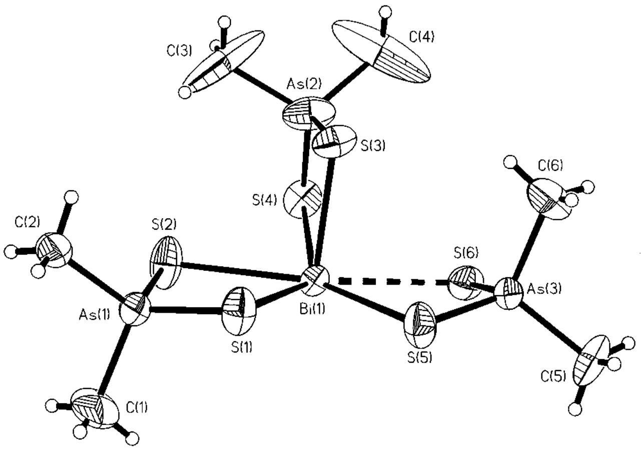


FIGURE 1 The molecular structure of the monomeric unit showing the atom-numbering scheme and the pentagonal pyramidal geometry.

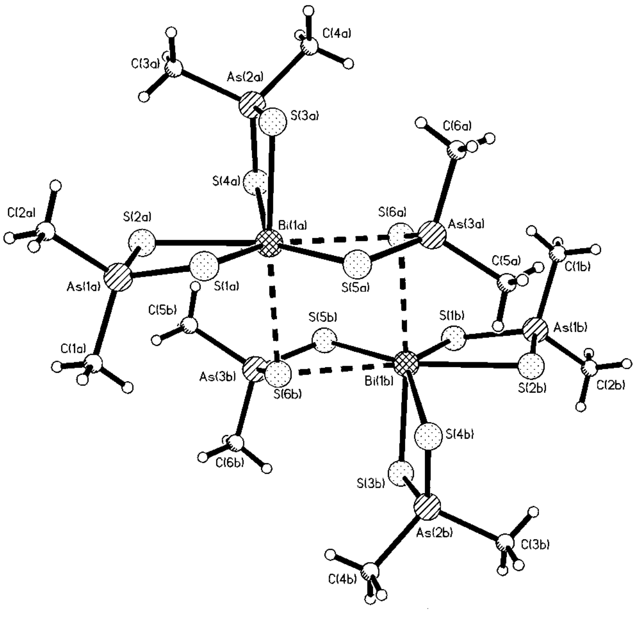


FIGURE 2 The structure of the dimer, showing the association of two monomeric units through secondary interactions.

Bi1–S1 2.735(4) Å, Bi1–S2 2.881(4) Å, and As1–S1 2.150(4) Å, and As1–S2 2.115(4) Å. The second chelate ring, containing the apical sulfur, is less symmetrical, and the ligand is anisobidentate (coordination pattern **3**) with strongly differing bismuth–sulfur and arsenic–sulfur interatomic distances; thus, Bi1–S3 2.658(4) Å (axial bond) and Bi1–S4 3.048(4) Å (equatorial bond), and As2–S3 2.138(4) Å and As2–S4 2.089(4) Å (probably double bond). In the third chelate ring, the ligand is actually bridging because of the intermolecular association (coordination pattern **5**), leading to strongly differing bismuth–sulfur interatomic distances Bi1–S5 2.802(4) Å and Bi1–S6 3.177(4) Å, while the arsenic–sulfur interatomic distances are practically identical, As3–S5 2.126(4) Å and As3–S6 2.120(4) Å.

The pentagonal pyramidal geometry of the monomeric units is clearly defined by the S–Bi–S bond angles, which also show significant distortions, caused by the small angles imposed by the formation of the four-membered chelate rings. Thus, axial-equatorial bond angles S3–Bi1–S1 90.1(1)°, S3–Bi1–S2 94.5(1)°, S3–Bi1–S5 88.6(1)° S3–Bi1–S6 90.1(1)° are practically perpendicular, but the S3–Bi1–S4 angle involved in a chelate ring is only 74.9(4)°. The bond angles in the equatorial plane are close to the theoretical value of 72° required by the axes of a pentagon, as shown by the values listed in Table 1.

TABLE 1 Bond Lengths (Å) and Bond Angles (°) in $Bi(S_2AsMe_2)_3$ (E = As, this work) Compared with Corresponding Values in $Bi(S_2PMe_2)_3$ (E = P, ref. [17])[a]

E	*As*	*P*
Bi1–S1	2.735(4)	2.714(3)
Bi1–S2	2.881(4)	2.891(3)
Bi1–S3	2.658(4)	2.641(3)
Bi1–S4	3.048(4)	3.025(3)
Bi1–S5	2.802(4)	2.782(3)
Bi1–S6	3.177(4)	3.165(3)
E1–S1	2.150(4)	2.030(4)
E1–S2	2.115(4)	1.987(4)
E2–S3	2.138(4)	2.035(4)
E2–S4	2.089(4)	1.969(5)
E3–S5	2.126(4)	2.013(4)
E3–S6	2.120(4)	2.000(4)
S1–Bi1–S2	74.6(1)	71.53(9)
S1–Bi1–S3	90.1(1)	90.32(10)
S1–Bi1–S4	142.0(1)	139.84(9)
S1–Bi1–S5	69.8(1)	71.84(9)
S1–Bi1–S6	140.6(1)	139.6(1)
S2–Bi1–S3	94.5(1)	95.39(11)
S2–Bi1–S4	72.1(1)	74.71(10)
S2–Bi1–S5	144.3(1)	143.03(9)
S2–Bi1–S6	144.6(1)	148.3(1)
S3–Bi1–S4	74.9(1)	71.72(9)
S3–Bi1–S5	88.6(1)	89.65(9)
S3–Bi1–S6	90.1(1)	90.8(1)
S4–Bi1–S5	142.1(1)	140.66(9)
S4–Bi1–S6	75.3(1)	77.8(1)
S5–Bi1–S6	70.8(1)	67.8(1)
S1–E1–S2	106.0(2)	109.4(2)
S3–E2–S4	110.9(2)	112.7(2)
S5–E3–S6	110.0(1)	112.3(2)
Bi1–S1–E1	90.2(1)	90.70(14)
Bi1–S2–E1	87.0(1)	86.59(14)
Bi1–S3–E2	91.2(1)	92.26(14)
Bi1–S4–E2	82.0(1)	82.82(14)
Bi1–S5–E3	92.9(1)	93.33(13)
Bi1–S6–E3	83.1(1)	
C1–E1–C2	105.5(7)	105.0(6)
C3–E2–C4	108.1(16)	105.7(13)
C5–E3–C6	104.1(8)	105.6(7)

[a] Note that S1 in Ref. [17] corresponds to S2 in this work and vice versa.

Dimerization of $Bi(S_2AsMe_2)_3$ molecules occurs through Bi(1a) . . . S(6b) secondary bonds (3.141(4) Å), which makes the bismuth atom seven-coordinate, and the actual coordination geometry becomes pentagonal bipyramidal. Since the coordination pattern of the As(3) ligand is bridging (bimetallic triconnective) of type **5**, one sulfur atom S(5) is connected only to Bi(1a), but the other, S(6a), is connected to both Bi(1a) and Bi(1b) through secondary bonds. The bond angles confirm that the nearly colinear S3a–Bi1a . . . S6b (170.2(4)°) is the axis of a pentagonal bipyramid in the dimeric molecule, with the Bi1a . . . S6b secondary bond basically perpendicular to the pentagonal basal plane (Table 2).

Figure 3 shows a structure diagram of isostructural dimeric bismuth(III) dithioarsinate and dithiophosphinate. The three different coordination patterns displayed by the dithioato ligands are clearly evidenced, and the comparison of bond lengths and bond angles given in Table 1 illustrates the remarkable similarity of the two structures. Moreover, the crystallographic data (very close unit cell dimensions) suggest that the two compounds are isomorphous.

The probable position of the lone electron pair at the Bi(III) atom was discussed in relation with the structure of the dithiophosphinate, $Bi(S_2PMe_2)_3$ [17], and similar considerations are valid here.

TABLE 2 Some Interactomic Distances (Å) and Bond Angles (°) in the Dimeric Pair of $Bi(S_2AsMe_2)_3$

Bi1a . . . S6b	3.141(4)
S1a–Bi1a . . . S6b	99.7(1)
S2a–Bi1a . . . S6b	88.8(1)
S3a–Bi1a . . . S6b	170.2(1)
S4a–Bi1a . . . S6b	97.4(1)
S5a–Bi1a . . . S6b	94.2(1)
S6a . . . Bi1a . . . S6b	81.9(1)
Bi1a . . . S6a . . . Bi1b	98.1(1)

TABLE 3 Crystal Data and Structure Determination

Empirical formula	$C_6H_{18}As_3BiS_6$
Formula weight	716.3 d
Temperature	298 K
Wavelength	MoK_α 0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 10.354\ (2)$ Å $b = 12.385(2)$ Å $c = 15.636(3)$ Å $\beta = 90.58(\ )$
Cell volume	2004.9(7) Å^3
Formula units in the cell Z	4
D calc	2.373 Mg/m^3
Absorption coefficient	14.311 mm^{-1}
F(000)	1328
Crystal size	0.96 × 0.52 × 0.38 mm
2 θ range	2.0 to 60.0°
Index range	$-1 < h < 14$ $-1 < k < 14$ $-21 < l < 21$
Reflections collected	6795
Independent reflections	5521 (R int = 7.67%)
Solution	Direct methods
Refinement method	Full-matrix least-squares
Goodness-of-fit	0.81
Final R indices (obs.data)	R = 0.0510, wR = 0.0621
R indices (all data)	R = 0.0881, wR = 0.0765
Largest difference peak	2.51 eÅ^{-3}
Largest difference hole	−4.54 eÅ^{-3}

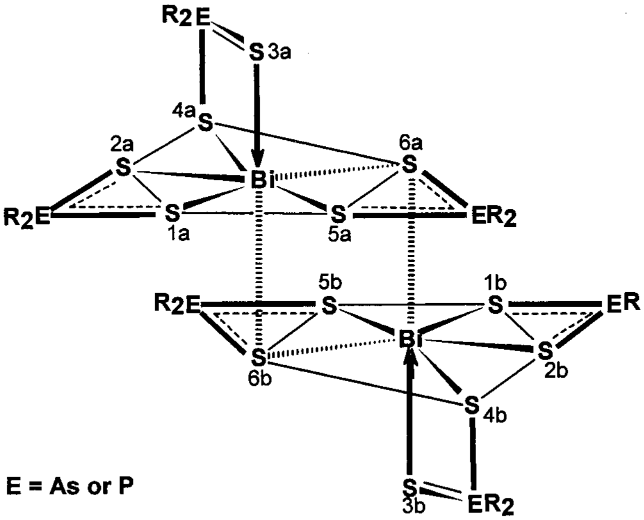


FIGURE 3 Structure diagram of isostructural bismuth(III) dimethyldithiophosphinate and dimethyldithioarsinate.

EXPERIMENTAL

Preparation of $Bi(S_2AsMe_2)_3$

The title compound was prepared by reacting bismuth(III) nitrate, $Bi(NO_3)_3 \cdot 5H_2O$ (0.23 g, 5 mmol) with sodium dimethyldithioarsinate, $NaS_2AsMe_2 \cdot 2H_2O$ (0.34 g, 5 mmol) in acetonitrile (15 mL), at room temperature. After 1 hour of stirring, the sodium nitrate was filtered off and the solution was concentrated. Light-yellow crystals were separated, mp 127°C. Single crystals for X-ray analysis were obtained by dissolving the product in a mixture of $CHCl_3$/hexane (1:1) and slow evaporation of the solvents. The FAB mass spectrum of $Bi(S_2AsMe_2)_3$ thus obtained shows peaks at m/e 717 M^+, 547 $[M-2Me_2AsS_2]^+$, 684 $[M-S]^+$, 579 $[C_4H_{12}As_2S_5]^+$, 515 $[C_4H_{12}As_2S_3Bi]^+$, 483 $[C_4H_{12}As_2S_2Bi]^+$, 346 $[C_2H_6AsS]^{+\cdot}$

Crystallographic Data (Table 2)

$C_6H_{18}BiAs_3S_6$: M = 716.3; monoclinic space group $P2_1/n$; $a = 10.354(2)$ Å, $b = 12.385(2)$ Å, $c = 15.636(3)$ Å, $\beta = 90.580(0)°$; V = 2004.9(7) Å^3, Z = 4; $D_{calc} = 2.373$ Mg/m^3, absorption coefficient 14.311 mm^{-1}. A yellow crystal of the dimensions 0.96 × 0.52 × 0.38 mm was measured at 298 K on a Siemens P4 four-circle diffractometer with graphite monochromatized MoK_α radiation. Within $2.0 < \theta < 60°$ range, 6795 reflections were measured, of which 5521 independent reflections ($R_{int} = 7.67\%$) were used in the full-matrix least-squares calculations (SHELX-76). The structure was solved by the direct method using the SHELX PLUS (PC Version), and the hydrogen atoms were positioned with a Riding model and fixed isotropic U. The final parameters were R = 0.051, wR = 0.0621 (observed data) and 0.0881, and wR = 0.0765 (all data). Further details of the crystal structure investigation and supplementary material were deposited with the Editor at the Cambridge Crystallographic Data Centre.

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