CRYSTAL AND MOLECULAR STRUCTURE OF TRIS(O-ETHYLDITHIOCARBONATO)BISMUTH(III)

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Abstract.

The crystal structure of the title compound, $[\text{Bi}(\text{S}_2\text{COEt})_3]$, shows that each bismuth atom exists in a highly distorted pentagonal bipyramidal geometry with one sulfur atom and the lone pair of electrons occupying the axial positions. Further association between the bismuth and sulfur atoms gives rise to a ladder-like structure.

Introduction.

The *O*-alkyl- or aryl-dithiocarbonates (i.e. xanthates, $^-\text{S}_2\text{COR}$) are known to coordinate metal centres in a variety of coordination modes [1]. The anion may function as mono-, bi- and tri- dentate ligands and of particular interest is the structural diversity of the main group element xanthates. The bismuth trisxanthates, $[\text{Bi}(\text{S}_2\text{COR})_3]$, have been characterized crystallographically for $\text{R} = \text{Me}$ [2], *i*Pr [3], *c*-hexyl [4] and benzyl [4] and different structures have been found, depending on the nature of the R group; these are discussed in detail later. Crystals of $[\text{Bi}(\text{S}_2\text{COEt})_3]$ suitable for X-ray analysis have proved elusive [3], however, this compound has been investigated in a carbon-13 solid state nmr study [5]. The conclusion from this study was that $[\text{Bi}(\text{S}_2\text{COEt})_3]$ exists as two polymorphs, having structures similar to those observed for other $[\text{Bi}(\text{S}_2\text{COR})_3]$ compounds [5]. The $[\text{Bi}(\text{S}_2\text{COEt})_3]$ compound crystallizes as thin yellow plates from a variety of organic solvents, however, prolonged standing results in decomposition. A full X-ray analysis has been precluded thus far owing to weak diffraction patterns and/or problems with twinning. The availability of a rotating Cu anode as a source of X-rays has enabled the measurement of a data set for a single crystal of $[\text{Bi}(\text{S}_2\text{COEt})_3]$ which has enabled full structure determination, the results of this study are reported herein.

Experimental.

The $[\text{Bi}(\text{S}_2\text{COEt})_3]$ compound was prepared as in the literature [6] and crystals suitable for the X-ray analysis were grown by the slow vapour diffusion of hexane into a chloroform solution of the compound. Intensity data for a yellow crystal (0.02 x 0.20 x 0.20 mm) were measured at room temperature on a Rigaku AFC6R four-circle diffractometer fitted with nickel-filtered $\text{CuK}\alpha$ radiation, $\lambda = 1.5412 \text{ \AA}$. A total of 5519 data were measured ($\omega:2\theta$ scan technique and θ_{max} was 60.0°), 5229 were unique and of these 3589 satisfied the $I > 3.0\sigma(I)$ criterion of observability and were used in the subsequent analysis. The data were corrected for Lorentz and polarization effects [7] and for absorption employing the DIFABS program [8] which resulted in a range of transmission coefficients of 0.883 to 1.036.

Crystal data for $[\text{Bi}(\text{S}_2\text{COEt})_3]$: $\text{C}_9\text{H}_{15}\text{BiO}_3\text{S}_6$, $M = 572.6$, triclinic, space group $P\bar{1}$, $a = 11.946(2)$, $b = 14.177(3)$, $c = 10.561(2) \text{ \AA}$, $\alpha = 90.42(2)$, $\beta = 100.53(1)$, $\gamma = 92.12(2)^\circ$, $V = 1757.2(5) \text{ \AA}^3$, $Z = 4$, $D_{\text{calcd}} = 2.164 \text{ g cm}^{-3}$, $F(000) = 1088$, $\mu = 262.89 \text{ cm}^{-1}$.

The structure was solved by direct methods [9] and refined by a full-matrix least-squares procedure based on F [7]. The Bi, S and O atoms were refined with anisotropic thermal parameters, the C atoms were refined isotropically and the H atoms were included in the model at their calculated positions (C-H $0.97 \text{ \AA}$). At convergence $R = 0.083$ and $R_w = 0.098$ (sigma weights [7]).* The analysis is less than optimum which may be due to the high value for the absorption coefficient owing to the use of Cu radiation (see Introduction). The final fractional atomic coordinates are listed in Table 1 and the crystallographic numbering scheme used is shown in Figure 1, which was drawn with ORTEP [10] at 30% probability ellipsoids. Data manipulation was performed with the teXsan package [7] installed on an Iris Indigo workstation.

Results and Discussion.

The triclinic unit cell of $[\text{Bi}(\text{S}_2\text{COEt})_3]$ is comprised of four molecules, two of which define the crystallographic asymmetric unit. The molecular structures of the two independent molecules of $[\text{Bi}(\text{S}_2\text{COEt})_3]$ are shown in Figure 1 and selected interatomic

* where $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma wF_o^2]^{1/2}$

Table 1. Fractional atomic coordinates for $[\text{Bi}(\text{S}_2\text{COEt})_3]$

Atom	x	y	z
Bi(1)	0.3230(1)	0.3552(8)	-0.1167(1)
Bi(2)	0.1832(1)	0.6307(8)	0.1055(1)
S(1a)	0.1194(7)	0.4287(6)	-0.0634(8)
S(1b)	0.2271(8)	0.7189(6)	-0.1117(9)
S(2a)	0.1948(8)	0.4723(7)	-0.3123(9)
S(2b)	0.0487(8)	0.7955(6)	0.0215(11)
S(3a)	0.2998(8)	0.2651(6)	0.1078(8)
S(3b)	0.3921(7)	0.5609(6)	0.0707(9)
S(4a)	0.4731(8)	0.2015(6)	-0.0445(10)
S(4b)	0.3000(8)	0.5112(7)	0.3059(10)
S(5a)	0.3909(8)	0.2952(7)	-0.3626(9)
S(5b)	0.0998(8)	0.6858(6)	0.3417(9)
S(6a)	0.1971(8)	0.2202(6)	-0.2458(8)
S(6b)	0.3020(8)	0.7657(6)	0.2452(9)
O(11a)	0.0162(21)	0.5396(17)	-0.2281(26)
O(11b)	0.1448(23)	0.8805(16)	-0.1577(23)
O(21a)	0.4398(22)	0.1369(16)	0.1816(24)
O(21b)	0.4913(19)	0.4537(15)	0.2437(23)
O(31a)	0.2426(20)	0.1574(15)	-0.4540(22)
O(31b)	0.2389(22)	0.8275(15)	0.4439(22)
C(11a)	0.1025(30)	0.4870(23)	-0.2068(35)
C(11b)	0.1391(28)	0.8070(21)	-0.0832(31)
C(12a)	-0.0091(38)	0.5925(29)	-0.3541(43)
C(12b)	0.1013(33)	0.9723(26)	-0.1231(38)
C(13a)	-0.0748(36)	0.6744(28)	-0.3325(42)
C(13b)	0.1893(37)	1.0137(29)	-0.0178(42)
C(21a)	0.4089(28)	0.1972(22)	0.0801(32)
C(21b)	0.4018(30)	0.5021(22)	0.2131(34)
C(22a)	0.5310(37)	0.0733(29)	0.1736(42)
C(22b)	0.5031(41)	0.3977(31)	0.3658(47)
C(23a)	0.5445(44)	0.0124(35)	0.2985(51)
C(23b)	0.5902(35)	0.3285(27)	0.3627(40)
C(31a)	0.2773(30)	0.2207(23)	-0.3594(35)
C(31b)	0.2121(27)	0.7620(21)	0.3496(31)
C(32a)	0.2948(34)	0.1481(26)	-0.5613(39)
C(32b)	0.1740(31)	0.8313(24)	0.5463(35)
C(33a)	0.2335(43)	0.0797(34)	-0.6552(49)
C(33b)	0.0754(38)	0.8897(30)	0.5145(43)

parameters are collected in Table 2. The structure analysis is of limited precision (see Experimental), however, the determined structure is unambiguous. The immediate coordination geometry about each of the bismuth atoms is defined by six sulfur atoms derived from three asymmetrically chelating xanthate ligands. The degree of asymmetry

Figure 1. Molecular structure and crystallographic numbering scheme for the two molecules comprising the asymmetric unit of $[\text{Bi}(\text{S}_2\text{COEt})_3]$.

in the mode of coordination of the three xanthate ligands (defined as the difference between the two Bi-S bond distances formed by each xanthate ligand, i.e. $\Delta\text{Bi-S}$) is not the same and indeed falls in two classes with one xanthate ligand chelating the bismuth atom

Table 2. Selected bond distances (Å) and angles (°) for [Bi(S₂COEt)₃]

Bi(1)-S(1a)	2.828(9)	Bi(2)-S(1b)	2.74(1)
Bi(1)-S(2a)	2.906(9)	Bi(2)-S(2b)	2.935(9)
Bi(1)-S(3a)	2.756(9)	Bi(2)-S(3b)	2.804(9)
Bi(1)-S(4a)	2.892(9)	Bi(2)-S(4b)	2.91(1)
Bi(1)-S(5a)	2.99(1)	Bi(2)-S(5b)	2.96(1)
Bi(1)-S(6a)	2.605(8)	Bi(2)-S(6b)	2.617(8)
S(1a)-Bi(1)-S(2a)	62.9(3)	S(1b)-Bi(2)-S(2b)	63.4(3)
S(1a)-Bi(1)-S(3a)	77.8(3)	S(1b)-Bi(2)-S(3b)	75.8(3)
S(1a)-Bi(1)-S(4a)	140.5(3)	S(1b)-Bi(2)-S(4b)	138.1(3)
S(1a)-Bi(1)-S(5a)	132.0(2)	S(1b)-Bi(2)-S(5b)	136.6(3)
S(1a)-Bi(1)-S(6a)	87.3(3)	S(1b)-Bi(2)-S(6b)	89.0(3)
S(2a)-Bi(1)-S(3a)	140.1(3)	S(2b)-Bi(2)-S(3b)	136.6(3)
S(2a)-Bi(1)-S(4a)	150.6(3)	S(2b)-Bi(2)-S(4b)	151.6(3)
S(2a)-Bi(1)-S(5a)	75.3(3)	S(2b)-Bi(2)-S(5b)	77.5(3)
S(2a)-Bi(1)-S(6a)	82.7(3)	S(2b)-Bi(2)-S(6b)	78.6(3)
S(3a)-Bi(1)-S(4a)	64.2(3)	S(3b)-Bi(2)-S(4b)	62.8(3)
S(3a)-Bi(1)-S(5a)	134.4(3)	S(3b)-Bi(2)-S(5b)	131.2(3)
S(3a)-Bi(1)-S(6a)	88.9(3)	S(3b)-Bi(2)-S(6b)	86.7(3)
S(4a)-Bi(1)-S(5a)	75.6(3)	S(4b)-Bi(2)-S(5b)	75.0(3)
S(4a)-Bi(1)-S(6a)	81.7(3)	S(4b)-Bi(2)-S(6b)	83.1(3)
S(5a)-Bi(1)-S(6a)	64.1(3)	S(5b)-Bi(2)-S(6b)	64.2(3)
Bi(1)-S(1a)-C(11a)	89(1)	Bi(2)-S(1b)-C(11b)	89(1)
Bi(1)-S(2a)-C(11a)	87(1)	Bi(2)-S(2b)-C(11b)	83(1)
Bi(1)-S(3a)-C(21a)	86(1)	Bi(2)-S(3b)-C(21b)	90(1)
Bi(1)-S(4a)-C(21a)	83(1)	Bi(2)-S(4b)-C(21b)	86(1)
Bi(1)-S(5a)-C(31a)	79(1)	Bi(2)-S(5b)-C(31b)	80(1)
Bi(1)-S(6a)-C(31a)	92(1)	Bi(2)-S(6b)-C(31b)	91(1)
S(1a)-C(11a)-S(2a)	121(2)	S(1b)-C(11b)-S(2b)	123(2)
S(3a)-C(21a)-S(4a)	127(2)	S(3b)-C(21b)-S(4b)	121(2)
S(5a)-C(31a)-S(6a)	125(2)	S(5b)-C(31b)-S(6b)	125(2)
S(1a)-C(11a)-O(11a)	115(3)	S(1b)-C(11b)-O(11b)	113(3)
S(2a)-C(11a)-O(11a)	124(3)	S(2b)-C(11b)-O(11b)	124(3)
S(3a)-C(21a)-O(21a)	110(3)	S(3b)-C(21b)-O(21b)	115(3)
S(4a)-C(21a)-O(21a)	123(3)	S(4b)-C(21b)-O(21b)	124(3)
S(5a)-C(31a)-O(31a)	121(3)	S(5b)-C(31b)-O(31b)	122(3)
S(6a)-C(31a)-O(31a)	114(3)	S(6b)-C(31b)-O(31b)	113(2)

decidedly more asymmetrically than the other two. Thus, $\Delta\text{Bi-S}$ is 0.385 Å for the S(5,6a) xanthate ligand compared to 0.072 and 0.136 Å for the S(1,2a) and S(3,4a) xanthate ligands, respectively; the comparable $\Delta\text{Bi(2)-S}$ values are 0.343, 0.195 and 0.106 Å, respectively. The more asymmetrically coordinating xanthate ligand can be thought to define an approximate mirror plane. The dihedral angles between the S_2CO atoms of the three xanthate ligands are 6.8, 91.8 and 85.4°, respectively for the first molecule and 28.7, 64.0 and 92.7° for the second molecule. The coordination geometry about each of the bismuth atoms is complicated owing to the presence of i) a stereochemically active lone-pair of electrons, ii) the restricted bite angle of the xanthate ligand, and iii) the close approach of symmetry related sulfur atoms.

There is a close intermolecular contact of 3.498(9) Å between the Bi(1) atom and the S(3b) atom of the second molecule comprising the asymmetric unit and a contact of 3.510(8) Å with a centrosymmetrically related S(3b) atom (symmetry operation: $1-x, 1-y, -z$). Similarly, the Bi(2) atom forms two close intermolecular contacts, one of 3.352(8) Å with the S(1a) atom and the other of 3.627(9) Å with a centrosymmetrically related S(1a) atom (symmetry operation: $-x, 1-y, -z$). The structure can thus be thought of in terms of associated dimers (connected via Bi...S contacts of 3.498(9) and 3.352(8) Å), i.e. the asymmetric unit, which are in turn connected with centrosymmetrically related dimers leading to an infinite chain that is propagated along the crystallographic *a* axis and approximately parallel to the *ab* plane. Such an association leads to the formation of a ladder-type arrangement as highlighted in Figure 2. If the intra- and inter- molecular interactions were considered as bonding interactions, each of the S(1a) and S(3b) atoms would be triply bridging and each of the Bi(1) and Bi(2) atoms would be considered eight-coordinate. It is likely, however, that while the Bi...S interactions greater than 3.2 Å exert some stereochemical influence, they do not represent significant bonding interactions.

The weak nature of the intermolecular attractions are seen in the Bi(1)-S(1a) and Bi(2)-S(3b) bond distances of 2.828(9) Å and 2.804(9) Å, respectively. These would be lengthened considerably, with respect to the remaining Bi-S separations, if involved in strong intermolecular interactions. The coordination geometries about each of the bismuth atoms may thus be discussed in terms of nearest neighbours, i.e. with Bi-S separations < 3.0 Å. The five atoms, S(1a), S(2a), S(3a), S(4a) and S(5a) have deviations of 0.112(8), -0.254(9), 0.043(8), -0.186(9) and 0.236(9) Å, respectively from the least-squares plane through them and describe a distorted

Figure 2. The association between molecules of $[\text{Bi}(\text{S}_2\text{COEt})_3]$.

pentagonal plane about the Bi(1) atom which lies 0.473(1) Å out of the plane in the opposite direction to the S(6a) atom. In this description the Bi(1) exists in a distorted pentagonal bipyramidal geometry with the S(6a) atom occupying one of the axial positions and the lone pair of electrons the other. The comparable deviations for the second molecule are -0.026(9), -0.101(9), 0.137(8), -0.26(1) and 0.171(9) Å, respectively with the Bi(2) atom lying 0.516(1) Å out of the plane. The distortions from the ideal geometry are significant for the reasons mentioned above.

There have been several other crystallographic investigations of $[\text{Bi}(\text{S}_2\text{COR})_3]$ derivatives [2-4]. There are basically two different structural motifs for these compounds as illustrated in Figure 3. The first motif, shown in the upper view of Figure 3 consists of centrosymmetric dimers, linked via intermolecular Bi...S separations similar to that found linking the two molecules comprising the asymmetric unit in the structure of $[\text{Bi}(\text{S}_2\text{COEt})_3]$. It is notable that the Bi...S' interactions were found to be 3.405(3), 3.375(1) and 3.210(2) Å for the R = Me [2], benzyl [4] and c-hexyl [4]

Figure 3. The two structural motifs for $[\text{Bi}(\text{S}_2\text{COR})_3]$.

xanthates, respectively and that the average Bi-S bond distance in each structure (excluding the intermolecular interactions) was 2.826(3), 2.832(2) and 2.829(1) Å, respectively. The average Bi-S bond distance in each of the molecules comprising the asymmetric unit in $[\text{Bi}(\text{S}_2\text{COEt})_3]$ is 2.815(4) and 2.814(4) Å, respectively, clearly in the same range as found in the other derivatives. The second motif, shown in the lower view of Figure 3, is polymeric owing to the presence of bridging isopropylxanthate ligands [3]. The polymer backbone is situated on a crystallographic mirror plane and is propagated by bridging xanthate ligands; related to each other across the mirror plane are two further xanthate ligands. The bismuth atom in this structure is seven coordinate and exists in a coordination geometry based on a distorted bicapped trigonal prism [3]. The structure of $[\text{Bi}(\text{S}_2\text{COEt})_3]$ appears to be intermediate between the dimeric and polymeric extremes shown in Figure 3. The crystal structure determination of $[\text{Bi}(\text{S}_2\text{COEt})_3]$ allows a reinvestigation of the carbon-13 solid state nmr spectrum of this compound [5].

A carbon-13 solid state nmr study of a series of arsenic, antimony and bismuth trisxanthates showed that the best resolution in the spectra was found in the methyl region [5]. In the methyl region of the spectrum of $[\text{Bi}(\text{S}_2\text{COEt})_3]$ five resonances were observed, in the ratio 1:1:2:1:1. This data was interpreted as being consistent with the presence of two polymorphs of $[\text{Bi}(\text{S}_2\text{COEt})_3]$, one analogous to the structure shown in the upper view of Figure 3 and the other similar to the polymeric structure shown in the lower view of Figure 3. A reinterpretation of this result is now appropriate given the availability of crystallographic data for $[\text{Bi}(\text{S}_2\text{COEt})_3]$. As suggested above, the two independent molecules approximate mirror symmetry. For the first molecule, containing the Bi(1) atom, there is a close correspondence between the two xanthate ligands related across the pseudo mirror plane. The degree of asymmetry in their mode of coordination is similar and further, the conformation of the two ethoxy residues confirm the presence of an approximate mirror plane. For the second molecule, i.e. with the Bi(2) atom, the disparity in the Bi-S bond distances is different for the two xanthate ligands related across the pseudo mirror plane and significantly there is no mirror relationship between the two ethoxy groups; see Figure 1. In summary, it is suggested that the first molecule of $[\text{Bi}(\text{S}_2\text{COEt})_3]$ is more symmetrical than the second. This observation leads to the conclusion that the two methyl groups related across the pseudo mirror plane in the first molecule are magnetically equivalent giving rise to one resonances of net intensity double that due to the carbon atom of the methyl group of the xanthate ligand defining the approximate mirror plane. In the second molecule the three methyl groups are sufficiently different from each other to resonate at different frequencies. In this interpretation, $[\text{Bi}(\text{S}_2\text{COEt})_3]$ exists as one polymorph, but with two molecules in the crystallographic unit. This conclusion is consistent with the observation that only thin plates have been observed for crystals of $[\text{Bi}(\text{S}_2\text{COEt})_3]$ isolated from a wide variety of solvent combinations and crystallization conditions.

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