Solid State Structures of Bis(diethylbismuthanyl)Sulfane, Selenane and Tellurane

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Dedicated to Prof. Gerd Meyer on the occasion of his 65th birthday

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KEYWORDS. Bismuth, Chalcogen, Metal-Metal Interactions.

ABSTRACT. Tetraethyldibismuthine Bi_2Et_4 reacts with elemental chalcogens with insertion into the Bi-Bi bond and formation of bis(diethylbismuthanyl)chalcogenanes $(\text{Et}_2\text{Bi})_2\text{E}$ (E = S **1**, Se **2**, Te **3**). The structures of **1**, **2**, and **3** were determined by single crystal X-ray diffraction. The complexes exclusively adopt *syn-anti* conformations in the solid state. The molecules show weak intermolecular $\text{Bi}\cdots\text{chalcogen}$ contacts, resulting in the formation of three-dimensional network of corner-shared Bi_4E -tetrahedrons (E = S, Se, Te).

Introduction

Heavier main group element compounds of group 15 and group 16 elements tend to form intermolecular interactions in the solid state. These interactions are rather weak and are often interrupted upon melting, resulting in a bathochromic shift between fluid and solid phases, the so-called "*thermochromic*" behavior.[1] Thermochromic behavior has been reported for instance for several distibines Sb_2R_4 and dibismuthines Bi_2R_4 as well as ditelluranes Te_2R_2 . [2] The formation of intermolecular interactions is typically observed for compounds containing small organic substituents, whereas sterically demanding substituents hamper the formation of intermolecular contacts. Moreover, electron withdrawing substituents such as perfluoroalkyl groups suppress the formation of intermolecular contacts as can be seen when comparing Te_2Me_2 and $\text{Te}_2(\text{CF}_3)_2$. Te_2Me_2 forms a chain-like structure in the solid state,[3] whereas $\text{Te}_2(\text{CF}_3)_2$ is monomeric in the solid state. In distibines and dibismuthines, the weak intermolecular interactions typically result in the formation of chain-like structures with $\text{E}\cdots\text{E}$ bond lengths below the sum of the *van-der-Waals* radii (4.12 Å).[4]

Aside from their tendency to form intermolecular contacts in the solid state, distibines and dibismuthines have been investigated within the last decades due to their interesting chemical properties. Due to the presence of electron lone pairs, they can react as Lewis bases toward main group metals[5] and transition metals.[6] However, the high s-character of the electron lone pair in dibismuthines render these very weak Lewis bases. In addition, distibines and dibismuthines, in which the metal centers adopt the formal oxidation state +II, are promising candidates for redox reactions due to their weak Sb-Sb and Bi-Bi bonds. For instance, insertion reactions with elemental chalcogens subsequently yielded the corresponding bis(dialkylstibanyl)chalcogenanes $\text{R}_2\text{Sb-E-SbR}_2$ (E = S, Se, Te) [7] and bis(dialkylbismuthanyl)chalcogenanes $\text{R}_2\text{Bi-E-BiR}_2$ (E = S,

Se, Te).[8] Some of as-prepared chalcogen-bridged complexes showed thermochromic behavior, pointing to weak intermolecular interactions in the solid state.[9]

In addition, dichalcogenanes E_2R_2 ($E = S, Se, Te$) were reported to react with distibines and dibismuthines M_2R_4 with formation of R_2M-ER' , [7b,8a,10] whereas the reactions with compounds of the general type MR ($M = Sb, Bi$), in which the group 15 metals adopt the formal oxidation state +I, occurred with E-E bond cleavage and subsequent formation of $RM(EAr)_2$, [11] These compounds form monomeric structures in the solid state due to the presence of the sterically demanding, chelating organic substituent.

Moreover, a very few organoantimony(III)[12] and organoantimony(V) chalcogenides [13] containing a terminal $Sb=E$ bond have been structurally characterized, whereas analogous organobismuth compounds are unknown, to date. However, Tokitoh et al. reported on the solid state structure of a telluradibismirane.[14]

We recently reported on the solid state structures of three bis(dialkylstibanyl)chalcogenanes $(R_2Sb)_2E$, ($R = Me, E = Te$; $R = Et, E = S, Te$), which showed different intermolecular interactions. The organic substituents were found to play a crucial role on the resulting packing mode in the solid state.[15] Unfortunately, only six sulfanes $(R_2Bi)_2S$ ($R = (Me_3Si)_2CH$; [16], 2,4,6- $Me_3C_6H_2$ [8b], 2-(Me_2NCH_2) C_6H_4 , [8d] $RN(CH_2C_6H_4)_2$, $R = Ph, Cy, t-Bu$ [17]) as well as one selenane ($[2,4,6-Me_3C_6H_2)_2Bi]_2Se$) [8b] and tellurane ($[{(Me_3Si)_2CH}_2Bi]_2Te$) [16] have been structurally characterized, to date. All of them contain sterically demanding, often donor functionalized, organic substituents, which effectively suppress the formation of intermolecular interactions. We therefore investigated reactions of sterically less demanding Bi_2Et_4 with

elemental chalcogens, and report now on the solid state structures of bis(dialkylbismuthanyl)chalcogenanes (Et₂Bi)₂S **1**, (Et₂Bi)₂Se **2**, and (Et₂Bi)₂Te **3**, respectively.

Results and Discussion.

(Et₂Bi)₂S (**1**), (Et₂Bi)₂Se (**2**), and (Et₂Bi)₂Te (**3**) were prepared in almost quantitative yields by reactions of Bi₂Et₄ with an excess of elemental S, Se and Te, respectively.[8b] **1** - **3** are thermally labile and decompose in solution with formation of BiEt₃, which can always be monitored in the ¹H and ¹³C NMR spectra (see Figures S3 - S8, Supporting Information). The ¹H NMR spectra of **1** and **2** show well separates multiplets even at ambient temperature, whereas that of **3** only contains a broad peak, which separates into two multiplets upon cooling to -30 °C. Further cooling resulted in crystallization of **3**.

Scheme 1. Synthesis of **1** - **3**.

Single-crystals of **1**, **2** and **3** were obtained upon storage of solution in pentane at -30 °C. Figures 1 - 3 show the crystal structures of **1**, **2** and **3**, which were determined by single-crystal X-ray diffraction (see Table S1, Supporting Information).

Figure 1. Solid state structure of **1** (thermal ellipsoids are shown at 50% probability levels; only one component of the disordered part is displayed; pale coloured atom are symmetry generated #1 *y,x,-z+2*; #2 *y,x,-z+1*); H atoms are omitted for clarity.

Figure 2. Solid state structure of **2** (thermal ellipsoids are shown at 50% probability levels; only one component of the disordered part is displayed); H atoms are omitted for clarity.

Figure 3. Solid state structure of **3** (thermal ellipsoids are shown at 50% probability levels, pale coloured atoms are symmetry generated #1 $y,x,-z$); H atoms are omitted for clarity.

1 crystallizes in the tetragonal space group $P4_32_12$ at $-30\text{ }^{\circ}\text{C}$ in rather poor quality and degraded at room temperature. The asymmetric unit consists of three independent molecules of which two are placed on special positions (two-fold axes). Though the refinement of the structure was successful in terms of R-values (R1: 3.37% wR2:6.30%) the final structure model is far from flawless. The shortest C-C bond lengths of $1.37(2)\text{ \AA}$ is far off the typical value of a single bond ($1.54\text{ \AA}$) however we consider the connectivity to be reliable. **2** crystallizes in the monoclinic space group $P2_1/n$ with two independent molecules in the asymmetric unit. **3** crystallizes in the tetragonal space group $P4_32_12$ with half an independent molecules in the asymmetric unit (SI, table S1) which is placed on a two-fold axis.

Table 1 summarizes the central structural parameters of **1**, **2** and **3** as well as selected structural data of previously structurally characterized bis(bismuthanyl)chalcogenanes (R_2Bi) $_2\text{E}$. Data of the corresponding bis(stibanyl)chalcogenanes (Et_2Sb) $_2\text{E}$ are given in the SI (Table S2).

(Table 1 here))

The molecules show a C_2 -symmetry which in some cases is crystallographically exact. Each Bi atom is connected to two carbon atoms and the central chalcogen atom, resulting in a distorted trigonal pyramidal coordination environment. The molecules form *syn-anti* conformers

according to the terms used in ref. 16, which was also observed for (Me₂Sb)₂Te, whereas (Et₂Sb)₂Te crystallizes as *syn-syn* conformer in the solid state.

The sum of the C-Bi-C and E-Bi-C bond angles (table 1) at each Bi atom is far away from tetrahedral (328.41°, 270° for perfectly orthogonal bonds), indicating a high s-character of the free electron pair as was previously observed for Bi₂Et₄ (C-Bi-C 281.8°) [2f] and BiR₃ (R = Me, 276.6(24)°; *i*-Pr 290.6(9)°),[18] respectively. Consequently, using the orientation of the lone-pair to describe the conformation of the molecule as suggested by Breunig et al. is more convenient than realistic. This summarizes the problem very well that though the electron lone-pair of heavier group 15 elements is of non-oriented s-type it shows a preferred direction in interactions. The average Bi-C bond lengths (**2** 2.243(5) Å; **3** 2.273(5) Å) are also comparable to those reported for Bi₂Et₄ (Bi-C 2.291(13) Å)[2f] and BiR₃ (R = Me, 2.259(17) Å; *i*-Pr 2.287(9) Å).[18] Most notably, the Bi-E-Bi bond angle steadily decreases with increasing atomic number of the chalcogen atom (**1** 94.84(2)°; **2** 91.69(2)°; **3** 86.61(2)°) as was expected due to the increasing s-character of the electron lone pairs and the increasing p-character of the E-Bi bonding electron pairs. Analogous trends have been previously reported for analogously substituted compounds (R₂Bi)₂E (R = (Me₃Si)₂CH, E = S 92.48(4)°, Te 88.00(7)°[16]; 2,4,6-Me₃C₆H₂, E = O 117.1(8)°, S 98.7(3)°, Te 91.2(1)°[8b]).

The Bi-E bond distances in **1** - **3** increase with increasing atomic number of the central chalcogen atom (av. values **1** 2.615(3) Å; **2** 2.765(3) Å; **3** 2.978(2) Å). The values are slightly elongated compared to the sum of the covalent radii as reported by Pyykkö *et al.* (Bi-E; E = S 2.54 Å, Se 2.67 Å, Te 2.87 Å).[19] According to a Cambridge structure database search, Bi-S distances (31 hits for Bi-S with bonding single bond and coordination numbers c.n. (Bi) = 3, c.n. (S) = 2) range from 2.450 to 2.727 (mean value 2.584(50) Å). In contrast, only seven compounds containing a

Bi-Se bond (2.569 - 2.717; mean value 2.676(35) Å) [8b,10e,20] and four compounds with a Bi-Te bond of the desired type (2.838 - 2.889; mean value 2.866(16) Å)[8b,14,16,21] have been reported. In table 1, the central structural parameters of compounds of the general type (R₂Bi)₂E are summarized. It is quite obvious, that the Bi-E bond lengths in **2** and **3** are significantly elongated by almost 10 pm, despite the sterically less demanding Et substituents. These findings point to intermolecular interactions between the molecules (table 2).

((Table 2 here))

We therefore analyzed the packing of **1** - **3** in more detail. The packing of the molecules of **1** to **3** shows a distorted diamond-like network with the chalcogen representing the C-atoms and BiEt₂ units bridging them. Figure 4 exemplarily shows the three-dimensional packing of **3** (those of **1** and **2** are given in the Si file, figure S1 and figure S2). The bond angles at the chalcogen atoms are close to the tetrahedral angle with exception of the intra-molecular angle (smaller) and the angle formed by E and the two inter-molecularly bonded atoms (larger) as can be seen in table 2. The intramolecular Bi-E-Bi diminishes while Bi⋯E⋯Bi increases with the atomic number of the chalcogen. This leads to a more distorted tetrahedral environment from S to Te and thus to a more distorted diamond-like network. Despite the distortion even in the Te compound a pseudo-cubic lattice can be found. In **1** [001], [$\frac{1}{2}$ - $\frac{1}{2}$ 0] and [$\frac{1}{2}$ $\frac{1}{2}$ 0], in **2** [121], [-101] and [1-21], and in **3** [001], [1-10] and [110] resemble the <100> directions of the corresponding cubic unit cell (table 3). Since both $P2_1/n$ and $P4_32_12$ are subgroups of $Fd-3m$, the space group of the diamond structure, the structures are related to diamond also symmetry-wise. A tetrahedral environment of S is also observed in the packing of (Me₂Sb)₂S,[22] even though the resulting network is not related to diamond or any other simple structure type involving tetrahedral coordination.

((Table 3 here))

Figure 4. Three-dimensional packing of **3**; C and H atoms are omitted for clarity, red bonds, blue, red and green line represents the basis of the pseudo-cubic lattice.

Conclusions. The solid structures of three analogously substituted bis(dialkylbismuthanyl)-chalcogenanes ($(\text{Et}_2\text{Bi})_2\text{S}$ (**1**), $(\text{Et}_2\text{Bi})_2\text{Se}$ (**2**), and $(\text{Et}_2\text{Bi})_2\text{Te}$ (**3**)) were determined by single crystal X-ray diffraction, allowing for the first time a detailed investigation on the role of the chalcogen atom on the central structural parameters. Even though **1** - **3** without exception form *syn-anti* conformers in the solid state, they show different intermolecular $\text{Bi}\cdots\text{chalcogen}$ contacts, resulting in three-dimensional networks of corner-shared Bi_4E -tetrahedrons ($\text{E} = \text{S}, \text{Se}, \text{Te}$).

Experimental Details. **1** - **3** were synthesized under an Ar atmosphere by reaction of the dibismuthine Bi_2Et_4 with an excess of the corresponding elemental chalcogen (S, Se, Te) in pentane according to a slightly modified literature procedure.[8b] Solvents were carefully dried over Na/K and degassed prior to use. A Bruker DMX 300 was used for NMR spectroscopy. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to THF-d_8 (^1H : $\delta = 3.580$; ^{13}C : $\delta = 25.31$).

(Et₂Bi)₂S (1): Yield: 1.72 g (81%). (300 MHz, THF-d₈): δ 2.02 (q, $^3J_{HH} = 7.88$ Hz, 8 H, CH₂), 2.34 (t, $^3J_{HH} = 7.83$ Hz, 12 H, CH₃). ¹³C NMR (75 MHz, THF-d₈): δ 12.16 (s, CH₃), 31.84 (s, CH₂).

(Et₂Bi)₂Se (2): Yield: 1.81 g (79%). (300 MHz, THF-d₈): δ 2.05 – 2.16 (m, 8 H, CH₂), 2.26 (t, 12 H, CH₃). ¹³C NMR (75 MHz, THF-d₈): δ 13.25 (s, CH₃), 24.95 (s, CH₂).

(Et₂Bi)₂Te (3): Yield: 2.08 g (84%). (300 MHz, THF-d₈): δ 2.28 – 2.32 (m (br), 20 H, CH₃ and CH₂). ¹³C NMR (75 MHz, THF-d₈): δ 15.22 (s, CH₃), 16.06 (s, CH₂).

Single crystal X-ray analyses. Crystallographic data of **1** - **3**, which were collected on a Bruker AXS APEX 2 diffractometer (MoK α radiation, $\lambda = 0.71073$ Å), are summarized in Table S1 (SI). Figures 1 - 3 show diagrams of the solid-state structures of **1** - **3**. Data were collected at 240(1) K (**1**), 100(1) K (**2**) and 100(1) K (**3**), respectively. The structures were solved by Direct Methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on F² (SHELXL-97/SHELXL2013).[23] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Some of the ethyl groups in **1** and **2** were disorder over two positions. **2** was pseudo-merohedrally twinned; **3** was refined as racemic twin.

The crystallographic data of **1** to **3** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-989136 (**1**), CCDC-989135 (**2**) and CCDC-989134 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam-ac.uk).

Supporting Information. Electronic Supplementary Information (ESI) available: Cif files of **1**, **2** and **3**. In addition, crystallographic details of **1**, **2** and **3** (Table S1), figures showing the intermolecular interactions in **1** and **2** (Figures S1 and S2) and interatomic distances for (R₂Sb)₂E derivatives (R=Me, Et, E= S, Se, Te; Table S2) can be found in the SI. Moreover ¹H (25 °C, -70 °C) and ¹³C NMR spectra of **1** - **3** are given (Figures S3 - S11). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

University of Duisburg-Essen and Mercator Research Center Ruhr (MERCUR)

ACKNOWLEDGMENT

S. Schulz thanks the Mercator Research Center Ruhr (MERCUR) and the University of Duisburg-Essen for financial support.

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Table 1. Comparative dimensional parameters (interatomic distances, pm, and angles, °) for (R₂Bi)₂E derivatives (R=mesityl, E=O, S, Se and R=bisyl, E=S, Te)

R	E	Conformation	ϕ Bi-E-Bi-lp		Bi-E-Bi	C-Bi-C	Σ (X-Bi-X)	Bi-E	Bi...Bi ^a	Ref.
			ϕ_1	ϕ_2						
Mesityl	O		86.51	92.99	124.6(3)	98.3(3)	294.5(9)	206.4(7)	366.5	[6]
						98.4(3)	295.6(9)	207.5(8)		
Mesityl	O ^b		84.17	86.46	117.1(8)	97.4(1)	286(3)	209.5(2)	359.5	[5]
						98.3(1)	289(3)	211.7(2)		
Mesityl	S	Near <i>syn-syn</i>	19.47	26.3	98.7(3)	97.4(1)	294(2)	252.0(7)	384.4	[5]
						98.9(9)	295(2)	254.5(6)		
Mesityl	Se	Near <i>syn-syn</i>	22.14	22.14	91.2(1)	100.6(3)	295.8(7)	265.1(1)	379.1	[5]
(Me ₃ Si) ₂ CH	S	Near <i>syn-syn</i>	21.39	59.12	92.48(4)	95.74(14)	300.0(4)	255.7(12)	370.5	
						104.63(15)	301.4(4)	257.2(12)		
(Me ₃ Si) ₂ CH	Te	Near <i>syn-syn</i>	21.33	62.64	88.0(7)	97.69(4)	302.4(10)	287.2(3)	400.2	
						104.96(4)	303.6(10)	288.9(2)		
Et (1)	S		137.57 ^c	137.57 ^c	94.87(15)	94.2(7) ^c	281.3(16) ^c	261.5(3) ^c	385.16(11)	^c

R	E	Conformation ϕ Bi-E-Bi-lp		Bi-E-Bi	C-Bi-C	$\Sigma(\text{X-Bi-X})$	Bi-E	Bi...Bi ^a	Ref.
		ϕ_1	ϕ_2						
Et (1)	S				94.2(7) ^c	281.3(16) ^c	261.5(3) ^c		^c
		137.57 ^c	137.57 ^c	94.87(15)	94.2(7) ^c	281.3(16) ^c	261.5(3) ^c	385.16(11)	^c
					94.2(7) ^c	281.3(16) ^c	261.5(3) ^c		^c
		96.19/ 111.58 ^{d,e}	96.19/ 111.58 ^{d,e}	100.97(15)	94.7(8)/ 131(2) ^{d,e}	284.6(18)/ 323(26) ^{d,e}	261.4(3) ^c	403.31(11)	^c
					94.7(8)/ 131(2) ^{d,e}	284.6(18)/ 323(26) ^{d,e}	261.4(3) ^c		^c
Et (2)	Se								
		98.09/ 131.14 ^d	98.09	98.58(11)	91.8(11)	283(3)/ 284(4) ^d	2.611(3)	396.16(8)	^c
					93.6(8)	288.8(18)	2.615(3)		^c
		87.62	94.09/ 128.16 ^d	98.825(16)	97.1(3)	285.5(6)	277.01(6)	420.84(4)	^c
					94.8(3)/ 97.3(3) ^d	280.4(7)/ 281.9(7) ^d	277.16(5)		^c
Et (3)	Te								
		136.52	141.05	91.689(16)	93.0(2)	279.6(5)	276.08(5)	396.75(4)	^c
					97.0(3)	271.0(6)	276.91(6)		^c
Et (3)	Te	138.33 ^c	138.33 ^c	86.606(13)	96.08(18) ^c	281.9(4) ^c	297.78(4) ^c	408.47(5)	^c

R	E	Conformation	ϕ	Bi-E-Bi-lp	Bi-E-Bi	C-Bi-C	$\Sigma(\text{X-Bi-X})$	Bi-E	Bi...Bi ^a	Ref.
			ϕ_1	ϕ_2						
						96.08(18) ^c	281.9(4) ^c	297.78(4) ^c		^c

^a Intramolecular Bi...Bi distance; ^b Crystallized with 0.5 EtOH; ^c This paper; ^d disorderd C α ; ^e equal because of symmetry equivalence, ϕ calculated from Bi-E-Bi-CT +180° where CT is the centroid of the C α , The vector Bi to CT' (generated from CT by inversion at Bi) corresponds to the assumed direction of the lone pair (lp) if considered stereochemically active (see ref. 13) Data of **1** is of limited reliability because of low crystal quality

Table 2: Geometrical data of intermolecular interactions (in ° and Å)

	E⋯Bi	Bi⋯E⋯Bi	
1 molecule “S1”	3.381(3) ^a	94.87(15)	110.07(13)
		112.72(2) ^a	112.90(2) ^a
1 molecule “S2”	3.423(2) ^a	100.98(15)	121.38(13)
		105.52(2) ^a	110.82(2) ^a
1 molecule “S3”	3.436(4)	98.58(11)	107.04(11)
	3.439(4)	108.41(12)	111.98(11)
		112.03(12)	117.24(9)
2 molecule “Se1”	3.2795(6)	98.83(2)	101.13(1)
	3.3103(5)	107.90(1)	108.31(2)
		108.54(1)	128.13(2)
2 molecule “Se11”	3.2706(5)	91.69(2)	108.63(2)
	3.2770(6)	109.24(1)	110.03(1)
		113.21(2)	120.26(2)
3	3.3894(3) ^a	86.61(2)	103.27(1) ^a
		104.10(1) ^a	142.06(2)

^a value appears twice because of a special position, i.e. symmetry equivalent bonds or angles. Data of **1** is of limited reliability because of low crystal quality.

Table 3. Pseudo cubic unit cells of **1** to **3**.

	<i>a</i>	<i>b</i>	<i>c</i>	<i>α</i>	<i>β</i>	<i>γ</i>
1	14.13	14.13	13.26	90	90	90
2	27.22	27.79	27.79	89.95	89.97	89.97
3	14.08	14.08	14.23	90	90	90

Graphic for Table of Content.

Tetraethyldibismuthine Bi_2Et_4 reacts with elemental chalcogens with insertion into the Bi-Bi bond and formation of bis(diethylbismuthanyl)chalcogenanes $(\text{Et}_2\text{Bi})_2\text{E}$ ($\text{E} = \text{S}$ **1**, Se **2**, Te **3**). The complexes exclusively adopt *syn-anti* conformations in the solid state and show weak intermolecular $\text{Bi}\cdots\text{chalcogen}$ contacts, resulting in the formation of three-dimensional network of corner-shared Bi_4E -tetrahedrons ($\text{E} = \text{S}, \text{Se}, \text{Te}$).

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DOI: 10.1021/om500208c

URN: urn:nbn:de:hbz:464-20201119-165944-8

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