Structural characterization of Sb₂Et₄ and Bi₂Et₄

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ABSTRACT: The solid state structures of Et₄Sb₂ **1** and Et₄Bi₂ **2** were determined by single crystal X-ray diffraction. Single crystals of **1** and **2** were grown in a closed quartz glass capillary under an inert argon atmosphere on the diffractometer using a specific IR-laser-assisted technique. **1** shows short intermolecular Sb···Sb interactions, whereas the closest Bi···Bi distances are longer than the sum of the van-der-Waals radii.

KEYWORDS. Dibismuthine, Distibine, Thermochromism, X-Ray crystal structure.

Introduction. The birth of organometallic chemistry dates back to 1760, when *Louis Cadet de Gassicourt* reported on the synthesis of the first organoarsenic compound. Cadet's "*fuming arsenical liquid*", also known as "*Cacodyl*", was later identified by *Robert Bunsen* as tetramethyldiarsine Me_4As_2 .¹ The heavier homologues, tetramethyldistibine Me_4Sb_2 and –dibismuthine Me_4Bi_2 ,² were synthesized in the thirties of the last century by reaction of methyl radicals with mirrors of elemental Sb and Bi, respectively. Starting in the eighties, efficient syntheses for alkyl and aryl substituted distibines and dibismuthines R_4E_2 were developed and their structures and chemical reactivity were investigated, in detail.³ Moreover, silyl, germyl and stannyl substituted complexes of the general type $(\text{R}_3\text{M})_4\text{Sb}_2$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}; \text{E} = \text{Sb},^4 \text{Bi}^5$) as well as mixed alkyl/aryl,⁶ alkyl/hydride⁷ and aryl/halide⁸ substituted distibines were synthesized and structurally characterized.

Low-valent distibines and dibismuthines R_4E_2 have specific properties, which are mainly determined by the organic substituents bound to the group 15 metal. For instance, the thermal stability of trialkyldibismuthines strongly depends on the steric bulkiness of the substituents. Those with little steric protection such as Bi_2Me_4 and Bi_2Et_4 are typically thermolabile, decomposing rapidly at ambient temperature with formation of trialkylbismuthines as well as elemental Bi, respectively, whereas dibismuthines containing sterically demanding substituents are thermally more robust. In contrast, Sb_2Me_4 and Sb_2Et_4 are thermally more stable and can be distilled at higher temperature without decomposition. Moreover, the formation of $\text{Me}_2\text{Bi}\cdot$ radicals upon fission of the Bi–Bi bond in Me_4Bi_2 , which has been considered as the first step of thermal or photochemical decomposition reactions, clearly reflects the limited stability of the Bi–Bi bond.⁹ In contrast, lighter group 15 homologues are thermally more robust and only sterically hindered diphosphines and diarsines tend to undergo homolytic E–E bond breakage reaction.¹⁰ The strength of the E–E bond has also been subject to quantum chemical calculations.¹¹

An even more interesting feature of distibines and dibismuthines is their different behavior upon melting. *Paneth* already reported that Me_4Bi_2 , which forms violet crystals at low temperature, melted to a red-yellow liquid prior to decomposition. This so-called "*thermochromic*" behavior, that was assigned

to distibines and dibismuthines which show a bathochromic shift upon melting or dissolution between the fluid (red or orange colors) and solid phases (violet, blue or green colors), has been intensely studied. *Ashe et al.* proved that again the specific organic substituents bound to the group 15 metal determine whether the complexes are thermochromic or nonthermochromic.¹² Thermochromic compounds show close intermolecular E $\cdots$ E contacts, leading to extended antimony and bismuth chain-like structures in the solid state, whereas these intermolecular contacts were not observed in nonthermochromic complexes.¹³ Upon melting, the extended bonding through intermolecular interactions is disrupted.

((Scheme 1 here))

The intermolecular E $\cdots$ E distances observed for thermochromic distibines and dibismuthines are elongated compared to the E–E single bond lengths observed in R₄E₂ (E = Sb, 2.827 – 2.883 Å; Bi, 2.983 – 3.209 Å)¹⁴ and the calculated E–E single-bond covalent radii (Sb: 2.80 Å; Bi: 3.02 Å),¹⁵ but are shorter than the sum of the van-der-Waals radii (Sb: 4.12 Å; Bi: 4.14 Å).¹⁶ Structurally characterized thermochromic distibines and dibismuthines are summarized in table 3.¹⁷ The chains are almost linear with the E–E $\cdots$ E bond angles typically ranging from 170 -180°.

((Table 3 here))

With a very few exceptions,¹⁸ analogously substituted distibines and dibismuthines are both either thermochromic or nonthermochromic. Therefore, *Ashe et al.* predicted that distibines and dibismuthines containing sterically less demanding substituents such as Me, Et or Pr are aligned in endless chains with close intermolecular metal $\cdots$ metal contacts in the solid state.⁹ Unfortunately, single crystal structures of these compounds, which are thermally and photochemically rather less stable, were limited to tetramethyldistibine, to date.^{17a,b} In addition, preliminary data on Me₄Bi₂ are mentioned.^{17d} Interestingly, the ratios of the intermolecular E $\cdots$ E distances and the "regular" E–E bond lengths (E $\cdots$ E/E–E) as observed for the tetramethyl complexes Me₄E₂ significantly decreases with increasing atomic number. Rather large ratios of 1.72 and 1.52 were reported for nonthermochromic diphosphine

and diarsine,^{17d} whereas the distibine (1.30,^{17b} 1.28^{17a}) and in particular the dibismuthine (1.15)^{17d} show much smaller ratios.

Due to our general interest in organoantimony and -bismuth chemistry, we investigated reactions of distibines and dibismuthines with group 13 metal trialkyls over the last decade. These studies led to the synthesis of mononuclear [*i*-Pr₄Sb₂][*Al*t-Bu₃]¹⁹ and dinuclear Lewis acid-base adducts [R₄Sb₂][*M*t-Bu₃]₂ (R = Me, Et; *n*-Pr, *i*-Bu; M = Al, Ga).²⁰ Moreover, the first structurally characterized dibismuthine adducts [Et₄Bi₂][*M*t-Bu₃]₂ were reported.²¹ In order to investigate the structural changes of dibismuthines and distibines occurring upon complexation in more detail, we became interested in the solid state structures of the pure distibines and dibismuthines. However, crystallization of these complexes, in particular those containing sterically less demanding substituents such as Me, Et or Pr groups, is rather difficult since they typically have low melting points and are very sensitive towards oxygen. We therefore investigated the crystallization of these complexes directly on the diffractometer.²²

Results and Discussion. Et₄Sb₂²³ and Et₄Bi₂²⁴ were prepared according to literature methods. Single crystals of **1** and **2** were grown on the diffractometer using a IR-laser-assisted technique in a closed quartz glass capillary under an inert argon atmosphere. The IR-laser allowed a very controlled and focused heating of the sample, which is frozen in a nitrogen stream, hence resulting in optimized growth conditions, in which the sample recrystallizes without decomposition. Figures 1 and 2 show the crystal structures of **1** and **2**, which were determined by single crystal X-ray diffraction studies.

((Figures 1 and 2 here))

((Tables 1 and 2 here))

1 crystallizes in the triclinic space group *P*-1 and **2** in the monoclinic space group *P*2₁/*c* with half a molecule in the asymmetric unit. The molecule is completed via inversion. The central structural parameters of **1** and **2** are summarized in table 2. The Sb-Sb bond length in **1** (2.8381(7) Å), which adopts an antiperiplanar conformation, belongs to the shortest Sb-Sb distances observed for distibines. Comparable Sb-Sb bond lengths were reported for Me₄Sb₂ (2.838(1),^{17b} 2.862(2) Å^{17a}), Ph₄Sb₂

(2.837(1),²⁵ 2.844(1) Å^{4a}) and [(Me₃Si)₂CHSb(H)]₂ (2.8304(8) Å^{7a}), respectively. In contrast, distibines containing N,C-chelating substituents such as [*o*-C₆H₄(CH=N-2,6-*i*-Pr₂C₆H₃)]₄Sb₂, which lead to an increase of the coordination number at the Sb centers, show significantly longer Sb-Sb bond lengths (2.9194(6) Å).²⁶ The C-Sb-C (96.0(3), 95.6(3)°) and C-Sb-Sb bond angles (95.18(18), 97.20(17), 95.36(18), 96.61(19)°) in **1** are slightly larger than those reported for Me₄Sb₂, most likely due to increased repulsive interactions between the organic substituents. Lewis acid-base adducts of tetraethyldistibine such as [*t*-Bu₃M]₂[Sb₂Et₄] (M = Al, Ga) show slightly wider C-Sb-C (Al: 96.78(6); Ga: 96.07(7)°) and C-Sb-Sb bond angles (Al: 97.47(4), 98.62(4); Ga: 97.04(5), 97.95(5)°),^{20a} indicating a slightly higher s-orbital contribution to the Sb-Sb and Sb-C bonding electron pairs, hence resulting in a closer to sp³-hybridization of the Sb atoms. Comparable findings have been observed for transition metal complexes of tetramethyldistibine such as [(OC)₅Cr]₂[Sb₂Me₄].²⁷

The Bi-Bi bond length as observed in **2** (2.9827(11) Å) is in the typical range reported for dibismuthines containing threefold-coordinated bismuth centers such as [(HC=CMe)₂]₂Bi₂ (2.9902(5) Å),¹³ (Me₃Si)₄Bi₂ (3.035(3) Å)^{5a} and Ph₄Bi₂ (2.990(2) Å²⁸). In contrast, a significantly longer Bi-Bi bond of 3.123 Å was reported for Me₄Bi₂ in a preliminary communication.^{17d} Unfortunately, the data set was reported to lack from severe disorder problem and to the best of our knowledge, the structural data of this compound was never published in detail. Since the difference of more than 13 pm can't be explained by sterical interactions, the reported bond length seems questionable. Hypervalent dibismuthines such as [R'N(CH₂C₆H₄)₂]₂Bi₂ (R' = Me 3.0707(3) Å, C(Me₂)CH₂CMe₃ 3.0547(2) Å, *t*-Bu 3.0648(2) Å) containing either 5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocine frameworks²⁹ or phenyl substituents with additional pendant arm ligands such as (2-Me₂NCH₂C₆H₄)₄Bi₂ (3.0657(5) Å³⁰) and [2,6-(CH₂NMe₂)₂C₆H₃]₄Bi₂, from which three polymorphic forms have been structurally characterized (3.0992(6), 3.1788(8), 3.2092(8) Å³¹), also show significantly longer Bi-Bi bonds. The C-Bi-C (92.7(4)°) and C-Bi-Bi bond angles (94.5(3), 94.6(3)°) in **2** are smaller than those in **1** as well as in [*t*-Bu₃M]₂[Bi₂Et₄] (M = Al: C-Bi-C 94.5(1), C-Bi-Bi 95.4(1), 97.8(1)°; Ga: C-Bi-C 93.7(6), C-Bi-Bi

94.7(5), 97.5(5)°),²¹ clearly indicating a higher p-character of the bonding electron pairs and a higher s-character of the electron lone pair.

((Figure 3 here))

Thermochromic distibines and dibismuthines typically exhibit short intermolecular interactions between the metal centers, leading to the formation of endless chains in the solid state. Upon melting, these intermolecular contacts are disrupted, leading to the bathochromic shift in the melt. Et₄Sb₂ **1** also shows short intermolecular Sb⋯Sb contacts of 3.688(1) Å between two distibine units (fig. 3), which agrees very well with values of reported for Me₄Sb₂ (3.645,^{17a} 3.678 Å^{17b}) and [(HC=CMe)₂]₂Sb₂ (3.63 Å),^{17c} respectively. As was observed for these distibines, the Sb-Sb⋯Sb angle of 177.94(2)° is also close to 180°. The conformation of **1** supports the formation of these endless chains. All Sb-Sb-C-C torsion angles show absolute values less than 90° [40.5(6), 79.3(6), 40.8(6), 78.9(5)°], i.e. the methyl groups are facing "inwards" thus minimizing steric hindrances for the intermolecular interactions.

((Figure 4 here))

In contrast, Et₄Bi₂ **2** doesn't form isolated Bi chains but exists as rather isolated molecules. The closest intermolecular Bi⋯Bi distances of 4.4598(4) Å, which are observed for every Bi atom to two adjacent dibismuthine molecules (symmetry equivalent via 2₁), is clearly longer than the sum of the van-der-Waals radii (4.14 Å).¹⁶ This finding is somehow unexpected since the analogously-substituted distibines and dibismuthines [(HC=CMe)₂]₂E₂ and (Me₃Si)₄E₂ (E = Sb, Bi) are isostructural, hence showing almost identical structural parameters. However, this is clearly not true for the tetraethyl derivatives **1** and **2**. In addition, Bi₂Et₄ was described as thermochromic compound that changes its color below -30 °C from red to almost black, whereas it is yellow at -196 °C.²⁴ As a consequence, close intermolecular contacts upon formation of Bi⋯Bi chain-like structure were expected for **2** in the solid state.⁹ However, we only observed an intensification of the red color to a deep red color rather than a color change when **2** was cooled to -103° C. Whether this color intensification, despite the long distance, results from very weak intermolecular Bi⋯Bi interactions needs to be clarified in the near future. At this point, the thermochromic behaviour of **2** seems at least questionable. In contrast, **1** changes its color upon cooling

from a yellow liquid at ambient temperature to a slightly more intense yellow oil, from which then red crystals began to grow at -85 °C. Interestingly, when the red crystalline solid is only slightly heated, it first turns to a yellow solid, which then melts to yellow liquid (fig. 5).

((Figure 5 here))

Conclusions. The solid state structures of Sb₂Et₄ **1** and Bi₂Et₄ **2** are described. Single crystals of **1** and **2** were grown by a laser-assisted technique on the diffractometer. According to our studies, only **1** shows thermochromic behaviour resulting from short intermolecular Sb···Sb interactions within the chain-type structure in the solid state. In contrast, the closest intermolecular Bi···Bi contacts observed for **2** are longer than the sum of the van-der-Waals radii. Additional studies are necessary in order to clarify, if these contacts are responsible for a color increase upon cooling **2** to -103 °C due to weak Bi···Bi interactions.

Experimental Details. **1** and **2** were synthesized under an Ar atmosphere according to literature methods. Solvents were carefully dried over Na/K and degassed prior to use.

Single crystal X-ray analyses. Crystallographic data of **1** and **2**, which were collected on a Bruker AXS SMART diffractometer (MoK α radiation, λ = 0.71073 Å), are summarized in Table 1. Figures 1 and 2 show diagrams of the solid-state structures of **1** and **2**. Data were collected at 169(1) K (**1**) and 170(1) K (**2**). The structures were solved by Direct Methods (SHELXS-97)³² and refined anisotropically by full-matrix least-squares on F² (SHELXL-97).³³ Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. Single crystals were formed by an *in-situ* zone melting process inside a quartz capillary using an IR-laser. The experimental setup does only allow for ω scans with χ set to 0° (ω scan of the single crystal). Any other orientation would have partially removed the capillary from the cooling stream and thus led to a melting of the crystals. This limits the completeness to 65% to 90% depending on the crystal system. The crystallization processes formed multiply non-merohedrally twinned crystals of which only the main components were used in the data reductions. The minor components were not suitable for proper twin refinements. The crystallographic

data of **1** and **2** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-831943 (**1**) and CCDC-808072 (**2**). 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).

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Supporting Information Available: A CIF file giving X-ray crystallographic data of **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Figure / Scheme Captions

Figure 1. Solid state structure of **1** (thermal ellipsoids are shown at 50% probability levels); H atoms are omitted for clarity.

Figure 2. Solid state structure of complex **2** (thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity; a: $-x+1, -y+1, -z+1$).

Figure 3. Solid state structure of **1** showing intermolecular Sb $\cdots$ Sb interactions resulting in an endless Sb chain; H atoms are omitted for clarity; Symmetry equivalent atoms generated by translation along a.

Figure 4. Solid state structure of **2** showing the shortest intermolecular Bi $\cdots$ Bi distances. If they can be regarded as interactions can't yet be clarified; H atoms are omitted for clarity.

Figure 5. Color change as observed upon solidification and melting of **1**.

Scheme 1. Intermolecular E $\cdots$ E interactions as observed for thermochromic distibines and dibismuthines such as Me₄Sb₂ and [(HC=CMe)₂]₄Bi₂.

TABLES.

Table 1. Crystallographic details of **1** and **2**.

	1	2
Empirical formula	C ₈ H ₂₀ Sb ₂	C ₈ H ₂₀ Bi ₂
Molecular mass	359.74	534.10
Crystal system	triclinic	monoclinic
Space group	P-1	P2 ₁ /c
a [Å]	6.5253(3)	9.3823(4)
b [Å]	8.7886(5)	7.3766(4)
c [Å]	11.8046(7)	9.7306(4)
α [°]	110.092(3)	90
β [°]	92.270(3)	112.638(3)
γ [°]	99.908(3)	90
V [Å ³]	622.72(6)	621.56(5)
Z	2	2
T [K]	169(1)	170(1)
μ [mm ⁻¹]	4.286	28.221
D _{calcd.} [g cm ⁻³]	1.919	2.854
2θ _{max} [°]	61.0	56.6
Crystal dim. [mm]	0.3 x 0.3 x 0.3	0.3 x 0.3 x 0.3
No. of reflections	9963	7925
No. of unique reflections	2631	1463
R _{int}	0.0259	0.0603
No. param. refined / restraints	91 / 0	46 / 0
R1 ^[a]	0.0445	0.0394
wR2 ^[b]	0.1212	0.0979
Goodness of fit ^[c]	1.084	1.083
Max./min. Transmission	0.75 / 0.42	0.75 / 0.24
Final max/min. Δρ, e Å ⁻³	2.133 (0.78 Å from Sb(1)) / -1.379	2.218(0.77 Å from Bi) / -2.988

^[a] $RI = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$ (for $I > 2\sigma(I)$). - ^[b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$. - ^[c] Goodness of fit = $\{\Sigma[w(|F_o^2| - |F_c^2|)^2] / (N_{\text{observns}} - N_{\text{params}})\}^{1/2}$. $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ with $P = [F_o^2 + 2F_c^2]/3$, a and b are constants chosen by the programme.

Table 2. Central structural parameters of **1** and **2**.

	1	2
E-E	2.8381(7)	2.9827(11)
E···E	3.6882(6)	4.4598(4) ^a
E-C	2.174(6)	2.276(11)
	2.157(7)	2.306(13)
	2.166(7)	
	2.182(7)	
E-E···E	177.94(2)	
C-E-C	96.0(3)	92.7(4)
	95.6(3)	
C-E-E	97.20(17)	94.5(3)
	95.18(18)	94.6(3)
	95.36(18)	
	96.61(19)	

^a shortest intermolecular Bi/Bi distance

Table 3. Metal-metal distances in thermochromic distibines and dibismuthines.

Distibine	Sb–Sb [Å]	Sb⋯Sb [Å]	∠Sb–Sb⋯Sb [°]	Reference
Me ₄ Sb ₂	2.862	3.645	179.2	17a
	2.838	3.678	179.2	17b
[(HC=CMe) ₂] ₂ Sb ₂	2.84	3.63	173.5	17c
(Me ₃ Si) ₄ Sb ₂	2.87	3.99	165.8	4a
	2.863	3.892	168.4	4b
(Me ₃ Ge) ₄ Sb ₂	2.851	3.860	170.5	4d
(Me ₃ Sn) ₄ Sb ₂	2.876	3.891	173.5	4c
	2.866	3.811	173.0	4b
	2.882	3.879	172.6	4b
Dibismuthine	Bi–Bi [Å]	Bi⋯Bi [Å]	∠Bi–Bi⋯Bi [°]	Reference
Me ₄ Bi ₂ ^a	3.123	3.582	178.2	17d
(Me ₃ Si) ₄ Bi ₂	3.035	3.804	169.0	5a
[(HC=CMe) ₂] ₂ Bi ₂	2.990	3.660	166.5	13

^a Only preliminary data are given.

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Scheme 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Graphic for Table of Content.

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