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## The bonding situation in triethylchalcogenostiboranes – polarized single bonds vs. double bonds†

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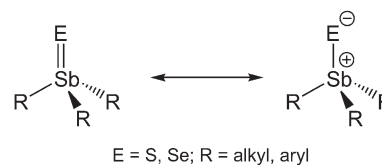
Triethylchalcogenostiboranes  $\text{Et}_3\text{Sb}=\text{E}$  ( $\text{E} = \text{S}$  **1**,  $\text{Se}$  **2**) were synthesized and their solid state structures were determined. The Sb–Se bond length is the shortest ever reported. Short  $\text{Sb}\cdots\text{E}$  contacts were not observed. According to quantum chemical calculations, the bonding situation in **1** and **2** is best described as a polarized Sb–E single bond.

### Introduction

The preparation and characterization of compounds containing double bonds between heavier main group 15 elements (Sb, Bi) and chalcogens (S, Se, or Te) have attracted much attention in the last few decades.<sup>1</sup> The stabilization of such compounds typically requires sterically overcrowded ligands (kinetic stabilization) to prevent self-condensation and/or polymerization (ring formation) of these compounds. Moreover, Dostál *et al.* recently demonstrated the promising effect of N,C,N-pincer-type ligands for the stabilization of monomeric antimony(III) chalcogenides of the general type  $\text{LSbE}$  ( $\text{E} = \text{S}, \text{Se}$ ).<sup>2</sup> These complexes contain terminal Sb–E bonds, which show a high polar bonding character,  $\text{Sb}^{\delta+}-\text{E}^{\delta-}$  ( $\text{E} = \text{Se}, \text{Te}$ ), due to the donation of electron density from the N atoms to the Sb atoms. However, theoretical studies proved that the terminal Sb–E bonds in hypothetical  $\text{PhSb}=\text{E}$  molecules are less polar and exhibit more double bond character due to the lack of extra donor atoms. In addition, Breunig *et al.* suggested the presence of a terminal antimony–selenium double bond in the tungsten complex  $(\text{CO})_5\text{W}(\text{CH}(\text{SiMe}_3)_2)\text{Sb}=\text{Se}$  in benzene solution, but this compound was shown to be dimeric with a central  $\text{Sb}_2\text{Se}_2$  core in the solid state by X-ray studies.<sup>3</sup> In remarkable contrast, solid state structures of organoantimony(V) chalcogenides  $\text{R}_3\text{SbE}$  bearing an unsupported terminal  $\text{Sb}=\text{E}$  double bond are almost unknown, to date, even though chalcogenostiboranes of the general type  $\text{R}_3\text{SbE}$  ( $\text{E} = \text{O}, \text{S}, \text{Se}; \text{R} = \text{alkyl, aryl}$ ) were initially prepared more than

150 years ago. Carl Jakob Löwig and Eduard Schweizer reported in 1850 on the redox reaction of  $\text{Et}_3\text{Sb}$  with elemental sulfur and selenium,<sup>4</sup> in which the Sb atom is oxidized from the formal oxidation state +III to +V. Even though the analogous Me-substituted thioantimony and other trialkylthio- and -selenostiboranes have been synthesized since then,<sup>5</sup> triphenylthioantimony  $\text{Ph}_3\text{SbS}$ , initially reported by Kaufmann by reaction of  $\text{Ph}_3\text{SbCl}_2$  with  $\text{H}_2\text{S}$ ,<sup>6</sup> represents the only structurally characterized triorganylthioantimony  $\text{R}_3\text{Sb}=\text{S}$ .<sup>7</sup> Pebler *et al.* described the short Sb–S bond in  $\text{Ph}_3\text{SbS}$  (2.244(1) Å) as a partial double bond, resulting from a  $d_\pi-p_\pi$  interaction.<sup>7</sup> In contrast, Otera *et al.* investigated the bonding situation in  $\text{Me}_3\text{SbS}$  and calculated a positive charge of +0.6 at the Sb atom, indicating the Sb–S bond to be best described as a polar single bond with some ionic stabilization.<sup>8</sup> In contrast, selenostiboranes  $\text{R}_3\text{Sb}=\text{Se}$ , which were also introduced as ligands in coordination chemistry,<sup>9</sup> have not been characterized by single crystal X-ray diffraction, to date. Therefore, it is still unclear whether the Sb–E bond in  $\text{Sb}(\text{v})$ chalcogenides should be described as a polar single bond or as a real double bond (Scheme 1).

Vibrational spectroscopy was used to clarify the bonding situation. The Sb–E stretching vibration frequencies for a Sb–E single bond (Sb–S 338  $\text{cm}^{-1}$ ; Sb–Se 234  $\text{cm}^{-1}$ ) and Sb=E double bond (Sb=S 485  $\text{cm}^{-1}$ ; Sb=Se 333  $\text{cm}^{-1}$ ) were calcu-



**Scheme 1** Mesomeric structures of triorganothio- and -selenostiboranes  $\text{R}_3\text{SbE}$ .

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lated using Gordy's rules<sup>10</sup> and compared with the experimental values of Et<sub>3</sub>Sb=S (439 cm<sup>-1</sup>, CCl<sub>4</sub> solution; 422 cm<sup>-1</sup>, KBr pellet) and Et<sub>3</sub>Sb=Se (272 cm<sup>-1</sup>, KBr pellet)<sup>11</sup> as well as Me<sub>3</sub>Sb=S (431 cm<sup>-1</sup>, KBr pellet), respectively.<sup>12</sup> However, since the experimental values fall in between the calculated values, a clear distinction between both bonding situations was not possible.

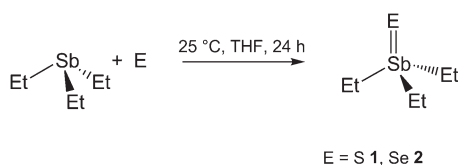
Due to our long-term interest in closed-shell compounds of heavy group 15 and group 16 elements, we recently started to investigate the solid state structures of trialkylbismuthanes R<sub>3</sub>Bi,<sup>13</sup> tetraalkyldistibanes and dibismuthanes R<sub>4</sub>E<sub>2</sub> (E = Sb, Bi)<sup>14</sup> as well as chalcogen-bridged compounds of the general type (R<sub>2</sub>Sb)<sub>2</sub>E<sup>15</sup>. We herein report on the synthesis and solid state structures of Et<sub>3</sub>Sb=S **1**, Et<sub>3</sub>Sb=Se **2** and Et<sub>3</sub>SbBr<sub>2</sub> **3**, respectively.

## Results and discussion

Et<sub>3</sub>SbS (**1**) and Et<sub>3</sub>SbSe (**2**) were synthesized by reaction of Et<sub>3</sub>Sb with elemental sulfur and selenium, respectively, according to a slightly modified literature method (Scheme 2).<sup>5c</sup> In contrast, any attempts to synthesize the corresponding triethyltellurostiborane Et<sub>3</sub>SbTe by reaction of Et<sub>3</sub>Sb with elemental Te or *n*-Bu<sub>3</sub>P=Te as well as by reaction of Et<sub>3</sub>SbBr<sub>2</sub> **3** with TeLi<sub>2</sub> failed.

Single crystals of **1** and **2** were grown upon storage of freshly prepared solutions in THF at -30 °C. Fig. 1 and 2 show the solid state structures of **1** and **2**, which crystallize as colorless needles in the trigonal space group *P*<sub>3</sub>*1**c* (**1**) and in the hexagonal space group *P*<sub>6</sub>*3**mc* (**2**). The C1 atom in **2** is disordered over two positions related *via* mirror-symmetry. The central structural parameters of **1** and **2** are summarized in Table 1. In addition, colorless crystals of Et<sub>3</sub>SbBr<sub>2</sub> **3** were obtained upon storage of a solution in ether at -30 °C (ESI†).

The Sb atoms in **1** and **2** adopt slightly distorted tetrahedral coordination spheres and the C–Sb–C bond angles (107.8(5)° **1**;



Scheme 2 Synthesis of **1** and **2**.

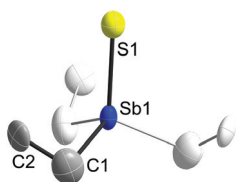


Fig. 1 Solid state structure of **1** (thermal ellipsoids are shown at 50% probability levels); H atoms are omitted for clarity. Symmetry generated part in pale colours (3-fold axis).

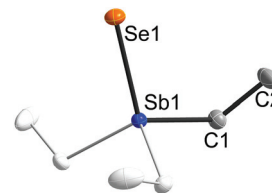


Fig. 2 Solid state structure of **2** (thermal ellipsoids are shown at 50% probability levels); H atoms second orientation of C1 are omitted for clarity. Symmetry generated part in pale colours (3-fold axis).

106.58(14)° **2**) are smaller compared to the C–Sb–E bond angles (111.1(5)° **1**; 112.23(13)° **2**). The Sb–C bond lengths in **1** (2.130(13) Å), **2** (2.142(4) Å) and **3** (av. 2.131(1) Å) are very similar and comparable to those observed for trialkylstibines SbR<sub>3</sub><sup>16</sup> and trialkyldihalostiboranes R<sub>3</sub>SbX<sub>2</sub><sup>17</sup> such as *i*-Bu<sub>3</sub>SbBr<sub>2</sub> (av. 2.130 Å),<sup>18</sup> [(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>3</sub>SbBr<sub>2</sub> (av. 2.149 Å),<sup>19</sup> and (PhCH<sub>2</sub>)<sub>3</sub>SbBr<sub>2</sub> (av. 2.185 Å).<sup>20</sup> Only Me<sub>3</sub>SbBr<sub>2</sub> showed significantly shorter Sb–C bond distances (av. 2.043 Å,<sup>21</sup> 2.047 Å<sup>22</sup>). In addition, simple Lewis-acid–base adducts of trialkylstibines with group 13 metal complexes, in which the Sb atom is also fourfold-coordinated,<sup>23</sup> also showed comparable Sb–C bond lengths except for Me<sub>3</sub>Sb–GaCl<sub>3</sub>, containing the strong Lewis acid GaCl<sub>3</sub> (av. 2.106(3) Å).<sup>24</sup>

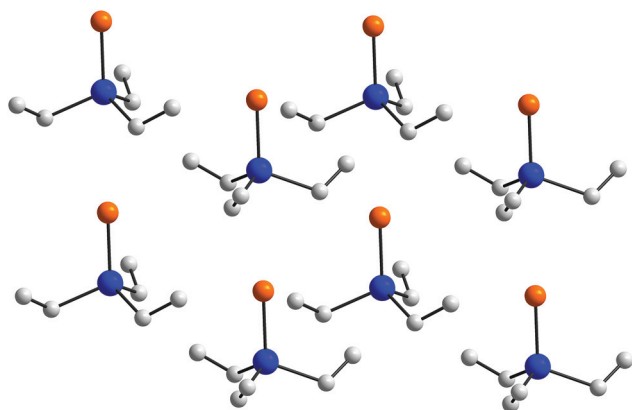
The most interesting bonding parameters are the Sb–chalcogen bond lengths. The Sb–S bond length of **1** (2.381(7) Å) is in between the calculated values for the Sb–S single bond (Sb–S 2.43 Å)<sup>25</sup> and the Sb=S double bond (2.27 Å).<sup>26</sup> In addition, the Sb–S bond lengths as observed in Ph<sub>3</sub>Sb=S (2.244(1) Å),<sup>7a,b</sup> the only triorganostiborane yet investigated by X-ray diffraction, (Me<sub>3</sub>Sb)<sub>2</sub>Me<sub>2</sub>SnCl<sub>2</sub> (2.305(1) Å),<sup>27</sup> and in the monomeric Sb(III)sulfide LSbS (2.2929(17) Å)<sup>2a</sup> are significantly shorter, whereas those observed in the corresponding dimeric, sulfur-bridged compounds [LSbS]<sub>2</sub> are elongated by almost 10 pm (2.4875(10), 2.4790(11) Å).<sup>28</sup> In contrast, the Sb–S bond lengths observed in Sb(III) sulfides such as S(SbEt<sub>2</sub>)<sub>2</sub> (2.429(5), 2.462(7) Å)<sup>15a</sup> and Sb(2,4,6-*i*-Pr<sub>3</sub>-SC<sub>6</sub>H<sub>2</sub>) (Sb–S 2.418(2), 2.420(2), 2.438(2) Å) are significantly elongated.<sup>29</sup>

**2** is the first structurally characterized trialkylselenostiborane and shows the shortest Sb–Se bond reported to date. The Sb–Se bond length (2.4062(8) Å) is significantly shorter than the corresponding calculated value for the respective Sb–Se single bond (Sb–Se 2.56 Å)<sup>25</sup> and is in perfect agreement with the calculated Sb=Se double bond value (Sb–Se 2.40 Å).<sup>26</sup> In addition, the Sb–Se bond lengths as observed in the N,C,N pincer-type complexes LSb=Se (2.4329(5), 2.4396(7) Å),<sup>2</sup> in Sb(III)–Se compounds such as [(CHSiMe<sub>3</sub>)<sub>2</sub>SbSe]<sub>2</sub>[W(CO)<sub>5</sub>] (2.5574(6), 2.5586(6) Å)<sup>3</sup> and (MeSe)<sub>3</sub>Sb (2.568(1)–2.588(1) Å)<sup>30</sup> as well as those reported for polyanions [Sb<sub>4</sub>Se<sub>9</sub>]<sup>4-</sup> (2.4232(9)–2.5154(9) Å)<sup>31</sup> are also elongated. Neither **1** nor **2** show short intermolecular Sb...E contacts, which is in remarkable contrast to those observed in chalcogen-bridged complexes of the general type (R<sub>2</sub>Sb)<sub>2</sub>E (E = S, Se, Te).<sup>15a</sup> Even though the Et<sub>3</sub>Sb=S as well as Et<sub>3</sub>Sb=Se molecules are perfectly linearly packed in the crystal as can be seen from Fig. 3, the intermolecular Sb...S (3.955(6) Å) and Sb...Se bond distances (4.1227(10) Å)



**Table 1** Bond lengths (Å) and angles (°) of **1**, **2**, **3**

	<b>1</b>	<b>2</b>	<b>3</b>
Sb–E [Å]	2.381(7)	2.4062(8)	2.6469(3), 2.6513(3)
Sb–C [Å]	2.130(13)	2.142(4)	2.127(3), 2.131(3), 2.134(3)
$\angle$ C–Sb–C [°]	107.8(5)	106.58(14)	115.10(10), 120.78(11), 124.10(10)
$\angle$ C–Sb–E [°]	111.1(5)	112.23(13)	88.25(8), 89.58(8), 89.77(8), 90.72(8), 90.77(8), 90.95(8)
$\angle$ Br–Sb–Br	—	—	177.655(12)
Sb...E [Å]	3.956(9)	4.1227(11)	—
$\angle$ E–Sb...E [°]	180	180	—

**Fig. 3** Packing of the Et<sub>3</sub>Sb=Se molecules (view along *y*; H atoms are omitted for clarity).

clearly exceed the sum of the van der Waals radii (Sb–S 3.86; Sb–Se 3.96 Å).<sup>32</sup>

### Quantum chemical calculations

The structures of trialkylchalcogenostiboranes can be generally described in terms of a ylid–ylen mesomerism (see Scheme 1) as is typically used for methylene phosphoranes, the so-called Wittig reagents.<sup>33</sup> In order to clarify the bonding situation in **1** and **2**, quantum chemical calculations were performed with density functional theory employing the B-P86 exchange correlation functional<sup>34</sup> and a third generation dispersion correction.<sup>35</sup> Geometry optimizations of the monomeric species **1a** and **2a** were carried out in the def2-QZVP basis set<sup>36</sup> of the TURBOMOLE program package<sup>37</sup> making use of the resolution of the identity approximation<sup>38</sup> and a relativistic effective core potential for Sb.<sup>39</sup> The calculated Sb–C bond lengths for the resulting *C*<sub>3</sub> symmetrical gas phase structures **1a** and **2a** were obtained as 2.175 Å and 2.176 Å, respectively, slightly longer (0.04 Å) than the crystal structure values. The C–Sb–C bond angles for **1a** (104.9°) and **2a** (104.2°) were also found to be virtually identical. They are roughly 2–3° smaller than the corresponding crystal structure parameters, indicating weak intermolecular interactions with the neighboring molecule in the solid state structure (*vide infra*). While the calculated Sb–S bond length of 2.257 Å is notably smaller (by 0.12 Å) than the corresponding crystal structure parameter, the calculated Sb–Se bond length of 2.393 Å is in agreement within 0.02 Å with the experimental value.

In order to get an idea of the packing effects within the linear chains we performed geometry optimizations of linear aggregates **1b** and **2b** of three monomers of **1** and **2**, respectively, within *C*<sub>3</sub> symmetry constraints. We verified that symmetry-unrestricted geometry optimizations destroy the linear chain arrangement, thus proving that it is not a minimum of the potential energy surface of the trimeric aggregate. The bond lengths of the central monomer (**1b**: C–Sb 2.169 Å, Sb–S 2.270 Å; **2b**: C–Sb 2.170 Å, Sb–Se 2.406 Å) change only slightly with respect to the gas phase monomers. Yet, the C–Sb–C bond angles (**1b**: 106.5°; **2b**: 105.8°) enlarge by more than 1°, improving agreement with the crystal structure data. The Sb...S intermolecular distance involving the Sb atom of the central monomer was calculated as 4.051 Å, the other one involving the S atom of the central monomer was obtained as 4.093 Å. They deviate by less than 0.14 Å from the crystal structure value of **1**. The corresponding Sb...Se intermolecular distances were determined as 4.219 and 4.255 Å, respectively, also deviating by less than 0.14 Å from the crystal structure value of **2**.

Dissociation of the linear trimeric aggregate **1b** into its monomers **1a** requires 57.7 kJ mol<sup>−1</sup>, a bit more than twice the calculated dissociation energy of a *C*<sub>3</sub> symmetry-constrained linear dimeric aggregate of **1** (26.3 kJ mol<sup>−1</sup>). It should be noted that the dissociation energy of the water dimer is about 20% lower (all dissociation energies without zero point vibration energy correction).<sup>40</sup> Dissociation of linear dimeric and trimeric aggregates of **2** requires 25.4 and 55.2 kJ mol<sup>−1</sup>, respectively. According to a natural population analysis (NPA)<sup>41</sup> of the monomeric structure **1a**, the sulfur atom bears a considerable charge of −0.73 *e*, and the Sb atom bears a charge of +1.53 *e*. The magnitudes of these partial charges increase even for the central monomer of the trimeric aggregate **1b** (S: −0.83 *e*, Sb: 1.57 *e*; similar yet smaller changes for the remaining monomers – see ESI†). This suggests a noticeable electrostatic contribution to the aforementioned dissociation energies. Yet, taking the empirical dispersion correction contained in the B-P86+D3 results as an indicator for the importance of dispersion interactions between the monomers, they also turn out to be highly important: the dispersion contribution to the dissociation energy of the linear dimer of **1** amounts to 18.4 kJ mol<sup>−1</sup> and for the trimer it amounts to 37.3 kJ mol<sup>−1</sup>, *i.e.* about 2/3 of the total interaction energy. The magnitudes of the dispersion contribution to the dissociation energies of the linear dimeric (19.1 kJ mol<sup>−1</sup>) and



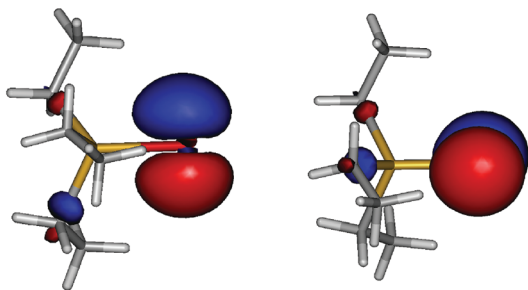


Fig. 4 HOMO (left) and HOMO-1 (right) of  $\text{Et}_3\text{Sb-Se}$  (isovalue  $\pm 0.05$  a.u.).

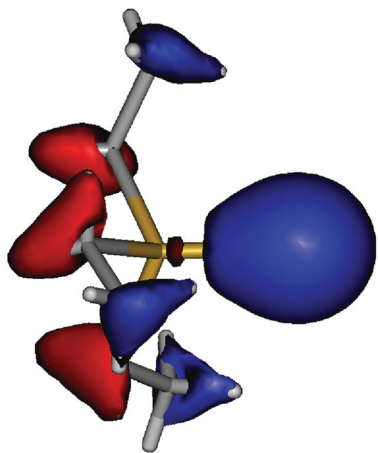


Fig. 5 HOMO-20 of  $\text{Et}_3\text{Sb-Se}$  (isovalue  $\pm 0.05$  a.u.).

trimeric ( $38.6 \text{ kJ mol}^{-1}$ ) aggregates of **2** are even slightly larger. On the other hand the partial charges on Se (**2a**:  $-0.64 e$ , central monomer of **2b**:  $-0.74 e$ ) and Sb (**2a**:  $+1.43 e$ , **2b**:  $+1.48 e$ ) are slightly smaller than in **1a/1b**, thus explaining the slight decrease in the total dissociation energies. According to these findings, one can conclude that the bond polarity decreases with an increasing chalcogen atomic number as was reported earlier.<sup>2a,42</sup> Moreover, dispersion interactions play a major role in the stabilization of the crystal structure.

Coming back to the question of the bonding situation in the monomers, natural bond orbital (NBO)<sup>41</sup> analysis suggests the presence of three lone pair orbitals on the sulfur atom in **1**, and similarly three lone pair orbitals on the selenium atom in **2**. One of the lone pair orbitals consists of the valence shell s orbital (**1**: 89%; **2**: 92%), the remaining two are pure valence shell p orbitals orthogonal to the Sb-E bond, thus precluding the existence of a Sb-E double bond in both cases. The remaining p orbital is involved in a single covalent bond between Sb and E. A glance at the canonical molecular orbitals confirms this picture: the degenerate HOMO/HOMO-1 (Fig. 4, ESI Fig. S1†) pair is strongly localized on the E atom, while HOMO-20 (Fig. 5, ESI Fig. S2†) mainly consists of a deformed s orbital on E.

Finally, a plot of the electron localization function (ELF)<sup>43</sup> also does not indicate a double bond character between Sb

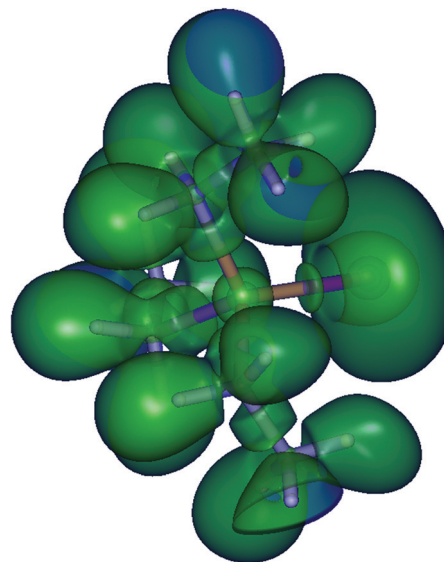


Fig. 6 ELF isosurfaces of  $\text{Et}_3\text{Sb-Se}$  (isovalue 0.670). The Se core electron domain is surrounded by a lone pair domain, the bond electron domain is located on the axis to the antimony core electron domain.

and E (Fig. 6 and ESI Fig. S3†). This and the large negative NPA partial charge on S in **1** and also on Se in **2** led us to conclude that the ylide form with one covalent and one ionic bond (*cf.* Scheme 1) is the dominant mesomeric structure in both cases. The relatively short Sb-Se bond thus must therefore be attributed to the strong ionic contribution to the overall bond.

## Conclusions

Two trialkylchalcogenostiboranes of the type  $\text{Et}_3\text{SbE}$  (E = S **1**, Se **2**) were structurally characterized. Even though the Sb-Se bond in **2** represents the shortest one ever reported, the shortening of the Sb-E bonds in **1** and **2** results from a strong electrostatic interaction between the central Sb atom and the chalcogen bonding partner as both bonds are strongly polarized,  $\text{Sb}(\delta^+)\text{-E}(\delta^-)$ . Computational calculations gave no hint on the presence of a Sb-E double bond due to  $\pi$ -interactions. Dispersion interactions play a major role in the stabilization of the crystal structure.

## Experimental

All manipulations were performed in a glovebox under an Ar atmosphere or using standard Schlenk techniques. Solvents were carefully dried over Na/K and degassed prior to use.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were referenced to internal deuterobenzene ( $\text{C}_6\text{D}_5\text{H}$ ,  $^1\text{H}$ :  $\delta = 7.154$ ;  $^{13}\text{C}$ :  $\delta = 128.0$ ).



## General synthesis of 1 and 2

Et<sub>3</sub>SbS **1** and Et<sub>3</sub>SbSe **2** were prepared according to a slightly modified literature method.<sup>5c</sup> 10 g (47.86 mmol) SbEt<sub>3</sub> was added dropwise at ambient temperature to a stirred suspension of 50 mmol E (E = S, 1.60 g; Se, 3.95 g) in 150 mL of THF and stirred for 24 h. Filtration through a P4 glass frit and removal of the solvent at reduced pressure gave **1** and **2** as colorless crystalline solids. Single crystals of **1** and **2** were obtained upon storage of a concentrated solution of **1** and **2** in THF at –30 °C for 48 h.

Et<sub>3</sub>SbS **1**. Yield: 11.30 g (98%). <sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ/ppm = 1.01 (t (br), 9H, CH<sub>3</sub>), 1.23 (q, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 6H, CH<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ/ppm = 8.6 (CH<sub>2</sub>), 13.4 (CH<sub>3</sub>).

Et<sub>3</sub>SbSe **2**. Yield: 13.50 g (98%). <sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ/ppm = 0.98 (t (br), 9H, CH<sub>3</sub>), 1.28 (q, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 6H, CH<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ/ppm = 9.9 (CH<sub>2</sub>), 12.7 (CH<sub>3</sub>).

**Synthesis of 3.** **3** was synthesized according to a slightly modified literature procedure.<sup>44</sup> 3.06 g (19.14 mmol) Br<sub>2</sub> was added dropwise to a cool solution (0 °C) of 4.00 g (19.14 mmol) SbEt<sub>3</sub> in 20 mL diethyl ether and stirred for 14 h at ambient temperature. After removal of the solvent at reduced pressure, **3** was obtained as an analytically pure orange liquid.

Et<sub>3</sub>SbBr<sub>2</sub> **3**. Yield: 6.71 g (95%). <sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ/ppm = 1.21 (t, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 9H, CH<sub>3</sub>), 2.44 (q, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 6H, CH<sub>2</sub>).

## Single crystal X-ray diffraction

Crystallographic data of **1–3**,<sup>†</sup> which were collected on a Bruker AXS SMART diffractometer (MoK<sub>α</sub> radiation, λ = 0.71073 Å) at 150(1) K (**1**), 100(1) K (**2**) and 100(1) K (**3**), are summarized in Table S1 (ESI<sup>†</sup>). The solid-state structures of **1–3** are shown in Fig. 1–3. The structures were solved by direct methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on F<sup>2</sup> (SHELXL-97).<sup>45,46</sup> **3** was refined as non-merohedral twin based on HKL4 data. Absorption corrections were performed semi-empirically from equivalent reflections on the basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups.

## Acknowledgements

St. S. and G. J. like to thank the University of Duisburg-Essen for financial support. St.S. is also grateful to the Mercator Research Center Ruhr (MERCUR) for financial support.

<sup>†</sup>The crystallographic data of **1**, **2**, and **3** (excluding structure factors) are deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1001646 (**1**), CCDC-1001644 (**2**) and CCDC-1001645 (**3**).

## Notes and references

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