Syntheses and Crystal Structures of Novel Antimony-Containing Cyclic Polysulfides[1]

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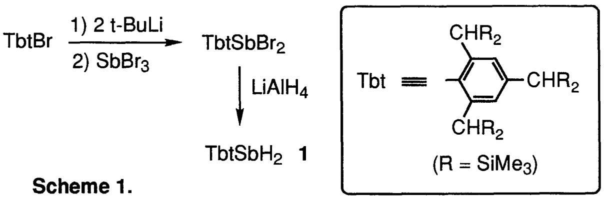
The reaction of a dihydrostibine bearing a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group, $TbtSbH_2$, with elemental sulfur resulted in the formation of two kinds of novel Sb-containing cyclic polysulfides, $TbtSbS_5$ and $TbtSbS_7$, together with another type of two cyclic polysulfides having two TbtSb units, 1,3,4,5,2,6-tetrathiadistibane and 1,3,5,2,4-trithiadistibolane derivatives.

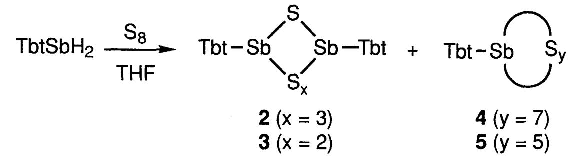
In contrast to the widely explored chemistry of the transition metal polychalcogenido complexes,[2] very little has been known for cyclic polychalcogenides containing a heavier main group element. Although there have been several examples of cyclic polysulfides containing a phosphorus or an arsenic atom, *e. g.*, $RP(=S)S_n$ (R = Me or *t*-Bu; n = 5, 6, and 7)[3] and $MeAsS_n$ (n = 5, 6, and 7),[4] as for cyclic antimony polysulfides only one example of a salt of antimony polysulfide anion, $[Mg(N\text{-}MeIm)_6][Sb_2S_{15}]$, has been isolated and characterized by Rauchfuss et al.[5] and no neutral species of antimony polysulfides have been reported. On the other hand, we have recently succeeded in the synthesis of novel tetrathiolanes containing a heavier group 14 element, $Tbt(Ar)MS_4$ [M = Si, Ge, Sn, or Pb; Ar = mesityl or 2,4,6-triisopropylphenyl (Tip)], by taking advantage of a new and efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter).[6] Here, we present the reactions of an overcrowded dihydrostibine, $TbtSbH_2$ (**1**), with elemental sulfur leading to the formation of the first cyclic polysulfides containing a trivalent antimony atom.



Scheme 1.

The starting dihydrostibine **1** was readily synthesized by the reaction of $SbBr_3$ with TbtLi in THF at -78 °C followed by the reduction of the resulting dibromostibine $TbtSbBr_2$ with lithium aluminum hydride at 0 °C as shown in Scheme 1. Although organometal(III) hydrides of group 15 metals such as arsenic, antimony, and bismuth are known to be highly reactive and unstable chemical species,[7] dihydrostibine **1** was isolated as white crystals stable toward air and moisture [mp 195 °C; $\delta_H(CDCl_3)$ 3.21 (SbH_2); $\nu_{Sb\text{-}H}$(KBr) 1855 cm^{-1}], suggesting the high efficiency of Tbt group for steric protection.

With the stable dihydrostibine **1** in hand, we examined its reaction with sulfur in the hope of obtaining antimony-containing cyclic polysulfides as in the case of the previously reported group 14 metal dihydrides.[6] When **1** (200 mg, 0.30 mmol) in THF (20 ml) was treated with elemental sulfur (78 mg, 0.30 mmol as S_8) at room temperature, two types of cyclic polysulfides having two TbtSb units, 1,3,4,5,2,6-tetrathiadistibane (**2**, 68 mg, 31%) and 1,3,4,2,5-trithiadistibolane (**3**, 33 mg, 15%) were isolated as yellow crystalline compounds along with a mixture (46 mg) of another type of two antimony polysulfides, $TbtSbS_7$ (**4**, 3%) and $TbtSbS_5$ (**5**, 15%), the yields of which were estimated by ^1H NMR (Scheme 2).[8] On the other hand, a dropwise addition of a THF solution (60 ml) of **1** (370 mg, 0.55 mmol) to a suspension of elemental sulfur (491 mg, 3 mmol as S_8) in THF (75 ml) at -30 °C resulted in quite a different distribution of the products, *i. e.*, a mixture (349 mg) of **4** (12%) and **5** (49%) together with a trace amount of **2** and **3** (Scheme 2). Although compounds **4** and **5** were unstable on silica gel, they were isolated as stable yellow cyrstals by means of gel permeation liquid chromatography with a recycling system.



Scheme 2.

Of the new antimony-containing cyclic polysulfides **2**-**5**, single crystals of **2** and **4** were obtained by slow evaporation of its $EtOH\text{-}CH_2Cl_2$ solution. X-ray crystallographic analysis of **2** and **4**, which are the first examples of these ring systems, revealed their unique molecualr geometry.[9]

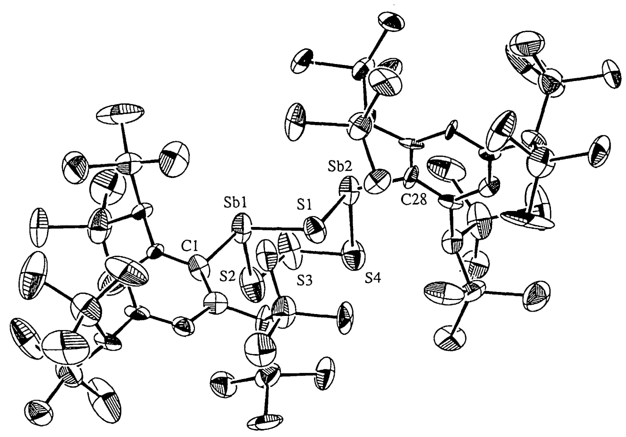


Figure 1. ORTEP drawing of **2** (one of the pair of independent molecules) with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles (deg): Sb(1)-S(1) 2.469(7), Sb(1)-S(2) 2.435(10), Sb(1)-C(1) 2.27(2), Sb(2)-S(1) 2.459(7), Sb(2)-S(4) 2.478(9), Sb(2)-C(28) 2.23(2), S(2)-S(3) 2.07(1), S(3)-S(4) 2.06(1), S(1)-Sb(1)-S(2) 98.2(3), S(1)-Sb(1)-C(1) 106.0(6), S(2)-Sb(1)-C(1) 95.3(7), S(1)-Sb(2)-S(4) 95.4(3), S(1)-Sb(2)-C(28) 93.8(6), S(4)-Sb(2)-C(28) 114.0(8), Sb(1)-S(1)-Sb(2) 94.0(3), Sb(1)-S(2)-S(3) 98.0(5), S(2)-S(3)-S(4) 106.6(5), Sb(2)-S(4)-S(3) 94.6(4).

As for **2**, one can see the chair conformation of the central tetrathiadistibane ring with both Tbt groups on the antimony atoms in equatorial positions as shown in Figure 1. Figure 2 clearly shows the crown-shaped heptathiastibocane ring of **4** which bears a close resemblance to the molecular geometry of cyclooctasulfur, and the S-S bonds are neither unusually long nor short but vary within a range from 2.009(5) to 2.039(6) Å. Of additional interest among the structural features of **4** is the nearly C_s symmetry of the SbS_7 ring though the molecules of **4** occupy general positions in the crystal.

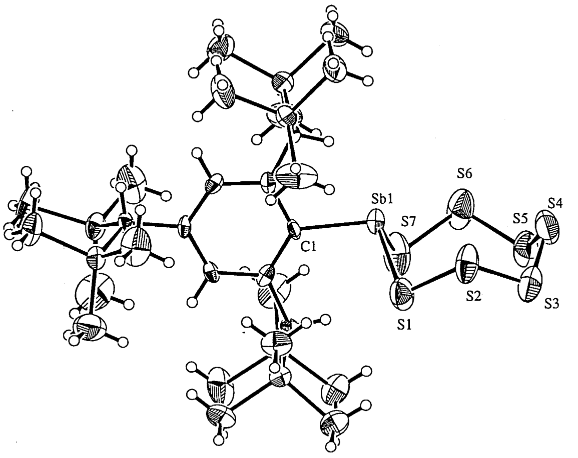


Figure 2. ORTEP drawing of **4** with thermal ellipsoid plot (30% probability for all non-hydrogen atoms). Selected bond lengths (Å) and angles (deg): Sb(1)-S(1) 2.408(4), Sb(1)-S(7) 2.408(5), Sb(1)-C(1) 2.150(10), S(1)-S(2) 2.025(5), S(2)-S(3) 2.009(5), S(3)-S(4) 2.011(7), S(4)-S(5) 2.037(7),. S(5)-S(6) 2.021(6), S(6)-S(7) 2.039(6), S(1)-Sb(1)-S(7) 100.2(2), S(1)-Sb(1)-C(1) 101.7(3), S(7)-Sb(1)-C(1) 101.5(3), Sb(1)-S(1)-S(2) 99.7(2), S(1)-S(2)-S(3) 109.7(3), S(2)-S(3)-S(4) 109.6(3), S(3)-S(4)-S(5) 109.8(3), S(4)-S(5)-S(6) 109.3(3), S(5)-S(6)-S(7) 108.8(3), Sb(1)-S(7)-S(6) 99.2(3).

Although the mechanism for the formation of **2–5** is not clear at present, compounds **2** and **3** most likely arise at high concentration and elevated temperature from a second attack of dihydrostibine **1** to the initially formed cyclic polysulfides **4** and **5**. Indeed, treatment of a mixture of **4** and **5** [molar ratio = 1:5 (^{1}H NMR)] with an equimolar amount of **1** at room temperature resulted in the formation **2** and **3** in 50 and 37%, respectively.

We have already succeeded in the synthesis of stable group 14 element–sulfur double bond compounds, *i. e.*, thiobenzaldehyde (TbtCH=S)[11] and metallanethiones [Tbt(Tip)M=S (M = Si, Ge, and Sn)][12] by the desulfurization of the corresponding overcrowded cyclic polysulfides containing group 14 elements such as octathionane ($TbtCHS_8$)[13] and tetrathiolanes [Tbt(Tip)MS_4].[6] Therefore, the formation of **4** and **5** is worthy of note not only as the first examples of stable antimony-containing cyclic polysulfides but also from the viewpoint of their potential utility as useful precursors of antimony–sulfur double-bond compounds, *e. g.* thioxostibine (TbtSb=S) and dithioxostiborane [TbtSb(S)=S], which are among a novel class of organoantimony compounds of current interest.

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References and Notes

1 Dedicated to Prof. Dr. Richard Neidlein of University of Heidelberg on the occasion of his 65th birthday.

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8 All the products described here showed satisfactory spectral [^{1}H and ^{13}C NMR, MS(FAB)] and analytical data.

9 *Crystal data* for **2**: $C_{54}H_{118}S_4Sb_2Si_{12}$,· M = 1476.29, monoclinic, space group $P2_1/n$, a = 25.66(2), b = 17.63(2), c = 39.62(2) Å, β = 106.03(4) °,V = 17228(24) Å^3, Z = 8, D_c = 1.138 g cm^{-3}, μ = 9.18 cm^{-1}. It has been revealed that in the unit cell there are two nonidentical molecules which have different geometry of the p-$CH(SiMe_3)_2$ group attached to one of the Tbt groups. Although all the non-hydrogen atoms were refined anisotropically, the refinement was performed without hydorgen atoms because of limitations of parameters. The final cycle of full-matrix least-squares refinement was based on 6813 observed reflections [$I > 2.00\sigma(I)$] and 1297 variable parameters with $R(R_w) = 0.093(0.082)$. *Crystal data* for **4**: $C_{27}H_{59}S_7SbSi_6$., M = 898.45, monoclinic, space group $P\bar{1}$, a = 11.980(5), b = 18.514(7), c = 11.337(3) Å, α = 92.68(3), β = 104.72(3), γ= 72.67(3) °, V = 2320(1) Å^3, Z = 2, D_c = 1.286 g cm^{-3}, μ = 10.81 cm^{-1}. All the non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located in calculated positioins. The final cycle of full-matrix least-squares refinement was based on 3092 observed reflections [$I > 3.00\sigma(I)$] and 370 variable parameters with $R(R_w) = 0.062\ (0.039)$. The intensity data for both **2** and **4** were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å), and the structure was solved by direct methods with *SHELXS-86*.[10] In order to avoid overlapping of the peaks ω scan technique was used for the data collection of **2** whose c axis was too large for ω-2θ scan.

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