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Nonconventional Behavior of NCN-Chelated Organoantimony(III) Sulfide and Isolation of Cyclic Organoantimony(III) Bis(pentasulfide)

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Organoantimony(III) sulfide (**1**) containing the NCN chelating ligand L [L = 2,6-(CH_2NMe_2)$_2C_6H_3$] displays unusual dual behavior, being dimeric (LSbS)$_2$, with the central Sb_2S_2 core, in the solid state but monomeric in solution. Sulfide **1** reacts with elemental S to give the unprecedented cyclic bis(pentasulfide) LSb(μ-S_5)$_2$SbL (**2**) with the central 12-membered ring Sb_2S_{10}.

Metallic polysulfides, as derivatives of S_x^{2-} anions ($x \geq 2$), may be prepared by a variety of methods using many types of sulfur sources (e.g., S_8, alkali-metal polysulfides, H_2S, etc.).[1] These compounds have attracted considerable attention not only with regard to their structure and reactivity but also for their potential uses. The majority of these works deal with transition-metal polysulfides[2] that were studied as catalysts and intermediates in important enzymatic processes.[3] On the contrary, the chemistry of stable heavier main-group 14 and 15 organometallic polysulfides remains nearly unexplored, with the exception of the works reported by Tokitoh and Lappert, who used effective steric protection of bulky ligands for the stabilization of such polysulfides derived from Si, Ge, Sn, Pb, Sb, and Bi.[4] These compounds may be divided into two general structural classes: (i) mononuclear compounds containing only one MS_n ring ($n = 4-6$);[4] (ii) dinuclear compounds containing two metal atoms bridged by two μ-sulfur bridges M(μ-S_n)$_2$M ($n = 1-3$).[4] Roesky et al. have reported on the preparation of a unique organoaluminum trisulfide, L′Al(μ-S_3)$_2$AlL′ [L′ = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2C_6H_3$], containing two μ-S_3 bridges by the reaction of an organoaluminum(I) precursor with sulfur as well.[5]

Recently, we have demonstrated that the oxidative addition of elemental Se or Te to the organoantimony(I) compound[6] (LSb)$_4$ supported by the NCN chelating, pincer-type, ligand L [L = 2,6-(CH_2NMe_2)$_2C_6H_3$] resulted in the formation of the monomeric organoantimony selenide LSbSe and telluride LSbTe with the preserved Sb−Se and Sb−Te terminal bonds.[7] We report here on the synthesis of corresponding sulfide **1** displaying an interesting dual monomer (solution)/dimer (solid) behavior. The addition of sulfur to **1** gave cyclic bis(pentasulfide) LSb(μ-S_5)$_2$SbL (**2**).

By analogy to the preparation of monomeric selenide LSbSe and telluride LSbTe, the first affords for the preparation of the sulfide **1** by the reaction of the organoantimony(I) compound (LSb)$_4$ with an excess of elemental S gave a mixture of the target compound **1** (characterized by NMR) and yellow single crystals characterized by the X-ray diffraction technique as the pentasulfide **2**. All attempts to drive this reaction to obtain selectively only one of these products failed, and the isolation of **1** was rather troublesome. In order to prepare compound **1** by a more reasonable reaction

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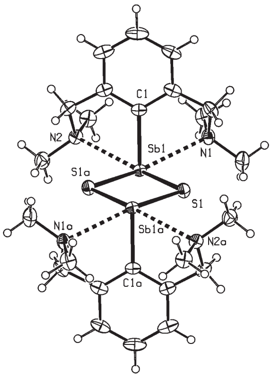
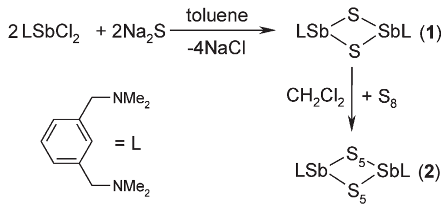


Figure 1. ORTEP plot of a molecule of **1** and the atom numbering scheme (symmetry code a: $-x$, $1-y$, $1-z$). The solvent (CH_2Cl_2) molecule was omitted for clarity. Selected bond lengths (Å) and angles (deg): Sb1−S1 2.4875(10), Sb1−S1a 2.4790(11), Sb1−C1 2.160(4), Sb1−N1 2.761(3), Sb1−N2 2.756(3); S1−Sb1−S1a 84.40(3), Sb1−S1−Sb1a 95.60(4), C1−Sb1−S1 98.34(11), C1−Sb1−S1a 96.22(11), N1−Sb1−N2 115.39(10).

Scheme 1

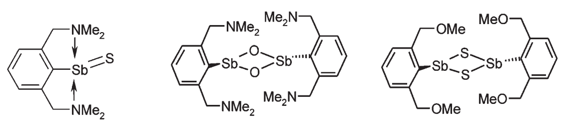


path, we reacted starting chloride[8] $LSbCl_2$ with anhydrous Na_2S, and this procedure gave sulfide **1** in moderate yield (Scheme 1).

The molecular structure of **1** was unambiguously established by X-ray diffraction studies[9] (Figure 1). The molecular structure is built up as a centrosymmetric dimer with the planar Sb_2S_2 core.[10] The Sb−S bond lengths within this ring are nearly identical, approaching the value for the covalent Sb−S bond [Sb1−S1 2.4875(10) Å and Sb1−S1a 2.4790(11) Å]. The angle at the antimony atom [S1−Sb1−S1a 84.40(3)°] is more acute than that at the bridging sulfur atoms [Sb1−S1−Sb1a 95.60(4)°]. Both ligands L are located mutually in the trans position with regard to the central four-membered ring. All nitrogen donor atoms of the ligands L are coordinated to the central metals through intramolecular interactions [range of the Sb−N bond lengths 2.756(3)−2.761(3) Å]. As a consequence of these dative Sb−N connections, polyhedra around the Sb atoms may be described as strongly distorted tetragonal pyramids, with the *ipso*-carbon atom C1 in the apical position.

Two sets of signals should be expected in the ^1H and ^{13}C NMR spectra of **1**because of the formation of two possible

Chart 1



1
(proposed structure in solution)

3

4

isomers, trans (as observed in the solid state) and cis in solution, of **1**. A similar situation was found in the dimeric oxide $(LSbO)_2$ (**3**; Chart 1) and also in other dimeric YCY-chelated systems (Y = O or N), containing the central Sb_2S_2, Bi_2S_2, and Sn_2S_2 cores, whose structures were described elsewhere.[11] However, the ^1H and ^{13}C NMR spectra of **1** revealed only one set of signals in $CDCl_3$. In the ^1H NMR spectra, an AX pattern was obtained for the NCH_2 moieties and two signals in a 1:1 intensity ratio were detected for the NMe_2 groups, indicating a nonsymmetric environment around the central atom and hindered rotation around the Sb−C bond due to the Sb−N intramolecular interactions. Similar results were obtained for the monomeric LSbSe and LSbTe compounds, pointing to a possible monomeric structure of **1** (LSbS, Chart 1)[12] in a $CDCl_3$ solution. The formation of monomeric structure LSbS was also observed in an acetonitrile solution in the case of electrospray mass spectral measurement (Figure S1a in the Supporting Information). In contrast to the low intensity of the dimeric ion at *m*/*z* 689 (9%), the most abundant ion at *m*/*z* 345 corresponds to the protonated molecule of the monomeric unit. On the other hand, the opposite observation was recorded for the related OCO antimony and bismuth sulfide compounds, where the most abundant ions belong to the dimeric structure and the ions corresponding to the monomeric structures are significantly less abundant (Figure S1 in the Supporting Information). Finally, the molecular weight of **1** was determined by ebulliometry in a $CHCl_3$ solution. The mean value from five experiments was estimated to 343 g/mol and corresponds well to the theoretical value (345 g/mol) for the monomeric structure of **1** (Chart 1).

The molecular structure of **1** was computed at the B3LYP level of theory[13] using the cc-pVDZ basis set[14] on all atoms, except for Sb, for which the cc-pVDZ-PP basis set[15] was used. The latter uses a cc-pVDZ like basis set for the valence region, together with a small-core relativistic pseudopotential. The Cartesian coordinates of the optimized structures are provided in the Supporting Information. The geometrical

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(9) **1**: $C_{24}H_{38}N_4S_2Sb_2 \cdot CH_2Cl_2$, $M = 775.13$, triclinic, $P\bar{1}$, colorless plate, $a = 8.9911(6)$ Å, $b = 9.7319(6)$ Å, $c = 10.3552(5)$ Å, $\alpha = 78.049(5)°$, $\beta = 84.599(5)°$, $\gamma = 77.526(4)°$, $V = 864.35(9)$ Å^3, $Z = 1$, $T = 150(1)$ K, 16 376 total reflections, 3949 independent [$R_{int} = 0.087$, R1 (obsd data) = 0.038, wR2 (all data) = 0.091]. CCDC 740163. **2**: $C_{24}H_{38}N_4S_{10}Sb_2$, $M = 946.68$, orthorhombic, *Fdd*2, yellow block, $a = 18.2391(8)$ Å, $b = 19.4562(11)$ Å, $c = 41.2517(8)$ Å, $V = 14638.6(3)$ Å^3, $Z = 16$, $T = 150(1)$ K, 60 294 total reflections, 8411 independent ($R_{int} = 0.082$, R1 (obsd data) = 0.046, wR2 (all data) = 0.115]. CCDC 740164.

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parameters of the trans isomer of **1** are in good agreement with the structural data obtained from the crystal structure. At this level of theory, we have also determined the dissociation energy of **1** into two monomers[16] and compared it with values for the NCN-chelated oxide **3** and the related OCO antimony sulfide compound **4** (Chart 1), which are known to be dimeric (both in the solid state and in solution). The calculations indeed indicate that the dissociation energy of **1** (15.8 kcal/mol) is substantially smaller than the dissociation energy of the oxide **3** (52.4 kcal/mol) and the OCO sulfide analogue **4** (27.9 kcal/mol).

In an attempt to synthesize the pentasulfide **2**, the reaction of **1** with 1 equiv of S_8 has been studied according to Scheme 1. The addition of a colorless CH_2Cl_2 solution of **1** to the stirred suspension of the elemental S resulted in a color change to yellow-orange, and all sulfur was consumed immediately. Compound **2** could be isolated as an orange powder (see the Supporting Information). The identity of **2** was established with the help of elemental analysis and single-crystal X-ray diffraction.[9] The purity of **2** was also studied using powder X-ray diffraction. The diffractogram of the bulk of **2** as obtained after the reaction[9] is essentially the same as that observed experimentally from comminuted single crystals and simulated from single-crystal measurements using *PLATON* software. It is noteworthy that diffractions of any unreacted sulfur are absent in the diffractogram of the bulk sample (see Figure S2 in the Supporting Information). Unfortunately, the low solubility of **2** in common organic solvents hampered NMR studies in solution; all spectra remain inconclusive.

The molecular structure of **2**, as determined in the solid state, is depicted in Figure 2. The molecular structure of **2** represents, to the best of our knowledge, an unknown structural type in the field of organometallic polysulfides.[1] Probably, the most similar compound containing two identical polysulfide bridges is, as was already mentioned, organoaluminum cyclic trisulfide $L'Al(\mu\text{-}S_3)_2AlL'$.[5]

The molecular structure of **2** is dominated by the central 12-membered ring Sb_2S_{10} formed through two identical μ-S_5 bridges. The S−S bond distances within these polysulfide chains vary between 2.032(3) and 2.052(4) Å and resemble the values found in elemental S_8 (ave 2.05 Å)[17] and also other organoantimony polysulfides (range 2.009−2.039 Å).[4h] The values of S−S−S angles fall within a narrow interval [107.96(15)−109.12(14)°]. The polysulfide chains are connected to the central antimony atoms, and the bond lengths [Sb1−S1 2.673(2) Å and Sb2−S5 2.677(2) Å] are longer than those found in sulfide **1** and in similar organoantimony polysulfides [range 2.408(4)−2.478(9) Å].[4h] Also, the comparison of these values to the value for the Sb−S covalent bond (2.48 Å) indicates a significant weakening (polarization) of the Sb−S bonds present in **2**. This fact is then reflected in a reinforcement of the Sb−N dative connections in **2** in comparison with **1** [the bond lengths in **2** are Sb1−N1 2.497(8) Å and Sb2−N2 2.467(7) Å, and those in **1** are 2.761(3) and 2.756(3) Å]. The coordination geometry around the central atoms Sb1 and Sb2 can be described as a distorted square pyramid with the sulfur and nitrogen atoms placed mutually in trans positions in the basal plane [the angles N−Sb−N 148.1(2) and 148.0(2)° and S−Sb−S 167.12(8) and 166.75(7)°]. This is in contrast to **1**, where the sulfur atoms as well as the nitrogen atoms are cis-arranged. The apex is occupied by the *ipso*-carbon atoms.

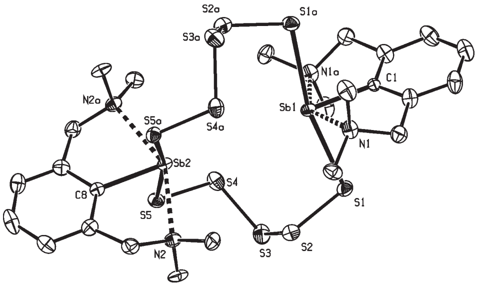

Figure 2. ORTEP plot of a molecule of **2** and the atom numbering scheme (symmetry code a: $-x, -y, -z$). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): S1−S2 2.032(3), S2−S3 2.052(4), S3−S4 2.047(4), S4−S5 2.033(3), Sb1−S1 2.673(2), Sb2−S5 2.677(2), Sb1−C1 2.068(12), Sb2−C8 2.127(12), Sb1−N1 2.497(8), Sb1−N2 2.467(7); S1−S2−S3 107.96(15), S2−S3−S4 108.32(14), S3−S4−S5 109.12(14), N1−Sb1−N1a 148.1(2), N2−Sb2−N2a 148.0(2), S1−Sb1−S1a 167.12(8), S5−Sb2−S5a 166.75(7).

The central intriguing cavity built up from 2 antimony atoms and 10 sulfur atoms is 4.5218(10) Å wide along the Sb1− Sb2 direction; the largest S−S distance across the cavity can be found between S3 and S3a, 8.274(3) Å.

In conclusion, organoantimony sulfide **1** displaying a monomeric structure in solution was synthesized. The reaction of **1** with sulfur gave unprecedented cyclic pentasulfide **2**, bearing two analogous μ-S_5 bridges connecting the central atoms. This motif represents a new structural type among organometallic polysulfides. The reactivity of **2**, especially concerning possible coordination of transition metals in the polysulfide cavity, is underway.

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Supporting Information Available: All experimental details, all crystal data and structure refinement, atomic coordinates, anisotropic displacement parameters, geometric data in CIF format, and details of all theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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