Extending the Time: Solvothermal Syntheses, Crystal Structures, and Properties of Two Non-isostructural Thioantimonates with the Composition [Mn(tren)]Sb₂S₄

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The two novel compounds, [Mn(tren)]Sb₂S₄ (1 and 2), were obtained by the reaction of elemental Mn, Sb, and S in aqueous solutions of tren (tren = tris(2-aminoethyl)amine, C₆H₁₈N₄) after different reaction times. Compound 1 is formed up to a reaction time of 13 d, and an extension of the reaction time leads to the formation of 2. Both compounds crystallize in monoclinic space groups (1, P2₁/c; 2, C₂/c). In 1, the two unique SbS₃ trigonal pyramids share a common S atom to form a Sb₂S₅ unit. Two S atoms of this group have a bond to Mn²⁺ yielding a MnSb₂S₃ heteroring in the boat conformation. The Sb₂S₅ moieties are joined via common corners into the final undulated [Sb₂S₄]₂⁻ anion which is directed along [001]. The structure of 2 contains the [Mn(tren)]²⁺ ion, one SbS₃ pyramid, and a Sb₂S₅ unit. Two symmetry-related SbS₅ groups share an edge, forming a Sb₂S₆ group containing a Sb₂S₂ ring. This group is joined via corners to two Sb₂S₃ pyramids on both sides producing a Sb₂S₄ ring. The Sb₂S₄ and Sb₂S₆ rings are condensed into the final [Sb₂S₄]₂⁻ anion which runs along [010]. The [Mn(tren)] groups are bound to the thioantimonate(III) backbone on opposite sides of the Sb₄S₄ ring, and a small MnSbS₂ ring is formed. In both structures, weak S⋯H bonds are found which may contribute to the stability of the materials. The two compounds decompose in one step upon heating, and only MnS and Sb₂S₃ could be identified as the crystalline part of the decomposition products. Both compounds can also be prepared under solvothermal conditions using MnSb₂S₄ as starting material. Compounds 1 and 2 are obtained from this ternary material in a high yield.

Introduction

During the past few years we demonstrated that Mn²⁺ is a very good candidate to be incorporated into thioantimonate(III) anionic frameworks: examples are the series of compounds with composition Mn₂Sb₂S₅⁻L (L = amine).¹⁻³ In these compounds Mn, Sb, and S atoms form heterocubanes which are joined into a neutral layered structure. One of the two independent Mn atoms is surrounded in a severely distorted octahedral environment of 6 S atoms, and the other Mn atom bonds two 2 N and 4 S atoms. The amines point into the empty space between successive layers, and the interlayer interactions are weak and of the van der Waals type. A spectacular compound with composition [Mn(C₆H₁₃N₃)]₂Mn₂Sb₄S₁₂ contains the formerly unknown heterometallic [Mn₂Sb₄S₁₂] core which is constructed by MnS₄ tetrahedra and SbS₃ pyramids being linked via common corners and edges.⁴ The [Mn(C₆H₁₃N₃)]²⁺ cations are located at the periphery of the core and are bound to the [Mn₂Sb₄S₁₂] unit via two S atoms. Interesting examples are the two new neutral thioantimonates(III) [Mn(tren)]₂Sb₂S₄ (tren = tris-(2-aminoethyl)amine, C₆H₁₈N₄) and [Mn(tren)]₂Mn₂Sb₄S₁₀.⁵ In the former compound trigonal SbS₃ pyramids are connected via common corners to give the tetradsenate [Sb₂S₅]⁴⁻.

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anion of which four S atoms have bonds to the manganese atoms of the [Mn(tren)]²⁺ ions. A remarkable feature is the comparably large angle of 134° around the S atom joining the two Sb atoms. In the structure of the second compound, MnS₄ tetrahedra and SbS₃ pyramids are linked via common corners and edges to form a new heterometallic [Mn₂SbS₁₀] core. The [Mn(tren)]²⁺ cations are located at the periphery and are bound to the central core via two S atoms. Finally, the new compounds [TM(tren)]Sb₂ were prepared with TM = Mn³⁺, Fe²⁺, Co²⁺, and Zn²⁺.6 In these isostructural compounds, the [Sb₄S₇]²⁻ anions are composed of three SbS₃ trigonal pyramids and one SbS₄ unit which share edges and corners to form semicubics (Sb₃S₄). The Sb₃S₄ moieties and SbS₃ pyramids are joined in an alternating fashion, yielding the [Sb₄S₇]²⁻ anionic chain. Weaker Sb–S bonding interactions between neighbored chains lead to the formation of layers within the (001) plane. The layers contain pockets that are occupied by the cations. The TM²⁺ ions are in a trigonal bipyramidal environment of four N atoms of the tren ligand and one S atom of the thioantimionate(III) anion.

Most syntheses are performed using the elements or binary compounds as starting materials. Very recently we demonstrated that the reaction of the ternary compound MnSb₂S₄ with dien (dien = diethylenetriamine) yielded the new thioantiminate(III) [Mn(dien)₂]Sb₂S₄·0.5H₂O which was not accessible by using the elements as educts.8 [Mn(dien)₂]-Sb₂S₄·0.5H₂O was obtained phase pure in high yields which encouraged us to perform more syntheses with MnSb₂S₄ as starting material. Here, we report on the synthesis, crystal structures, and properties of the two novel thioantiminate(III) compounds with the composition [Mn(tren)]Sb₂S₄.

Experimental Section

Synthesis. The title compounds were synthesized under solvothermal conditions from elemental manganese (54.9 mg, 1 mmol), antimony (243.5 mg, 2 mmol), and sulfur (128.3 mg, 4 mmol) in 5 mL of a tren/H₂O solution (50%). The mixtures were heated at 140 °C for 7 days (1) and 33 days (2) in Teflon-lined steel autoclaves with an inner volume of approximately 30 mL. The products consisting of dark orange (1) and red-orange (2) colored crystals with a polyhedral shape were filtered off, washed with distilled water, and dried in air. The yield was about 80% for 1 and 40% for 2.

Both compounds were also obtained using MnSb₂S₄ (200 mg, 0.468 mmol)7 in 5 mL of an 90% aqueous solution of tris(2-aminoethyl)amine (yield of 65–70%). The only byproduct of the procedure presented above was elemental antimony which was detected in the X-ray powder patterns.

Long time experiments from 7 to 33 d were performed using the first synthetic procedure to determine the time when compound 1 disappears and compound 2 is formed.


Structure Determination. The intensity data were collected with an Imaging Plate diffraction system (Fa. Stoe). The raw intensities were treated in the usual way and were corrected for absorption effects using X-Red⁹ and X-Shape.¹⁰ The structures were solved with direct methods using SHELXS-97,¹¹ and structure refinement was performed against F² using SHELXL-97.¹² All non-hydrogen atoms except some of the disordered carbon atoms were refined anisotropically. The hydrogen atoms were positioned with idealized geometry and were refined isotropically using a riding model. Three carbon atoms of the ligand in compound 1 are disordered and were refined using a split model with anisotropic displacement factors for the major occupied atoms (sof = 0.8) and isotropic displacement factors for the minor occupied atoms (sof = 0.2). In 2, some carbon atoms of the ligand are disordered and were refined anisotropically using a split model (sof = 0.65: 0.35). Crystal data, results of the structure refinement, and bond lengths and angles are found in Tables 1 and 2.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC185044 (2) and CCDC 600580 (1). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax (+44)1223–336–033; e-mail: deposit@ccdc.cam.ac.uk).

X-ray Powder Diffractometry. The X-ray powder patterns were recorded on a Stoe Stadi-P diffractometer (Cu Kα₁ radiation, λ = 1.540598 Å) in transmission geometry.

Thermanalytical Measurements. Thermal investigations were performed on a Netzsch STA-409CD DTA-TG measurement device. All measurements were corrected for buoyancy and current effects. They were performed using a heating rate of 4 K/min in Al₂O₃ crucibles under a dynamic nitrogen atmosphere (flow rate 75 mL/min; purity 99.999%; sample weight 11.9 (1) and 15.1 mg (2)).

Results and Discussion

Crystal Structures. In the two new compounds, [Mn(tren)]Sb₂S₄ (1 and 2), all atoms are in general positions. The Mn²⁺ ions are located in a distorted octahedral environment of four N atoms of the tren ligand and two S atoms of the [Sb₄S₇]²⁻ anions (Figures 1 and 2). The Mn–N bonds range from 2.240(3) to 2.375(3) Å in 1 and from 2.235(3) to 2.350(3) Å in 2. The Mn–S bond lengths are 2.5181(9) and 2.7494(10) Å in 1 and 2.4774(10) and 2.7947(9) Å in 2 (Table 2). As expected the longer Mn–N distances are on the opposite side of the short Mn–S bond (Table 2).⁵,⁵,¹⁴,¹⁵

In 1, two SbS₃ trigonal pyramids share a common S atom to form a Sb₂S₅ unit. Two S atoms of this group have a bond to Mn²⁺ yielding a MnSb₂S₄ heterotetragonal in the boat conformation (Figures 1 and 2). The SbS₃ moieties are joined via common corners into the final undulated [Sb₂S₄]²⁻ anion (Figure 2) which is directed along [001]. Otherwise, the

References:

(10) X-Shape, version 1.03; Stoe & Cie GmbH: Darmstadt, Germany, 1998.
structure may be described as \( \text{MnSb}_2\text{S}_3 \) rings being interconnected by \( \text{S} \) atoms.

The \( \text{S}--\text{S} \) bond lengths (range of 2.3556(8)–2.5991(8) Å) and \( \text{S}--\text{S} \)–\( \text{S} \) angles (range of 87.13(3)–107.66(3)°) are

### Table 1: Selected Data of Data Collection and Refinement Results for Compounds 1 and 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Empirical Formula</th>
<th>FW</th>
<th>Temp (K)</th>
<th>Wavelength (Å)</th>
<th>Cryst Syst</th>
<th>Space Group</th>
<th>Unit Cell Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{C}<em>6\text{H}</em>{18}\text{MnN}_4\text{S}_4\text{Sb}_2 )</td>
<td>572.92</td>
<td>293(2)</td>
<td>0.70173 Å</td>
<td>monoclinic</td>
<td>( P2_1/c )</td>
<td>( a = 4.0116(6) ) Å, ( b = 15.2439(12) ) Å, ( c = 11.2964(6) ) Å</td>
</tr>
<tr>
<td>2</td>
<td>( \text{C}<em>6\text{H}</em>{18}\text{MnN}_4\text{S}_4\text{Sb}_2 )</td>
<td>572.92</td>
<td>293(2)</td>
<td>0.70173 Å</td>
<td>monoclinic</td>
<td>( C2/c )</td>
<td>( a = 23.4380(12) ) Å, ( \beta = 96.89(3) ) Å, ( \gamma = 119.565(10) ) Å</td>
</tr>
</tbody>
</table>

**Refinement**:
- \( R \) (int) \( = 0.0283 \)
- \( R_p \) \( = 0.0259 \)
- \( wR_p \) \( = 0.0294 \)

**Extinction Coeff.**
- \( 0.0063(3) \)
- \( -0.946 \) e Å\(^{-3} \)

### Table 2: Selected Bond Lengths (Å) and Angles (deg) in Compounds 1 and 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{Mn}--\text{S} )</td>
<td>( \approx 2.2 ) Å</td>
</tr>
<tr>
<td>2</td>
<td>( \text{Sb}--\text{S} )</td>
<td>( \approx 2.4 ) Å</td>
</tr>
</tbody>
</table>

*Estimated standard deviations are given in parentheses. 

*Symmetry transformation codes: A \( x, y + 1/2, z \); B \( x, -y + 1/2, z \); C \( 1/2-x, y, z/2 \). 

Typical for thiostannate(III) compounds (Table 2), 1–6, 16–23

The analysis of the packing and orientation of neighboring chains yields some interesting results. Along [010], the \( [\text{Mn}](\text{tren})\)\(^2+\) ions of neighboring chains show an antiparallel orientation; along [100], they are oriented in the same direction (Figure 3), and along [011], they are packed so that the organic parts are always oriented face-to-face (Figure 3 bottom). 

The \( \text{Sb} \) atoms each have one long contact to a \( \text{S} \) atom in the chain \( \text{Sb}--\text{S} = 3.113(3) \) Å, \( \text{Sb}(1)--\text{S}(3) = 3.113(3) \) Å,

3.257(3) Å). Thus, ψ-trigonal bipyramidal polyhedra result when the lone electron pair located in the equatorial plane is taken into account. The presence of five intermolecular H⋯S distances ranging from 2.630 to 2.963 Å and N−H⋯S angles between 133.55 and 178.70° indicate weak hydrogen bonding.

The $\infty^{1}{[Sb\,S_{4}]}^{2-}$ anion in 2 is composed of one Sb(1)S$_{3}$ trigonal pyramid and a Sb(2)S$_{4}$ unit. Sb−S bond lengths and S−Sb−S angles for Sb(1)S$_{3}$ are in the typical range (Table 2).

In the Sb(2)S$_{4}$ unit, two longer Sb−S bonds are observed (2.6143(9) and 2.8564(8) Å) (Table 2) which are trans to each other with an angle of 175.83(3)°. Such SbS$_{4}$ groups are not uncommon and were observed in [Zn(tren)]-$\text{Sb}_{4}$S$_{8}$, [Co(tren)]Sb$_{4}$S$_{8}$, [Fe(dien)$_{2}$]Sb$_{6}$S$_{10}$.$\text{H}_{2}$O, and Cs$_{2}$Sb$_{8}$S$_{13}$. The S(1) and S(2) atoms are bound to the Mn$^{2+}$ ion forming a MnSbS$_{2}$ heteroring. Two symmetry-related Sb(2)S$_{4}$ moieties share an edge, forming a Sb$_{2}$S$_{6}$ group containing a Sb$_{2}$S$_{2}$ ring. This group is joined via corners to two Sb(1)S$_{3}$ pyramids on both sides yielding a SbS$_{4}$ ring. The Sb$_{2}$S$_{2}$ and Sb$_{2}$S$_{4}$ rings are condensed to the final $\infty^{1}{[Sb\,S_{4}]}^{2-}$ anion which runs along [010] (Figure 4). The $\text{Mn(tren)}$ groups are bound to the thioantimonate(III) backbone on opposite sides of the Sb$_{2}$S$_{4}$ ring (Figure 4).

The Sb(1) atom has two long contacts to S atoms within the chain (Sb(1)−S(1)= 3.225(1) Å, Sb(1)−S(4) = 3.281(1) Å), and the environment may be regarded as a distorted rectangular pyramid with the lone electron pair most likely occupying the free apical position (i.e., the coordination polyhedron is a distorted ψ-octahedron). In Figure 5, two different views of the packing of the chains are shown. Neighboring chains along [010] are arranged such that the tren ligand points into pockets which are formed by the interconnected SbS$_{4}$ units (Figure 5, top). In the (010) plane, the chains are arranged in a layerlike fashion (Figure 5, bottom).

Five short H⋯S distances between 2.610 and 2.818 Å with corresponding N−H⋯S angles ranging from 140.33 to 166.91° indicate weak hydrogen bonding between adjacent chains.

Thioantimonates with the composition [M(amine)]Sb$_{2}$S$_{4}$ are rare, and only two other examples exist. In the two-dimensional compound [Co(tren)]Sb$_{2}$S$_{4}$, the anion is built...
up from a SbS$_3$ trigonal pyramid and a SbS$_4$ unit. Two of the SbS$_4$ units share a common edge, forming the well-known Sb$_2$S$_2$ heterorings. Four Sb$_2$S$_2$ heterorings are joined via four SbS$_3$ units yielding a squarelike net with a large Sb$_{10}$S$_{10}$ ring. The cavities of the rings are filled by the [Co(tren)$_2$]$^{2+}$ ions. In [Ni(tren)]Sb$_2$S$_4$, the anion is composed of two SbS$_3$ pyramids sharing a common corner to form a one-dimensional chain. An interesting feature of this compound is a NiSb$_2$S$_3$ ring in the twist conformation. In (CH$_3$NH$_3$)$_2$Sb$_2$S$_4$, two pyramidal SbS$_3$ groups are linked via an edge to give dimeric Sb$_2$S$_4^{2-}$ anions, which are then joined via longer Sb–S bonds into one-dimensional chains.

**Synthetic Aspects.** The two new compounds were obtained under identical synthesis conditions but after different reaction times. This observation demonstrates that under solvothermal conditions after short reaction times the less stable material is formed first and the more stable compound crystallizes at later stages of the reaction. According to our long-term experiments, compound 1 is formed up to about 13 days, and via the extension of the syntheses beyond this time compound 2 is formed. The X-ray powder patterns gave no hints for the coexistence of the two compounds independently of the reaction time. One interesting finding is that compound 1 has a higher density than compound 2 (Table 1). In another experiment, some crystals of 2 were added to the reaction mixture. After 7 days only crystals of compound 2 were found in the reaction product. When the syntheses are performed in Teflon liners which were formerly used for the preparation of compound 2 only this material crystallized. These observations are hints that compound 2 is more stable than 1.

Normally, one would expect that the more stable material exhibits the higher density. However, this is just a crude rule and several exceptions are known. The observations for 1 and 2 agree well with the unusual behavior of MnSb$_2$S$_4$ which exhibits a high-density high-pressure polymorph, oP$_{28}$, first reported in ref 25 and a lower density room-temperature polymorph, mC$_{28}$, which is supposed to be more stable.

Another interesting result was obtained with syntheses which used MnSb$_2$S$_4$ as the starting material. The ratio of the elements is identical with that found in the products. But according to the results of X-ray powder diffraction, elemental Sb was formed as a byproduct clearly indicating that a redox reaction occurred. It is highly likely that this redox reaction took place with the amine. During the reaction with MnSb$_2$S$_4$, the primary building units, SbS$_3$ pyramids and MnS$_6$ octahedra, must be fully destroyed. In the final products, only MnN$_4$S$_2$, SbS$_3$, and SbS$_4$ units are observed. In situ X-ray scattering experiments are under way for a better understanding of this complex reaction.

**Thermal Investigations.** The thermal stability of the title compounds were investigated using simultaneous differential thermoanalysis (DTA) and thermogravimetry (TG) measurements under a N$_2$ atmosphere. Compound 1 decomposes in two steps with a total weight loss of 23.4% which is accompanied by two endothermic events with peak temperatures at $T_p = 277.4 \, ^\circ\text{C}$ and 295.0 $^\circ\text{C}$ (Figure 6). Unfortunately, the two thermal reactions are too close, preventing a more detailed study of the decomposition mechanism. In the

![Figure 5. Two different views of the arrangement of the chains in compound 2: (top) view along [001] and (bottom) view along [010].](image)

![Figure 6. DTA, TG, and DTG curves for compound 1 ($T_p$ = peak temperature).](image)
X-ray powder pattern of the gray decomposition product elemental Sb, MnS, and Sb₂S₃ could be identified.

The decomposition of compound 2 starts at approximately 150 °C in one step with a total weight loss of 25.3% which is accompanied by a broad endothermic event at \( T_p = 296.0 \) °C. The endothermic signal shows a shoulder at the lower temperature side indicating that the material is decomposed in two very close steps which cannot be resolved (Figure 7). Again, the X-ray powder pattern shows only reflections from MnS and Sb₂S₃. In both cases, the weight loss can be attributed to the removal of the tren ligand. The slightly different values for \( \Delta m_{\text{exp}} \) can be attributed to a contamination of the decomposition products with small amounts of C and N.

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