Infinite Anionic Chains Formed by Alternating Bidentately Acting [SbS$_4$]$^{3-}$ Anions and [Mn(dien)]$^{2+}$ Complexes in the Compound [Mn(dien)$_2$][Mn(dien)SbS$_4$]$_2$

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

The new compound [Mn(dien)$_2$][Mn(dien)SbS$_4$]$_2$ (dien = diethylenetriamine) was synthesized under solvothermal conditions. It crystallizes in the non-centrosymmetric monoclinic space group $P2_1$ with $a = 7.5736(5)$, $b = 19.1081(16)$, $c = 13.1174(11)$ Å, $\beta = 90.022(9)^\circ$, $V = 1898.3(3)$ Å$^3$, and $Z = 2$. The crystal structure is composed of one [Mn(dien)$_2$]$^{2+}$ cation and an anionic chain composed of [SbS$_4$]$^{3-}$ anions and [Mn(dien)$_2$]$^{2+}$ cations. The [SbS$_4$]$^{3-}$ anions connect [Mn(dien)$_2$]$^{2+}$ ions in a $\mu_2$-fashion to form an undulated [([Mn(dien)SbS$_4$])$^{-}_2$ chain running along [001]. The Mn$^{2+}$ ions in the chain are in a rare distorted rectangular pyramidal coordination environment with 3 N and 1 S atom forming the base and one S atom being located at the apex of the pyramid. The anionic chains and the cations alternate along [010]. Several relatively strong intra- and inter-chain N–H···S bonding interactions are observed. From the Raman spectrum the reduction of the ideal $T_d$ symmetry of the [SbS$_4$]$^{3-}$ anions is obvious because more resonances occur than expected for the undistorted geometry.

Key words: Thioantimonates, Solvothermal Syntheses, Crystal Structure

Introduction

During the past decades a large number of fascinating thiometallate compounds were prepared either under solvothermal or ambient conditions as recently reviewed [1 – 5]. A subgroup of these compounds mainly prepared under solvothermal conditions are thioantimonates(III) which are characterized by a large variety of chemical compositions, Sb:S ratios and structural dimensionalities. It can be assumed that Sb(III)S$_x$ units ($x = 3 – 5$) generated at the early stages of a hydrothermal reaction have a pronounced tendency for further condensation thus leading to the formation of higher hierarchical building blocks with different structural complexity. Compounds with isolated thioantimonate(III) anions like [Sb$_3$S$_6$]$^{3-}$, [Sb$_2$S$_8$]$^{3-}$, [Sb$_8$S$_{12}$]$^{6-}$ [6 – 8] have been isolated, but also very complex three-dimensional networks have been observed. Some selected examples are given in refs. [9 – 19]. There are only three examples for the coexistence of Sb(III) and Sb(V) in thioantimonate compounds obtained under solvothermal conditions [20 – 22], and another mixed valent thioantimonate, Cs$_3$Ag$_2$Sb$_3$S$_8$, was prepared in supercritical ammonia [23].

While thioantimonates(III) exhibit a variable and diverse structural chemistry, compounds containing Sb(V) are rare and mainly structurally characterized by isolated [SbS$_4$]$^{3-}$ anions and counterions. There are few examples where bonding interactions between the [SbS$_4$]$^{3-}$ anions and transition metal or lanthanoid cations occur. The [SbS$_4$]$^{3-}$ anion can act as a monodentate ligand like in e.g. [Mn(tren)(trenH)]SbS$_4$ (tren = tris(2-aminoethyl)amine) and [Mn(trans-1,2-dach)$_3$]$_2$[Mn(trans-1,2-dach)$_2$(SbS$_4$)$_2$]·6H$_2$O (trans-1,2-dach = trans-1,2-diaminocyclohexane) [24], as
a bidentate bridging ligand as observed in e.g. [Nd(en)(H$_2$O)($\mu$-SbS$_4$)] [25], or as a tridentate ligand like in e.g. [La(en)$_3$($\mu$-SbS$_3$)] [25], [Ce(dien)$_2$($\mu$-SbS$_4$)$_2$] [26]. [La(teta)(en)SbS$_4$] (teta = tri ethylenetetramine) [27], [Ln(dien)$_2$($\mu$-$\eta^1$-$\eta^2$-SbS$_4$)$_2$]$_n$ (Ln = Pr, Nd, Sm) and [Ln(dien)$_2$($\eta^2$-SbS$_4$)] (Ln = Eu, Dy) [28], and [Pr(en)$_3$(H$_2$O)($\mu$-SbS$_4$)] [29].

In the past we often observed that Mn$^{2+}$ can easily be integrated into thiometallate networks [30 – 35], and during further explorative work we obtained and characterized the new compound [Mn(dien)$_2$]$_2$MnSb$_4$S$_7$ featuring anionic chains composed of tetrahedral bidentately acting [SbS$_4$]$^{3-}$ moieties interconnected [Mn(dien)]$_2$$^{2+}$ complexes and additional [Mn(dien)$_2$]$^{2+}$ ions which are located between the chains.

Experimental Section

Synthesis

All chemicals were purchased and used without further purifications. The title compound was obtained as yellow-orange thin needles upon heating 64.4 mg S (2 mmol), 61.1 mg Sb (0.5 mmol) and 54.8 mg Mn (1 mmol) in 2 mL diethylentetriamine (dien) for 2 d at 140 °C in a Teflon-liner placed in a steel autoclave. Despite a large variation of the synthesis conditions, the yield based on Mn was always only between 5 and 15%. Changing the educt ratio and/or the reaction time led to crystallization of the mixed-valent compound [Mn(dien)$_2$]$_2$MnSb$_2$S$_7$ [22]. The most sensitive synthesis parameter is the reaction time. An increase beyond 2 d afforded the formation of dense phases like MnS and Sb$_2$S$_3$ together with unknown compounds. – Elemental analysis CHN (%): calc. C 17.8, N 15.6; H 4.9; found C 18.1, N 15.3, H 5.1.

Crystal structure determination

The intensity data were collected using a Stoe IPDS-1 (Imaging Plate Diffraction System) with MoK$_\alpha$ radiation at room temperature. The structure was solved with Direct Methods using the program SHELXL-97 [36], and the refinement was carried out against F$^2$ with SHELXL-97 [37]. All non-hydrogen atoms were refined anisotropically. All H atoms were positioned with idealized geometry and refined isotropically using a riding model. An empirical absorption correction was performed. The crystal metric as well as the internal R value indicated orthorhombic symmetry, and an analysis of the systematically absent reflections led to space group $P2_2_1$. However, structure refinement in this space group always led to strong disorder and very poor reliability factors which clearly demonstrated that the crystal symmetry is too high. Further analysis has shown that the compound crystallizes monoclinically in space group $P2_1$, and that the crystal is non-merohedrally twinned with a 2-fold axis as the twin element (BASF parameter: 0.529(1)). In this space group no disorder is present, and the absolute structure can easily be determined and is in agreement with the selected setting; x (Flack) parameter: 0.06(2).

CCDC 929165 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Raman spectroscopy

The Raman spectrum was recorded with a Bruker IFS 66 Fourier transform Raman spectrometer (wavelength: 541.5 nm) in the region from 100 to 3500 cm$^{-1}$.

UV/Vis spectroscopy

The UV/Vis spectroscopic investigation was carried out at room temperature using an UV-Vis/NIR two-channel spectrometer Cary 5 from Varian Technot Pty., Darmstadt. The optical band gap was determined by analyzing the UV/Vis reflectance spectrum of the powdered sample (with BaSO$_4$ powder used as reference material). The absorption data were calculated applying the Kubelka-Munk relation for diffuse reflectance data.

Results and Discussion

The compound crystallizes in the non-centrosymmetric monoclinic space group $P2_1$ with all atoms being located on general positions. Selected data of the data collection and refinement results are summarized in Table 1.

In the crystal structure the crystallographically unique $\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\delta\d
Table 1. Selected details of the data collection and structure refinement result.

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Fig. 1 (color online). The Mn²⁺ cation in the title compound. C atoms are not labeled, and H atoms are not displayed for clarity.

The Mn–S bond lengths are between 2.452(2) and 2.509(2) Å, and the Mn–N bonds vary from 2.211(7) to 2.326(6) Å, thus being in the range reported for other Mn containing thiometaaltes [42]. The MnN₅S₂ coordination environment in the thioantimonate chain is rather unusual, and only few examples are known for such a coordination geometry, and the bridging Sb–S bond length is less pronounced than the remaining bonds to the terminal S atoms (2.3078(10)–2.3196(11) Å) [44]. In [Ni(tren)SbS₄]− with the bidentately acting [SbS₄]³⁻ ion the difference is less pronounced with two longer (2.3467(8) and 2.3333(12) Å) and two shorter (2.3150(8) and 2.3071(10) Å) distances [45], and in the [Mn(chxn)₂(SbS₄)₂]³⁻ anion of [Mn(chxn)₃]₂[Mn(chxn)₂(SbS₄)₂]·6H₂O (chxn = 1,2-diaminocyclohexane) all Sb–S bonds are in a narrow range between 2.323(1) and 2.348(1) Å [24]. In the compound [Sm(en)₃(H₂O)(μ-SbS₄)] one of the bridging Sb–S bonds (2.3137(12) Å) is even shorter than the bond to the terminal S atom of 2.3341(8) Å [46], while in [La(teta)(en)SbS₄] the three bridging Sb–S bonds (2.3262(11)–2.3334(10) Å) are longer than the Sb–Sterm bond (2.3141(12) Å) [27].

Fig. 2 (color online). The unique [SbS₄]³⁻ ions and the [Mn(dien)]²⁺ cations in the {[Mn(dien)SbS₄]₂} chain. Note that not all atoms are labeled, and that H atoms are omitted for clarity.

The S–S bond lengths (Table 2) can be grouped into two short terminal bonds (Sb–S: 2.300(2)–2.3070(17) Å) and two bridging bonds (2.3478(16)–2.3674(18) Å). The elongation of the Sb–S bonds to S atoms which are also bound to a transition metal is not unusual. E.g., in [Co(dien)]₂[Co(tren)SbS₄]·0.5H₂O the [SbS₄]³⁻ anion has one bond to the Co²⁺ cation, and the bridging Sb–S bond length of 2.3701(8) Å is significantly longer than the remaining bonds to the terminal S atoms (2.3078(10)–2.3196(11) Å) [44]. In [Ni(tren)SbS₄]− the difference is less pronounced with two longer (2.3467(8) and 2.3333(12) Å) and two shorter (2.3150(8) and 2.3071(10) Å) distances [45], and in the [Mn(chxn)₂(SbS₄)₂]³⁻ anion of [Mn(chxn)₃]₂[Mn(chxn)₂(SbS₄)₂]·6H₂O (chxn = 1,2-diaminocyclohexane) all Sb–S bonds are in a narrow range between 2.323(1) and 2.348(1) Å [24]. In the compound [Sm(en)₃(H₂O)(μ-SbS₄)] one of the bridging Sb–S bonds (2.3137(12) Å) is even shorter than the bond to the terminal S atom of 2.3341(8) Å [46], while in [La(teta)(en)SbS₄] the three bridging Sb–S bonds (2.3262(11)–2.3334(10) Å) are longer than the Sb–Sterm bond (2.3141(12) Å) [27].

The S–S bonds angles around Sb₁ range from 142.68 to 167.50°, and for Sb₂ they are between 105.56(7) and 113.25(8)°, i.e., the distortion from ideal tetrahedral geometry is very similar for both [SbS₄]³⁻ units.

The anionic chains and the [Mn(dien)]²⁺ cations are packed in alternating fashion along a[010] (Fig. 3). Several intra- and inter-chain S–H–N bonding interactions are observed with S–H separations between 2.472 and 2.970 Å and N–H–S angles ranging from 142.68 to 167.50°. We note that all S atoms are
involved in inter-chain interactions generating a three-
dimensional network.

Analyzing the transition metal cation containing
thiometallate chemistry, the Mn$^{2+}$ ion behaves very
differently from other first row transition metal ions
due to its ease of bond formation to both S and N. While cations like Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$ or Zn$^{2+}$ must
be forced to form bonds to S atoms of a thiometallate
framework using multidentate N-donor ligands which
do not coordinatively saturate the cations, Mn$^{2+}$ is eas-
ily integrated in such networks. Examples are e. g. the
series of compounds Mn$_2$(L)Sb$_2$S$_5$ (L = amine) [31,
33, 34, 47 – 52]. Mn$^{2+}$ can also easily be inte-
grated into thiostannate networks as shown by the
compounds (1,4-dabH)$_2$MnSnS$_4$ [53], {[Mn(trien)$_2$]
SnS$_4$}·4 H$_2$O [54] (trien = triethylenetetramine), or
{[Mn(tren)$_2$]Sn$_2$S$_6$} [55], and in thiogermanates like
in [C$_{14}$H$_{29}$N(CH$_3$)$_3$]MnGe$_4$S$_{10}$ (C$_{14}$H$_{29}$N(CH$_3$)$_3$ =
mesityltrimethylammonium) [56], which demonstrates
that the special behavior of Mn$^{2+}$ is not restricted to
thioantimonates.

The free tetrahedral [SbS$_4$]$^{3-}$ anion with ideal sym-
metry is expected to show four normal modes of vi-

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| Sb(1)–S(1) | 2.3573(18) | Sb(2)–S(5) | 2.3478(16) |
| Sb(1)–S(2) | 2.300(2)   | Sb(2)–S(6) | 2.3555(19) |
| Sb(1)–S(3) | 2.3707(17) | Sb(2)–S(7) | 2.3031(18) |
| Sb(1)–S(4) | 2.3674(18) | Sb(2)–S(8) | 2.3010(18) |

S(2)–Sb(1)–S(1) 108.46(9) S(8)–Sb(2)–S(7) 113.25(8)
S(3)–Sb(1)–S(1) 109.23(6) S(8)–Sb(2)–S(5) 111.85(7)
S(2)–Sb(1)–S(4) 110.51(7) S(7)–Sb(2)–S(5) 107.94(7)
S(3)–Sb(1)–S(4) 105.56(6) S(8)–Sb(2)–S(6) 105.56(7)

Mn(1)–S(4) 2.4423(18) N(13)–Mn(2)–N(11) 134.3(4)
Mn(1)–S(5) 2.501(2)   N(13)–Mn(2)–N(12) 76.4(3)
Mn(1)–N(1) 2.231(7)   N(11)–Mn(2)–N(12) 76.2(3)
Mn(1)–N(2) 2.326(6)   N(13)–Mn(2)–S(6) 110.9(4)
Mn(1)–N(3) 2.220(6)   N(11)–Mn(2)–S(6) 110.94(19)
Mn(2)–S(1) 2.509(2)   N(12)–Mn(2)–S(6) 104.78(19)
Mn(2)–S(6) 2.452(2)   N(13)–Mn(2)–S(1A) 94.8(3)
Mn(2)–N(13) 2.211(7)  N(11)–Mn(2)–S(1A) 95.61(17)
Mn(2)–N(11) 2.233(7)  N(12)–Mn(2)–S(1A) 155.83(18)
Mn(2)–N(12) 2.281(6)  N(33)–Mn(3)–N(23) 91.4(2)
Mn(3)–N(33) 2.269(6)  N(33)–Mn(3)–N(22) 162.9(2)
Mn(3)–N(21) 2.288(5)  N(31)–Mn(3)–N(22) 96.4(2)
Mn(3)–N(23) 2.298(6)  N(33)–Mn(3)–N(21) 94.2(2)
Mn(3)–N(32) 2.307(6)  N(31)–Mn(3)–N(21) 93.7(2)
Mn(3)–N(31) 2.283(7)  N(22)–Mn(3)–N(21) 79.2(2)
Mn(3)–N(22) 2.283(6)  N(33)–Mn(3)–N(23) 91.4(2)
N(3)–Mn(1)–N(1) 141.5(2) N(31)–Mn(3)–N(23) 158.0(2)
N(3)–Mn(1)–N(2) 76.3(3)  N(22)–Mn(3)–N(23) 77.1(2)
N(1)–Mn(1)–N(2) 76.1(2)  N(22)–Mn(3)–N(21) 105.0(2)
N(3)–Mn(1)–S(4) 104.18(19) N(33)–Mn(3)–N(21) 76.9(2)
N(1)–Mn(1)–S(4) 109.91(17) N(31)–Mn(3)–N(21) 93.7(2)
N(2)–Mn(1)–S(4) 112.16(17) N(22)–Mn(3)–N(21) 94.2(2)
N(3)–Mn(1)–S(5) 95.66(17) N(22)–Mn(3)–N(22) 165.9(3)
N(1)–Mn(1)–S(5) 93.23(17) N(21)–Mn(3)–N(22) 112.5(2)
N(2)–Mn(1)–S(5) 93.23(17) N(23)–Mn(3)–N(22) 77.3(3)
S(4)–Mn(1)–S(5) 103.70(7) N(23)–Mn(3)–N(23) 76.9(2)
vibrations viz. \( \nu_1(A_1) \), \( \nu_2(E) \), \( \nu_3(F_2) \) and \( \nu_4(F_2) \). All four vibrations are Raman-active while only \( \nu_3 \) and \( \nu_4 \) are infrared-active. For solid \( \text{Na}_3\text{SbS}_4 \) these bands are located at 410, 389 (asymmetric Sb–S stretch, \( \nu_2 \)), 368 (symmetric Sb–S stretch, \( \nu_3 \)), 198, and 162 cm\(^{-1}\) (Sb–S bending vibrations) [57]. The strongest band in the Raman spectrum of the title compound (Fig. 4) at 358 cm\(^{-1}\) is most likely the symmetric Sb–S stretching vibration, while the band at 387 cm\(^{-1}\) is most probably the asymmetric stretching. The two lines at 188 and 158 cm\(^{-1}\) are then due to bending vibrations. Because the two independent \( [\text{SbS}_4]^{3-} \) ions have bonds to Mn\(^{2+}\) cations, the local symmetry is reduced from \( T_d \) to \( C_3v \) for Sb1 and to \( C_{2v} \) for Sb2. This reduction of the symmetry leads to the appearance of further bands in the Raman spectrum. The resonances not marked in the Raman spectrum cannot be unambiguously assigned.

The UV/Vis spectrum of the title compound (Fig. 5) shows a not very steep absorption edge, and the optical band gap is estimated to 2.75 eV corresponding to a wavelength of 450.8 nm which is in line with the yellow-orange color of the compound.

In summary, the crystallization of the title compound has provided another illustrative example of the solvothermal approach yielding unexpected thioantimonate compounds with unparalleled structures. It is highly likely that a systematic variation of the synthesis conditions will afford more new thiometalates.

**Acknowledgement**

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