Thioantimonate Networks

[Mn(terpy)Sb$_2$S$_4$]$_n$, a 1D Network of MnSb$_4$S$_5$ Rings Exhibiting a Pronounced Magnetocaloric Effect and Luminescence

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Dedicated to Prof. Dr. Yuri Grin on the occasion of his 65th birthday

Abstract: The solvothermal reaction of an aqueous solution of Na$_3$Sb$_5$ or Schlippe’s Salt (Na$_3$Sb$_2$S$_9$·H$_2$O) in the presence of Mn(ClO$_4$)$_2$·6H$_2$O and terpy (terpy = 2,2′:6′,2″-terpyridine) or the [Mn(terpy)]$^{2+}$ complex led to crystallization of the new compound [Mn(terpy)Sb$_2$S$_4$]$_n$ (I). The unique crystal structure of I features chains formed by fused MnSb$_4$S$_5$ rings. The Mn$^{2+}$ ion is coordinated by one terpy ligand and two S$_2$– anions resulting in a distorted Mn$_2$S$_2$ trigonal bipyramid. The terpy ligands point to the exterior of the chains, distances between neighbored ligands indicate π···π stacking. Magnetic investigations show paramagnetic behavior ($\mu_{\text{eff}} = 5.92\, \mu_B$/Mn$^{2+}$ at room temperature). Field-dependent magnetic susceptibility measurements at different temperatures evidence a significant magnetocaloric effect of $-\Delta S = 20.54\, J\, kg^{-1}\, K^{-1}$ at $T = 2\, K$ for a magnetic field change of $\Delta B = 9\, T$. The compound exhibits blue luminescence, and a detailed analysis allowed assignment of the emission and excitation bands to the different constituents of the compound.

Introduction

With the rising number of thioantimonates and antimony sulfide compounds, the possibilities regarding their applications increased significantly. It was shown that such compounds exhibited promising properties in photocatalytic hydrogen evolution reaction$^{[1–3]}$ photocatalytic dye degradation$^{[4,5]}$ or as anode materials for lithium ion batteries.$^{[6]}$

Due to the flexible coordination geometries of Sb(III), Sb–S bond lengths and S–Sb–S angles, a large variety of thioantimonate(III) structures ranging from discrete anions up to three-dimensional networks have been synthesized and characterized. Many of these thioantimonates have been prepared applying elemental transition metals (TM) or TM salts, Sb, and S, in reactions$^{[1–3]}$ photocatalytic dye degradation$^{[4,5]}$ or as anode materials for lithium ion batteries.$^{[6]}$

Works$^{[18,19]}$ have shown that the aliphatic amine molecules may form complexes with the TM$^{n+}$ cations, thus preventing formation of TM complexes with aromatic amine molecules.

In comparison to the properties of divalent late transition metal cations, the Mn$^{2+}$ ion behaves quite different, as it shows a similar affinity to N donor atoms and S$_2$– anions, and thus is readily integrated into a variety of thioantimonate networks$^{[3,10,12,17,18,20–27,28]}$. The amine molecules act as structure-directing agents as well as mineralizers, generating a basic medium necessary for the formation of polysulfides that are required for dissolving the elemental starting materials. Solvothermal syntheses are rather sensitive to changes of reaction parameters like reaction time, temperature or molecular ratios of the starting materials. Attempts to further develop the chemistry of thioantimonates by e.g. integrating TM complexes containing solid aromatic amines requires us to overcome some challenges: Most of the relevant amines are only weakly soluble in water and thus do not generate the required basic conditions. In the past, several antimony sulfides with aromatic amine molecules integrated in the anionic network could be obtained using aliphatic amines as mineralizers.$^{[18,19]}$ However, this synthetic approach has the drawback that the aliphatic amine molecules may form complexes with the TM$^{n+}$ cations, thus preventing formation of TM complexes with aromatic amine molecules.

Recently, we reported the synthesis of new thioantimonates using TM$^{n+}$ complexes and Schlippe’s salt, Na$_3$Sb$_2$S$_9$·H$_2$O, as a water-soluble precursor.$^{[29]}$ This reaction system is characterized by a short reaction time for product formation and a remarkable robustness against changes of the reaction parameters. We successfully synthesized [Mn$_2$(bipy)$_4$Sb$_5$S$_9$(ClO$_4$)$_3$(bipy) = 2,2″-bipyridine, dibipy = 4,4″-dimethyl-2,2″-bipyridine] and [TM(bipy)$_3$][Sb$_5$S$_{10}$] (TM = Ni, Fe), [Ni(dibipy)$_3$][Sb$_5$S$_{10}$] by applying Na$_3$Sb$_2$S$_9$·H$_2$O and the corresponding TM$^{n+}$ complexes.

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The $\text{[Sb}_3\text{S}_6\text{]}^{2-}$ anions solely contain Sb(III), formed by redox reactions under the synthesis conditions, while in the Mn$^{2+}$-containing compound Sb(V) is preserved. The $\text{[Mn(bipy)}_2\text{]}^{2+}$ complex applied in the reaction mixture is relatively labile, loosing bipy ligands followed by instantaneous bond formation to the Sb$\text{S}_4^{2-}$ anion. To avoid the redox reactions using Na$_3$SbS$_4$·9H$_2$O, we successfully employed aqueous solutions of Na$_3$SbS$_3$ as precursor together with TM$^{2+}$ complexes.$^{[31]}$

In further solvothermal experiments we used the $\text{[Mn(terpy)}_2\text{]}^{2+}$ complex ($\text{terpy} = 2,2’$-$’$,2”-terpyridine) or Mn(ClO$_4$)$_2$·6H$_2$O and terpy and aqueous solution of Na$_3$SbS$_3$ leading to crystallization of the new antimony sulfide $\text{[Mn(terpy)Sb}_2\text{S}_4\text{]}^{2-}$ (I). Syntheses performed with aqueous solutions of Na$_3$SbS$_3$·9H$_2$O applying the Mn sources mentioned above also led to crystallization of I. The crystal structure of this compound was determined by single-crystal structure analysis. Since it was demonstrated that Mn$^{2+}$-containing compounds are interesting candidates as luminescence materials because the emission significantly depend on the coordination environment,$^{[32,33]}$ we are also investigated the luminescence properties. The Mn$^{2+}$ cation with a $S = 5/2$ spin ground state is a promising cation for the magnetocaloric effect, which was determined for the title compound.

**Results and Discussions**

**Synthetic Details**

To avoid the redox and condensation reactions necessary to form Sb(III) species applying Na$_3$SbS$_3$·9H$_2$O, syntheses were undertaken with aqueous solutions of Na$_3$SbS$_3$ in a Mn:Sb molar ratio of 1:2. With $\text{[Mn(terpy)}_2\text{]}^{2+}$, red crystals of the new compound $\text{[Mn(terpy)Sb}_2\text{S}_4\text{]}_{\text{n}}$ (I) appeared after 1 d together with an unknown crystalline phase as can be seen in the powder X-ray diffraction (PXRD) pattern (Figure S1). Prolongation of the reaction times up to 7 d yielded I as main product, but the amount of the impurity could not be reduced (Figure S1). Using Mn(ClO$_4$)$_2$·6H$_2$O and terpy separately, compound I crystallized after 3 h as a pure phase, while prolongation to 7 d led to the appearance of the crystalline side-phase already observed in the syntheses mentioned above (Figure S1). Recently, we performed solvothermal syntheses with Na$_3$SbS$_3$·9H$_2$O (Schlippe’s salt), Mn(ClO$_4$)$_2$·6H$_2$O and terpy and successfully obtained a new compound with composition $\text{[Mn(terpy)}_2\text{Sb}_3\text{S}_6\text{]}_{\text{n}}$·0.5H$_2$O$_{\text{n}}$ and a by-product which could not be identified at this time. For the preparation of this compound 2 mL of H$_2$O was added in a glass tube to a mixture of 36.2 mg (0.1 mmol) Mn(ClO$_4$)$_2$·6H$_2$O, 46.7 mg (0.2 mmol) terpy and 96.2 mg (0.2 mmol) Na$_3$SbS$_3$·9H$_2$O ($T = 140^\circ$, $t = 3$ d). Dark brown blocks crystallized next to tiny amounts of red needles, which in the meantime were identified as compound I.

To examine whether I is only a small by-product using Na$_3$SbS$_3$·9H$_2$O further, syntheses were performed at $T = 140^\circ$ C using $\text{[Mn(terpy)}_2\text{]}^{2+}$ or Mn(ClO$_4$)$_2$·6H$_2$O and terpy with Na$_3$SbS$_3$·9H$_2$O dissolved in H$_2$O varying the reaction time. In the presence of $\text{[Mn(terpy)}_2\text{]}^{2+}$ the title compound crystallized together with an additional phase within a reaction time of 6 h (Figure S2). Increasing the reaction time to 7 d the amount of the by-product could be significantly reduced (Figure S2). Reacting the aqueous solution of Schlippe’s salt with terpy and Mn(ClO$_4$)$_2$·6H$_2$O for 7 h led to a product consisting of the title compound and large amounts of a by-product (Figure S3). An increase of the time to 9 d significantly reduced the quantity of the side phase. This observation encouraged us to extend the reaction times and after 16 d only minute amounts of the by-product could be detected in the PXRD pattern apart from reflections of $\text{[Mn(terpy)Sb}_2\text{S}_4\text{]}_{\text{n}}$ (Figure S3). The remaining small impurities could be successfully removed by treating the sample in an ultrasonic bath as evidenced by the PXRD pattern (Figure S4) and the according Pawley fit (Figure S5). It is highly remarkable that both the thioantimonate(V) and the thioantimonate(III) anions of the precursors condense to form an identical thioantimonate network, especially keeping in mind that Sb(V) in the [Sb$_3$S$_6$]$^{2-}$ anion must be reduced to Sb(III).

**Crystal Structure**

Compound $\text{[Mn(terpy)Sb}_2\text{S}_4\text{]}_{\text{n}}$ (I) crystallizes in the monoclinic space group P2$_1$/c with two formula units in the unit cell, and all unique atoms on general positions. In the structure of I the unique Mn$^{2+}$ cation is surrounded by one terpy ligand and two S$^{2-}$ anions to form an asymmetric polyhedron that may be described as a distorted trigonal bipyramid with two S and one N atoms forming the trigonal base and the two remaining N atoms in the apical positions (Figure 1). This type of environment is rare for Mn$^{2+}$, which prefers an octahedral environment. A similar polyhedron was observed in $\text{[Mn(dien)}_2\text{Sb}_2\text{S}_6\text{]}^{2-}$ or in $\text{[Mn(dien)}_2\text{Sb}_2\text{S}_6\text{]}^{2-}$ (dien = diethylenetriamine)$^{[36]}$ The angles around Mn$^{2+}$ in the “trigonal” plane range from 111.85 to 131.16°, while the angle N–Mn–N is 142.16° (Table S1). The Mn–N bond lengths are between 2.204 and 2.274 Å (Table S1). The Mn–S bond lengths are almost identical (2.417 Å) being remarkably short compared to the sum of ionic radii of Mn$^{2+}$ (CN5) = 0.75 Å and of S$^{2-}$ = 1.84 Å. Similar short Mn–S bonds were observed in $\text{[Mn(terpy)}_2\text{Sb}_2\text{S}_4\text{]}^{2-}$ with 2.426(2) and 2.425(3) Å and a corresponding S–Mn–S angle of 115.57°. For a somewhat smaller S–Mn–S angle of 99.4° the

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Figure 1. View of a segment of the structure of $\text{[Mn(terpy)Sb}_2\text{S}_4\text{]}_{\text{n}}$ (I) with labelling of selected atoms. H atoms are omitted for clarity.
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Mn–S bonds are slightly larger at 2.45 and 2.51 Å than in the title compound. An increase of the S–Mn–S angle to 103.7° leads to even shorter Mn–S bonds with 2.442 and 2.501 Å. In the structure of the recently published compound ([(Mn(tren))Sb2S4]·H2O), a one-dimensional chain is observed consisting of MnSbS2S4 rings which are interconnected by S2– anions. Like in the structure of the title compound, the unique Mn2+ cations are in a strongly distorted environment of three N atoms of the terpy ligand and two S2– anions of SbS3 pyramids, reminiscent to that of the polyhedron observed in I.

The distortion of the polyhedra may be described based on interatomic distances d defining Δd = d2/⟨d2⟩ – 1 (⟨d⟩ means an average, variance d2 = ⟨d2⟩ – ⟨d⟩2). However, in this approach variations of the angles around the central cation are not taken into account. A more general approach based on an ellipsoidal approximation of coordination polyhedra by calculating the minimum bounding ellipsoid (MBE) as recently demonstrated using the program PIEFACE. Using this approach, the volume of the Mn2+-centered polyhedron was calculated as 52.4 Å3 and the shape parameter S of 0.024 indicates axially stretching of the trigonal-bipyramid. The terpy ligand is not planar as evidenced by the torsion angles ranging from 4.79 to 18.65°. The unique Sb atoms are in a trigonal pyramidal environment of three S atoms (Figure 1) with shorter Sb–S bond lengths to S2– anions that also bind to Mn2+ (2.369 and 2.374 Å). The Sb(2)S3 pyramid is joined to two Sb(1)S3 moieties sharing common corners thus generating a chain along [010] (Figure 2, left). The remaining two S atoms (S(1,4)) have bonds to Mn2+ so that MnSb4S5 rings are formed that are condensed along [1–1–1] showing the condensed MnSb4S5 rings, and right: packing of the chains viewed along [010]. H Atoms are omitted.

Figure 2. Two different views of the arrangement of the interconnected SbS3 pyramids with bonds to Mn2+ cations generating chains. Left: view nearly along [1–1–1] showing the condensed MnSb4S5 rings, and right: packing of the chains viewed along [010]. H Atoms are omitted.

Comparison with Crystal Structures Containing the [Sb2S4]2– Anion

The [Sb2S4]2– anion present in I was also observed in the dimorphic compound (Mn[tren]Sb2S4). In contrast to I, in one polymorph MnSb2S3 heterocycles are joined by S2– anions to form a chain (Figure 3a), while in the second polymorph a chain is constructed from alternating Sb4S4 and Sb2S2 rings (Figure 3b). The Mn2+ centers are located at the periphery of the central chain and MnSbS2 moieties are generated. In the structure of [Ni(tren)Sb2S4], a network topology similar to the first polymorph of [Mn(tren)Sb2S4] was reported. In contrast, the structure of [Co(tren)Sb2S4] features Sb11S10 rings condensed to form a thioantimoniate(III) layer with Co2+ cations located in pores comprising Co–S bonds to the network (Figure 3c). Anionic chains of composition [Sb2S4]2– and isolated transition metal complexes are found in the isotypic compounds [TM(en)3][Sb2S4] (TM = Ni, Co; en = ethylenediamine) (Figure 3d), while the structure of (maH)2[Sb2S4] (ma = methylamine) consists of methylammonium cations and a dimeric [Sb2S4]2– anion (Figure 3e).

Magnetic Investigations

The temperature dependence of the magnetic susceptibility of I is typical for a paramagnet with a χmT value of 4.38 cm³ K mol⁻¹ expected for one spin-only Mn2+ center per formula unit. The analysis of the data with the Curie–Weiss law yields an effective magnetic moment of 5.92 μB/Mn2+, which is in perfect agreement with the spin only value for S = 5/2 (Figure 4), and a Weiss temperature of 0 K indicating that the magnetic Mn2+ d5 centers are virtually uncoupled. Depending on the structural dimensionality and linkage pattern of Mn2+ cations, Mn/Sb/S phases exhibit a variety of magnetic properties. For layered compounds with general formula Mn2(L)Sb2S3 (L = ligand) strong antiferromagnetic interactions were reported. Despite
large negative values for the Weiss constant $\theta$ no long-range ordering of the magnetic moments could be detected, indicative for magnetically frustrated systems.$^{[9,44]}$ A similar strong magnetic frustration was reported for layered $\text{Mn}_3\text{Sb}_2\text{S}_6(\text{C}_6\text{H}_{18}\text{N}_4)$ ($\text{C}_6\text{H}_{18}\text{N}_4 = \text{triethylenetetramine}$) with $\theta = -62$ K, but in this case a Neel temperature $T_N = 2.9$ K was observed,$^{[27]}$ while for the 2D compound $[\text{Mn(dien)}]_2\text{Sb}_{18}\text{S}_{30}$ $[\text{Mn(dien)}]_2$ only moderate antiferromagnetic interactions ($\theta = -7.9$ K) were found.$^{[20]}$ Antiferromagnetic ordering was observed at $T_N = 40.5$ K for $\text{Mn}_2\text{Sb}_4\text{S}_8(\text{N}_2\text{H}_4)_2$ exhibiting a 3D structure. But moderate magnetic frustration was present as indicated by the value for the Weiss constant of $\theta = -77.3$ K.$^{[45]}$ Weak respectively moderate antiferromagnetic exchange interactions were observed for $(\text{dienH}_3)[(\text{dienH})\text{MnSb}_8\text{S}_{15}]\cdot\text{H}_2\text{O}$ ($\text{dien} = \text{diethylenetriamine}$) and $[\text{Mn(teta)}(\text{H}_2\text{O})_2][\text{Mn(tren)}]_2\text{Sb}_3\text{S}_{12}\cdot\text{H}_3\text{O}$ crystallizing in a 1D structure, with $\theta = -1.5$ and $-13.9$ K.$^{[17]}$ The effective magnetic moment for Mn$^{2+}$ was close to the spin-only value and strong deviation with 4.24 $\mu_B$ for $\text{Mn}_2\text{Sb}_4\text{S}_8(\text{N}_2\text{H}_4)_2$ was not further discussed.

The magnetocaloric effect (MCE) is an intrinsic property of compounds containing paramagnetic centers, and well documented for e.g. compounds that contain rare earth elements,$^{[46–53]}$ alloys,$^{[54]}$ coordination compounds$^{[55]}$ Cr-based complexes,$^{[56]}$ complexes containing Mn$^{2+}$ and Gd$^{3+}$ cations,$^{[57]}$ oxidic spinels,$^{[58]}$ or transition metal cluster compounds$^{[59]}$ to mention just a few examples. The spins of a paramagnetic compound, which are randomly oriented, align in a magnetic field leading to a decrease of the magnetic entropy, $\Delta S_M$. The magnetic entropy is related to the spin multiplicity ($2S + 1$) representing the degrees of freedom, and a large value for $S$ is beneficial for a large entropy change. The anisotropy and zero field splitting (zfs) should be small because large values reduce the maximum of $\Delta S_M$ due to ordering and splitting of the ground state, leading to reduction of $\Delta S_M$. The d$^5$ Mn$^{2+}$ ion exhibits a negligible zfs and insignificant anisotropy, rendering compounds with this cation interesting MCE candidates. $S = 5/2$ gives a maximal molar magnetic entropy of $S_{\text{max}} = \ln(2S + 1) = 14.9$ J K$^{-1}$ mol$^{-1}$. To examine whether the title compound shows an MCE, isothermal magnetization data at different temperatures were measured and the $\Delta S_M$ values were calculated using the Maxwell equation

$$\Delta S_M(T) = \int_{B_{\text{min}}}^{B_{\text{max}}} \mu_0 \frac{\partial M}{\partial T} dB' = \int_{B_{\text{min}}}^{B_{\text{max}}} \frac{\partial M}{\partial T} dB'$$

with $B_{\text{min}}$ and $B_{\text{max}}$ representing the initial and final value of the magnetic field.

The evolution of $-\Delta S_M$ at the different temperatures from 2 to 50 K is displayed in Figure 6 integrating from $B_{\text{min}} = 0$ T to $B_{\text{max}}$. The largest value for $-\Delta S_M$ amounts to $20.54$ J kg$^{-1}$ K$^{-1}$ ($13.55$ J K$^{-1}$ mol$^{-1}$) for $\Delta B = 9$ T at 2 K, which is close to the maximum theoretical value. With increasing temperature and decreasing values for $\Delta B$ the entropy change decreases.

Investigations of the MCE of Mn-containing compounds were mainly done on clusters featuring a large number of Mn$^{n+}$ centers, on alloys or oxides. E.g., the mixed-valent compound $[\text{Mn}^{III}_6\text{Mn}^{II}_4\text{O}_4\text{Br}_4(\text{amp})_6(\text{ampH}_2)_3(\text{HampH}_2)]\text{Br}_3\cdot 8(\text{hexane})$ has a $S = 22$ ground state caused by ferromagnetic coupling of all
spins exhibiting $-\Delta S_M = 13.0 \text{ J kg}^{-1} \text{ K}^{-1}$ at $T = 2.2 \text{ K}$ and $\Delta B = 0–7 \text{ T}$.\[60\] Another example is $[\text{Mn}^{\text{III}}_{6}\text{Mn}^{\text{II}}_{8}(\text{OH})_{2}(\text{Hpeol})_{4}(\text{H}_{2}\text{peol})_{6}\text{I}_{4}](\text{EtOH})_{6}$ with dominating antiferromagnetic exchange interaction and a $S = 7 \pm 1$ ground state for which a maximal MCE of $-\Delta S_M = 25.0 \text{ J kg}^{-1} \text{ K}^{-1}$ at $T = 3.8 \text{ K}$ and $\Delta B = 0–7 \text{ T}$ was reported.\[55\] In comparison, for $\text{Cd}_{0.9}\text{Gd}_{0.1}\text{F}_{2.1}$ the magnetic susceptibility follows Curie–Weiss behavior between 5 and 300 K, and evaluation of isothermal magnetization curves yielded $-\Delta S_M = 7.2 \text{ J kg}^{-1} \text{ K}^{-1}$ at $T = 5 \text{ K}$ and $\Delta B = 5 \text{ T}$.\[61\] The compound $\{[\text{Mn}(\text{pyrazole})_{4}]_{2}[\text{Nb}(\text{CN})_{8}]\cdot4\text{H}_{2}\text{O}\}_{n}$ shows a magnetic ordering at $T \approx 23 \text{ K}$ and a maximum value for $-\Delta S_M = 6.65 \text{ J kg}^{-1} \text{ K}^{-1}$ at $24.3 \text{ K}$ and $\Delta B = 5 \text{ T}$.\[62\] These comparisons demonstrate that the MCE of the title compound can compete with that reported for a variety of samples exhibiting much larger spin multiplicity ground states.

**Luminescence Properties**

Under UV irradiation, compound I emits blue light, which is strongly quenched due to its brownish color and consequent light absorption in the visible spectral range (Figure 7a). Accordingly, the emission spectrum of I (Figure 7b) is composed of two main bands, distributed over the UV to bluish-green spectral range, with maxima at 20000 and 27616 cm$^{-1}$. The respective excitation spectrum is located at approximately 22000–37000 cm$^{-1}$, with maxima at $\approx 27027, 31347$ and 35460 cm$^{-1}$.

![Figure 7. (a) Compound I under visible (left) and UV (right) light. (b) Emission (green curve, $\lambda_{\text{em}} = 325 \text{ nm}$) and excitation (blue curve, $\lambda_{\text{ex}} = 500 \text{ nm}$) spectra of the title compound.](image)

Similarly as for I, the emission spectrum of $[\text{Mn}(\text{terpy})_{2}(\text{ClO}_4)_{2}]$ also comprises two emission bands, a high-energy in the blue spectral range (20000 cm$^{-1}$) and a low-energy one (25000 cm$^{-1}$) in the green spectral range (Figure 8a). This behavior is in accordance with the respective photograph of the precursor compound under UV light (Figure 8a, inset). In this context, it is important to notice the similarity in shape and position between the emission spectrum of I to those of $[\text{Mn}(\text{terpy})_{2}(\text{ClO}_4)_{2}]$, indicating that the emission properties of this sample are caused by Mn$^{2+}$ and terpy instead by Sb$^{3+}$. A s often reported in the literature,\[68–71\] this behavior is expected due to the strong energy transfer between Sb$^{3+}$ and Mn$^{2+}$ ions.

In Figure 8b, it is shown that the emission spectrum of terpy exhibits a maximum at ca. 18000 cm$^{-1}$, similar to the observation reported by Fink et al.\[72\] for $2,2',2''$-terpyridine, without a high-energy emission band in the $\nu \approx 25000 \text{ cm}^{-1}$ spectral range. This broad luminescence band over the visible range of the electromagnetic spectrum results in the emission of white light, as observed in the photograph of this sample under UV light (Figure 8b, inset). Therefore, considering the emission spectra of I (Figure 7b) and of $[\text{Mn}(\text{terpy})_{2}(\text{ClO}_4)_{2}]$ (Figure 8a), it is possible to conclude that the respective low-energy bands are most probably assigned to the $\pi^* \rightarrow \pi$ electronic transitions of the organic ligand and the high-energy band could be attributed to the $3d \rightarrow 3d$ Mn$^{2+}$ electronic transitions.

**Thermogravimetric Investigations**

The TG curve of compound I shows a mass loss of 37.1 % accompanied by an endothermic event at $T_{\text{peak}} \approx 317 \text{ °C}$ (Figure...
The mass loss matches to the loss of the terpy molecule but without further experiments like the simultaneous use of mass spectroscopy the interpretation of the weight loss remains speculative.

**Spectroscopic Investigations**

An IR spectrum of compound I was measured and compared to the spectra of terpy and Mn(terpy)_2(ClO_4)_2 showing a good agreement of the absorptions in the products with those of the starting materials (Figure S7). The characteristic vibrations as well as their assignments are listed in Table S5.

**Conclusions**

We demonstrated that the title compound can be synthesized applying different synthetic routes. A fast reaction was observed using Na_3SbS_3, the Mn^{2+} salt and terpy and a phase pure sample is formed after 3 h. Longer reaction times led to appearance of a side-product. Using Na_3SbS_3·9H_2O, a Mn^{2+} salt and terpy a reaction time of 16 d was necessary until a nearly phase pure sample could be obtained. Some of the differences observed for Na_3SbS_3 and Na_3SbS_3·9H_2O can be explained with the fact that the latter sample contains Sb(V) which must be reduced to Sb(III) during chemical reactions. The crystal structure features interconnected MnSb_4S_5 rings with a 1D network topology significantly different from all other thioantimonate compounds containing the [Sb_2S_4]^{2-} anion, demonstrating the pronounced flexibility of thioantimonate(III) structures. Characterization of the magnetic properties evidences a pronounced magnetocaloric effect, which is comparable to examples reported in literature. Analysis of the luminescence spectra demonstrate that both Mn^{2+} and terpy contribute to the luminescence properties of the title compound.

**Experimental Section**

**Materials**

Chemicals were used as purchased without further purification. Mn(ClO_4)_2·6H_2O (99 %), terpy (97 %), sulfur (min. 99 %) and Sb_2S_3 (98 %) were purchased from Alfa Aesar. Na_3SbS_3·9H_2O was synthesized from aqueous solution of Na_3SbS_3·9H_2O (technical grade, purchased from Acros Organics), Sb_2S_3 and sulfur.

[Mn(terpy)_2](ClO_4)_2 was synthesized following an analogous method to prepare [Ni(bipy)_2](ClO_4)_2 described by Ruiz-Pérez et al.[73] and Na_3SbS_3 was synthesized after Pompe and Pfitzner.[74] Generally, the reaction products were filtered off, washed with small amounts of water and dried under ambient conditions. For the magnetic and luminescent investigations, the products were additionally cleaned with numerous ultrasonic treatment steps in acetone and ethanol.

**Caution:** Perchlorates are potentially explosive when heated and must be handled with care.

**Syntheses**

Compound I was synthesized by adding 2 mL of H_2O in a glass tube to a mixture of 72.0 mg (0.1 mmol) [Mn(terpy)_2](ClO_4)_2 and 57.4 mg (0.2 mmol) Na_3SbS_3. The sealed tube was heated to 140 °C and reaction times between 6 h and 7 d were applied. Red needles with a yield of 10 % based on Sb were obtained after 6 h, and the yield could be increased to 25 % after 7 d. Using Mn(ClO_4)_2·6H_2O 36.2 mg (0.1 mmol), terpy 46.7 mg (0.2 mmol) and 57.4 mg (0.2 mmol) Na_3SbS_3 dissolved in 2 mL of H_2O led also to formation of the title compound between 3 h and 7 d with comparable yields.

Syntheses were also performed by adding 2 mL of H_2O to a mixture of 72.0 mg (0.1 mmol) [Mn(terpy)_2](ClO_4)_2 and 96.2 mg (0.2 mmol) Na_3SbS_3·9H_2O which were deposited in a glass tube. The tube was sealed and heated to 140 °C with reaction times between 6 h and 7 d. The yields ranged between 12 % (6 h) and 28 % (7 d). Using a mixture of 36.2 mg (0.1 mmol) Mn(ClO_4)_2·6H_2O, 46.7 mg (0.2 mmol) terpy and 96.2 mg (0.2 mmol) Na_3SbS_3·9H_2O with 2 mL of H_2O afforded crystallization of the title compound after 8 d (T = 140 °C; yield: 10 %). Extending the time to 16 d the yield increased to about 79 %.

**Conclusions**

We demonstrated that the title compound can be synthesized applying different synthetic routes. A fast reaction was observed using Na_3SbS_3, the Mn^{2+} salt and terpy and a phase pure sample is formed after 3 h. Longer reaction times led to appearance of a side-product. Using Na_3SbS_3·9H_2O, a Mn^{2+} salt and terpy a reaction time of 16 d was necessary until a nearly phase pure sample could be obtained. Some of the differences observed for Na_3SbS_3 and Na_3SbS_3·9H_2O can be explained with the fact that the latter sample contains Sb(V) which must be reduced to Sb(III) during chemical reactions. The crystal structure features interconnected MnSb_4S_5 rings with a 1D network topology significantly different from all other thioantimonate compounds containing the [Sb_2S_4]^{2-} anion, demonstrating the pronounced flexibility of thioantimonate(III) structures. Characterization of the magnetic properties evidences a pronounced magnetocaloric effect, which is comparable to examples reported in literature. Analysis of the luminescence spectra demonstrate that both Mn^{2+} and terpy contribute to the luminescence properties of the title compound.
Luminescence measurements: The emission and excitation spectra were recorded at room temperature in quartz ampoules, using a FL3–22 Fluorolog-3 fluorescence spectrometer (HORIBA Jobin Yvon GmbH, Unterhaching, Germany), equipped with a R928P Photomultiplier and a 450 W xenon lamp.

Supporting Information (see footnote on the first page of this article): Crystal data and refinement results; powder X-ray diffraction patterns of the title compound; distances and angles; X-ray powder patterns of the pristine samples and the raw products; infrared spectrum of the title compound; graph of a TG analysis of the title compound.

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