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Solvothermal Synthesis, Crystal Structure, and Properties of the First Zinc Containing Thioantimonate(III) $[Zn(\textit{tren})]_2Sb_4S_8 \cdot 0.75\ H_2O$

Michael Schaefer, Christian Näther, and **Wolfgang Bensch***

Institut für Anorganische Chemie der Christian-Albrechts-Universität Kiel, D-24098-Kiel, Germany

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Summary. Yellow crystals of the title compound were obtained under solvothermal conditions reacting elemental Zn, Sb, and S in a solution of tris(2-aminoethyl)amine (= *tren*) and water. The compound crystallises in the monoclinic space group $P2_1/c$ with $a = 13.0247(7)$, $b = 22.308(2)$, $c = 12.1776(6)$ Å, and $\beta = 105.352(6)°$. In the structure of $[Zn(\textit{tren})]_2Sb_4S_8 \cdot 0.75\ H_2O$ two $[Zn(\textit{tren})]^{2+}$ cations are bound to the $[Sb_4S_8]^{4-}$ anion via S atoms. The Zn^{2+} ions are in a trigonal bipyramidal environment of four N atoms of the tetradentate *tren* ligand and one S atom of the $[Sb_4S_8]^{4-}$ anion. The anion is formed by SbS_3 and SbS_4 units which share common corners and edges. The interconnection mode yields three different non-planar Sb_2S_2 heterorings. The shortest intermolecular Sb–S distance amounts to about 3.7 Å, and taking this long separation into account undulated chains running along [001] are formed with the water molecules residing in the pocket-like cavities. Upon heating the compound decomposes in one step starting at about 240°C. The final decomposition product was identified as ZnS and Sb_2S_3 by X-ray powder diffractometry. Additionally, spectroscopic data as well as synthetic procedures for $[Zn(\textit{tren})]_2Sb_4S_8 \cdot 0.75\ H_2O$ are reported.

Keywords. Thioantimonates; Solvothermal synthesis; Crystal structure; Physical properties.

Introduction

The thioantimonates(III) are an attractive group of compounds because different degrees of condensation and dimensionalities are observed [1–10]. Many thioantimonates(III) are synthesised under solvothermal conditions applying amines as solvents and structure directing molecules. A few years ago we started investigations whether transition metal cations (TM^{n+}) can be incorporated into the thioantimonate(III) networks with the final goal to enhance the structural diversity and to modify

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* Corresponding author. E-mail: wbensch@ac.uni-kiel.de

the physical properties. The main problem is that the overwhelming number of amines form very stable isolated [*TM*(amine)]$^{n+}$ cations which cannot form bonds to the S atoms of the thioantimonate(III) anions. There are two different approaches which may overcome this problem. One way is to choose cations like Mn^{2+} or Fe^{2+} that have a comparable affinity to S and N atoms. Using Mn we successfully synthesised a series of compounds with the general formula $Mn_2Sb_2S_5 \cdot L$ ($L = 2$ ethylamine, 2 methylamine, 2 ethylenediamine, 1,3-diaminopropane) [10–12]. In these compounds one of the unique Mn^{2+} ions is coordinated by six S atoms and the second by four S and two N atoms. Despite the more than 60 fold excess of the amine with respect to S the Mn^{2+} cations form bonds to both the S and N atoms reflecting the similar affinity of this cation to these two atoms. The concept of "similar affinity" does not work for other TM^{n+} ions. Therefore, a different strategy must be chosen. This strategy relies on the electronic configuration of the transition metal cation and the sterical requirements of a suitable amine which both forces that the [*TM*(amine)]$^{n+}$ complex has free coordination sites to form bonds to the S atoms of the thioantimonate network. Simply, applying a tetradentate amine and Ni^{2+} with the d^8 electronic configuration the Ni^{2+} ion prefers an octahedral environment and the geometrical requirements of the amine let two positions at the Ni^{2+} free for bond formation to S atoms of the thioantimonate. For Co^{2+} with a d^7 configuration the octahedral and trigonal bipyramidal environment is energetically comparable. Hence, the steric demands of the amine forces whether the former or latter coordination is adopted by Co^{2+}. Using the tetradentate ligand tris(2-aminoethyl)amine (= *tren*) we synthesised several new TM^{n+} containing thioantimonates like $Co(C_6H_{18}N_4)]_2Sb_4S_8$ [13], $[Co(C_6H_{18}N_4)]_2Sb_2S_5$ [13], $[Co(C_6H_{18}N_4)]Sb_2S_4$ [14], $[Ni(C_6H_{18}N_4)]Sb_2S_4$ [14], and $[Fe(C_6H_{18}N_4)]_2FeSbS_4$ [15] demonstrating that our synthesis strategy works. Very recently, we presented that TM^{n+} containing thioantimonates(III) exhibit an interesting thermal behaviour [16]. Starting with an amine rich Mn-thioantimonate(III) the directed thermal decomposition yields an amine poorer compound. This is a new synthetic route which was established for coordination polymers [17–20]. Until now no investigations were reported with TM^{2+} ions with a d^{10} electronic configuration. We note that in antimony sulfosalts elements like Zn are present besides other transition metals as Ag, Fe, and Cu.

Based on the ideas presented above we explored the Zn–Sb–S system applying *tren* as the amine ligand. Here we report on the synthesis and properties of the first Zn thioantimonate(III), [Zn(*tren*)]$_2Sb_4S_8 \cdot 0.75\ H_2O$.

Results and Discussion

The new compound [Zn(*tren*)]$_2Sb_4S_8 \cdot 0.75\ H_2O$ (*tren* = tris(2-aminoethyl)amine) crystallises in the monoclinic space group $P2_1/c$ with four formula units in the unit cell (Table 1). All atoms are located on general positions. The primary building units are distorted ZnN_4S trigonal bipyramids, SbS_3 trigonal pyramids, and SbS_4 units. Both crystallographically independent Zn atoms are in a distorted trigonal bipyramidal environment (ZnN_4S) of the four N atoms of the *tren* ligand and one S atom from the thioantimonate(III) anion (Fig. 1).

The Zn–S distances of 2.385(1) Å for Zn(1)–S(1) and 2.381(1) Å for Zn(2)–S(8) are nearly equal and are similar to those reported in the literature [21].

Table 1. Technical details of data acquisition and selected refinement results for $[Zn(\mathit{tren})]_2Sb_4S_8 \cdot 0.75\ H_2O$

space group	$P2_1/c$
a/Å	13.0247(7)
b/Å	22.308(2)
c/Å	12.1776(6)
β/°	105.352(6)
V/Å^3	3412.0(3)
Z	4
T/K	293
μ/mm^{-1}	5.02
MM/g · mol^{-1}	1178.71
density (calc.)/g · cm^{-3}	2.295
2θ range/°	5–54
data collected	29718
unique data	7072
data ($F_o > 4.0\ \sigma(F_o)$)	5831
R_{int}	0.0334
$\Delta\rho$ [e/Å^3]	−0.71/0.77
$R1$ ($F_o > 4.0\ \sigma(F_o)$)[a]	0.0270
$wR2$ (all data)[b]	0.0650
Goodness of Fit	1.078

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; [b] $wR2 = [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o{}^2) + (y \cdot P)^2 + z \cdot P]$, $P = (\mathrm{Max}(F_o{}^2, 0) + 2 \cdot F_c{}^2)/3$, $y = 0.0367$, $z = 1.2288$

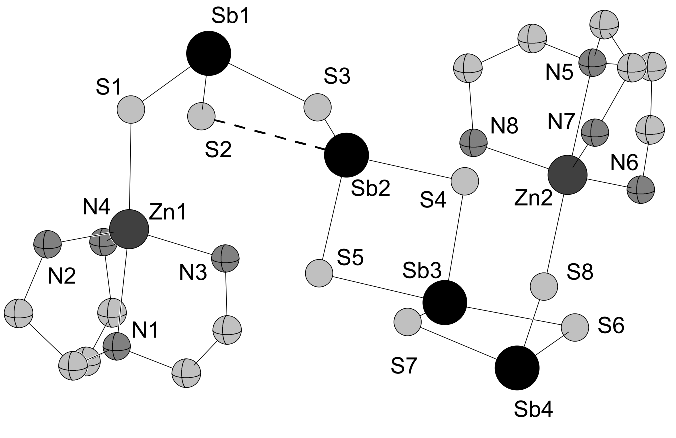

Fig. 1. View of $[Zn(\mathit{tren})]_2Sb_4S_8 \cdot 0.75\ H_2O$ with labelling; the long Sb(2)–S(2) bond of about 3 Å is shown as dotted line; the disordered atoms, the hydrogen atoms, and the oxygen atoms are omitted for clarity

The Zn–N bond lengths vary between 2.062(4) and 2.344(3) Å and are in the range reported for Zn-*tren* complexes except for the longer distances [22–25]. The longer Zn–N bonds (Zn(1)–N(1) = 2.318(3) Å and Zn(2)–N(5) = 2.344(3) Å) are in *trans* position to the Zn–S bonds (Table 3). The angles around the Zn atoms deviate from

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[\mathrm{Zn}(\mathit{tren})]_2\mathrm{Sb}_4\mathrm{S}_8 \cdot 0.75\ \mathrm{H_2O}$

	x	y	z	U_{eq}
Zn(1)	−808(1)	6055(1)	5061(1)	31(1)
Zn(2)	6294(1)	5455(1)	6831(1)	32(1)
Sb(1)	439(1)	5479(1)	8225(1)	36(1)
Sb(2)	2358(1)	6736(1)	8509(1)	42(1)
Sb(3)	3885(1)	7407(1)	6736(1)	44(1)
Sb(4)	5276(1)	6853(1)	4711(1)	41(1)
S(1)	−662(1)	5244(1)	6370(1)	42(1)
S(2)	79(1)	6501(1)	8462(1)	48(1)
S(3)	2161(1)	5699(1)	7795(1)	45(1)
S(4)	4282(1)	6712(1)	8324(1)	50(1)
S(5)	1875(1)	7312(1)	6776(1)	44(1)
S(6)	6012(1)	7312(1)	6513(1)	54(1)
S(7)	3524(1)	6724(1)	5107(1)	53(1)
S(8)	5927(1)	5835(1)	4940(1)	41(1)
N(1)	−1089(2)	6759(1)	3611(2)	30(1)
C(1)	−12(3)	6951(2)	3582(3)	37(1)
C(2)	751(3)	6426(2)	3824(3)	37(1)
N(2)	−1953(3)	5620(2)	3763(3)	46(1)
C(3)	−1666(3)	6456(2)	2558(3)	40(1)
C(4)	−2453(4)	6009(2)	2790(3)	48(1)
N(3)	727(3)	6148(2)	4920(3)	40(1)
C(5)	−1707(3)	7244(2)	3946(3)	40(1)
C(6)	−1373(4)	7331(2)	5227(4)	46(1)
N(4)	−1416(3)	6758(2)	5808(3)	41(1)
N(5)	6700(3)	5015(2)	8643(3)	39(1)
C(7)	7534(4)	5389(2)	9359(4)	52(1)
C(8)	7375(4)	6043(2)	9023(4)	56(1)
N(6)	7276(3)	6099(2)	7794(3)	46(1)
C(9)	7030(6)	4399(2)	8523(4)	71(2)
C(10)	7541(8)	4327(4)	7582(9)	47(2)
C(10′)	6968(15)	4180(6)	7453(11)	54(4)
N(7)	6936(3)	4631(2)	6532(3)	46(1)
C(11)	5703(4)	5043(2)	8991(3)	47(1)
C(12)	4741(4)	4967(2)	8004(4)	47(1)
N(8)	4784(3)	5378(2)	7069(3)	46(1)
O(1)	403(7)	6390(3)	1134(5)	69(2)
O(2)	5492(12)	6311(5)	10811(10)	58(4)

The equivalent isotropic displacement parameter U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor

the ideal value of a trigonal bipyramidal environment and spread from 78.6(1) to 175.77(8)°. The Zn(1) atom is 0.3793 Å above the plane formed by N(2), N(3), and N(4), and Zn(2) lies 0.4020 Å above the plane built by N(6), N(7), and N(8). The Sb(1), Sb(2), and Sb(4) atoms are coordinated by three S atoms to form trigonal pyramids whereas Sb(3) has four S atoms as nearest neighbours. The $[\mathrm{Sb_4S_8}]^{4-}$

anion is constructed in the following way: In the central part of the anion the $Sb(2)S_3$ pyramid shares a common edge with the $Sb(3)S_4$ unit forming a Sb_2S_2 heteroring. The $Sb(2)S_3$ moiety shares one S atom with the $Sb(1)S_3$ unit, and finally the $Sb(3)S_4$ moiety is joined to the $Sb(4)S_3$ unit via a common edge to form a second Sb_2S_2 heteroring. The rings are not planar with mean deviations from the least-squares planes of 0.0787 Å (Sb(2)–S(4)–S(5)–Sb(3)) and 0.1409 Å (Sb(3)–S(6)–S(7)–Sb(4)). The angle between the two planes amounts to 68.2° (Fig. 1). The terminal S atoms of the anion (S(1) and S(8)) each have a bond to the Zn^{2+} ions.

The Sb–S distances in the SbS_3 pyramids range from 2.361(1) to 2.574(1) Å and are typical for Sb–S single bonds [1–5, 7, 10–16]. Interestingly, the $Sb(3)S_4$ unit has two short bonds (2.425(1), 2.446(1) Å) and two relatively long separations of 2.638(1) and 2.863(1) Å, respectively. We note that the two long Sb–S distances are nearly *trans* to each other (see Table 3). The SbS_4 unit with two short and two longer Sb–S distances is not uncommon and is often found in thioantimonates(III) exhibiting different compositions and dimensionalities [26–28].

The S–Sb–S angles are between 81.93(4) and 170.18(3)°. The structure becomes more complex when secondary Sb–S bonds up to 3.8 Å are considered. The Sb(1) atom has one contact to S(2) of 3.000(1) Å forming a SbS_4 unit. Considering this long distance as a weak bond another Sb_2S_2 heteroring may be identified (mean deviation from least-squares plane: 0.1498 Å; angle to the Sb(2)–S(4)–S(5)–Sb(3) plane: 67.2°; angle to the Sb(3)–S(6)–S(7)–Sb(4) plane: 135.3°). If the long Sb(4)–S(4a) separation of 3.691(1) Å is treated as a weak contact the individual molecules are interconnected into an undulated chain which is directed along [001] (Fig. 2). The arrangement of the undulated chains yields pocket-like

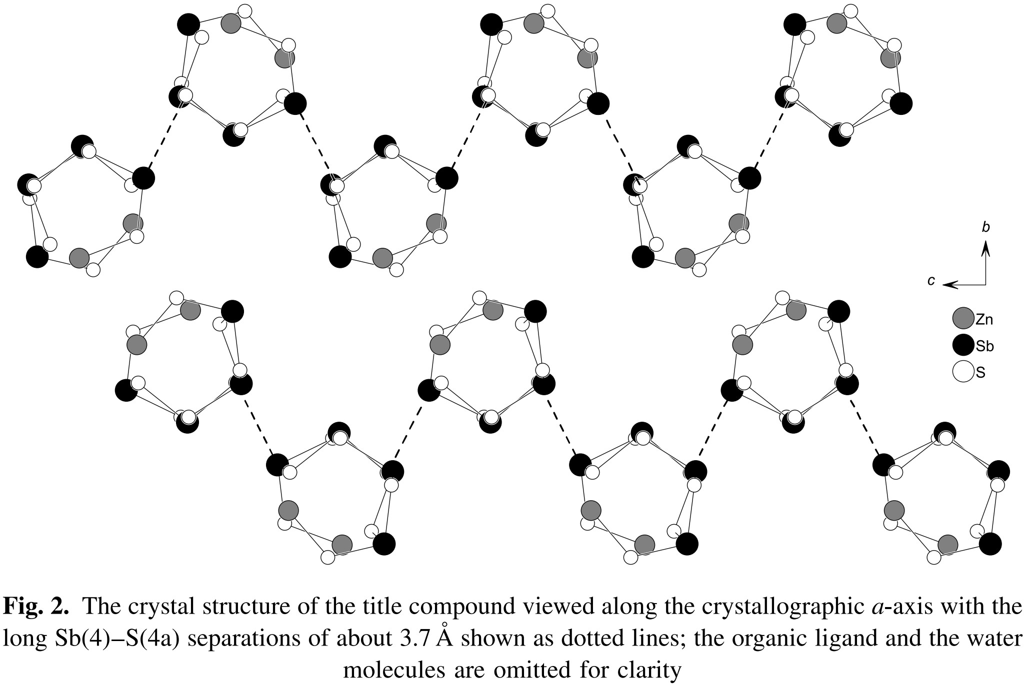

Fig. 2. The crystal structure of the title compound viewed along the crystallographic *a*-axis with the long Sb(4)–S(4a) separations of about 3.7 Å shown as dotted lines; the organic ligand and the water molecules are omitted for clarity

Table 3. Selected distances (Å) and angles (°) for $[\mathrm{Zn}(\mathit{tren})]_2\mathrm{Sb}_4\mathrm{S}_8 \cdot 0.75\ \mathrm{H}_2\mathrm{O}$

Sb(1)–S(1)	2.391(1)	Sb(1)–S(2)	2.361(1)
Sb(1)–S(3)	2.484(1)	Sb(2)–S(2)	3.000(1)
Sb(2)–S(3)	2.461(1)	Sb(2)–S(4)	2.574(1)
Sb(2)–S(5)	2.408(1)	Sb(3)–S(4)	2.425(1)
Sb(3)–S(5)	2.638(1)	Sb(3)–S(6)	2.863(1)
Sb(3)–S(7)	2.446(1)	Sb(4)–S(4)[a]	3.691(1)
Sb(4)–S(6)	2.381(1)	Sb(4)–S(7)	2.471(1)
Sb(4)–S(8)	2.415(1)		
Zn(1)–S(1)	2.385(1)	Zn(2)–S(8)	2.381(1)
Zn(1)–N(1)	2.318(3)	Zn(1)–N(2)	2.101(3)
Zn(1)–N(3)	2.062(4)	Zn(1)–N(4)	2.072(3)
Zn(2)–N(5)	2.344(3)	Zn(2)–N(6)	2.070(4)
Zn(2)–N(7)	2.089(3)	Zn(2)–N(8)	2.071(4)
S(1)–Sb(1)–S(2)	103.80(4)	S(1)–Sb(1)–S(3)	101.14(4)
S(2)–Sb(1)–S(3)	93.15(4)	S(3)–Sb(2)–S(4)	87.86(4)
S(3)–Sb(2)–S(5)	102.32(4)	S(4)–Sb(2)–S(5)	88.21(4)
S(4)–Sb(3)–S(5)	86.41(4)	S(4)–Sb(3)–S(6)	91.21(4)
S(4)–Sb(3)–S(7)	101.72(5)	S(5)–Sb(3)–S(6)	170.18(3)
S(5)–Sb(3)–S(7)	89.23(4)	S(6)–Sb(3)–S(7)	81.93(4)
S(6)–Sb(4)–S(8)	104.75(4)	S(6)–Sb(4)–S(7)	92.16(4)
S(7)–Sb(4)–S(8)	100.48(4)		
N(1)–Zn(1)–N(2)	78.6(1)	N(1)–Zn(1)–N(3)	80.2(1)
N(1)–Zn(1)–N(4)	79.6(1)	N(2)–Zn(1)–N(3)	119.7(2)
N(2)–Zn(1)–N(4)	113.7(2)	N(3)–Zn(1)–N(4)	116.9(2)
N(1)–Zn(1)–S(1)	172.44(8)	N(2)–Zn(1)–S(1)	93.9(1)
N(3)–Zn(1)–S(1)	102.99(9)	N(4)–Zn(1)–S(1)	104.59(9)
N(5)–Zn(2)–N(6)	78.8(1)	N(5)–Zn(2)–N(7)	78.2(1)
N(5)–Zn(2)–N(8)	79.6(1)	N(6)–Zn(2)–N(7)	119.6(2)
N(6)–Zn(2)–N(8)	116.4(2)	N(7)–Zn(2)–N(8)	113.0(2)
N(6)–Zn(2)–S(8)	103.7(1)	N(8)–Zn(2)–S(8)	102.1(1)
N(7)–Zn(2)–S(8)	97.6(1)	N(5)–Zn(2)–S(8)	175.77(8)
Zn(1)–S(1)–Sb(1)	112.78(4)	Zn(2)–S(8)–Sb(4)	114.90(4)

[a] Symmetry code: *x*, 1.5-*y*, *z*-0.5

cavities where the water molecules are located. Several short S···N separations (Table 4) indicate hydrogen bonding which may contribute to the stability of the compound despite the fact that S···H bonds are weak.

Table 4. Hydrogen bond parameters for $[\mathrm{Zn}(\mathit{tren})]_2\mathrm{Sb}_4\mathrm{S}_8 \cdot 0.75\ \mathrm{H}_2\mathrm{O}$

D–H	*A*	*d*(*D*–H)	*d*(H···*A*)	<*DHA*	*d*(*D*···*A*)	
N3–H1N3	S5	0.900	2.638(3)	162.16(0)	3.506(6)	
N4–H2N4	S2	0.900	2.493(8)	159.95(0)	3.352(1)	
N6–H1N6	S2	0.900	2.877(5)	142.98(1)	3.637(5)	[*x* + 1, *y*, *z*]
N6–H2N6	S6	0.900	2.453(4)	165.16(1)	3.331(4)	
N8–H1N8	S4	0.900	2.620(1)	161.27(0)	3.485(2)	

Compounds with general composition [*TM*(amine)]$_2$Sb$_4$S$_8$ are very rare and to the best of our knowledge only three examples exist. In [Ni(*dien*)$_2$]$_2$Sb$_4$S$_8$ (*dien* = diethylenetriamine) the two crystallographically independent [Ni(*dien*)$_2$]$^{2+}$ cations and the two crystallographically independent [Sb$_4$S$_8$]$^{4-}$ anions are isolated [29]. The [Sb$_4$S$_8$]$^{4-}$ anions are formed by the interconnection of four pyramidal SbS$_3$ units sharing common corners. The main feature of the anions is a Sb$_4$S$_4$ heteroring in a chair-like conformation. An isolated [Sb$_4$S$_8$]$^{4-}$ ring anion is also found in [Mn(*pn*)$_3$]$_2$Sb$_4$S$_8$ $\cdot$ 2 H$_2$O (*pn* = 1,2-diaminopropane) [30]. A comparable anionic part to the presented compound is found in [Co(*tren*)]$_2$Sb$_4$S$_8$ where the [Sb$_4$S$_8$]$^{4-}$ anions are bound to the [Co(*tren*)]$^{2+}$ cations through the terminal S atoms [13]. The [Sb$_4$S$_8$]$^{4-}$ anions are also constructed from SbS$_3$ and SbS$_4$ units by sharing common corners and edges forming three Sb$_2$S$_2$ heterorings. We note that the conformations of the [Sb$_4$S$_8$]$^{4-}$ anions in the Zn and Co compound are quite different. In the latter compound the mean root square deviations from planarity amount to 0.1132 and 0.2701 Å in the two crystallographically independent molecules with angles between the Sb$_2$S$_2$ rings of 110.6 and 115.8°, respectively. Due to symmetry reasons one ring in each molecule of [Co(*tren*)]$_2$Sb$_4$S$_8$ is planar. The mean deviations from the best planes as well as the angles between the Sb$_2$S$_2$ are significantly larger than in the Zn thioantimonate.

In the Raman spectra intensive bands are located between 375 and 319 cm^{-1} (Fig. 3). The strongest resonance at 356 cm^{-1} may be due to the Zn–S symmetric stretch vibration. The assignment of the other resonances is not straightforward, but according to the literature the band located at 375 cm^{-1} could be assigned to the Sb(1,4)S$_3$ units [14, 31]. The resonance with lower frequency at 319 cm^{-1} is due to the Sb(3)S$_4$ unit. The other absorption at 346 and 338 cm^{-1} may be caused by the Sb(2)S$_3$ unit which has an elongated bond to S(2) with 3 Å.

Figure 4 shows the DTA-TG-DTG curves recorded during thermal decomposition of the sample. Just above 125°C decomposition starts which may be caused by

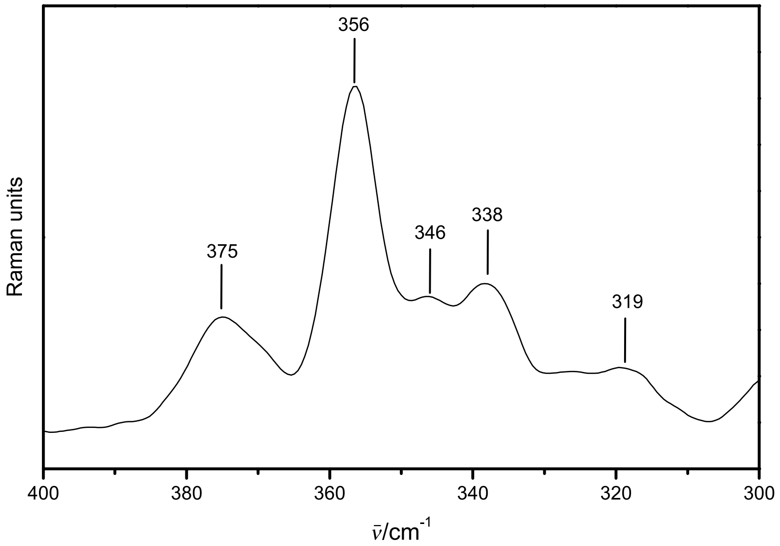

Fig. 3. Raman spectra of [Zn(*tren*)]$_2$Sb$_4$S$_8$ $\cdot$ 0.75 H$_2$O

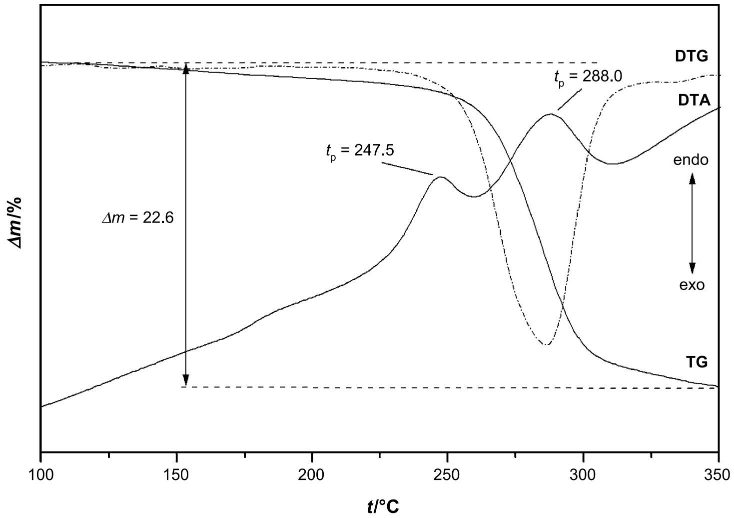

Fig. 4. DTA-TG-DTG curves of [Zn(*tren*)]$_2$Sb$_4$S$_8$ · 0.75 H$_2$O obtained in nitrogen atmosphere with a heating rate of 4 K/min; t_p are the peak temperatures in °C and the weight loss is given in %

the removal of the water molecules. A strong weight loss starts at about 240°C and extends up to 350°C. At the beginning of the weight change an endothermic event is seen in the DTA curve with a peak temperature $t_p = 247$°C. A second endothermic signal follows at $t_2 = 288$°C (Fig. 4). The DTG curve gave no hints for a two step reaction and hence the nature of the first endothermic event is not clear. The total weight loss amounts to 22.6% and is lower than expected for the removal of only two *tren* molecules and the water molecule (26.0%). But in the grey residue a total of 3.9% of C and N was found explaining the difference. In the X-ray powder pattern ZnS and Sb$_2$S$_3$ could be unambiguously identified. Formally, the decomposition of [Zn(*tren*)]$_2$Sb$_4$S$_8$ · 0.75 H$_2$O may be described by the equation: [Zn(*tren*)]$_2$Sb$_4$S$_8$ · 0.75 H$_2$O → 2 ZnS + 2 Sb$_2$S$_3$ + 0.75 H$_2$O + 2 tren.

Experimental

Physical Methods

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 Al$_2$O$_3$ crucibles under a dynamic nitrogen atmosphere (flow rate: 75 cm^3/min, purity: 5.0; sample weight: 12.6 mg). Raman spectra were measured in the region from $\bar{\nu} = 100$ to 3500 cm^{-1} with a Bruker IFS 66 Fourier transform Raman spectrometer. The X-ray powder patterns were recorded on a STOE Stadi-P diffractometer (Cu-K$_{\alpha 1}$ radiation, $\lambda = 1.540598$ Å) in transmission geometry. The elemental analysis was performed using an EuroEA Elemental Analyser from Eurovector and the EDX spectra were measured with an Environmental Scanning Electron Microscope ESEM XL30 from Philips being equipped with an EDAX microanalysis system.

Synthesis

Yellow coloured square-like crystals of [Zn(*tren*)]$_2$Sb$_4$S$_8$ · 0.75 H$_2$O were synthesised from elemental Zn (65.38 mg, 1 mmol), Sb (121.75 mg, 1 mmol) and S (80 mg, 2.5 mmol) in an aqueous solution of

50% *tren* (5 cm^3; 16.7 mmol). The mixture was heated to 140°C for 7 days in a Teflon-lined steel autoclave ($\sim$30 cm^3) and cooled within 3 h to room temperature. The product was filtered off, washed with acetone, and stored under vacuum. The yield based on Zn is about 35%. Besides the title compound an unknown amorphous phase and crystalline Sb were observed. The EDX analysis of $[\mathrm{Zn}(tren)]_2\mathrm{Sb}_4\mathrm{S}_8 \cdot 0.75\ \mathrm{H_2O}$ gave a Zn:Sb:S ratio of 1:2.08:3.97. C, H, N, S analysis: calc.: C 12.23, H 3.08, N 9.51, S 21.77%; found: C 11.85, H 3.15, N 9.03, S 20.98%.

Crystallography

The intensity data were collected with an Image Plate Diffraction System (Fa. STOE). The raw intensities were treated in the usual way and were corrected for absorption effects using X-Red [32] and X-Shape [33]. The structure was solved with direct methods using SHELXS-97 [34] and structure refinement was performed against F^2 using SHELXL-97 [35]. All non-hydrogen atoms were refined anisotropically. The C(10) atom is disordered over two positions and was refined using a split model with anisotropic displacement parameters and varying site occupation factors of 60:40%. Both crystallographic independent O atoms were refined anisotropically with site occupation factors of 50% for O(1) and 25% for O(2). The hydrogen atoms were positioned with idealised geometry and refined with individual isotropic displacement parameters using the riding model. The O–H hydrogen atoms were not considered. Crystal data, results of the structure refinement, as well as lists with atomic coordinates, bond lengths, and angles are found in Tables 1, 2, 3, and 4.

The supplementary material has been sent to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, as supplementary material No. CCDC 215365 and can be obtained by contacting the CCDC (quoting the article details and the corresponding CCDC number).

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