

Solvothermal Syntheses and Characterization of Three Lanthanide Thioantimonates(V) with Mixed Ethylene Polyamines

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Three new lanthanide thioantimonates(V) $[Ln(en)(teta)(SbS_4)]$ $\{Ln = Sm$ (**1**), Eu (**2**), Gd (**3**); en = ethylenediamine; $teta$ = triethylenetetramine $\}$ have been solvothermally synthesized and structurally characterized. Compounds **1–3** are isostructural. The $[SbS_4]^{3-}$ anion acting as bichelating ligand is bound to the $[Ln(en)(teta)]^{3+}$ ion, resulting in a neutral complex $[Ln(en)(teta)(SbS_4)]$. The central Ln^{3+} ion lies within an eight-coordinate environment forming a distorted bicapped trigonal prism LnN_6S_2 . Although a few lanthanide thioantimonates have been reported to date, they only contain one type of ethylene polyamine. Compounds **1–3** are rare examples of lanthanide thioantimonates with mixed ethylene polyamine ligands. The absorption edges of 1.75 eV for **1** and 2.27 eV for **3** have been derived from optical absorption spectra.

Key words: Lanthanide, Thioantimonates, Complex, Solvothermal Syntheses, Crystal Structure

Introduction

The incorporation of transition metal (*TM*) or lanthanide (*Ln*) ions into group 13–15 chalcogenidometalate frameworks under solvothermal conditions has received much attention, because it may generate various exciting structural architectures with interesting properties [1–9]. Since Kanatzidis *et al.* reported the first thioantimonate $[Co(en)_3][CoSb_4S_8]$ [10], where parallel $[SbS_2]^-$ chains are linked by tetrahedrally coordinated Co(II) atoms into $[CoSb_4S_8]^{2-}$ layers, a large number of the anionic $[Sb_xS_y]^{z-}$ frameworks incorporating *TM* ions through *TM*–S bonds have been obtained by solvothermal methods, as exemplified by $[Cr(en)_2SbS_3]$ [11], $[Cr(teta)(SbS_3)]$ [12], $[Fe(tren)]FeSbS_4$ [13], $[Fe(dien)_2]Fe_2Sb_4S_{10}$ [13], $[TM(tren)]Sb_4S_7$ (*TM* = Mn, Fe, Co, Zn) [14], $[Mn(tren)]_2Sb_2S_5$ [15], $[Mn(tren)]_2Mn_2Sb_4S_{10}$ [15], $[Mn(tren)]_4Mn_2Sb_4S_{12}$ [16], $(H_2dien)_{0.5}Cu_2SbS_3$ [17], $(Hdien)Cu_3Sb_2S_5$ [17], $(H_2teta)_{0.5}Cu_3Sb_2S_5$ [17], $[Hen][Ag_2SbS_3]$ [18], and $[Hen]_2[Ag_5Sb_3S_8]$ [18], where segmental or whole *TM* ions are encapsulated within the thioantimonate anions. However, the thioantimonates incorporating Ln^{3+} ions prepared under solvothermal conditions are still a less

explored area [18–24], because they are comparatively unstable with respect to heat, water, oxygen, and light. Moreover, the soft Lewis-basic S^{2-} ligand coordinates with difficulty to the hard Lewis-acidic Ln^{3+} ions via *Ln*–S bonds in solvents. More recently, we have attempted the preparation of lanthanide thioantimonates in chelating amine solutions by the solvothermal method and prepared the organic hybrid lanthanide thioantimonates $[Eu(dien)_2SbS_3]$ [25], $\{[Eu(dien)_2]_2(\mu_4-Sb_2S_5)\} Cl_2$ [25], $\{[Eu(teta)]_2[\mu_2-SbS_3](\mu_2-H_2O)\} [Eu(teta)In_4S_9] \cdot 0.25teta$ [3], $[Sm_4(teta)_4(\mu-\eta^2, \eta^3-Sb_3S_7)_2(\mu-Sb_2S_4)]$ [26], $[Eu_2(teta)_2(\mu-SbS_3)(\mu-OH)]_2(SbS_4)(OH) \cdot H_2O$ [26], $\{[Ln(teta)]_2[\mu_2-Sb^{III}S_3](\mu_2-OH)\}_2\{[Ln(teta)]_2(\mu_2-OH)_2(Sb^VS_4)_2\} Cl_2$ (*Ln* = Y, Eu, Er) [27], and $[Gd_2(teta)_2(\mu_2-OH)_2(\mu_2-SbS_4)]Cl \cdot 0.25H_2O$ [27], where the typical soft base-donor ligands $[SbS_3]^{3-}$, $[SbS_4]^{3-}$, $[Sb_2S_5]^{4-}$, $[Sb_3S_7]^{5-}$, and $[Sb_2S_4]^{2-}$ are bound to the hard Lewis-acidic Ln^{3+} ions. Notably, the reported transition metal or lanthanide thioantimonates generally contain only one type of ethylene polyamine, but mixed ethylene polyamines acting as ligands or structure-directing agents are relatively rare, the only example being the 1-D lanthanide thioantimonate $La(teta)(en)(\mu-\eta^1, \eta^2-SbS_4)$ [28], which is

constructed from $[\mu-\eta^1, \eta^2-\text{Sb}^{\text{V}}\text{S}_4]^{3-}$ tetrahedra and the complex cations $[\text{La}(\text{teta})(\text{en})]^{3+}$. In this paper, we report the solvothermal syntheses and crystal structures of three lanthanide thioantimonates(V) with mixed ethylene polyamines as ligands.

Results and Discussion

The lanthanide thioantimonates(V) $[\text{Ln}(\text{en})(\text{teta})(\text{SbS}_4)]$ $\{\text{Ln} = \text{Sm}$ (**1**), Eu (**2**), Gd (**3**); en = ethylenediamine; teta = triethylenetetramine $\}$ are isostructural and crystallize in the monoclinic space group $P2_1/c$ with four formula units in the unit cell. Therefore, only **1** is discussed here in detail. The molecular structure of **1** is depicted in Fig. 1a. The $[\text{SbS}_4]^{3-}$ anion acts as bichelating ligand bound to the $[\text{Sm}(\text{en})(\text{teta})]^{3+}$ ion leading to a neutral complex $[\text{Sm}(\text{en})(\text{teta})(\text{SbS}_4)]$. The Sm^{3+} ion is in an eight-coordinate environment with four N atoms of one teta ligand, two N atoms of one en ligand and two S atoms of one $[\text{SbS}_4]^{3-}$ ion to give a distorted bicapped trigonal prism (Fig. 1b). The $\text{Sm}-\text{N}$ bond lengths are 2.536(12)–2.590(2) Å, and the $\text{Sm}-\text{S}$ bond lengths are 2.866(4)–2.9016(8) Å, comparable to those in other reported lanthanum thioantimonates with amino ligands [26, 27]. Each $\text{Sb}(\text{V})$ ion is surrounded by four S^{2-} ions to form a distorted $[\text{SbS}_4]$ tetrahedron, which is manifested by the $\text{S}-\text{Sb}-\text{S}$ angles deviating from the ideal value of 109.5° . The coordination of the $[\text{SbS}_4]^{3-}$ anion to the Sm^{3+} ion is much influenced by the mixed ethylene polyamines used in the syntheses. The reaction of Sb and S with Ln_2Cl_3 in teta yielded ionic complexes $[\text{Ln}(\text{teta})_2]\text{SbS}_4$ $[\text{Ln} = \text{Eu}, \text{Gd}, \text{Er}]$ [27], where $[\text{SbS}_4]^{3-}$ exists as a discrete ion not coordinated to the metals. The Ln^{3+} ions are coordinated by two teta ligands to form coordinatively saturated eight-coordinate complexes $[\text{Ln}(\text{teta})_2]^{3+}$, which have no opportunity to be further connected to the $[\text{SbS}_4]^{3-}$ ions, while in **1**, **2** and **3** the coordinatively unsaturated complexes $[\text{Ln}(\text{en})(\text{teta})]^{3+}$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$) containing two additional coordination sites at the Ln^{3+} ions are able to form two bonds to the S atoms of an $[\text{SbS}_4]^{3-}$ ion. Notably, the La^{3+} ionic radius is larger than that of the Ln^{3+} ions ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$), leading to an even larger coordination sphere of the central metal. For instance, the La^{3+} cation in $[\text{La}(\text{en})(\text{teta})(\text{SbS}_4)]$ [28] is nine-coordinated forming bonds to three S atoms of $[\text{SbS}_4]^{3-}$ anions in addition to the amine N atoms. As a consequence, this complex is not isostructural with

the complexes **1**, **2** and **3** despite an analogous composition.

Even more interestingly, the ionic radius of trivalent Gd^{3+} (0.938 Å) is slightly smaller than that of the Eu^{3+} ion (0.950 Å) [29], which might result in a more compact $[\text{Gd}(\text{en})(\text{teta})]^{3+}$ cation leaving less space for the coordination of the $[\text{SbS}_4]^{3-}$ anions. This difference might account for the observation that the $\text{Gd}\cdots\text{Sb}$ distance [3.753(1) Å] is slightly longer than the $\text{Eu}\cdots\text{Sb}$ distance [3.746(1) Å], which also leads to a slightly larger cell volume of **3** of 1910.5(7) Å³ as compared to 1901.9(7) Å³ of **2**. In any case these differences are at the margin of significance and probably not too much importance should be given to them.

In **1**, the uncoordinated S atoms of $[\text{Sm}(\text{en})(\text{teta})(\text{SbS}_4)]$ are involved in intermolecular $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds with adjacent molecules, leading to a chain-like arrangement of $[\text{Sm}(\text{en})(\text{teta})(\text{SbS}_4)]$ molecules parallel to the a axis. These chains are aligned in an antiparallel fashion and connected *via*

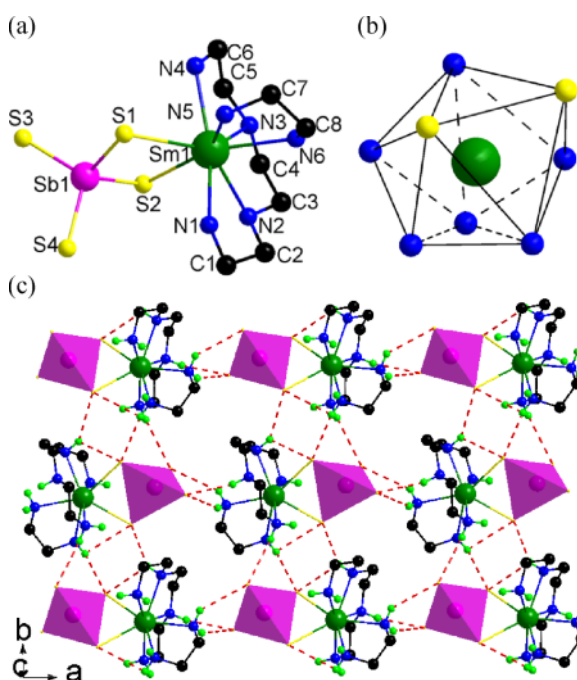


Fig. 1 (color online). a) Molecular structure of **1** in the crystal with the labelling scheme adopted (H atoms are omitted for clarity); b) the coordination environment of the Sm^{3+} ion in **1**; c) the layer built up from the $[\text{Sm}(\text{en})(\text{teta})(\text{SbS}_4)]$ units *via* $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonding interactions (shown by dashed lines, H atoms bonded to C atoms are omitted for clarity).

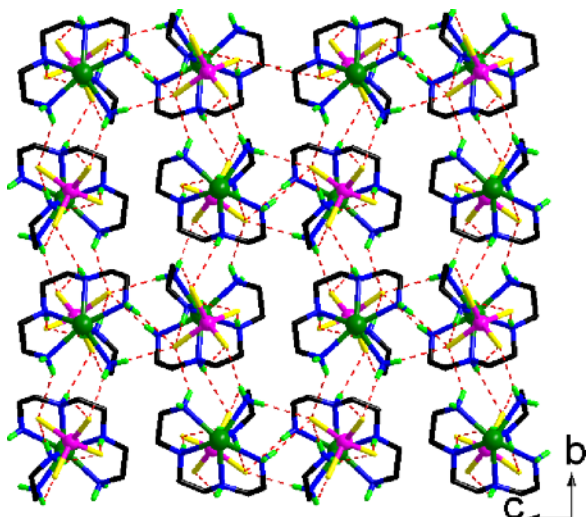


Fig. 2 (color online). 3-D hydrogen-bonded network structure of **1** (H atoms bonded to C atoms are omitted for clarity).

N–H···S hydrogen bonds forming a layer parallel to the (001) plane (Fig. 1c). The layers interact also via N–H···S hydrogen bonds resulting in a 3-D hydrogen-bonded network (Fig. 2). The N···S distances are in the range of 3.371(2) to 3.622(3) Å and the N–H···S angles vary from 140 to 167°, which are consistent with the values reported in the literature [18–26]. Similar intermolecular hydrogen bonds are found in both **2** and **3**.

The solid-state UV/Vis absorption spectra of compounds **1** and **3** were measured at room temperature

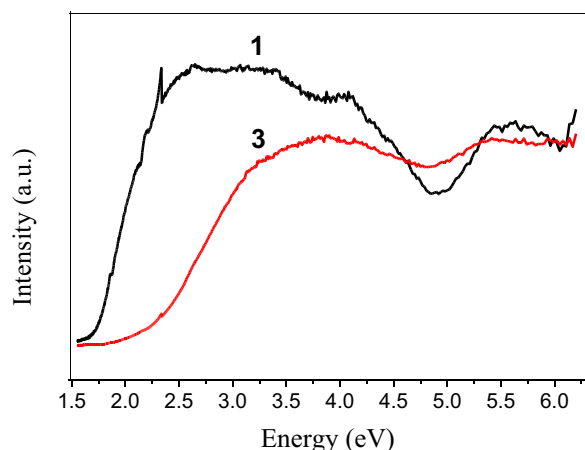


Fig. 3 (color online). Optical absorption spectra of compounds **1** and **3**.

(Fig. 3). The absorption edges are 1.75 eV for **1** and 2.27 eV for **3**, which lie in the energy range suitable for visible-light photocatalytic applications [30]. These absorption edges are comparable with values of the lanthanide thioantimonates [Eu(dien)₂SbS₃] (1.77 eV) [25], {[Eu(dien)₂]₂(μ₄-Sb₂S₅)} Cl₂ (1.71 eV) [25], [Pr(en)₃(H₂O)(μ₂-SbS₄)] (2.35 eV) [23], and {[Eu(tepa)]₂[μ₂-Sb^{III}S₃](μ₂-OH)}₂{[Ln(tepa)]₂(μ₂-OH)₂(Sb^VS₄)₂} Cl₂ (2.00 eV) [27], which exhibit the properties of a semiconductor.

Experimental Section

General: All analytically pure starting materials were purchased and used without additional purification. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr pellets. Elemental analysis was carried out on an EA-1110 elemental analyzer. The UV spectra were recorded at room temperature using a computer-controlled PE Lambda 900 UV spectrometer equipped with an integrating sphere in the wavelength range of 200–800 nm.

Synthesis of [Sm(en)(teta)(SbS₄)] (**1**)

A mixture of Sb (0.05 mmol, 0.0057 g), S (0.70 mmol, 0.0220 g), SmCl₃ (0.10 mmol, 0.0257 g), en (0.5 mL), and tetra (0.5 mL) was placed in a thick Pyrex tube. The sealed tube was heated at 160 °C for 6 d to yield yellow block-shaped crystals. The crystals were washed with ethanol, dried and stored under vacuum (67% yield based on Sb). – Anal. for C₈H₂₆N₆S₄SbSm: calcd. C 15.84, H 4.32, N 13.85; found C 15.77, H 4.42, N 13.78. – IR (cm^{−1}): ν = 3411(s), 3232(s), 2952(m), 1560(s), 1512(s), 1380(m), 1338(m), 1111(vs), 984(s), 810(vw), 758(vw), 668(s), 515(m).

Synthesis of [Eu(en)(teta)(SbS₄)] (**2**)

A mixture of Sb (0.05 mmol, 0.0057 g), S (0.60 mmol, 0.0188 g), Eu₂O₃ (0.05 mmol, 0.0176 g), en (0.5 mL), and tetra (0.5 mL) was placed in a thick Pyrex tube. The sealed tube was heated at 160 °C for 7 d to yield yellow block-shaped crystals. The crystals were washed with ethanol, dried and stored under vacuum (57% yield based on Sb). – Anal. for C₈H₂₆EuN₆S₄Sb: calcd. C 15.80, H 4.31, N 13.82; found C 15.77, H 4.39, N 13.76. – IR (cm^{−1}): ν = 3433(s), 3353(s), 2979(m), 2873(m), 1634(m), 1559(w), 1406(s), 1348(m), 1042(s), 953(m), 800(m), 695(m), 584(w), 477(m).

Synthesis of [Gd(en)(teta)(SbS₄)] (**3**)

A mixture of Sb (0.05 mmol, 0.0057 g), S (0.70 mmol, 0.0220 g), GdCl₃ (0.10 mmol, 0.0264 g), en (0.5 mL), and

	1	2	3
Formula	C ₈ H ₂₆ N ₆ S ₄ SbSm	C ₈ H ₂₆ EuN ₆ S ₄ Sb	C ₈ H ₂₆ GdN ₆ S ₄ Sb
<i>M_r</i>	606.75	608.36	613.64
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	9.898(2)	9.871(2)	9.880(2)
<i>b</i> , Å	13.329(3)	13.277(3)	13.333(3)
<i>c</i> , Å	14.655(3)	14.651(3)	14.646(3)
β, deg	98.02(3)	97.90(3)	98.00(3)
<i>V</i> , Å ³	1914.5(7)	1901.9(7)	1910.5(7)
<i>Z</i>	4	4	4
<i>D</i> _{calcd} , g cm ^{−3}	2.11	2.13	2.13
μ(MoK _α), cm ^{−1}	4.9	5.1	5.3
<i>F</i> (000), e	1172	1176	1180
Refl. measured	10683	9622	10591
Refl. unique / <i>R</i> _{int}	3400 / 0.0165	3344 / 0.0753	3400 / 0.0164
Param. refined	181	181	182
<i>R</i> (<i>F</i>) / <i>wR</i> (<i>F</i> ²) (all refl.)	0.0154 / 0.0348	0.0837 / 0.2177	0.0145 / 0.0329
GoF (<i>F</i> ²)	1.099	1.027	1.109
Δρ _{fin} (max / min), e Å ^{−3}	0.28 / −0.43	2.08 / −4.39	0.48 / −0.44

Table 1. Crystal structure data for **1–3**.

	1 (<i>Ln</i> = Sm)	2 (<i>Ln</i> = Eu)	3 (<i>Ln</i> = Gd)
<i>Ln</i> –N	2.562(2)–2.590(2)	2.536(12)–2.581(11)	2.538(2)–2.564(2)
<i>Ln</i> –S	2.8777(9)–2.9016(8)	2.866(4)–2.892(4)	2.8628(9)–2.8972(8)
Sb–S	2.2926(10)–2.3487(8)	2.294(4)–2.346(4)	2.2907(10)–2.3520(8)
N– <i>Ln</i> –N/S	65.59(7)–160.37(8)	64.7(4)–159.8(4)	65.82(7)–158.95(7)
S– <i>Ln</i> –S	76.66(2)	76.72(10)	76.78(2)
S–Sb–S	99.60(3)–113.65(3)	99.36(13)–113.81(15)	99.12(3)–113.84(3)

Table 2. Selected bond lengths (Å), and angles (deg) for **1, 2** and **3**.

teta (0.5 mL) was placed in a thick Pyrex tube. The sealed tube was heated at 160 °C for 7 d to yield orange sheet-shaped crystals. The crystals were washed with ethanol, dried and stored under vacuum (71 % yield based on Sb). – Anal. for C₈H₂₆GdN₆S₄Sb: calcd. C 15.66, H 4.27, N 13.70; found C 15.67, H 4.25, N 13.63. – IR (cm^{−1}): ν = 3380(s), 3222(s), 2937(m), 2865(m), 1572(vs), 1507(s), 1375(m), 1098(s), 1058(m), 986(s), 808(w), 669(m), 590(m), 478(m).

Crystal structure determination

Data collections were performed on a Rigaku Mercury CCD diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 296(2) K with a maximum 2θ value of 50.20°. The intensities were corrected for Lorentz and polarization effects. The structures were solved with Direct Methods using the program SHELXS-97 [31, 32], and the refinement was performed against *F*² using SHELXL-97 [33, 34]. All non-hydrogen atoms were refined anisotropically. The H atoms of the en and tetra ligands were positioned

with idealized geometry and refined with fixed isotropic displacement parameters. Relevant crystal data and refinement results can be found in Table 1. Selected bond lengths and angles for **1** are listed in Table 2.

CCDC 898419 (**1**), 898420 (**2**) and 898421 (**3**) contain 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.

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