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The First Example of Solvothermally Synthesized Thioantimonates(V) with Ethylenediamine Coordinated Lanthanide(III): [Sm(en)$_4$]SbS$_4$·0.5en and [Sm(en)$_3$(H$_2$O)(μ-SbS$_4$)]$_\infty$

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Under mild solvothermal conditions two novel thioantimonates(V) [Sm(en)$_4$]SbS$_4$·0.5en (**1**) and [Sm(en)$_3$(H$_2$O)(μ-SbS$_4$)]$_\infty$ (**2**) were synthesized; the structure of **1** contains discrete [Sm(en)$_4$]$^{3+}$ and [SbS$_4$]$^{3-}$ ions, while **2** consists of neutral [Sm(en)$_3$(H$_2$O) (μ-SbS$_4$)] one-dimensional chains.

Recently, extensive interest has been focused upon the synthesis and characterization of ternary and quternary lanthanide chalcogenides due to their promising photo-, thermo-, and electroluminescence and nonlinear optical properties.[1-3] These compounds are usually prepared by flux technique at high temperature. The mild solvothermal reaction in amine has proven to be a versatile route for the syntheses of chalcogenometalates.[4] With this method, a number of thioantimonates, in which transition metal complex cations act as charge balancing ions for Sb$_x$S$_y$$^{z-}$ anions, have been synthesized.[5,6] Transition metal ions, such as Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Ag$^+$, are proven to be able to incorporate into the Sb$_x$S$_y$$^{z-}$ network.[7] However, the synthetic method of incorporation of lanthanide metal cations (Ln^{3+}) into the thioantimonate anionic network under mild solvothermal conditions has not been reported till now. In our systematic syntheses of thiometalates in ethylenediamine (en) solution,[8] we obtained two novel organic–inorganic hybrid thioantimonates, [Sm(en)$_4$]SbS$_4$·0.5en (**1**) and [Sm(en)$_3$(H$_2$O)(SbS$_4$)] (**2**). The two compounds are the first examples of lanthanide thioantimonates synthesized in en solution under solvothermal conditions.

Compound **1** was prepared by a reaction of Sm$_2$O$_3$ with Sb and S in en at 150 °C for 7 days.[9] Compound **2** was obtained in a different procedure. A clear yellow solution was previously obtained by a reaction of Sb with S in en for 2 days at 150 °C. After Sm$_2$O$_3$ was added to the resulted solution, the solvothermal reaction went on for another 5 days at the same temperature, and then **2** was achieved.[9]

Compound **1**[10] is composed of an eight-coordinated [Sm(en)$_4$]$^{3+}$ cation, a tetrahedral [SbS$_4$]$^{3-}$ anion, and a solvent molecule of en (Figure 1a). The coordination geometry

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(9) Synthesis: colorless prism crystals of [Sm(en)$_4$]SbS$_4$·0.5en (**1**) were synthesized by reacting Sm$_2$O$_3$ (174.4 mg, 0.5 mmol) and Sb (121.7 mg, 1 mmol) with S (96.19 mg, 3 mmol) in 4 mL of ethylenediamine. The mixture was loaded into a Teflon-lined stainless steel autoclave (the filling rate of the autoclave is about 30%). Then, the autoclave was heated to 150 °C for 7 days (yield 50% based on Sb). Colorless block crystals of [Sm(en)$_3$(H$_2$O)(SbS$_4$)] (**2**) were synthesized with the same starting material and molar ratio as **1** but in a different procedure. A clear yellow solution was previously obtained by reacting Sb with S in ethylenediamine for 2 days at 150 °C. After Sm$_2$O$_3$ was added to the resulting solution, the solvothermal reaction was carried on for 5 days at the same temperature (yield 55% based on Sb).

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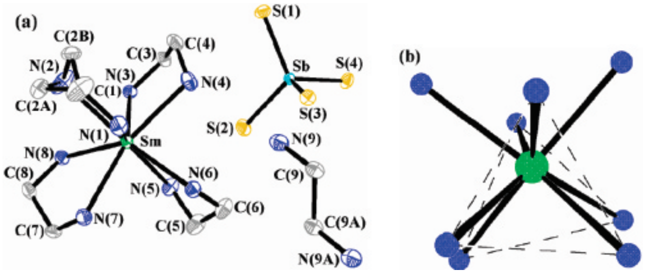

Figure 1. (a) Crystal structure of **1**, the atom of C(2) being disordered. Hydrogen atoms are omitted for clarity. (b) Coordination environment of the Sm^{3+} ion. Selected bond distances (Å): Sb−S(1) 2.3160(10), Sb−S(2) 2.3259(10), Sb−S(3) 2.3421(9), Sb−S(4) 2.3294(10), Sm−N(1) 2.578(3), Sm−N(2) 2.592(3), Sm−N(3) 2.552(3), Sm−N(4) 2.545(3).

around Sm^{3+} ion is a bicapped trigonal prism of N atoms (Figure 1b). The Sm−N bond distances varying from 2.545(3) to 2.578(3) Å are comparable to those observed in other samarium complexes with amine donor atoms.[11] The Sb−S bond distances vary from 2.3160(10) to 2.3421(9) Å, distances which are similar to those found in other discrete tetrahedral $[SbS_4]^{3-}$ anions.[12] All the geometrical parameters indicate a significantly distorted SbS_4 tetrahedron.

The crystal structure[10] of **2** consists of neutral $[Sm(en)_3(H_2O)(\mu\text{-}SbS_4)]$ one-dimensional chains. The Sm^{3+} ion is coordinated by three en ligands and one H_2O. The $[SbS_4]^{3-}$ anion acts as a bridging ligand connecting neighboring $[Sm(en)_3(H_2O)]^{3+}$ cations to form one-dimensional coordination polymer of $[Sm(en)_3(H_2O)(\mu\text{-}SbS_4)]_\infty$ (Figure 2a). Being different from the Sm^{3+} ion in **1**, in **2** the Sm^{3+} ion is in a nine-coordinated environment with six N atoms from three en ligands, two S atoms from two different $[SbS_4]^{3-}$ anions, and one O atom from H_2O (Figure 2a). The novel mixed ligands coordinated polyhedron SmN_6S_2O is a distorted top-capped square antiprism (Figure 2b). The atoms of Sb, Sm, O, S(1), and S(2) form a mirror plane (Figures 2a and 3). The en ligands of N(1)−C(1)−C(2)−N(2) and N(1A)−C(1A)−C(2A)−N(2A) are mirror images of each other. Similar to $[SbS_4]^{3-}$ in **1**, the tetrahedral $[SbS_4]^{3-}$ anion in **2** is also distorted, as evidenced by the S−Sb−S angles ranging from 106.58(4)° to 111.19(3)°. The average distance of Sm−N (2.624 Å) is elongated by ca. 0.058 Å compared with that of eight-coordinated $[Sm(en)_4]^{3+}$ ion (av. Sm−N 2.566 Å). The Sm−S distances (2.9749(10) and 3.0739(12) Å) are comparable to the corresponding distances of multinary samarium sulfides with S donor atoms of thiometalate anions.[13]

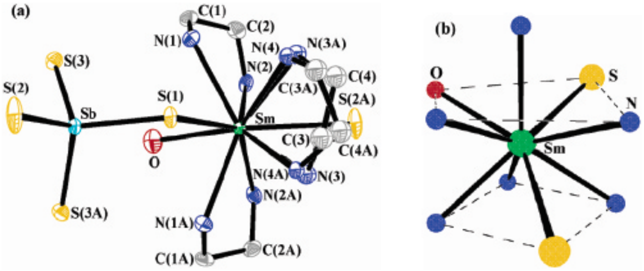

Figure 2. (a) Crystal structure of **2**, one of the en molecules being disordered. Hydrogen atoms are omitted for clarity. (b) Coordination environment of the Sm^{3+} ion. selected bond distances (Å): Sb−S(1) 2.3254(11), Sb−S(2) 2.3137(12), Sb−S(3) 2.3341(8), Sm−N(1) 2.609(3), Sm−N(2) 2.601(3), Sm−N(3) 2.647(7), Sm−N(4) 2.640(7), Sm−O 2.616(4), Sm−S(1) 2.9749(10), Sm−S(2A) 3.0739(12).

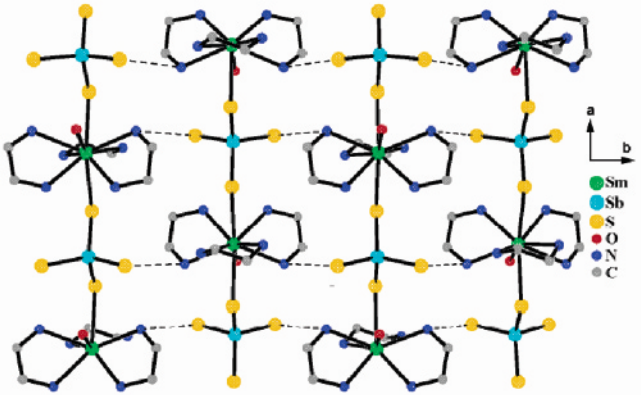

Figure 3. View of the layer (viewing along *c*-axis) formed by $[Sm(en)_3(H_2O)(SbS_4)]_\infty$ chains via N−H···S hydrogen bonds (shown in dashed lines). Hydrogen atoms are omitted for clarity.

Except for in a few cases[12] where $[SbS_4]^{3-}$ is bound to transition-metal cations, coordinated by amine, thioantimonates(V) usually exist as an isolated tetrahedral $[SbS_4]^{3-}$ anion.[6] In **2** the $[SbS_4]^{3-}$ anion is bound to $[Sm(en)_3(H_2O)]^{3+}$ ion and acts as a μ-bridging ligand to connect the cations. Compound **2** is the first example of thioantimonate(V) with $[SbS_4]^{3-}$ anion coordinated to lanthanide metal complex cations of $[Ln(en)_3]^{3+}$. All the $[Sm(en)_3(H_2O)(\mu\text{-}SbS_4)]_\infty$ chains are parallel to the *a* axis, and their orientations alternate in neighbors (Figure 3). The chains are connected via N−H···S hydrogen bonds forming a layered arrangement parallel to the (001) plane. Then, the layers interact also via N−H···S hydrogen bonds resulting in a three-dimensional network.

Optical diffuse reflection spectra in the 250−700 nm range were measured at room temperature. The absorption (α/S)

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(10) Crystal structure determination: $[Sm(en)_4]SbS_4{\cdot}0.5en$ (**1**), M_w = 670.81. Monoclinic, space group $P2_1/n$ (No. 14) with a = 11.0520(13) Å, b = 12.8847(15) Å, c = 16.116(2) Å, β = 91.861(3)°, V = 2293.7(5) Å^3. T = 193 K, Z = 4, D_{calcd} = 1.943 g·cm^{-3}, and μ = 4.090 mm^{-1}. 24981 reflections collected in the range $6.82 \leq 2\theta \leq 54.96$, 5225 unique reflections. $[Sm(en)_3(H_2O)(SbS_4)]$ (**2**), M_w = 598.67. Orthorhombic, space group *Pnma* (No. 62) with a = 9.2725(6) Å, b = 13.3851(9) Å, c = 14.6863(9) Å, V = 1822.8(2) Å^3. T = 193 K, Z = 4, D_{calcd} = 2.182 g·cm^{-3}, and μ = 5.131 mm^{-1}. 19104 reflections collected in the range $6.02 \leq 2\theta \leq 54.96$, 2162 unique reflections. An empirical absorption correction was applied to the data; structures were solved with SHELXS-97 (Sheldrick, G. M. University of Göttingen); structures refinement against F^2 using SHELXL-97 (Sheldrick, G. M. University of Göttingen). For **1**, 243 variables; $R1$ for 5035 reflections $[I > 2\sigma(I)]$ = 0.0300, $wR2$ for all 5225 data = 0.0605, GOF 1.255. For **2**, 94 variables; $R1$ for 2121 reflections $[I > 2\sigma(I)]$ = 0.0214, $wR2$ for all 2162 data = 0.0503, GOF 1.149. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located by calculation except that H atoms of N(2) and N(9) in **1** were located by difference Fourier maps. In **1**, the atom of C(2) is disordered, and the occupancies of C(2A)/C(2B) were assigned as 60% and 40%. In **2**, one en ligand is disordered, and the occupancies of disordered N(3)−C(3)−C(4)−N(4)/N(4A)−C(4A)−C(3A)−N(3A) atoms were assigned as 50% and 50% respectively.

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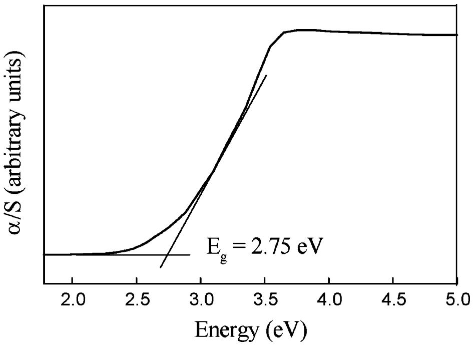

Figure 4. Solid state optical absorption spectrum of **2**, showing the band gap value of E_g.

data were calculated from the reflectance using the Kubelka–Munk function.[14] The obtained absorption versus energy spectra show band gaps at 2.73 eV for **1** and 2.75 ev for **2** (Figure 4). Both band gaps of **1** and **2** are larger than those of multinary lanthanide polythioantimonates(III) free of organic ligands, such as $K_2La_2Sb_2S_9$ (2.20 eV),[2] La_2SbS_5Br (2.08 eV), and $CeLaSbS_5Br$ (2.07 eV).[3]

Compound **1** loses its free en at 90 °C (0.5en, 4.4%). It removes coordinated en ligands between 100 and 250 °C in two steps with mass losses of 17.6% and 18.2%, which is in good agreement with complete removal of four en ligands (calculated: 35.8%). Compound **1** loses 1 molar S element with mass loss of 4.5% between 340 and 450 °C. Compound **2** loses its H_2O molecule below 127 °C with a mass loss of 2.8% (calculated: 3.0%). Above 127 °C, **2** removes en ligands in two steps with total mass loss of 30.8% (calculated: 30.1%), which is accompanied by two endothermic signals at 154 and 231 °C on a DSC curve, respectively. Compound **2** also loses sulfur but at lower temperature between 250 and 350 °C (see Supporting Information). The residues of **1** and **2** were checked by XRD, but the decomposition products could not been clearly assigned, because the reflection intensities are weak and the peaks are broadened.

In conclusion, although numerous main group chalcogenometalates were obtained from en systems by mild solvothermal reaction, up to now only transition metal complex cations are involved in incorporation with the chalcogenometalate anions in this synthetic method. Compounds **1** and **2** are the first example of thioantimonates(V) with lanthanide metal complex cations acting as counterions. The structure of **2** is a novel example of a $[SbS_4]^{3-}$ anion acting as a bridging ligand. Therefore, the solvothermal method is a new route for synthesis of multinary lanthanide sulfides modified with organic components.

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Supporting Information Available: Figures of TGA-DSC curves and crystallographic data of **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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