Inorganic Chemistry

Solvothermal Syntheses of [Ln(en)$_3$(H$_2$O)$_x$(μ_{3-x}-SbS$_4$)] (Ln = La, x = 0; Ln = Nd, x = 1) and [Ln(en)$_4$]SbS$_4$·0.5en (Ln = Eu, Dy, Yb): A Systematic Study on the Formation and Crystal Structures of New Lanthanide Thioantimonates(V)

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Received August 17, 2005

New lanthanide thioantimonate(V) compounds, [Ln(en)$_3$(H$_2$O)$_x$(μ_{3-x}-SbS$_4$)] (en = ethylenediamine, Ln = La, x = 0, **Ia**; Ln = Nd, x = 1, **Ib**) and [Ln(en)$_4$]SbS$_4$·0.5en (Ln = Eu, **IIa**; Dy, **IIb**; Yb, **IIc**), were synthesized under mild solvothermal conditions by reacting Ln$_2$O$_3$, Sb, and S in en at 140 °C. These compounds were classified as two types according to the molecular structures. The crystal structure of type I (**Ia** and **Ib**) consists of one-dimensional neutral [Ln(en)$_3$(H$_2$O)$_x$(μ_{3-x}-SbS$_4$)]$_\infty$ (x = 0 or 1) chains, in which SbS$_4{}^{3-}$ anions act as tridentate or bidentate bridging ligands to interlink [Ln(en)$_3$]$^{3+}$ ions, while the crystal structure of type II (**IIa**, **IIb**, and **IIc**) contains isolated [Ln(en)$_4$]$^{3+}$ cations, tetrahedral SbS$_4{}^{3-}$ anions, and free en molecules. A systematic investigation of the crystal structures of the five lanthanide compounds, as well as two reported compounds, clarifies the relationship between the molecular structure and the entity of the lanthanide(III) series, such as the stability of the lanthanide(III)−en complexes, the coordination number, and the ionic radii of the metals.

Introduction

Lanthanide chalcogenides have attracted increased attention in recent years, because of their promising photo-, thermo-, and electroluminescence and nonlinear optical properties,[1−4] as well as potential applications in an extended infrared transparency region.[4] These compounds are generally prepared by flux methods at high temperature. The mild solvothermal synthesis, in which reaction is performed in the presence of a structure-directing agent such as an organic amine, has proven to be a versatile route for the preparation of chalcogenides containing the main group elements germanium, tin, arsenic, and antimony.[5] In the case of antimony, transition-metal (TM) ions have been introduced into the solvothermal system of Sb (or SbS$_3{}^{3-}$)/amines and a large number of TM-containing thioantimonates have been prepared by the solvothermal route.[6,7] The transition metals and

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amines lead to a structural diversity of thioantimonates. Amines coordinate to the TM, forming isolated $M(amine)_m^{n+}$ complex ions to balance the charge of $Sb_xS_y^{z-}$ anion, such as $[M(en)_3]Sb_2S_4$ (M = Co, Ni),[6a] $[M(en)_3]Sb_4S_7$ (M = Mn, Co, Ni),[6a,b] $[Co(en)_3]Sb_{12}S_{19}$ (en = ethylenediamine),[6c] $[Ni(dien)_2]Sb_4S_8$,[6d] $[Ni(dien)_2]Sb_4S_9$,[6e] $[Ni(dien)_2]_3(Sb_3S_6)_2$,[6f] $[Ni(dien)_2]_9Sb_{22}S_{42}\cdot0.5H_2O$,[6g] and $[Fe(dien)_2]Sb_6S_{10}\cdot0.5H_2O$,[6h] (dien = diethylenediamine). On the other hand, $M(amine)_m^{n+}$ complexes or TM ions can be incorporated into the anionic $Sb_xS_y^{z-}$ network through M–S bonds,[7] giving $[Co(en)_3]$-$CoSb_4S_8$,[7a] $(en)_{0.5}[Cu_2SbS_3]$,[7b] $[M(tren)]Sb_2S_4$ (M = Co, Ni),[7c] $[Co(tren)]_2Sb_4S_8$ (tren = tris(2-aminoethyl) amine),[7d] and $[Fe(dien)_2]Fe_2Sb_4S_{10}$,[7h] for examples. But, there has been very little exploration of the chemistry in the area of the syntheses of thioantimonates integrating lanthanide metal ions (Ln^{3+}) via the solvothermal method. The combination of lanthanide metal ions with the chalcogenometalates should lead to a new series of chalcogenometalates.

During our systematic synthesis of chalcogenometalates in superheated en,[8] we initiated exploration of the synthetic system $Ln_2O_3/Sb/S/en$ (Ln = lanthanide) under solvothermal conditions with the aim of obtaining thioantimonates containing lanthanide metals. Recently, we have successfully synthesized two novel samarium thioantimonates(V), $[Sm(en)_3(H_2O)(\mu_2-SbS_4)]$ (**Ic**) and $[Sm(en)_4]SbS_4\cdot0.5en$ (**IId**),[9a] from this solvothermal system. The two compounds are the first examples of lanthanide thioantimonates synthesized by the solvothermal method. During the continuing work on the synthesis of lanthanide-containing thioantimonates, two types of organic–inorganic hybrid lanthanide thioantimonates(V), $[Ln(en)_3(H_2O)_x(\mu_{3-x}-SbS_4)]$ (Ln = La, x = 0; Ln = Nd, x = 1) and $[Ln(en)_4] SbS_4\cdot0.5en$ (Ln = Eu, Dy, Yb), were obtained. The present contribution reports the synthesis and crystal structures of the series of lanthanide thioantimonates(V) and the factors influencing the crystal structures across the lanthanide series.

Experimental Section

General. All analytical grade chemicals were obtained commercially and used without further purification. Elemental analysis was conducted on a MOD 1106 elemental analyzer. FT-IR spectra

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were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr disks in the $4000−400$ cm^{-1} range. UV–vis spectra were measured with a Shimadzu UV-3150 spectrometer at room temperature. The absorption (α/S) data were calculated from the reflectance using the Kubelka–Munk function, $\alpha/S = (1 − R)^2/2R$,[10] where R is the reflectance at a given energy, α is the absorption, and S is the scattering coefficient. Thermoanalytical measurements were performed using a DCS-TGA microanalyzer (SDT 2960), and all samples were heated at a rate of 5 °C min^{-1} under a nitrogen stream of 100 mL min^{-1}. Powder X-ray diffraction (XRD) patterns were collected on a D/MAX-3C diffractometer using graphite monochromatized Cu Kα radiation ($\lambda = 1.5406$ Å).

Syntheses. All compounds were solvothermally synthesized in ethylenediamine (en). In a typical synthetic procedure, reactants in the stoichiometric molar ratio were dispersed in 3 mL en under stirring; then the mixture was loaded into a Teflon-lined stainless-steel autoclave with inner volume of 15 mL. The sealed autoclave was heated to 140 °C for 7 days. After the reaction mixture cooled to ambient temperature, the crystals were filtered off, washed with ethanol and ether, and stored under vacuum.

$[La(en)_3(\mu_3-SbS_4)]$ (Ia). Colorless prism crystals of **Ia** were obtained from the reaction of La_2O_3 (163 mg, 0.5 mmol), Sb (122 mg, 1 mmol), and S (128 mg, 4 mmol) in en with a yield of 165 mg (29% based on La_2O_3). Anal. Calcd for $C_6H_{24}N_6S_4LaSb$: C, 12.66; H, 4.25; N, 14.76. Found: C, 12.62; H, 4.34; N, 14.58. IR (KBr): 3308m, 3287m, 3265m, 3240s, 3218s, 3197s, 3123s, 2931s, 2898m, 2873m, 2854m, 1586vs, 1515s, 1469m, 1457m, 1384m, 1331m, 1290w, 1277w, 1257w, 1154w, 1112w, 1082w, 1065w, 1031vs, 999s, 953vs, 864w, 810w, 601m, 574m, 482w, 451m cm^{-1}.

Synthesis of $[Nd(en)_3(H_2O)(\mu_2-SbS_4)]$ (Ib). Light blue-red block crystals of **Ib** were obtained from the reaction of Nd_2O_3 (168 mg, 0.5 mmol), Sb (122 mg, 1 mmol), and S (128 mg, 4 mmol) in en in a yield of 308 mg (52% based on Nd_2O_3). Anal. Calcd for $C_6H_{26}N_6OS_4NdSb$: C, 12.16; H, 4.42; N, 14.18. Found: C, 12.10; H, 4.44; N, 14.04. IR (KBr): 3335s, 3316s, 3248s, 3128s, 2937s, 2882s, 2857s, 2369m, 1574vs, 1505s, 1459s, 1386m, 1329m, 1214w, 1171w, 1149w, 1109w, 1069w, 1011m, 957m, 874w, 812w, 774w, 663w, 614m, 582m, 527w, 494w, 434w cm^{-1}.

$[Eu(en)_4]SbS_4\cdot0.5en$ (IIa). Colorless block crystals of **IIa** were obtained from the reaction of Eu_2O_3 (176 mg, 0.50 mmol), Sb (122 mg, 1 mmol), and S (128 mg, 4 mmol) in en with a yield of 216 mg (32% based on Eu_2O_3). Anal. Calcd for $C_9H_{36}N_9S_4EuSb$: C, 16.08; H, 5.40; N, 18.75. Found: C, 16.04; H, 5.44; N, 18.72. IR (KBr): 3299vs, 3276s, 3249s, 3127s, 2924vs, 2880s, 1570vs, 1505s, 1385m, 1331s, 1157w, 1011m, 983m, 868w, 814w, 776w, 660w, 590m cm^{-1}.

$[Dy(en)_4]SbS_4\cdot0.5en$ (IIb). Colorless block crystals of **IIb** were obtained from the reaction of Dy_2O_3 (187 mg, 0.5 mmol), Sb (122 mg, 1 mmol), and S (128 mg, 4 mmol) in en with a yield of 253 mg (37% based on Dy_2O_3). Anal. Calcd for $C_9H_{36}N_9S_4DySb$: C, 15.83; H, 5.31; N, 18.46. Found: C, 15.81; H, 5.36; N, 18.42. IR (KBr): 3332vs, 3285s, 3251s, 3127s, 2926vs, 2885s, 1572vs, 1504s, 1460m, 1385m, 1330s, 1215w, 1158w, 1010m, 984m, 870w, 812w, 780w, 659w, 593m cm^{-1}.

$[Yb(en)_4]SbS_4\cdot0.5en$ (IIc). Colorless block crystals of **IIc** were obtained from the reaction of Yb_2O_3 (197 mg, 0.5 mmol), Sb (122 mg, 1 mmol), and S (128 mg, 4 mmol) in en with a yield of 208 mg (30% based on Yb_2O_3). Anal. Calcd for $C_9H_{36}N_9S_4YbSb$: C, 15.59; H, 5.23; N, 18.18. Found: C, 15.56; H, 5.30; N, 18.12. IR

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Table 1. Crystallographic Data for Compounds **Ia**, **Ib**, **IIa**, **IIb**, and **IIc**

	Ia	**Ib**	**IIa**	**IIb**	**IIc**
formula	$C_6H_{24}N_6S_4LaSb$	$C_6H_{26}N_6OS_4NdSb$	$C_9H_{36}N_9S_4EuSb$	$C_9H_{36}N_9S_4DySb$	$C_9H_{36}N_9S_4YbSb$
fw (g mol^{-1})	569.21	592.56	672.42	682.96	693.50
cryst size (mm^3)	$0.30 \times 0.14 \times 0.11$	$0.40 \times 0.30 \times 0.25$	$0.34 \times 0.18 \times 0.10$	$0.25 \times 0.21 \times 0.20$	$0.30 \times 0.18 \times 0.10$
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$Pnma$ (No. 62)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	8.7230(15)	9.2634(15)	11.047(2)	11.0395(7)	11.0482(7)
b (Å)	10.2043(19)	13.418(2)	12.881(2)	12.8756(8)	12.8801(8)
c (Å)	20.277(4)	14.757(2)	16.080(3)	16.0131(9)	16.0753(10)
β (deg)	93.818(5)	90.00	91.931(4)	92.117(2)	91.966(2)
V (Å^3)	1800.9(6)	1834.2(5)	2286.6(7)	2274.6(2)	2286.2(2)
Z	4	4	4	4	4
ρ_{calcd} (g cm^{-3})	2.099	2.146	1.953	1.994	2.015
μ (mm^{-1})	4.298	4.729	4.277	4.827	5.625
$F(000)$	1096	1148	1324	1336	1352
temp (K)	193(2)	193(2)	193(2)	193(2)	193(2)
no. reflns with $F_o > 2\sigma(F_o)$	3900	2170	4693	4863	3891
no. params	164	94	243	235	235
R1 ($F_o > 2\sigma(F_o)$)	0.0385	0.0243	0.0627	0.0306	0.0429
wR2 (all data)	0.0577	0.0837	0.0776	0.0585	0.0926

(KBr): 3336vs, 3279s, 3244m 3130s, 2922s, 2876s, 1582s, 1458m, 1385m, 1328m, 1278w, 1147m, 1008vs, 864w, 718m, 621m, 605w cm^{-1}.

General Procedures for X-ray Crystallography. Data collections were performed on a Rigaku Mercury CCD diffractometer using a ω-scan method with graphite monochromated Mo Kα radiation ($\lambda = 0.071073$ nm) at 193(2) K to a maximum 2θ value of 54.96° for **Ia**, **Ib**, **IIa**, and **IIb** and 50.70° for **IIc**. The intensities were corrected for Lorentz and polarization effects. The structures were solved with direct methods using the SHELXS-97 program.[11] The refinement was performed against F^2 using SHELXL-97.[12] All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters. The third en ligand in **Ib** is disordered with the occupancies of disordered C/C′ and N/N′ atoms assigned as 50 and 50%, respectively. The C(2) atoms in **IIa**−**IIc** are also disordered, and the occupancies of disordered C/C′ are assigned as 60 and 40%, 55 and 45%, and 58 and 42% for **IIa**, **IIb**, and **IIc**, respectively. The H atoms of the disordered en ligand were not dealt with. Relevant crystal and collection data parameters and refinement results can be found in Table 1. Additional details of crystal data in CIF format can be found in the Supporting Information.

Results and Discussion

Synthesis and Valence of the Lanthanide Thioantimonates. Synthesis. The title compounds, **Ia**, **Ib**, **IIa**, **IIb**, and **IIc**, were conveniently prepared from the Ln$_2$O$_3$/Sb/S/ en synthetic system in the stoichiometric molar ratio of the reactants under mild solvothermal conditions. The heterogeneous reaction under solvothermal conditions is complex and little is known about the reaction mechanism. It is believed that polysulfide S_x^{2-} ions are formed during the reaction of S in the basic solution of en and oxidize the metals.[7k] Some reported studies have shown the presence of polysulfide S_x^{2-} ions in basic solutions.[13] In the reaction

medium, the solid material of Ln$_2$O$_3$ is transformed to $[Ln(en)_3]^{3+}$ or $[Ln(en)_4]^{3+}$ species to balance charges of SbS$_4{}^{3-}$ anions. In a few dozen experiments with varying conditions, the elemental molar ratio of Ln/Sb/S ranging from 1:1:2.5 to 1:1:5 and using different volumes of en as well as at different temperatures (from 140 to 180 °C), the same compounds were obtained. The results suggest that the title lanthanide thioantimonates(V) are formed and are thermally stable under a wide variety of synthetic conditions. It is notable that, although a less stoichiometric amount of elemental S was used, no lanthanide thioantimonates(III) were obtained.

Formation of Lanthanide Thioantimonates(V). The products of the solvothermal reactions from the M/Sb/S/ amine (M = transition metal) synthetic system are mainly compounds of thioantimonates(III).[6,7] In only rare cases, Sb is oxidized to Sb^V in the very basic solution of amine, and few examples of thioantimonates(V) were reported.[14,15] The excess amount of elemental S seems to be beneficial to oxidize Sb^{III}S$_3{}^{3-}$ to Sb^{V}S$_4{}^{3-}$. For example, thioantimonate-(III) compound [Ni(en)$_3$]Sb$_2$S$_4$ was obtained with the molar ratio Ni^{2+}/Sb/S of 1:1:3, while thioantimonate(V) compound, [Ni(en)$_3$(Hen)]SbS$_4$, was formed with the molar ratio of 1:1:6 under the same synthetic conditions.[8c] But in the case of lanthanide metals, only thioantimonates(V) are obtained within a wide range of Ln/Sb/S molar ratios (varying from 1:1:2.5 to 1:1:5). Furthermore, the structure and composition of the lanthanide thioantimonates(V) are not influenced by the molar ratios of reactants, the volume of amine, or the temperature.

Structure Types of the Lanthanide Thioantimonates. Crystal of Type I. The general feature of the crystal structures of type I is that the lanthanide(III)−en complex cations are interconnected by multidentate SbS$_4$ ligands to

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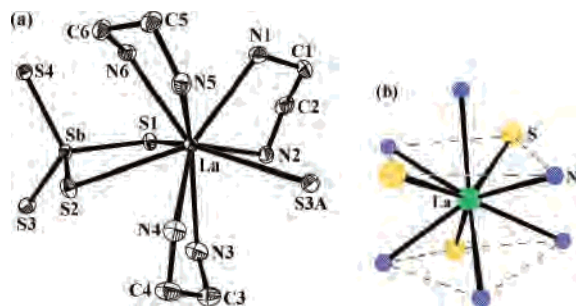
Figure 1. (a) Crystal structure of **Ia** with the labeling scheme. Displacement ellipsoids are drawn at the 50% level. Hydrogen atoms are omitted for clarity. Symmetry operation: (A) $x - 1$, y, z. (b) Coordination environment of the La^{3+} ion.
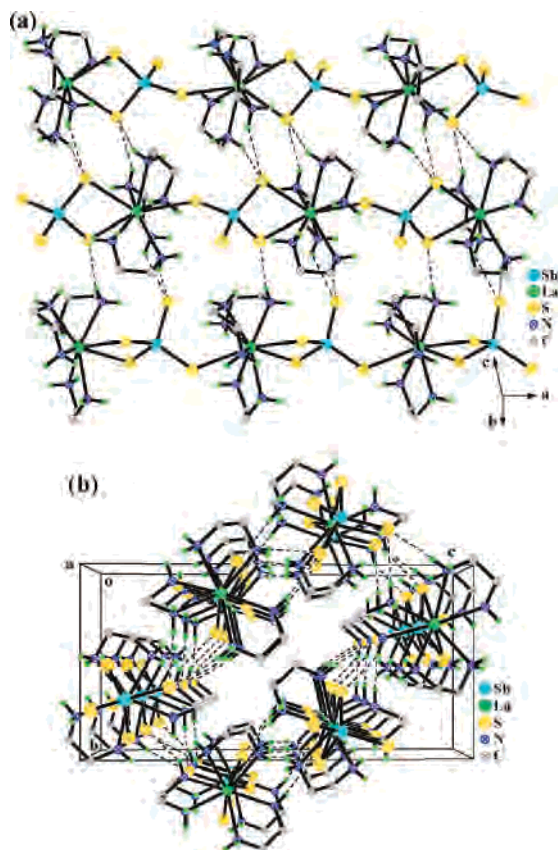

Figure 2. (a) View of N−H···S hydrogen bonds (shown in dashed lines) between the [La(en)$_3$(μ-SbS$_4$)]$_\infty$ chains and (b) the crystal packing diagram of **Ia** showing the N−H···S hydrogen bonds (viewed along a axis). The hydrogen atoms of C−H are omitted for clarity.

form one-dimensional chains. In compound **Ia**, the SbS$_4^{3-}$ anion acts as a μ_3-SbS$_4$ bridging ligand with S(1) and S(2) coordinated to one [La(en)$_3$]$^{3+}$ ion and S(3) coordinating to another [La(en)$_3$]$^{3+}$ ion to link the [La(en)$_3$]$^{3+}$ ions into a one-dimensional coordination polymer, [La(en)$_3$(μ_3-SbS$_4$)]$_\infty$ (Figures 1a and 2a). The La^{3+} ion is in a nine-coordinated environment with six amino N atoms of three bidentate en ligands and three S atoms of two different SbS$_4^{3-}$ anions. The novel mixed-ligand-coordinated polyhedron LaN$_6$S$_3$ is a distorted monocapped square antiprism (Figure 1b). The La−N distances, ranging from 2.662(4) to 2.742(4) Å (Table 2), are comparable with those observed in four en-ligand-coordinated [La(en)$_4$]$^{3+}$ cation.[16] The La−S distances, ranging from 3.0508(11) to 3.1698(12) Å, are slightly longer than
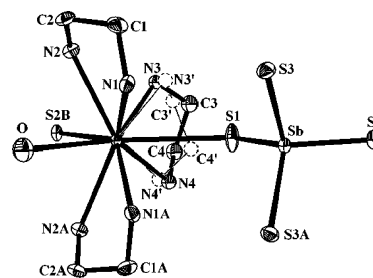
Figure 3. Crystal structure of **Ib** with the labeling scheme. Displacement ellipsoids are drawn at the 50% level. Hydrogen atoms are omitted for clarity. Symmetry operation: (A) x, $-y + 3/2$, z; (B) $x - 1$, y, z.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **Ia** and **Ib**

	Ia (Ln = La)	**Ib** (Ln = Nd)
Sb−S	2.3181(11)−2.3361(11)	2.3161(15)−2.3323(10)
Ln−N	2.662(4)−2.742(4)	2.637(3)−2.677(8)
Ln−S	3.0508(11)−3.1698(12)	2.9987(13), 3.0445(15)
Ln−O		2.648(5)
Ln−S−Sb	91.68(3)−122.80(4)	114.38(5), 125.84(6)
S−Sb−S	101.09(4)−113.04(4)	106.22(5)−111.22(3)
N−Ln−N	64.30(11)−144.97(12)	63.87(16)−147.3(2)
S−Ln−S	71.87(3)−137.81(3)	133.99(4)
S−Ln−N	66.02(8)−145.70(8)	64.9(2)−135.99(7)
S−Ln−O		84.02(11)−141.99(11)
O−Ln−N		71.31(8)−141.68(19)

those of lanthanum thioantimonates(III).[2,3] The SbS$_4^{3-}$ anion is a distorted tetrahedron with Sb−S distances varying from 2.3181(11) to 2.3361(11) Å, which are comparable to those observed in other tetrahedral SbS$_4^{3-}$ anions.[14] The distances of Sb−S(1), Sb−S(2), and Sb−S(3) (av Sb−S = 2.3287-(11) Å) are expectedly longer than that of Sb−S(4) (2.3181-(11) Å) because of the coordination of S(1), S(2), and S(3) to the [La(en)$_3$]$^{3+}$ ions. The [La(en)$_3$(μ_3-SbS$_4$)]$_\infty$ chains are parallel to the a axis, and their orientation alternates in adjacent chains (Figure 2a). The N−H···S hydrogen-bonding interactions between the chains (N···S = 3.385(4)−3.467-(4) Å, N−H···S = 149.7−173.8°) result in a 3D network (shown in Figure 2b).

The crystal structure of **Ib** is similar to that of **Ia** and also consists of neutral one-dimensional [Nd(en)$_3$(H$_2$O)(μ_2-SbS$_4$)]$_\infty$ chains except that the SbS$_4^{3-}$ anion acts as a bidentate bridging ligand other than a tridentate one in **Ia**, and the nine-coordinate environment of [Nd(en)$_3$]$^{3+}$ ion is satisfied by the coordination of one H$_2$O molecule (Figure 3). The water molecule must be from the solvent en, since commercial en is not an absolute reagent. The 9-coordinate polyhedron NdN$_6$S$_2$O is a distorted monocapped square antiprism similar to the LaN$_6$S$_3$ polyhedron in **Ia**. The third en ligand is disordered (Figure 3) with the occupancies of disordered C/C′ and N/N′ atoms assigned as 50 and 50%, respectively. The crystal structure of **Ib** is isostructural to a Sm analogue, [Sm(en)$_3$(H$_2$O)(μ_2−SbS$_4$)] (**Ic**), reported by our group.[9a] The average distances of Nd−N (2.656 Å) and Nd−S (3.0216(14) Å) are comparable to those observed in other Nd^{3+} complexes with amine donor atoms[17] and those

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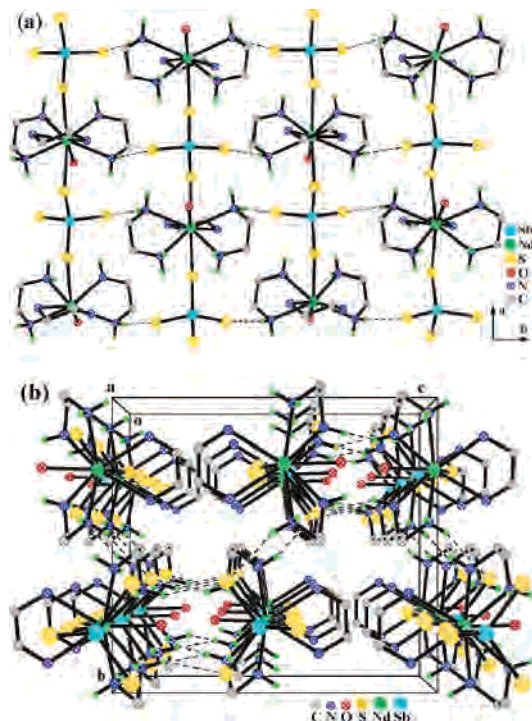
Figure 4. (a) View of the layer (viewed along *c* axis) formed by [Nd-(en)$_3$(H$_2$O)(SbS$_4$)]$_\infty$ chains via N−H···S hydrogen bonds (shown in dashed lines) and (b) the crystal packing of **Ib** showing the N−H···S hydrogen bonds (viewed along *a* axis). The hydrogen atoms of C−H are omitted for clarity.

of multinary neodymium sulfides with S donor atoms of thiometalate anions,[18] respectively.

The [Nd(en)$_3$(H$_2$O)(μ-SbS$_4$)]$_\infty$ chains are parallel to the *a* axis and their orientations alternate in adjacent chains (Figure 4a). The chain contacts neighbors through N−H···S hydrogen bonds with N···S distances varying from 3.555(3) to 3.667(3) Å and N−H···S angles varying from 152.4 to 165.7°, forming a layered arrangement parallel to the (001) plane. The layers also interact via N−H···S hydrogen bonds leading to a 3D network (Figure 4b).

Crystal Structure of Type II. Compounds **IIa**, **IIb**, and **IIc**, which have the general formula [Ln(en)$_4$]SbS$_4$·0.5en, are isostructural (Table 1), and compound **IIa** is discussed here in detail. **IIa** consists of an isolated four-en-coordinated [Eu(en)$_4$]$^{3+}$ cation, a tetrahedral SbS$_4{}^{3-}$ anion, and one half of a free en molecule. The crystal structure of **IIa** is depicted in Figure 5a. The C(2) atom is disordered, and the occupancies of disordered C/C′ are assigned as 60% and 40%. The Eu^{3+} ion is in an eight-coordinate environment with eight amino N atoms of four bidentate en ligands forming a distorted bicapped trigonal prism (Figure 5b). The Eu−N distances (2.532(5)−2.576(6) Å) are comparable to those observed in the literature.[19] The Sb−S distances and S−Sb−S angles are in agreement with the values of other four compounds (Table 2 and Table 3). In **IIa**, SbS$_4{}^{3-}$ anions

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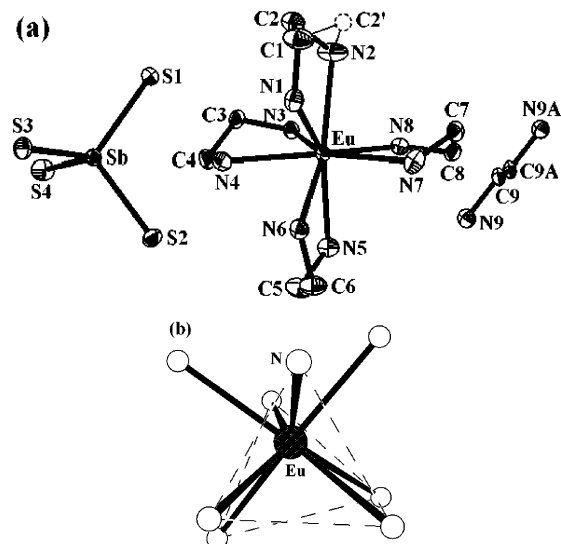
Figure 5. (a) Crystal structure of **IIa** with the labeling scheme with the displacement ellipsoids drawn at the 50% level and (b) the coordination environment of the Eu^{3+} ion.
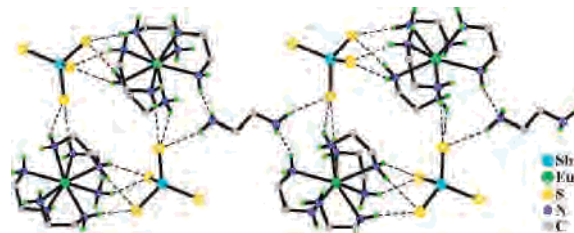

Figure 6. View of intermolecular N−H···S and N−H···N hydrogen-bonding interactions (shown in dashed lines) in **IIa**. The hydrogen atoms of C−H are omitted for clarity.

contact [Eu(en)$_4$]$^{3+}$ and the free en ligand via N−H···S hydrogen bonds with N···S distances varying from 3.308-(5) to 3.598(6) Å and N−H···S angles varying from 147.2 to 173(8)°, and the [Eu(en)$_4$]$^{3+}$ cations are connected by an en molecule via the N−H···N hydrogen bond (N···N = 3.061(8) Å, N−H···N = 157.7°). A network structure is assembled via the two types of interactions of hydrogen-bonding (Figure 6). The same hydrogen bonding interactions are found in compounds **IIb** and **IIc**. Meanwhile, the crystal structures of **IIa−IIc** are isostructural to that of a analogue of [Sm(en)$_4$]SbS$_4$·0.5en (**IId**).[9a]

Factors Influencing the Structures of the Lanthanide Thioantimonates. Structural Changes Across the Lanthanide Series. Under the same synthetic conditions, lanthanide(III)−en complexes form two types and three different structures of lanthanide thioantimonates(V) with the SbS$_4{}^{3-}$ anion. La^{3+} and Nd^{3+} form thioantimonate(V) compounds of type I, which are reformulated [Ln(en)$_3$(H$_2$O)$_x$(μ_{3-x}-SbS$_4$)] (Ln = La, **Ia**; Nd, **Ib**), in which SbS$_4{}^{3-}$ anions act as μ_3-SbS$_4$ and μ_2-SbS$_4$ bridging ligands, respectively, leading to one-dimensional neutral polymeric structures, while Eu^{3+}, Dy^{3+}, and Yb^{3+} form thioantimonates(V) of type II, [Ln-

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Table 3. Selected Bond Distances (Å) and Angles (deg) for **IIa**, **IIb**, and **IIc**

	IIa (Ln = Eu)	**IIb** (Ln = Dy)	**IIc** (Ln = Yb)
Sb−S	2.3132(16)−2.3397(16)	2.3145(10)−2.3424(10)	2.3186(18)−2.3448(18)
Ln−N	2.532(5)−2.576(6)	2.482(3)−2.546(4)	2.519(6)−2.573(6)
S−Sb−S	106.69(6)−113.29(6)	106.33(4)−113.52(4)	106.57(7)−113.40(7)
N−Ln−N	65.84(17)−153.52(17)	66.67(11)−152.61(11)	66.23(19)−154.2(2)

Table 4. Trivalent Lanthanide Metal Ionic Radius and the Stability Constant of $[Ln(en)_3]^{3+}$ Complexes in Dimethyl Sulfoxide at 25 °C

	ionic radius[20] (Å)		stability constant[21] (log K_3)
La^{3+}	1.061	$[La(en)_3]^{3+}$	3.31(10)
Pr^{3+}	1.013	$[Pr(en)_3]^{3+}$	3.50(11)
Nd^{3+}	0.995	$[Nd(en)_3]^{3+}$	3.80(12)
Sm^{3+}	0.964	$[Sm(en)_3]^{3+}$	4.3(2)
Eu^{3+}	0.950	$[Eu(en)_3]^{3+}$	4.43(24)
Gd^{3+}	0.938	$[Gd(en)_3]^{3+}$	4.98(12)
Tb^{3+}	0.923	$[Tb(en)_3]^{3+}$	5.28(7)
Dy^{3+}	0.908	$[Dy(en)_3]^{3+}$	5.49(14)
Ho^{3+}	0.894	$[Ho(en)_3]^{3+}$	5.68(12)
Er^{3+}	0.881	$[Er(en)_3]^{3+}$	6.76(12)
Tm^{3+}	0.869	$[Tm(en)_3]^{3+}$	7.04(6)
Yb^{3+}	0.858	$[Yb(en)_3]^{3+}$	7.70(7)
Lu^{3+}	0.848	$[Lu(en)_3]^{3+}$	7.76(6)

$(en)_4]SbS_4 \cdot 0.5en$ (Ln = Eu, **IIa**; Dy, **IIb**; Yb, **IIc**), which are constructed by isolated $[Ln(en)_4]^{3+}$ and SbS_4^{3-} ions. In particular, the Sm^{3+} ion forms both type I ($[Sm(en)_3(H_2O)-(\mu_2-SbS_4)]$, **Ic**) and type II ($[Sm(en)_4]SbS_4 \cdot 0.5en$, **IId**) compounds; this is related to the synthetic procedure.[9a] Compound **IId** is obtained by a one-step solvothermal reaction, while **Ic** is obtained by a two-step reaction.[9a] The two kinds of synthetic procedures were described in detail in the literature. [9b] However, only one type of compound is formed for other lanthanide elements with either a one-step or two-step solvothermal reaction, for example, $[La(en)_3(\mu_3-SbS_4)]$ (**Ia**) were obtained using both of the synthetic procedures. As a consequence of these results, the samarium-(III) ion just locates at the dividing point of type I and type II structures.

Influence of the Stability of Lanthanide(III)−en Complexes. The formation and structures of the two types of thioantimonates(V) are obviously related to the lanthanide-(III) ionic radii and the stability of Ln(III)−en complexes. The stability of Ln(III)−en complexes can be elucidated by their stability constants (in a dimethyl sulfoxide solution), which are listed in Table 4.[20,21] It can be seen from Table 4 that the stability constants of $[Ln(en)_3]^{3+}$ complexes rise monotonically with the decrease in the ionic radius of the trivalent lanthanide ions. This trend reveals that the capacity of coordination of the SbS_4^{3-} anion to lanthanides(III) in competition with that of the en ligand decreases across the lanthanide series. Thus, the SbS_4^{3-} anion can bond to lighter lanthanide ions (La−Nd) as a tridentate or bidentate ligand, resulting in compounds of type I, whereas it is incapable of coordinating to the heavier ones (Eu−Lu) resulting in the formation of compounds of type II. The competition of the two coordinating reactions balances at samarium(III), which

has a suitable radius and stability constant of the en complex and forms compounds of both type I and type II.

Influence of the Coordination Number of Lanthanides-(III) Ions. The lanthanide(III) ions do not exhibit the restricted stereochemistry in coordination complexes typical of transition metals but, rather, are characterized by variable coordination numbers and geometries.[21] It is also well-known that the coordination numbers of lanthanide(III) ions prefer nine for lighter lanthanide ions and eight for heavier ones in aqueous solution.[22] Because en is a bidentate ligand, the lighter lanthanide ions (La−Sm) leave at least one coordination site free at the Ln^{3+} ion allowing it to bond to the SbS_4^{3-} anion or water molecule. In fact, lanthanum is bound to three sulfur (μ_3-SbS_4) and six nitrogen donor atoms (**Ia**). Neodymium and samarium are coordinated by two sulfur (μ_2-SbS_4) and six nitrogen donor atoms, and both ions combine one H_2O ligand to maintain the coordination number of nine (**Ib** and **Ic**). But the en ligands have saturated the coordination number of heavier lanthanide ions, thus, the SbS_4^{3-} anion has less opportunity to coordinate to the metal center, and compounds of type II (**IIa**−**IId**) are formed.

Optical and Thermal Properties of the Lanthanide Thioantimonates. Optical Properties. The optical absorption spectra of compounds **Ia** and **Ib** in the range of 1.7 to 6 eV show well-defined abrupt absorption edges from which the band gaps can be estimated as 3.68 eV for **Ia** and 2.29 eV for **Ib** (Figure 7). Both band gaps of **Ia** and **Ib** are larger than those of lanthanide polythioantimonates(III) free of organic components, such as, $K_2La_2Sb_2S_9$ (2.20 eV),[2a] La_2-SbS_5Br (2.08 eV),[3] and $CeLaSbS_5Br$ (2.07 eV).[3] The band gaps are similar for both water-coordinated type I and type II compounds, for example, the band gaps of **Ic** and **IId** are 2.73 and 2.75 eV, respectively.[9a] However, the difference in the energy for **Ia** and **Ib** is very large (ΔE = 1.39 eV), which might be the result of their different structures.

Thermal Properties. Upon heating in the nitrogen stream, compound **Ia** loses en ligands in one step with a mass loss of 31.5% (theoretical values: 31.7%) accompanied by one endothermic signal in the DSC curve with peak temperature, T_p, of 230 °C. It releases one molar elemental sulfur with mass loss of 5.0% between 250 and 400 °C. The decomposition of **Ib** is similar to that of **Ia** except that compound **Ib** loses its coordinated H_2O at T_p = 112 °C with mass loss of 3.1%. Compound **IIa** decomposes in three steps with mass losses of 4.0, 35.5, and 5% for free en molecule, coordinated en ligands, and one molar elemental sulfur, respectively. The decomposition of compounds **IIb** and **IIc** is similar to that of **IIa**. It is not uncommon that thioantimonate(V) compounds release elemental sulfur upon heating.[8c,14b] The self-

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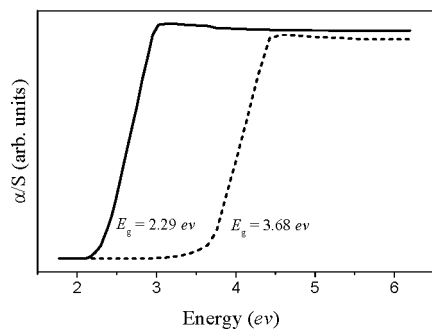
Figure 7. Solid-state optical absorption spectra of **Ia** (dashed line) and **Ib** (solid line). The band gap value, E_g, is shown.

redox reaction of $Sb^VS_4{}^{3-}$ species can produce thioantimonate-(III) compound and elemental S. This assumption is supported by the decomposition product, Sb_2S_3, found in residue of $[Ni(en)_3(Hen)]SbS_4$.[8c] The phases of the decomposition residues of compounds **Ia**, **Ib**, and **IIb** at 450 °C were checked by X-ray diffraction. In the X-ray powder pattern of the decomposition products of **Ia**, lanthanum antimony sulfide, $La_6Sb_8S_{21}$ (JCPDS No. 37-583), and lanthanum sulfide, La_2S_3 (JCPDS No. 22-645), were identified (see Supporting Information). But the decomposition products of **Ib** and **IIb** are amorphous to X-ray powder diffraction.

Conclusion

The lanthanides(III) exhibit typically "hard" acid cations and preferentially bond to oxygen and nitrogen donor atoms in solution, so the strategy to solvothermally combine Ln^{3+} ions with thiometalate anions requires a nonaqueous system to avoid the hydrolysis of lanthanides(III) in aqueous solutions. We have successfully synthesized a series of novel crystalline lanthanide thioantimonates(V) in en solvent under solvothermal conditions. The solvothermal method is a new route for the synthesis of multinary lanthanide sulfides decorated by organic components. Unlike transition-metal ions, which mainly produce thioantimonate(III) compounds in an Sb/S/amine solvothermal system, lanthanides(III) always lead to thioantimonate(V) compounds in a similar synthetic system. Furthermore, the products are not mutable and can be obtained under a wide variety of synthetic conditions.

The lanthanide thioantimonates(V) can be classified as two types, according to the crystal structures, which are related to the entities of lanthanide(III) ions. The lighter lanthanides-(III) form compounds of type I and the heavier ones form type II. The types of lanthanide thioantimonates(V) are related to the stability of the lanthanide(III)−en complexes and the coordination number and ionic radii of lanthanides-(III). The $SbS_4{}^{3-}$ anion has proven to be able to coordinate to lighter lanthanide(III) ions with a μ_3-SbS_4 or μ_2-SbS_4 coordination mode. The result demonstrates that the hard acid lanthanide(III) ions can be coordinated by a "soft" base-donor atom of sulfur in amine solution, in addition the hard ones of oxygen and nitrogen. The synthesis and structural characterization of the title compounds would be helpful for a more complete understanding of the coordination chemistry of lanthanides(III).

Supporting Information Available: Figures of TGA−DSC curves (PDF), powder X-ray diffraction pattern, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC051402G