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Solvothermal Synthesis, Crystal Structures, and Properties of New Selenidoantimonates $[Ln(en)_4(SbSe_4)]$ (Ln = La, Nd) and $[Sm(en)_4]SbSe_4 \cdot 0.5en$: The First Example of an $SbSe_4^{3-}$ Anion Acting as a Ligand to a Lanthanide Complex

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Three new lanthanide selenidoantimonates $[Ln(en)_4(SbSe_4)]$ [Ln = La (**1**), Nd (**2**)] and $[Sm(en)_4]SbSe_4 \cdot 0.5en$ (**3**) (en = ethylenediamine) were first synthesized by treating $LnCl_3$, Sb, and Se in a stoichiometric ratio with en under mild solvothermal conditions. Compounds **1** and **2** are isostructural. The Ln^{3+} ion has a nine-coordinate environment involving eight N atoms from four en ligands and one Se atom from the $SbSe_4^{3-}$ anion forming a distorted bicapped pentagonal bipyramid. $[La(en)_4(SbSe_4)]$ and $[Nd(en)_4(SbSe_4)]$ are the first examples of solvothermally synthesized selenidoantimonates with an $SbSe_4^{3-}$ anion acting as a ligand in a lanthanide complex. The crystal structure of **3** contains an isolated bicapped trigonal-prismatic coordinated $[Sm(en)_4]^{3+}$ cation, a tetrahedral $SbSe_4^{3-}$ anion, and half a free en molecule in its asymmetric unit. The bandgaps of 2.22 eV for **1**, 2.33 eV for **2**, and 2.54 eV for **3** have been derived from optical absorption spectra. Compound **1** loses the en ligands in one step, whereas compound **2** loses them in two steps.

Introduction

The mild solvothermal reaction in amine has proven to be a versatile route for the synthesis of main group chalcogenometalates.[1–3] In the case of chalcogenoantimonates, since the compound $[Co(en)_3]CoSb_4S_8$[4] was prepared, a large number of thioantimonates have been synthesized using amino transition metal (TM) complexes $[TM(amine)_m^{n+}]$ as structural directors under solvothermal conditions, giving $[M(en)_3]Sb_2S_4$ (M = Co, Ni),[5] $[M(en)_3]Sb_4S_7$ (M = Mn, Co, Ni),[5,6] $Mn_2(en)Sb_2S_5$,[7] $[Co(en)_3]Sb_{12}S_{19}$,[8] $[Ni(dien)_2]Sb_4S_8$,[9] $[Fe(dien)_2]Sb_6S_{10} \cdot 0.5H_2O$,[10] $[Ni(dien)_2]Sb_4S_9$,[11] $[Ni(dien)_2]_9Sb_{22}S_{42} \cdot 0.5H_2O$,[12] $[Ni(dien)_2]_3(Sb_3S_6)_2$,[13] $[Fe(dien)_2]Fe_2Sb_4S_{10}$[14] (dien = diethylenediamine), $[M(tren)]Sb_2S_4$ (M = Co, Ni),[15] $[M(tren)]Sb_4S_7$ (M = Mn, Fe, Co, Zn),[16] $[Co(tren)]_2Sb_4S_8$,[17] $[Mn(tren)]_4Mn_2Sb_4S_{12}$,[18] and $[Mn(tren)]_2Sb_2S_5$[19] [tren = tris(2-aminoethyl)amine], for example. The thioantimonates exhibit rich structural diversity because of the variable coordination behaviors of Sb^{III} atoms caused by the stereochemically active lone pair.[20] However, compared with the bewildering thioantimonates, the selenidoantimonates combined with transition metals are less explored under mild solvothermal conditions and only a few examples have been reported.[21–25]

The combination of lanthanide metals with chalcogenometalates should lead to new architectural features with unique properties. However, the chemistry explored involving the synthesis of chalcogenometalates integrating with lanthanide metal ions (Ln^{3+}) by the solvothermal methodology is very limited. It is a challenge to combine the Ln^{3+} ion with the so-called soft-base chalcogenometalate anions in solution because of the weak coordination of chalcogenometalate anions and the hydrolysis of lanthanide ions. Very recently, templated by (en)lanthanide(III) complexes, two series of lanthanide thioantimonates(V), $[Ln(en)_3(H_2O)_x(\mu_{3-x}\text{-}SbS_4)]$ (x = 0, 1; Ln = La, Nd, Sm) and $[Ln(en)_4]SbS_4 \cdot 0.5en$ (Ln = Sm, Eu, Dy, Yb),[26,27] were obtained from the synthetic system Ln^{3+}/Sb/S/en under solvothermal conditions during our systematic synthesis of chalcogenometalates in superheated en.[28–31] The present contribution reports the synthesis, crystal structures, and properties of new lanthanide selenidoantimonates(V) $[La(en)_4(SbSe_4)]$, $[Nd(en)_4(SbSe_4)]$, and $[Sm(en)_4]SbSe_4 \cdot 0.5en$, which were obtained from a solvothermal route. To the best of our knowledge, the present compounds are the only examples of selenidoantimonates combined with lanthanide(III) complex cations.

Results and Discussion

The compounds **1** and **2** crystallize in the monoclinic space group $P2_1/n$ with four formula units in the unit cell and are isostructural. The molecular structure of **1** is de-

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picted in Figure 1. The lanthanide(III) ion is coordinated by four bidentate en ligands and a monodentate $SbSe_4^{3-}$ anion leading to a neutral complex $[Ln(en)_4(SbSe_4)]$ [Ln = La (**1**), Ln = Nd (**2**)]. The central Ln^{3+} ion lies within a nine-coordinate environment forming a distorted monocapped square antiprism LnN_8Se. The Ln–N bond lengths are 2.648(4)–2.773(3) Å for La–N and 2.628(3)–2.725(3) Å for Nd–N, and are consistent with those in other compounds containing (en)lanthanide(III) complexes.[27,32] The La–Se [3.3197(5) Å] and Nd–Se [3.2992(6) Å] bond lengths are comparable to those in multinary lanthanum and neodymium selenides [3.1070(12)–3.3625(12) Å for La–Se in $KLaP_2Se_6$[33] and 2.979(1)–3.245(1) Å for Nd–Se in Nd_4MnOSe_6[34]]. The Ln–N and Ln–Se bond lengths decrease from La to Nd, as expected from the lanthanide contraction. The $SbSe_4^{3-}$ anion is a distorted tetrahedron, as evidenced by Sb–Se bond lengths ranging from 2.4654(5) to 2.4851(7) Å and Se–Sb–Se angles ranging from 107.715(18) to 111.558(17)°. Both lengths and angles are comparable to those observed in other compounds containing tetrahedral $SbSe_4^{3-}$ anions.[21–24] The Sb–Se(1) bonds [2.4848(5) Å for **1**, 2.4851(7) Å for **2**] are expectedly longer than other Sb–Se bonds (Table 1) because of the coordination of Se(1) with the lanthanide(III) ion.

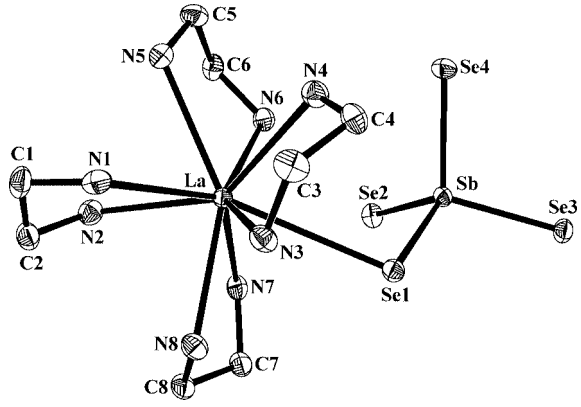

Figure 1. Crystal structure of **1** with labeling scheme; the probability ellipsoids are drawn at the 50% level. Hydrogen atoms are omitted for clarity.

In **1**, the terminal Se atoms of $[La(en)_4(SbSe_4)]$ are involved in intermolecular N–H···Se hydrogen bonding with adjacent molecules resulting in a chainlike arrangement of $[La(en)_4(SbSe_4)]$ moieties parallel to the *a* axis (Figure 2). The chains are further connected through N–H···Se hydrogen bonds leading to a three-dimensional network. The N···Se distances vary from 3.443(4) to 3.755(4) Å and the N–H···Se angles vary from 138.1 to 167.7° (Table 2), and are consistent with the values reported in the literature.[35] Similar intermolecular hydrogen bonding is observed in compound **2** (Table 2).

Compound **3** crystallizes in the space group $P2_1/n$ with four formula units in the unit cell. Its molecular structure is quite different from those of **1** and **2**, but it is isostructural to the thio analog of $[Sm(en)_4]SbS_4 \cdot 0.5en$.[26] The crystal structure of **3** consists of an isolated four-en-coordinated $[Sm(en)_4]^{3+}$ cation, a tetrahedral $SbSe_4^{3-}$ anion, and half a free en molecule in its asymmetric unit (Figure 3). The atom C(2) is disordered and the occupancies of disordered C and C′ are assigned as 55% and 45%, respectively. The Sm^{3+} ion is in an eight-coordinate environment with eight amino N atoms from four bidentate en ligands forming a distorted bicapped trigonal prism. The Sm–N bond lengths [2.532(5)–2.576(6) Å] are comparable with those reported in the literature.[26] The Sb–Se distances and Se–Sb–Se angles are in agreement with those in **1** and **2** (see Tables 1 and 3). The Se atoms of the $SbSe_4^{3-}$ anion are in contact with $-NH_2$ groups with N···Se distances ranging from 3.402(5) to 3.764(5) Å and N–H···Se angles ranging from 142.1 to 171.9°, indicating weak hydrogen bonds. An N(6)–H(6A)···N(9) hydrogen bond is formed with an N(6)···N(9) distance of 3.100(8) Å and an N(6)–H(6A)···N(9) angle of 156.2°. The N–H···Se and N–H···N hydrogen-bonding interactions lead to a three-dimensional network structure. The crystal packing of **3** is illustrated in Figure 4.

In our systematic investigation of lanthanide thioantimonate compounds in superheated en, two types of compounds were obtained across the lanthanide series. The lighter (en)lanthanide(III) complex cations are bridged by μ_3-SbS_4 or μ_2-SbS_4 ligands to form one-dimensional neutral polymers $[Ln(en)_3(H_2O)_x(\mu_{3-x}\text{-}SbS_4)]$ (Ln = La, Nd, Sm),[26,27] whereas the heavier ones form compounds

Table 1. Selected bond lengths [Å] and angles [°] for **1** and **2**.

	1	**2**		**1**	**2**
Sb–Se(1)	2.4848(5)	2.4851(7)	Sb–Se(2)	2.4671(5)	2.4654(5)
Sb–Se(3)	2.4675(5)	2.4719(6)	Sb–Se(4)	2.4701(5)	2.4665(6)
Ln–Se(1)	3.3197(5)	3.2992(6)	Ln–N(1)	2.648(4)	2.623(3)
Ln–N(2)	2.737(4)	2.725(3)	Ln–N(3)	2.702(3)	2.678(3)
Ln–N(4)	2.700(4)	2.592(3)	Ln–N(5)	2.773(3)	2.646(3)
Ln–N(6)	2.686(3)	2.646(3)	Ln–N(7)	2.735(3)	2.681(3)
Ln–N(8)	2.692(4)	2.628(3)			
Se(1)–Sb–Se(2)	108.852(17)	111.395(19)	Se(1)–Sb–Se(3)	111.017(18)	108.248(16)
Se(1)–Sb–Se(4)	108.424(17)	108.882(16)	Se(2)–Sb–Se(3)	109.311(18)	107.715(18)
Se(2)–Sb–Se(4)	111.521(18)	109.06(2)	Se(3)–Sb–Se(4)	107.722(18)	111.558(17)
Se(1)–Ln–N	69.60(7)–141.18(8)	68.88(7)–141.04(7)	Sb–Se(1)–Ln	102.926(15)	103.837(17)
N–Ln–N	62.77(10)–145.40(11)	63.72(9)–144.65(9)			

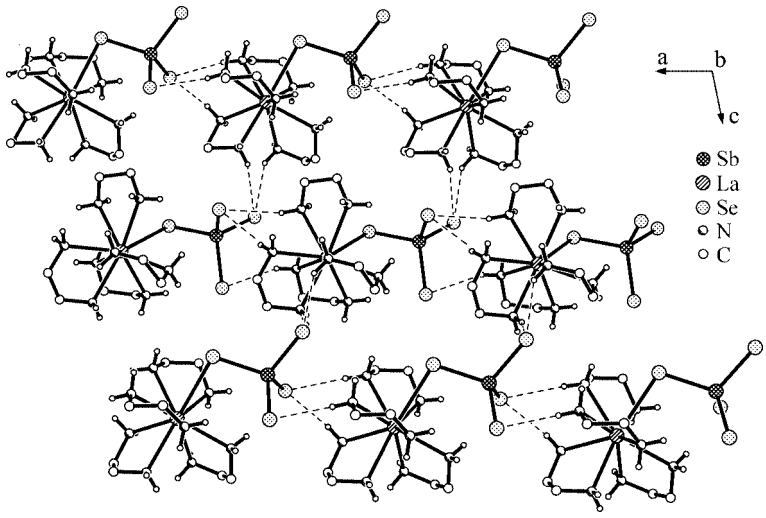

Figure 2. N–H···Se hydrogen bonds between the $[La(en)_4(SbSe_4)]$ molecules viewing along the *b* axis. Hydrogen atoms of C–H are omitted for clarity.

Table 2. Selected N···Se distances [Å] and N–H···Se angles [°] for **1** and **2**.

N–H	Se	N···Se	N–H···Se
1			
N(1)–H(1A)	Se(4)[a]	3.443(4)	149.2
N(1)–H(1B)	Se(3)[b]	3.508(4)	161.4
N(2)–H(2A)	Se(3)[c]	3.651(4)	160.0
N(3)–H(3A)	Se(4)[a]	3.755(4)	156.6
N(5)–H(5A)	Se(3)[c]	3.650(3)	147.9
N(6)–H(6A)	Se(4)	3.589(4)	164.3
N(6)–H(6B)	Se(2)	3.477(4)	138.1
N(7)–H(7B)	Se(2)	3.597(4)	167.7
N(8)–H(8B)	Se(2)[a]	3.546(4)	149.1
2			
N(1)–H(1A)	Se(4)	3.476(3)	139.4
N(1)–H(1B)	Se(3)	3.590(3)	166.1
N(2)–H(2A)	Se(2)[d]	3.768(3)	139.5
N(2)–H(2B)	Se(2)[c]	3.627(3)	147.8
N(4)–H(4A)	Se(2)[d]	3.493(3)	160.4
N(4)–H(4B)	Se(3)[a]	3.432(3)	148.9
N(5)–H(5B)	Se(3)[a]	3.784(3)	154.4
N(6)–H(6B)	Se(3)	3.616(3)	173.0
N(7)–H(7A)	Se(4)	3.596(3)	166.5
N(8)–H(8A)	Se(4)[a]	3.550(3)	147.9

[a] Symmetry code: $x + 1, y, z$. [b] Symmetry code: $-x + 3/2, y - 1/2, -z + 3/2$. [c] Symmetry code: $x + 1/2, -y + 3/2, z - 1/2$. [d] Symmetry code: $-x + 3/2, y + 1/2, -z + 1/2$.

$[Ln(en)_4]SbS_4 \cdot 0.5en$ (Ln = Sm, Eu, Dy, Yb)[26,27] that are constructed from isolated $[Ln(en)_4]^{3+}$ and SbS_4^{3-} ions. The two types of thioantimonates are related to the stability of the (en)lanthanide(III) complexes, coordination number, and the radii of the metal ions.[27] A similar situation is observed in the case of selenidoantimonate. The (en)lanthanide(III) complexes also form two kinds of selenidoantimonates with the $SbSe_4^{3-}$ anion in en. In **1** and **2**, $[Ln(en)_4]^{3+}$ (Ln = La, Nd) cations combine with $SbSe_4^{3-}$ through an Ln–Se bond, while $[Sm(en)_4]^{3+}$ does not bond with $SbSe_4^{3-}$ in **3**. Although the lanthanide(III) ions do not exhibit restricted stereochemistry in coordination complexes and are characterized by variable coordination numbers and geometries in the solid state,[36] it is commonly observed that the lighter lanthanide ions prefer coordination numbers of nine and heavier ones prefer coordination numbers of eight in solution.[37] Because en is a bidentate ligand, the $[La(en)_4]^{3+}$ and $[Nd(en)_4]^{3+}$ ions are bonded to the monodentate ligand $SbSe_4^{3-}$ to maintain the coordination number of nine for La^{3+} and Nd^{3+}, and $[La(en)_4(SbSe_4)]$ and $[Nd(en)_4(SbSe_4)]$ are formed. It is worth noting

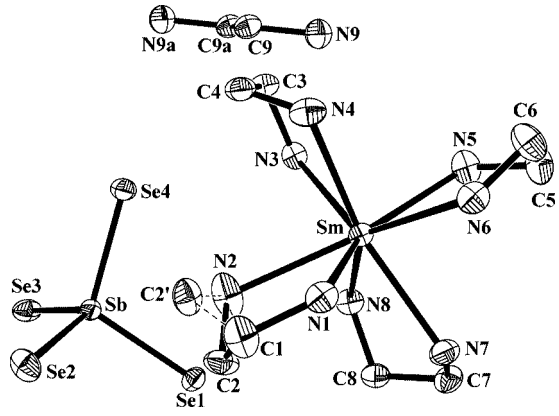

Figure 3. Crystal structure of **3** with labeling scheme. The probability ellipsoids are drawn at the 50% level; hydrogen atoms are omitted for clarity.

Table 3. Selected bond lengths [Å] and angles [°] for **3**.

Sb–Se(1)	2.4793(7)	Sb–Se(2)	2.4601(8)
Sb–Se(3)	2.4548(8)	Sb–Se(4)	2.4640(8)
Sm–N(1)	2.580(5)	Sm–N(2)	2.615(6)
Sm–N(3)	2.559(5)	Sm–N(4)	2.533(5)
Sm–N(5)	2.569(6)	Sm–N(6)	2.580(5)
Sm–N(7)	2.560(5)	Sm–N(8)	2.547(5)
Se(1)–Sb–Se(2)	105.33(3)	Se(1)–Sb–Se(3)	109.28(3)
Se(1)–Sb–Se(4)	110.06(3)	Se(2)–Sb–Se(3)	113.74(3)
Se(2)–Sb–Se(4)	108.99(3)	Se(3)–Sb–Se(4)	109.35(3)
N–Sm–N		66.08(16)–154.23(17)	

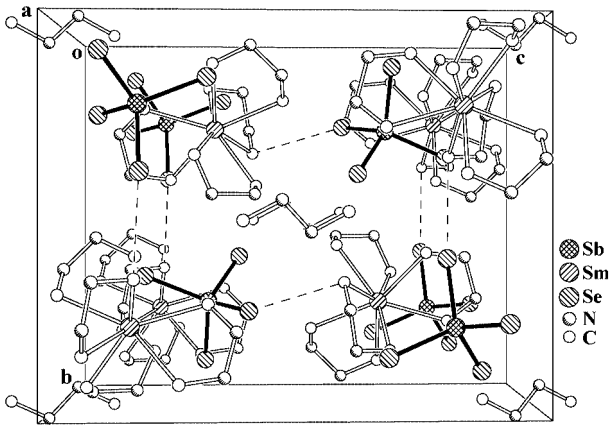

Figure 4. Crystal structure of $[Sm(en)_4]SbSe_4 \cdot 0.5en$ viewed along the *a* axis; hydrogen atoms are omitted for clarity.

that SbS_4^{3-} and $SbSe_4^{3-}$ exhibit different coordination modes when bound to the same lanthanide ions. For example, in $[La(en)_3(\mu_3\text{-}SbS_4)]$, SbS_4^{3-} acts as a μ_3-SbS_4 tridentate ligand to interlink $[La(en)_3]^{3+}$ ions, while $SbSe_4^{3-}$ coordinates to the $[La(en)_4]^{3+}$ ion as a monodentate ligand in the compound $[La(en)_4(SbSe_4)]$. This structural difference can be interpreted in terms of the lower coordination ability of the $SbSe_4^{3-}$ anion with respect to SbS_4^{3-}. Compared with the SbS_4^{3-} ligand, $SbSe_4^{3-}$is a soft-base ligand for the hard-acid cations of lanthanide(III) because of the larger radius of the selenium atom. Therefore, lanthanum can be coordinated with three sulfur atoms (μ_3-SbS_4) and six nitrogen atoms to form the μ_3-SbS_4 compound $[La(en)_3(\mu_3\text{-}SbS_4)]$ in a sulfide solution, but with one selenium atom and eight nitrogen atoms to form the mono-$SbSe_4$ compound $[La(en)_4(SbSe_4)]$ in a selenide solution.

Optical Properties

The optical absorption spectra of compounds **1**–**3** show well-defined abrupt absorption edges from which the bandgaps were estimated as 2.22 eV for **1**, 2.33 eV for **2**, and 2.54 eV for **3** (see Figure 5). These bandgaps are larger than those of the multinary lanthanide polythioantimonates(III), such as $K_2La_2Sb_2S_9$ (2.20 eV)[38] and La_2SbS_5Br (2.08 eV),[39] which are free of organic components.

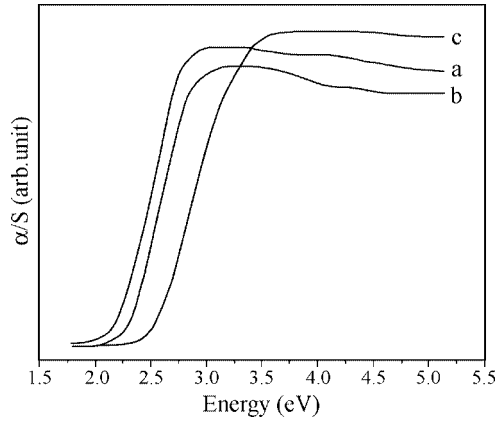

Figure 5. Optical absorption spectra of compounds **1** (a), **2** (b), and **3** (c).

Thermal Investigations

On heating in a nitrogen stream, compound **1** starts to decompose at T_{onset} = 190 °C with a weight loss of 29.2% (calcd. 29.4% for four en ligands) in one step. The weight loss is in good agreement with the theoretical value of 29.4% involving the complete removal of four en ligands. The decomposition process is accompanied by a strong endothermic signal in the DSC curve with peak temperature T_p = 222 °C (Figure 6a). In the IR spectrum of the residue no H–N, H–C, C–N, and C–C vibrations could be detected. For **3**, thermal decomposition occurs in two steps with a weight loss of 3.0% (calcd. 3.5% for 0.5 en ligands) and 28.0% (calcd. 28.0% for four en ligands), which correspond with the removal of free en and coordinated en ligands, respectively. The two decomposition steps are accompanied by two endothermic signals in the DSC curve with peak temperatures of T_p = 118 °C and T_p = 236 °C (Figure 6b).

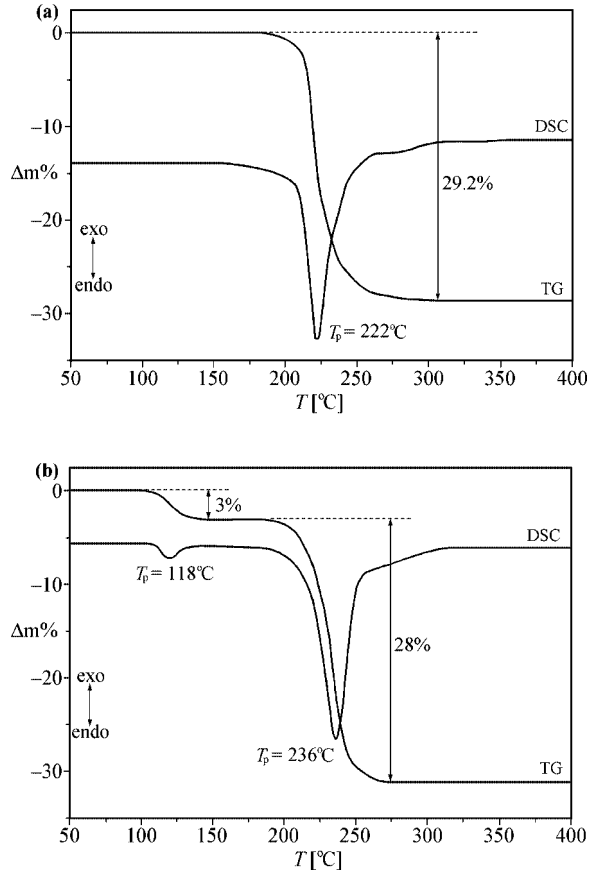

Figure 6. TG-DSC curves of compounds **1** (a) and **3** (b).

Conclusions

The lanthanides(III) typically produce "hard"-acid cations, which preferentially bond to oxygen and nitrogen donor atoms in solution so it is a challenge to combine Ln^{3+} ions with the so-called soft-base chalcogenometalate anions in an amine solvent. We have successfully synthesized novel selenidoantimonates containing lanthanide(III) in an en solvent under solvothermal conditions. $[Ln(en)_4(SbSe_4)]$ (Ln = La, Nd) and $[Sm(en)_4]SbSe_4{\cdot}0.5en$ are the first examples of solvothermally synthesized selenidoantimonates. The solvothermal method is a new route for the synthesis of multinary lanthanide selenides decorated by organic components. The synthesis and solid-state structural studies described in this article show that the soft-base ligand $SbSe_4^{3-}$ can coordinate to lanthanide(III) ions in an amine solution. This will shed light on a more complete understanding of the coordination chemistry of lanthanides(III) and preparation of lanthanide selenidometalates by mild solvothermal methods.

Experimental Section

General: All analytical grade chemicals were obtained commercially and used without further purification. Elemental analysis was conducted with an MOD 1106 elemental analyzer. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer using dry KBr discs in the 4000–400 cm^{-1} range. Room-temperature optical diffuse reflectance spectra of the powdered samples were obtained with a Shimadzu UV-3150 spectrometer. The absorption (α/S) data were calculated from the reflectance using the Kubelka–Munk function $\alpha/S = (1 - R)^2/2R$,[40] where R is the reflectance at a given energy, α is the absorption, and S is the scattering coefficient. Thermoanalytical measurements were performed with a DCS-TGA microanalyzer of SDT 2960, and all the samples were heated under a nitrogen stream of 100 mL min^{-1} with a heating rate of 5 °C min^{-1}.

Synthesis of $[La(en)_4(SbSe_4)]$ (1): The reactants $LaCl_3$ (122.6 mg, 0.5 mmol), Sb (61 mg, 0.5 mmol), and Se (158 mg, 2 mmol) were mixed in ethylenediamine (3 mL) whilst stirring. The mixture was loaded into a Teflon-lined stainless steel autoclave with an inner volume of 15 mL, and the sealed autoclave was then heated to 140 °C for 7 d. After cooling to ambient temperature, orange block crystals of **1** were obtained. The crystals were washed with ethanol and diethyl ether, dried and stored under vacuum. Yield: 188 mg (46%). $C_8H_{32}LaN_8SbSe_4$ (816.92): calcd. C 11.86, H 3.95, N 13.72; found C 11.81, H 3.92, N 13.66. IR (KBr): $\tilde{\nu}$ = 3383 (s), 3241 (s), 3106 (s), 2924 (s), 2870 (m), 1582 (vs), 1489 (s), 1454 (s), 1385 (m), 1327 (s), 1277 (m), 1146 (w), 1103 (w), 1007 (vs), 860 (w), 822 (w), 633 (m), 494 (m) cm^{-1}.

Synthesis of $[Nd(en)_4(SbSe_4)]$ (2): Orange-yellow platelet crystals of **2** were obtained by using a similar synthesis procedure to that used in **1** except that reactant $LaCl_3$ was replaced by $NdCl_3$. Yield: 226 mg (55%). $C_8H_{32}N_8NdSbSe_4$ (822.25): calcd. C 11.69, H 3.92, N 13.63; found C 11.54, H 3.88, N 13.60. IR (KBr): $\tilde{\nu}$ = 3335 (s), 3240 (s), 3167 (s), 2940 (s), 2870 (s), 1597 (s), 1578 (s), 1481, 1459 (s), 1385 (m), 1354 (s), 1214 (w), 1157 (w), 1080 (s), 1030 (vs), 822 (w), 779 (w), 640 (s), 513 (w), 440 (m) cm^{-1}.

Synthesis of $[Sm(en)_4]SbSe_4{\cdot}0.5en$ (3): Yellow prism crystals of **3** were obtained by using a similar synthesis procedure to that used in **1** except that reactant $LaCl_3$ was replaced by $SmCl_3$. Yield: 223 mg (52%). $C_9H_{36}N_9SbSe_4Sm$ (858.41): calcd. C 12.59, H 4.23, N 14.68; found C 12.54, H 4.25, N 14.62. IR (KBr): $\tilde{\nu}$ = 3301 (vs), 3280 (s), 3245 (s), 3132 (s), 2930 (vs), 2880 (s), 1570 (vs), 1515 (s), 1385 (m), 1331 (s), 1157 (w), 1007 (s), 868 (w), 814 (w), 776 (w), 660 (w), 498 (m) cm^{-1}.

X-ray Crystal Structure Determinations: A summary of crystal data and refinement parameters is given in Table 4. Data were collected with a Rigaku Mercury CCD diffractometer at 193(2) K using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) by an ω-scan method with a maximum 2θ value of 54.96°. An orange $0.22 \times 0.15 \times 0.10$ mm block crystal of **1**, an orange-yellow $0.46 \times 0.28 \times 0.05$ mm platelet crystal of **2**, and a yellow $0.35 \times 0.06 \times 0.05$ mm prism crystal of **3** were used for data collection. An absorption correction was applied for all the compounds using a multi-scan correction method. The structures were solved by direct methods using the SHELXS-97 program.[41] The refinement was performed against F^2 using the SHELXL-97 program.[42]

Table 4. Crystallographic data for **1**, **2**, and **3**.

	1	**2**	**3**
Empirical formula	$C_8H_{32}N_8Se_4LaSb$	$C_8H_{32}N_8Se_4NdSb$	$C_9H_{36}N_9Se_4SmSb$
Formula mass [g mol^{-1}]	816.92	822.25	858.41
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a [Å]	9.4711(6)	9.473(2)	11.3777(8)
b [Å]	14.6905(9)	14.625(3)	13.1107(9)
c [Å]	16.0388(10)	15.937(3)	16.3772(11)
β [°]	98.920(2)	98.847(4)	92.400(2)
V [Å^3]	2204.6(2)	2181.6(8)	2440.8(3)
Z	4	4	4
T [K]	193(2)	193(2)	193(2)
$D_{calcd.}$ [g cm^{-3}]	2.461	2.503	2.336
μ(Mo-K_α) [mm^{-1}]	9.749	10.273	9.466
Measured reflections	24400	24034	26983
Independent reflections	5034	4996	5575
Reflections with $I > 2\sigma(I)$	4537	4496	4659
R_{int}	0.0396	0.0533	0.0653
$R(F)$ [$F^2 > 2\sigma(F^2)$][a]	0.0308	0.0276	0.0444
$R_w(F^2)$ (all data)[b]	0.0595	0.0609	0.0930
Largest difference peak/hole [e Å^{-3}]	0.670/–1.111	1.087/–1.762	1.207/–1.497

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned with idealized geometries and refined with fixed isotropic displacement parameters using a riding model. The H atoms of C(1), C(2), and N(2) in **3** were not dealt with because of the disorder of atom C(2). CCDC-299097 (**1**), -299098 (**2**), and -299099 (**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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