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The First Example of the Tetraselenidostannate Anion $[SnSe_4]^{4-}$ as a Chelating Ligand to a Lanthanide Complex Ion: Solvothermal Synthesis and Characterization of Lanthanoid Selenidostannates $[Hdien][Ln(dien)_2(\mu\text{-}SnSe_4)]$ (Ln = Sm, Eu) and $[Eu_2(dien)_4(\mu\text{-}OH)_2]Sn_2Se_6$

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New lanthanoid selenidostannates $[Hdien][Ln(dien)_2(\mu\text{-}SnSe_4)]$ [Ln = Sm (**1**), Eu (**2**); dien = diethylenetriamine] were solvothermally prepared by reaction of Ln_2O_3 (Ln = Sm, Eu) with Sn and Se in dien. The structures of **1** and **2** consist of the tetraselenidostannate anion $[SnSe_4]^{4-}$ coordinating to a $[Ln(dien)_2]^{3+}$ fragment as a bidentate chelating ligand. The reaction of Ln_2O_3 and Se with $SnCl_4{\cdot}5H_2O$ under the same solvothermal conditions produces the selenidostannate $[Eu_2(dien)_4(\mu\text{-}OH)_2]Sn_2Se_6$ (**3**), which is constructed from the two dinuclear ions $[Eu_2(dien)_4(\mu\text{-}OH)_2]^{4+}$ and $[Sn_2Se_6]^{4-}$. The water molecule prevents the $[SnSe_4]^{4-}$ anion from coordinating to the lanthanide center. As far as we know, compounds **1** and **2** are the first selenidostannates integrated within lanthanoid complexes prepared under mild solvothermal conditions. Upon heating, compounds **1** and **2** decompose in three steps, whereas compound **3** undergoes a one-step decomposition procedure. The band gaps of 2.52, 2.08, and 2.43 eV were derived from optical absorption spectra for compounds **1**, **2**, and **3**, respectively.

Introduction

The mild solvothermal synthetic technique has proven to be a versatile route to the preparation of main-group chalcogenometalates containing transition-metal complexes, and a number of these chalcogenometalates have been synthesized by solvothermal methods in amine solutions.[1] The solvothermal synthesis of main-group chalcogenometalates containing lanthanoid complexes, however, is a scarcely explored route.

Recently, by introducing lanthanide(III) oxides Ln_2O_3 into the synthetic system M(M = Sb, As)/S(or Se)/en(or dien) (en = ethylenediamine), we successfully synthesized lanthanoid chalcogenoantimonates $[Ln(en)_3(H_2O)_x(\mu_{3-x}\text{-}SbS_4)]_\infty$ (Ln = La, x = 0; Ln = Nd, Sm, x = 1), $[Ln(en)_4]SbS_4{\cdot}0.5en$ (Ln = Sm, Eu, Dy, Yb),[2] and $[Ln(en)_4(SbSe_4)]$ (Ln = La, Nd),[3] and lanthanoid selenidoantimonate $[Ln(dien)_2(\mu_3\text{-}AsSe_4)]_\infty$ (Ln = Nd, Sm)[4] by using the solvothermal method. The formation of these lanthanoid chalcogenometalates in en and dien solvents proves that the tetrachalcogenometalate ligands $[SbS_4]^{3-}$, $[SbSe_4]^{3-}$, and $[AsSe_4]^{3-}$, which are regarded as typical soft-base ligands, can coordinate to Ln^{3+} complexes in the competition with the amino chelating ligands of en and dien. The tetrathioantimonate anion $[SbS_4]^{3-}$ acts as an μ_2-SbS_4 or μ_3-SbS_4 ligand to bridge the $[Ln(en)_3(H_2O)_x]^{3+}$ fragments to form a neutral polymer $[Ln(en)_3(H_2O)_x(\mu_{3-x}\text{-}SbS_4)]_\infty$,[2] whereas the tetraselenidoantimonate anion $[SbSe_4]^{3-}$ coordinates to Ln^{3+} as a monodentate ligand in compounds $[Ln(en)_4(SbSe_4)]$.[3] The tetraselenidoarsenate $[AsSe_4]^{3-}$ anion acts as an μ_3-$AsSe_4$ bridging ligand in polymeric $[Ln(dien)_2(\mu_3\text{-}AsSe_4)]_\infty$.[4] These compounds are the first examples of lanthanoid chalcogenometalates with tetrahedral $ME_4{}^{3-}$ (M = Sb, As; E = S, Se) anions coordinating to lanthanide metal centers, although these tetrahedral anions acting as ligands to transition-metal centers have been known for a long time.[5] Here we report the solvothermal synthesis and structural characterization of the novel lanthanoid tetraselenidostannate compounds $[Hdien][Sm(dien)_2(\mu\text{-}SnSe_4)]$ (**1**), $[Hdien][Eu(dien)_2(\mu\text{-}SnSe_4)]$ (**2**), and $[Eu_2(dien)_4(\mu\text{-}OH)_2]Sn_2Se_6$ (**3**). Compounds **1** and **2** are the only examples where the $SnSe_4{}^{4-}$ anion acts as a ligand in the Ln^{3+} complexes.

Results and Discussion

Syntheses of the Compounds

The reaction of Sm_2O_3 and Eu_2O_3 with Sn and Se in dien under solvothermal conditions produces yellow crystals of **1** and orange-red crystals of **2**, respectively. When

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$SnCl_4 \cdot 5H_2O$ was used instead of Sn in the synthesis of **2**, compound **3** was obtained. This result shows that the coordination of $[SnSe_4]^{4-}$ with lanthanide ions is greatly influenced by the existence of water molecule in the reactants. In the syntheses, the solid materials Sm_2O_3 and Eu_2O_3 are transformed into lanthanide(III)–dien complex cations to combine with selenidostannate anions. Our present and previous works have shown that the Ln_2O_3/en (or dien) system is a convenient source of lanthanide(III)–en and lanthanide(III)–dien complex cations under the solvothermal conditions.[2–4]

Description of Structures

Single-crystal X-ray analysis revealed that compounds **1** and **2** are isostructural and crystallize in the monoclinic space group *P*2/*c* with two formula units in the unit cell. They are composed of the $[Ln(dien)_2(\mu\text{-}SnSe_4)]^-$ ion and isolated with protonated dien ligands. The structures of the $[Ln(dien)_2(\mu\text{-}SnSe_4)]^-$ units in **1** and **2** are depicted in Figures S1 (Supporting Information) and Figure 1, respectively. The Ln^{3+} ion is coordinated to two tridentate dien ligands and a bidentate $\mu\text{-}SnSe_4$ ligand. The LnN_6Se_2 polyhedron (Ln = Sm, Eu) may be described as a distorted bicapped trigonal prism. The $[SnSe_4]^{4-}$ anion acting as a bidentate ligand to $[Ln(dien)_2]^{3+}$ exhibits a distorted tetrahedral geometry. Because Se1 (Se1A) has a bond to Sm^{3+}/Eu^{3+}, the Sn–Se1 bond [2.5413(7) Å for **1**, 2.5407(9) Å for **2**] is significantly longer than the Sn–Se2 bond [2.5041(7) Å for **1**, 2.5024(8) Å for **2**], and the Se1–Sn–Se1A angle [105.15(3)° for **1**, 104.89(4)° for **2**] is the smallest among all the Se–Sn–Se angles (Table 1). In **1** and **2**, a four-membered $LnSe_2Sn$ heterocycle is formed, and the Ln1, Sn1, Se1, and Se1A atoms are coplanar with zero torsion angles of Ln1–Se1–Sn1–Se1a and Sn1–Se1–Ln1–Se1a for both **1** and **2**. The most related chelating coordination mode of the $\mu\text{-}SnSe_4$ ligand is observed in the $[Cr(en)_2(SnSe_4)]^-$ ion,[6] but the $[SnSe_4]^{4-}$ anion is more distorted in $[Cr(en)_2(SnSe_4)]^-$ owing to the formation of a nonplanar $CrSe_2Sn$ ring. The bond lengths Sm–Se [2.9468(7) Å] and Eu–Se [2.9345(9) Å] are shorter than those observed in nine-coordinate lanthanide selenides, such as the bond lengths 2.9543(4)–3.2336(9) Å for the Sm–Se bond of the $SmOSe_8$ polyhedron in Sm_4FeOSe_6,[7] and 3.0575(9)–3.323(2) Å for the Eu–Se bond of the $EuSe_9$ polyhedron in $Eu_8(Sn_4Se_{14})(Se_3)_2$[8a] and $EuSbSe_3$.[8b] The Ln–N bond lengths are 2.590(5)–2.615(5) Å for Sm–N and 2.572(5)–2.597(6) Å for Eu–N (Table 1), and they are in the range observed in other Sm^{3+}/Eu^{3+} compounds with amino-chelating ligands.[2a,9] The Ln–Se and Ln–N distances decrease from Sm to Eu, as expected from the lanthanoid contraction.

In **1** and **2**, a chain-like arrangement of the $[Ln(dien)_2(\mu\text{-}SnSe_4)]^-$ moieties along [010] is generated through weak N–H···Se hydrogen bonds (Figure 2). The chains form layers perpendicular to the (001) plane through weak N–H···Se bonding interactions. The protonated amine molecules are located between the layers (Figure 3). Two terminal Se atoms (Se2 and Se2A) of the $[Ln(dien)_2(\mu\text{-}SnSe_4)]^-$ unit are involved in the intermolecular hydrogen bond contacts with the NH and NH_2 groups of three neighboring $[Ln(dien)_2(\mu\text{-}SnSe_4)]^-$ moieties forming eight N–H···Se hydrogen bonds for which the N···Se lengths vary from 3.484(5) to 3.597(5) Å for **1** and 3.483(6) to 3.599(6) Å for **2**. The N···Se separations are in agreement with those observed in the literature.[10]

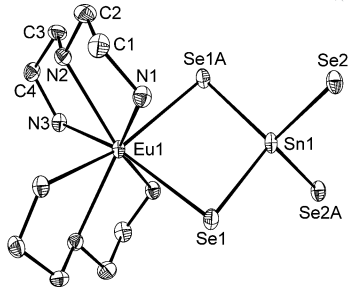

Figure 1. Crystal structure of the $[Eu(dien)_2(\mu\text{-}SnSe_4)]^-$ unit in **2** with the labeling scheme (30% displacement ellipsoids). Hydrogen atoms are omitted for clarity.

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

	1 (Ln = Sm)	**2** (Ln = Eu)
Sn1–Se1	2.5413(7)	2.5407(9)
Sn1–Se2	2.5041(7)	2.5024(8)
Ln1–Se1	2.9468(7)	2.9345(9)
Ln1–N1	2.615(5)	2.597(6)
Ln1–N2	2.590(5)	2.585(6)
Ln1–N3	2.591(5)	2.572(5)
Se–Sn–Se	105.15(3)–116.08(4)	104.89(4)–116.25(4)
Sn–Se–Ln	84.20(2)	84.21(3)
Se–Ln-Se	86.45(3)	86.69(3)
Se–Ln–N	74.59(11)–154.08(11)	74.55(13)–153.89(13)
N–Ln-N	64.95(15)–148.8(2)	65.17(18)–148.2(3)

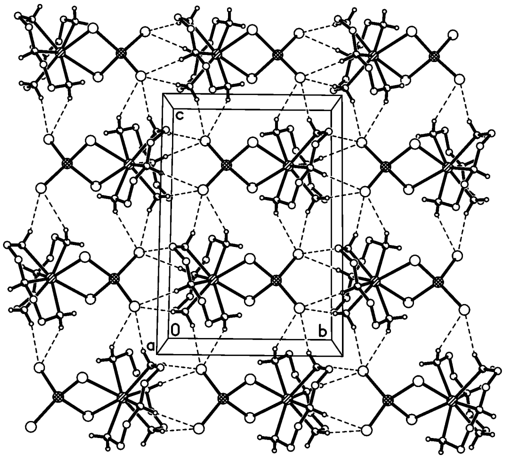

Figure 2. Crystal packing of the $[Eu(dien)_2(\mu\text{-}SnSe_4)]^-$ unit in **2** viewed along the *a* axis, showing N–H···Se intermolecular interactions in dashed lines. Hydrogen atoms of CH_2 are omitted for clarity.

Compound **3** consists of a dimeric $[Sn_2Se_6]^{4-}$ anion and a binuclear complex cation $[Eu_2(dien)_4(\mu_2\text{-}OH)_2]^{4+}$. The dimer $[Sn_2Se_6]^{4-}$ is formed by two $SnSe_4$ tetrahedra sharing a

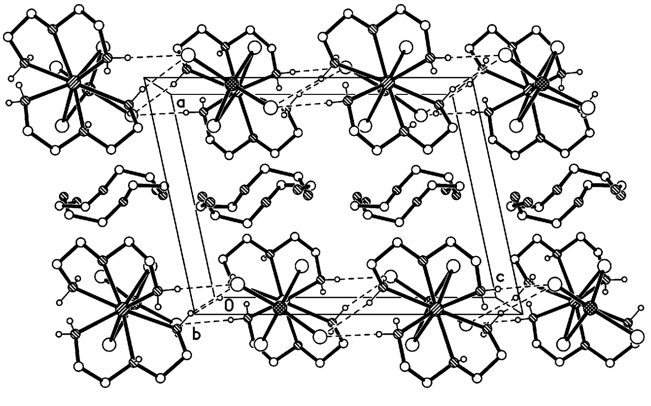

Figure 3. Crystal packing of **2** viewed along the *b* axis. Hydrogen atoms of CH_2 are omitted for clarity.

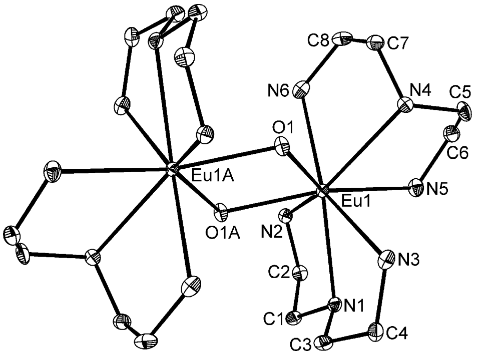

Figure 4. Crystal structure of the $[Eu_2(dien)_4(\mu\text{-}OH)_2]^{4+}$ cation in **3** with the labeling scheme (30% displacement ellipsoids). Hydrogen atoms are omitted for clarity.

common edge, and its Sn–Se lengths and Se–Sn–Se angles are consistent with the literature values[10] and need no further comment. The binuclear complex cation $[Eu_2(dien)_4(\mu_2\text{-}OH)_2]^{4+}$ is constructed of two [Eu(dien)$_2$] moieties joined by two μ_2-OH bridging ligands to form a centrosymmetric dimer with a Eu_2O_2 rhomboidal core (Figure 4). The $Eu_2O_2(\mu_2\text{-}OH)$ core has only been observed once before in the complex $[Eu(tpa)(\mu_2\text{-}OH)(OTf)_2]_2$ [tpa = tris(2-pyridylmethyl)amine].[11] In **3**, the europium ion is in an eightfold coordination and the coordination geometry can be described as a bicapped trigonal prism. The Eu–N bond lengths [2.556(5)–2.624(4) Å; Table 2] are consistent with those in compound **2**. The Eu–O(μ_2-OH) bond lengths [2.304(4) and 2.268(4) Å] are in agreement with those of $[Eu(tpa)(\mu_2\text{-}OH)(OTf)_2]_2$,[11] and are, as expected, shorter than the bonds for Eu–O(μ_3-OH) and Eu–O(μ_4-OH) in polynuclear europium complexes like $[Eu(\mu_4\text{-}OH)(\mu_3\text{-}OH)_4(DBM)_{10}]$ (DBM = dibenzoylmethide) [Eu–O 2.321(12)–2.691(10) Å],[12a] and $[Eu_9(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_8(\mu\text{-}BA)_8(BA)_8]^-$ (BA = benzoylacetone) [Eu–O 2.333(4)–2.6090(8) Å].[12b] The Eu1···Eu1A separation [3.8019(6) Å], however, is longer than that in $[Eu_9(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_8(\mu\text{-}BA)_8(BA)_8]^-$ [Eu···Eu 3.6725(4)–3.7590(3) Å].[12b] All Se atoms of $[Sn_2Se_6]^{4-}$ are involved in intermolecular N–H···Se hydrogen-bonding interactions with $[Eu_2(dien)_4(\mu_2\text{-}OH)_2]^{4+}$ cations (Figure 5). Each $[Sn_2Se_6]^{4-}$ anion has contacts with six $[Eu_2(dien)_4(\mu_2\text{-}OH)_2]^{4+}$ moieties with N···Se separations varying from 3.547(4) to 3.837(5) Å, resulting in a three-dimensional hydrogen-bonding network.

Table 2. Selected bond lengths [Å] and angles [°] for **3**.

Sn1–Se1	2.6103(7)	Sn1–Se1[a]	2.5776(7)
Sn1–Se2	2.4697(7)	Sn1–Se3	2.4572(7)
Eu1–O1	2.304(4)	Eu1–O1[b]	2.268(4)
Eu1–N1	2.597(5)	Eu1–N2	2.578(4)
Eu1–N3	2.602(5)	Eu1–N4	2.624(4)
Eu1–N5	2.599(4)	Eu1–N6	2.556(5)
Eu1···Eu1[b]	3.8019(6)		
Sn–Se–Sn	87.10(2)	Eu–O–Eu	112.52(15)
Se–Sn–Se	92.90(2)–118.68(2)	O–Eu–O	67.48(15)
O–Eu–N	74.40(13)–151.24(14)	N–Eu–N	64.71(15)–148.47(15)

[a] $-x + 1, -y + 2, -z$. [b] $-x + 1, -y + 1, -z + 1$.

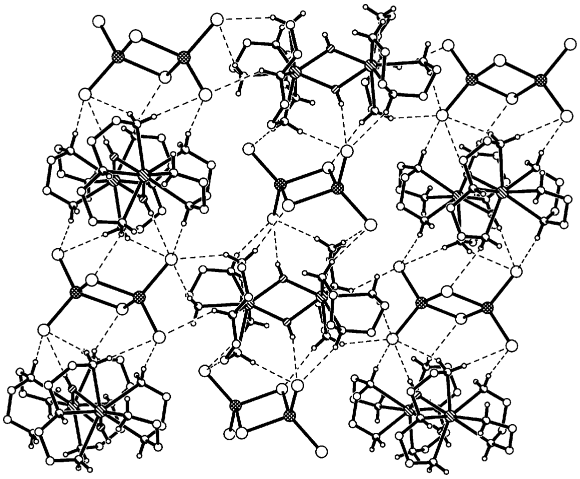

Figure 5. Section of the crystal packing of **3** viewed along the *c* axis, showing N–H···Se and N–H···O intermolecular interactions in dashed lines. Hydrogen atoms of CH_2 are omitted for clarity.

The tetraselenidostannate anion $[SnSe_4]^{4-}$ acting as a chelating ligand to transition metal complex ions was already observed in selenidostannate anions $[Cr(en)_2(SnSe_4)]^-$[6] and $[M_4(\mu_4\text{-}Se)_2(SnSe_4)_4]^{10-}$ (M = Co, Mn, Zn, Cd).[13] This coordination mode has not been observed for lanthanide metal complex ions until now. Compounds **1** and **2** are the first examples of solvothermally synthesized selenidostannates with the $[SnSe_4]^{4-}$ anion acting as a ligand in the lanthanide complexes. The syntheses of **1** and **2** in dien demonstrate that the soft-base ligand $[SnSe_4]^{4-}$ can coordinate to lanthanide(III) ions in competition with N atoms of the amine molecules. Compounds **2** and **3** were prepared under identical conditions, but with Sn and $SnCl_4\cdot 5H_2O$ as starting materials, respectively. Determination of the crystal structure confirms that the hydrate water molecule in starting material $SnCl_4{\cdot}5H_2O$ could prevent the $[SnSe_4]^{4-}$ anion from coordinating with the lanthanide ions. As a harder base and a less sterically hindered ligand than the $[SnSe_4]^{4-}$ anion, the OH^- group, which is derived from protonation of dien, exhibits higher coordination ability with lanthanide ions than with the $[SnSe_4]^{4-}$ anion. So, the $SnCl_4{\cdot}5H_2O$ starting material produces the dinuclear lanthanide hydroxy complex $[Eu_2(dien)_4(\mu\text{-}OH)_2]Sn_2Se_6$ rather than the $[SnSe_4]^{4-}$ coordinated lanthanide selenidostannate $[Hdien][Eu(dien)_2(\mu\text{-}SnSe_4)]$.

Thermal Analysis

The thermal stabilities of compounds **1**–**3** were investigated under a N_2 atmosphere, and representative TG-DSC curves of **1** and **3** are shown in Figure 6. Compound **1** decomposes in three steps with a total weight loss of 34.7% between 100 and 350 °C (Figure 6a), which corresponds to the complete removal of the dien molecules (calcd. 34.57% for three dien units). The decomposition is accompanied by three endothermic signals in the DSC curve with peak temperatures 154.2, 184.5, and 264.3 °C, respectively. Compound **2** exhibits a similar decomposition pattern with a total weight loss of 34.1% (Figure S2 in the Supporting Information). Compound **3** decomposes in one step with a total weight loss of 28.7% (Figure 6b), which is attributed to removal of the water molecules (calcd. 1.2% for H_2O) and the dien ligands (calcd. 28.2% for four dien units), accompanied by an endothermic signal in the DSC curve with a peak temperature of 263.2 °C.

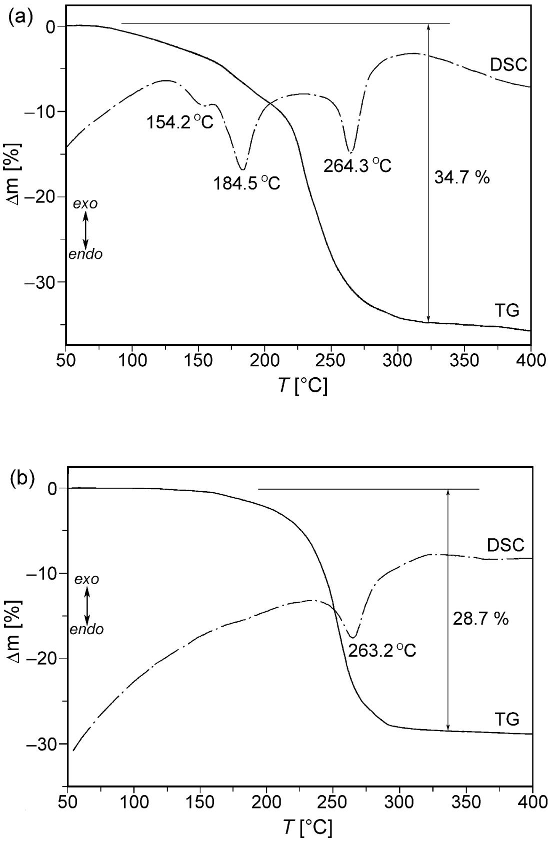

Figure 6. TG-DSC curves of compounds **1** (a) and **3** (b).

Optical Properties

Solid-state optical absorption spectra were recorded from powder samples at room temperature. The absorption spectra of compounds **1**–**3** show well-defined abrupt absorption edges, from which the band gaps can be estimated: 2.52 eV for **1**, 2.08 eV for **2**, and 2.43 eV for **3** (Figure 7). These band gaps are much larger than those of lanthanide selenidostannates free of organic components, $Eu_8(Sn_4Se_{14})(Se_3)_2$ (1.07 eV),[8a] and are smaller than those of transition-metal selenidostannates, such as, $[Rb_{10}(H_2O)_{14.5}][Zn_4(\mu_4\text{-}Se)(SnSe_4)_4]$ (2.68 eV),[13d] $[Ba_5(H_2O)_{32}][Zn_5(\mu_3\text{-}Se)_4(SnSe_4)_4]$ (2.71 eV),[13d] and $[K_{10}(H_2O)_{16}(MeOH)_{0.5}][M_4(\mu_4\text{-}Se)(SnSe_4)_4]$ [M = Mn (2.56 eV), Zn (2.90 eV)].[13e]

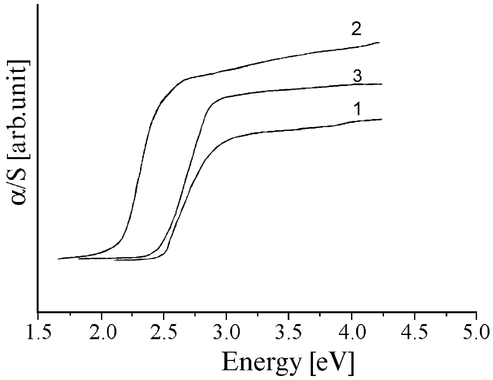

Figure 7. Optical absorption spectra of compounds **1**, **2**, and **3**.

Conclusions

A one-pot synthesis under solvothermal conditions at relatively low temperatures was employed for the preparation of lanthanide selenidostannates $[Hdien][Ln(dien)_2(\mu\text{-}SnSe_4)]$ (Ln = Sm, Eu), which are the first examples of selenidostannates integrated within lanthanide complexes. We have shown that the soft-base tetraselenidostannate anion $[SnSe_4]^{4-}$ can coordinate to hard-acid lanthanide ions Ln^{3+} in competition with chelating dien ligands in solution, but the coordination of $[SnSe_4]^{4-}$ with lanthanide ions is prevented by the existence of water; therefore, thoroughly dried starting materials should be used to prepare $[SnSe_4]^{4-}$ coordinated lanthanide compounds. We believe the solvothermal syntheses of the lanthanide selenidostannates $[Hdien][Ln(dien)_2(\mu\text{-}SnSe_4)]$ and $[Eu_2(dien)_4(\mu\text{-}OH)_2]Sn_2Se_6$ are beneficial to a more-complete understanding of the coordination chemistry of lanthanide ions, and new lanthanide selenidometalates can be prepared by this mild solvothermal method.

Experimental Section

Materials and Methods: All analytical-grade chemicals were obtained commercially and used without further purification. Elemental analysis was conducted with a MOD 1106 elemental analyzer. FTIR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr discs in the 4000–400 cm^{-1} range. Thermoanalytical measurements was performed by using a TG-DSC microanalyzer SDT 2960, and all samples were heated under a nitrogen stream of 100 $mL\,min^{-1}$ with a heating rate of 5 °C min^{-1}. Room-temperature optical diffuse reflectance spectra of the powdered sample were obtained with a Shimadzu UV-3150 spectrometer. The absorption (α/S) data were calculated from the reflectance by using the Kubelka-Munk function $\alpha/S = (1 - R)^2/2R$,[14] where R is the reflectance at a given energy, α is the absorption, and S is the scattering coefficient.

[Hdien][Sm(dien)$_2$(μ-SnSe$_4$)] (1): A mixture of Sm_2O_3 (174 mg, 0.5 mmol), Sn (119 mg, 1 mmol), and Se (237 mg, 3 mmol) in diethylenetriamine (6 mL) was loaded into a Teflon-lined stainless steel autoclave with an inner volume of 22 mL. The sealed autoclave was heated under autogenous pressure at 170 °C for 5 d. Upon cooling to ambient temperature, yellow block crystals of **1** were obtained in ca. 46% yield (based on Sn). $C_{12}H_{40}N_9Se_4SmSn$ (895.41): calcd. C 16.10, H 4.50, N 14.08; found C 15.83, H 4.45, N 13.82. IR (KBr): ṽ = 3404 (s), 3210 (vs), 3095 (vs), 2917 (vs), 2863 (s), 1568 (vs), 1520 (vs), 1466 (s), 1397 (m), 1368 (m), 1335 (m), 1150 (m), 1073 (s), 1011 (s), 972 (s), 903 (s), 826 (m), 756 (m), 594 (w), 586 (w), 471 (w) cm^{-1}.

[Hdien][Eu(dien)$_2$(μ-SnSe$_4$)] (2): A mixture of Eu_2O_3 (176 mg, 0.5 mmol), Sn (119 mg, 1 mmol), and Se (237 mg, 3 mmol) in diethylenetriamine (6 mL) was loaded into a Teflon-lined stainless steel autoclave with an inner volume of 22 mL. The sealed autoclave was heated under autogenous pressure at 170 °C for 5 d. Upon cooling to ambient temperature, orange-red block crystals of **2** were obtained in ca. 48% yield (based on Sn). $C_{12}H_{40}EuN_9Se_4Sn$ (897.02): calcd. C 16.07, H 4.46, N 14.05; found C 15.88, H 4.41, N 13.84. IR (KBr): ṽ = 3404 (s), 3327 (vs), 3195 (vs), 3087 (s), 2886 (vs), 1652 (m), 1574 (m), 1459 (m), 1219 (m), 1211 (m), 1135 (w), 1081 (m), 972 (m), 895 (w), 818 (w), 765 (w), 695 (w), 563 (m), 464 (m) cm^{-1}.

[Eu$_2$(dien)$_4$(μ-OH)$_2$]Sn$_2$Se$_6$ (3): A mixture of Eu_2O_3 (176 mg, 1 mmol), $SnCl_4\cdot5H_2O$ (351 mg, 1 mmol), and Se (237 mg, 3 mmol) in diethylenetriamine (6 mL) was loaded into a Teflon-lined stainless steel autoclave with an inner volume of 22 mL. The sealed autoclave was heated under autogenous pressure to 170 °C for 5 d. Upon cooling to ambient temperature, yellow block crystals of **3** were obtained in ca. 51% yield (based on $SnCl_4\cdot5H_2O$). $C_{16}H_{54}Eu_2N_{12}O_2Se_6Sn_2$ (1461.77): calcd. C 13.15, H 3.98, N 11.50; found C 12.94, H 3.91, N 11.36. IR (KBr): ṽ = 3349 (vs), 3117 (vs), 2938 (s), 2878 (s), 1568 (vs), 1510 (vs), 1386 (s), 1335 (s), 1156 (m), 1037 (w), 998 (w), 978 (w), 810 (w), 591 (w) cm^{-1}.

X-ray Crystallography: A summary of crystal data and refinement parameters is given in Table 3. The intensity data were collected with a Rigaku Mercury CCD diffractometer at 193(2) K by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) with a ω-scan method. An absorption correction was applied for all compounds by using multiscan method. The structures were solved with direct methods by using the SHELXS-97 program[15a] and refinement was performed against F^2 by using the SHELXL-97 program.[15b] All non-hydrogen atoms were refined anisotropically. The isolated protonated dien molecules in **1** and **2** are disordered with the occupancies of disordered C/C′ and N/N′ atoms assigned as 50 and 50%, respectively. The hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters by using a riding model.

CCDC-686887 (for **1**), -686888 (for **2**), and -686889 (for **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.

Supporting Information (see footnote on the first page of this article): Crystal structure of the [Sm(dien)$_2$(μ-SnSe$_4$)]$^-$ unit in **1**; TG-DSC curves of compound **2**.

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

	1	**2**	**3**
Formula	$C_{12}H_{40}N_9Se_4SmSn$	$C_{12}H_{40}EuN_9Se_4Sn$	$C_{16}H_{54}Eu_2N_{12}O_2Se_6Sn_2$
Formula mass	895.41	897.02	1461.77
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2/c$ (no.13)	$P2/c$ (no.13)	$P2_1/n$ (no.14)
a [Å]	10.1850(16)	10.1846(19)	12.0268(13)
b [Å]	9.4712(14)	9.4531(16)	11.8025(12)
c [Å]	13.808(2)	13.791(3)	13.8271(15)
β [°]	102.256(3)	102.165(4)	99.179(2)
V [Å^3]	1301.7(3)	1297.9(4)	1937.6(4)
Z	2	2	2
T [K]	173(2)	173(2)	173(2)
$D_{calcd.}$ [g cm^{-3}]	2.285	2.295	2.506
$F(000)$	846	848	1360
μ [mm^{-1}]	8.803	8.982	10.136
θ range [°]	3.13–25.34	3.02–25.35	3.43–25.35
Measured reflections	12185	12130	18435
Independent reflections (R_{int})	2385(0.0361)	2383(0.0346)	3530 (0.0370)
Reflections with $I > 2\sigma(I)$	2229	2233	3289
Parameters	120	120	186
R_1[a] [$I > 2\sigma(I)$]	0.0351	0.0388	0.0293
wR_2[b] [$I > 2\sigma(I)$]	0.0847	0.0856	0.0529
Goodness-of-fit on F^2	1.084	1.127	1.222

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

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