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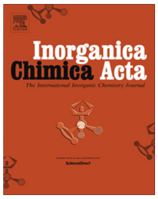

Solvothermal syntheses and characterizations of the first example of lanthanide selenidostannates prepared in mixed ethylene polyamines

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ABSTRACT

Samarium selenidostannates [Hen][Sm(dien)$_3$]Sn$_2$Se$_6$ (**1**), [Sm(trien)(tren)(Cl)]$_2$Sn$_2$Se$_6$·0.5en (**2**), and [{Sm(en)(trien)}$_2$(μ-OH)$_2$]Sn$_2$Se$_6$ (**3**) (en = ethylenediamine, dien = diethylenetriamine, trien = triethylenetetramine, tren = tris(2-aminoethyl)amine) were prepared by solvothermal methods in mixed solvents of en/dien and en/trien, respectively. Compounds **1** and **2** consist of [Sn$_2$Se$_6$]$^{4-}$ anion and mononuclear Sm(III)-complex cations, and/or a protonated en and half a free en molecule. Compound **3** is composed of a [Sn$_2$Se$_6$]$^{4-}$ anion and a binuclear [{Sm(en)(trien)}$_2$(μ-OH)$_2$]$^{4+}$ complex cation. As far as we know, **1**–**3** are the first examples of the lanthanide selenidostannates prepared in mixed ethylene polyamines. In the crystal structures of **1**–**3**, the cations and anions are connected into three-dimensional supramolecular networks by N–H···Se and/or N–H···N, N–H···Cl and O–H···Se hydrogen bonds. Compounds **1**–**3** exhibit bandgaps in the range of 2.18–2.41 eV, and a distinct blue-shift of the bandgap from **2** to **1** and **3** is observed.

1. Introduction

Multinary chalcogenostannates incorporated with transition metal (TM) components have attracted increasing attention because of their structural diversity and optical and electronic properties [1]. A series of TM-contained chalcogenostannates have been prepared using TM-organic cations as structure-directing agents under solvothermal conditions [2]. This templating synthesis is usually conducted in protic solutions containing coordinating amine ligands. The [TM(amine)$_m$]$^{n+}$ complex cations formed *in situ* act as charge compensating ions or structural components in the final ternary chalcogenostannates, depending on the structures of the amine ligands. In ethylenediamine (en) and diethylenetriamine (dien) solutions, TM^{n+} ions often form saturated complexes [TM(en)$_3$]$^{n+}$ and [TM(dien)$_2$]$^{n+}$, which lead to compounds containing free chalcogenostannate anions, such as [M(en)$_3$]$_2$Sn$_2$S$_6$ (M = Mn, Co, Zn) [3], [M(en)$_3$]$_2$Sn$_2$Se$_6$ (M = Mn, Ni, Zn) [4,5], [Zn(en)$_3$]$_2$Sn$_2$Te$_6$·en [6], [M(en)$_3$]$_2$Sn$_2$Te$_6$ (M = Mn, Zn) [7], and [Ni(dien)$_2$]$_2$Sn$_2$S$_6$ [8]. The only chalcogenidostannates incorporated with TM-en complex components are [{Mn(en)$_2$}$_2$(*μ*-en)(*μ*-Sn$_2$S$_6$)]$_\infty$ [9] and [K$_6$(MeOH)$_9$][Sn$_2$Se$_6$][Cr(en)$_2$(SnSe$_4$)]$_2$ [10]. But in the presence of tetradentate triethylenetetramine (trien) and tris(2-aminoethyl)amine (tren), and pentadentate tetraethylenepentamine (tepa) ligands, or bidentate ligands with higher steric hindrance (such as 1,10-Phenanthroline, phen), unsaturated TM-amine complexes can be formed, and TM-incorporated chalcogenidostannates are obtained. The examples include {[Mn(trien)]$_2$SnS$_4$}·4H$_2$O [11], [{TM(tren)}$_2$(μ-Sn$_2$S$_6$)] (TM = Co, Ni) [12], [{TM(tepa)}$_2$(μ-Sn$_2$S$_6$)] (TM = Fe, Co, Ni) [13], [{TM(phen)}$_2$(μ-Sn$_2$Se$_6$)] (TM = Mn, Fe) [14], [{Zn(trien)}$_2$(μ-SnTe$_4$)], and [{Zn(tren)}$_2$(μ-Sn$_2$Te$_6$)] [15]. The unsaturated coordination site of TM center in TM-amine complexes is completed by the chalcogen atom of the chalcogenidostannate anions in these compounds.

The ethylene polyamines en, dien, trien, and tepa are also excellent chelating ligands to the lanthanide (Ln) centers [16]. This provides the possibility to prepare chalcogenidometalates containing Ln-amine complexes. In recent years, we have successfully prepared a series of lanthanide-containing thiostannates [17] and selenidostannates [18] in the ethylene polyamine solvents using solvothermal technique. Unlike TMs which resulted in compounds containing free chalcogenostannate anions in dien, Lns gave complexes [{Ln(dien)$_2$}$_4$(μ$_4$-Sn$_2$Se$_9$)(μ-Sn$_2$Se$_6$)]$_\infty$ (Ln = La, Ce, Nd) and [Hdien][Gd(dien)$_2$(μ-SnSe$_4$)] (Ln = Sm, Eu, Gd) [18a–c], in which the chalcogenostannate anions coordinate to the Ln(III) centers with chalcogen atoms. Now the lanthanide system Sm/Sn/Se are firstly investigated in the mixed ethylene polyamines en/dien and en/trien, and new lanthanide selenidostannates [Hen]$_2$[Sm(dien)$_3$]$_2$(Sn$_2$Se$_6$)$_2$ (**1**), [Sm(trien)(tren)(Cl)]$_2$Sn$_2$Se$_6$·0.5en (**2**), and

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[{Sm(en)(trien)}$_2$(μ-OH)$_2$]Sn$_2$Se$_6$ (**3**) were prepared and characterized.

2. Experimental

2.1. Materials and physical measurements

Anhydrous chloride SmCl$_3$ was prepared according to the literature methods [19]. The rest of the starting materials were of analytical grade and were used as received. Elemental analyses were conducted using an EA1110-CHNS-O elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Magna-IR 550 spectrometer using dry KBr discs over the 4000–400 cm^{-1} range. Optical diffuse reflectance spectra of powder samples were obtained at room temperature using a Shimadzu UV-3150 spectrometer. Thermal gravimetric analyses (TGA) were conducted on an SDT 2960 microanalyzer; the samples were heated at a rate of 5 °C min^{-1} under a nitrogen stream of 100 mL min^{-1}. Absorption (α/S) data were calculated from the reflectance using the Kubelka–Munk function $\alpha/S = (1 - R)^2/2R$ [20].

2.2. Synthesis of [Hen][Sm(dien)$_3$]Sn$_2$Se$_6$ (**1**)

A mixture of SmCl$_3$ (128 mg, 0.50 mmol), Sn (59 mg, 0.50 mmol), and Se (158 mg, 2.0 mmol) and 3 mL of mixed en/dien (1:1(v/v)) were loaded into a Teflon-lined stainless steel autoclave with an inner volume of 10 mL. The sealed autoclave was heated under autogenous pressure at 140 °C for 6 days. Upon cooling to room temperature, the resulting yellow plank crystals of **1** were filtered off, washed with ethanol and stored under a vacuum (58% yield based on Sn). The crystals are stable in dried air and ethanol. *Anal.* Calc. for C$_{14}$H$_{48}$N$_{11}$Se$_6$SmSn$_2$ (1232.12): C, 13.75; H, 3.93; N, 12.50. Found: C, 13.89; H, 3.83; N, 12.45%. IR (KBr): 3321(s), 3037(w), 2928(s), 2850(s), 2664(w), 1624(s), 1573(s), 1534(m), 1437(w), 1308(m), 1237(m), 1187(w), 1095(m), 1051(w), 895(w), 650(m), 535(w), 417(w) cm^{-1}.

2.3. Synthesis of [Sm(trien)(tren)(Cl)]$_2$Sn$_2$Se$_6$·0.5en (**2**)

A mixture of SmCl$_3$ (128 mg, 0.50 mmol), Sn (59 mg, 0.50 mmol), and Se (158 mg, 2.0 mmol) and 3 mL of mixed en/trien (1:1(v/v)) were loaded into a Teflon-lined stainless steel autoclave with an inner volume of 10 mL. The sealed autoclave was heated under autogenous pressure at 140 °C for 6 days. Upon cooling to room temperature, the resulting orange–red block crystals of **2** were filtered off, washed with ethanol and stored under a vacuum (45% yield based on Sn). The crystals are stable in dried air and ethanol. *Anal.* Calcd. for C$_{25}$H$_{76}$N$_{17}$Cl$_2$Se$_6$Sm$_2$Sn$_2$ (1697.77): C, 17.69; H, 4.51; N, 14.03. Found: C, 17.55; H, 4.44; N, 13.87%. IR (KBr): 3253(s), 2964(m), 2895(m), 1517(s), 1440(s), 1332(s), 1286(s), 1260(s), 1171(s), 1027(w), 989(w), 963(w), 756(w), 640(m), 594(s), 502(m), 413(w) cm^{-1}.

2.4. Syntheses of [{Sm(en)(trien)}$_2$(μ-OH)$_2$]Sn$_2$Se$_6$ (**3**)

A mixture of Sm$_2$O$_3$ (87 mg, 0.25 mmol), Sn (59 mg, 0.50 mmol), and Se (158 mg, 2.0 mmol) and 3 mL of mixed en/trien (1:1(v/v)) were loaded into a Teflon-lined stainless steel autoclave with an inner volume of 10 mL. The sealed autoclave was heated under autogenous pressure at 180 °C for 6 days. Upon cooling to room temperature, the resulting yellow crystals of **3** were filtered off, washed with ethanol and stored under a vacuum (51% yield based on Sn). The crystals are stable in dried air and ethanol. *Anal.* Calcd. for C$_{16}$H$_{54}$N$_{12}$O$_2$Se$_6$Sm$_2$Sn$_2$ (1458.55): C, 13.18; H, 3.73; N, 11.52. Found: C, 13.07; H, 6.68; N, 11.39%. IR (KBr): 3536(w), 3218(s), 3109(m), 3016(m), 2936(s), 2816(s), 2665(w), 1569(s), 1517(s), 1448(s), 1344(m), 1286(s), 1229(s), 1148(m), 1102(m), 981(m), 894(m), 814(w), 762(m), 640(m), 565(m), 520(w), 460(w), 411(w) cm^{-1}.

2.5. X-ray crystallography

All data were collected on a Rigaku Saturn CCD diffractometer at 293(2) K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) with a ω-scan method to a maximum 2θ value of 50.70° for **1**–**2**, and 50.05° for **3**. An absorption correction was applied for all the compounds using multi-scan. The structures were solved with direct methods using the program of SHELXS-97 [21a], and refined by a full matrix least-squares technique based on F^2 using SHELXL-97 [21b]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added geometrically and refined using the riding model. The atoms C(27) and N(21) in **1** are disordered. Both C(27) and N(21) are refined as 60% and 40%. The disordered C(5) and N(8) in **2** are refined as 54% and 46%, and 80% and 20%, respectively. Hydrogen atoms were added

Table 1
Crystal data and experimental details for compounds **1**–**3**.

	1	**2**	**3**
Empirical formula	C$_{14}$H$_{48}$N$_{11}$Se$_6$SmSn$_2$	C$_{25}$H$_{76}$N$_{17}$Cl$_2$Se$_6$Sm$_2$Sn$_2$	C$_{16}$H$_{54}$N$_{12}$O$_2$Se$_6$Sm$_2$Sn$_2$
Formula weight	1232.12	1697.77	1458.55
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	10.044(2)	10.3481(18)	12.063(2)
b (Å)	12.803(3)	10.5750(15)	13.095(3)
c (Å)	15.811(3)	14.043(3) A	12.469(3)
α (°)	66.32(3)	77.265(12)	90
β (°)	72.86(3)	87.779(15)	95.17(3)
γ (°)	68.35(3)	61.410(9)	90
V (Å^3)	1704.8(6)	1312.2(4)	1961.7(7)
Z	2	1	2
T (K)	293(2)	293(2)	293(2)
R_{int}	0.0498	0.0439	0.0521
Total reflections	16547	12859	17039
Unique reflections	6194	4764	3455
No. of parameters	310	262	175
R_1 [$I > 2\sigma(I)$]	0.0484	0.0444	0.0494
wR_2 (all data)	0.0974	0.1097	0.0970
Goodness-of-fit (GOF) on F^2	1.095	1.115	1.184