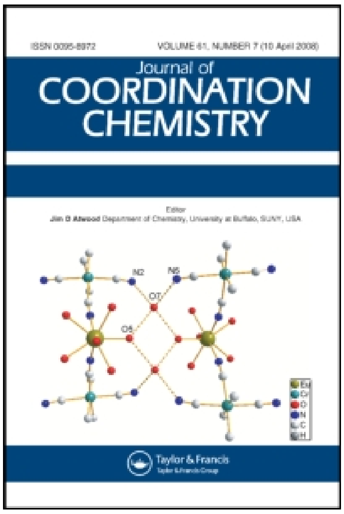

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Solvothermal syntheses and optical properties of hexathiostannates containing samarium(III) complexes with different ethylene polyamines

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Four samarium thiostannates, $[Sm_2(en)_6(\mu_2\text{-}OH)_2]Sn_2S_6$ (**1**), $[Sm(dien)_3]_2[(Sn_2S_6)Cl_2]$ (**2a**), $[Sm(dien)_3]_2[(Sn_2S_6)(SH)_2]$ (**2b**), and $[Sm(trien)(tren)(Cl)]_2Sn_2S_6 \cdot en$ (**3**) (en = ethylenediamine, dien = diethylenetriamine, trien = triethylenetetraamine, tren = tris(2-aminoethyl)amine), were solvothermally synthesized and characterized. Compounds **1–3** consist of the hexathiostannate anion $[Sn_2S_6]^{4-}$ and Sm(III) complex cations. In addition, **2a** and **2b** contain monovalent anions Cl^- and SH^-, respectively. In **1**, the Sm(III) ion forms a binuclear complex $[Sm_2(en)_6(\mu_2\text{-}OH)_2]^{4+}$, in which Sm(III) is eight coordinate. In **2a**, **2b,** and **3**, Sm(III) ions form mononuclear nine-coordinate complexes. The coordination modes of Sm(III) are influenced by the denticity of ethylene polyamines, and the monovalent OH^- and Cl^- as well. The complex $[Sm(trien)(tren)(Cl)]^{2+}$ in **3** is the first example of a lanthanide complex with mixed ethylene polyamine ligands. The optical properties of **1–3** were measured.

Keywords: Samarium; Thiostannates; Solvothermal synthesis; X-ray structure determination; Optical properties

1. Introduction

Binary chalcogenidostannates have attracted increasing attention because of the structural diversity based on the condensation of tetrahedral $[SnQ_4]^{4-}$ (Q = S, Se and Te) [1–4] and potential applications as semiconductors, optical, and ion exchange materials [5–9]. Among the oligomeric and polymeric chalcogenidostannates $[Sn_xQ_y]^{n-}$ anions, the dimeric hexachalcogenidodistannate anions $[Sn_2Q_6]^{4-}$ can be easily crystallized with a variety of counterions. A series of $[Sn_2Q_6]^{4-}$ compounds with the general formula $A[Sn_2Q_6]$ (A = cation) have been prepared by molten flux or extraction methods with alkali metal cations [10–14] and organic cations [15–22] as structure-directing agents. Solvothermal synthesis, conducted in the presence of transition metals with ethylene polyamine as a solvent, has proved to be a useful method to prepare the hexachalcogenidodistannates $[Sn_2Q_6]^{4-}$ with transition metal

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complex cations as the counterions. Examples include $[M(en)_3]_2Sn_2S_6$ (M=Mn, Co, Ni, and Zn) [23, 24], $[M(en)_3]_2Sn_2Te_6$ (M = Mn and Zn) [25], $[Zn(en)_3]_2Sn_2Te_6 \cdot en$ [26] (en = ethylenediamine), $[Ni(dap)_3]_2Sn_2S_6 \cdot 2H_2O$ (dap = 1,2-diaminopropane), $[Co(tren)]_2Sn_2S_6$, $[Ni(tren)]_2Sn_2S_6$ (tren = tris(2-aminoethyl)amine) [27], $[M(tepa)]_2Sn_2S_6$ (M=Fe, Co, Ni) (tepa = tetraethylenepentamine) [28], and $[\{Mn(cyclam)\}_2(\mu\text{-}Sn_2Se_6)]$ (cyclam =1,4,8,11-tetraazacyclotetradecane) [29]. The ethylene polyamines act not only as the reaction solvents, but also as chelating ligands to the transition metal ions.

Although formation and thermodynamic properties of the lanthanide complexes with polyamine ligands such as en [30], dien [31], and tren [32] had been studied in the solution, structurally characterized examples are still rare. Recently, in the light of the solvothermal synthesis of transition metal chalcogenidometalates, we successfully synthesized a number of main group chalcogenidometalates combined with lanthanide–en and lanthanide–dien complexes using the solvothermal method [33–38]. Now we investigate the Sm/Sn/S solvothermal system in different ethylene polyamine solvents, and four new lanthanide thiostannates, $[Sm_2(en)_6(\mu_2\text{-}OH)_2]Sn_2S_6$ (**1**), $[Sm(dien)_3]_2[(Sn_2S_6)Cl_2]$ (**2a**), $[Sm(dien)_3]_2[(Sn_2S_6)(SH)_2]$ (**2b**), and $[Sm(tren)(trien)(Cl)]_2Sn_2S_6 \cdot en$ (**3**), were synthesized and characterized.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were of analytical grade and were used without purification. Elemental analysis was conducted on a MOD 1106 elemental analyzer. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr discs from 4000 to 400 cm^{-1}. 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 $\alpha/S = (1-R)^2/2R$ [39], where R is the reflectance at a given energy, α is the absorption, and S is the scattering coefficient. The microprobe analysis by energy dispersive X-ray spectroscopy (EDXS) was performed on a Hitachi S-4700 spectrometer.

2.2. *Synthesis of the complexes*

2.2.1. Synthesis of $[Sm(en)_3(\mu_2\text{-}OH)]_2Sn_2S_6$ (1). Complex **1** was synthesized by a solvothermal reaction of $SmCl_3$ (257 mg, 1 mmol), Sn (119 mg, 1 mmol), and S (96.2 mg, 3 mmol) in en (4 mL). The reactants are mixed and loaded into a Teflon-lined stainless steel autoclave with 15 mL inner volume, and then the sealed autoclave was heated under autogenous pressure at 170°C for 6 days. Upon cooling to ambient temperature, colorless block crystals of **1** were obtained in *ca* 36% yield (based on Sn). Complex **1** can also be obtained with Sm_2O_3 as a starting material. The compound is stable in dry air and in C_2H_5OH and CH_3OCH_3 solvents. Anal. Calcd for $C_{12}H_{50}N_{12}O_2S_6Sm_2Sn_2$ (%): C, 12.81; H, 4.48; and N, 14.94. Found (%): C, 12.73; H, 4.32; and N, 14.83.

2.2.2. Synthesis of [Sm(dien)$_3$]$_2$[(Sn$_2$S$_6$)Cl$_2$] (2a). Yellowish block crystals of **2a** were prepared with a procedure similar to the synthesis of **1,** except that dien was used instead of en as the solvent (52% yield based on Sn). The compound is stable in dry air and in C_2H_5OH and CH_3OCH_3. Anal. Calcd for $C_{24}H_{78}N_{18}Cl_2S_6Sm_2Sn_2$ (%): C, 20.29; H, 5.53; and N, 17.75. Found (%): C, 20.05; H, 5.28; and N, 17.62. A microprobe analysis by EDXS gave the heavy atom component of $Sm_{2.17}Sn_2S_{6.15}Cl_{1.89}$, in agreement with the result of the X-ray structure determination.

2.2.3. Synthesis of [Sm(dien)$_3$]$_2$[(Sn$_2$S$_6$)(SH)$_2$] (2b). Yellow cubic crystals of **2b** were prepared with a procedure similar to the synthesis of **2a,** except that Sm_2O_3 was used instead of $SmCl_3$ (56% yield based on Sn) as a starting material. The compound is stable in dry air and in C_2H_5OH and CH_3OCH_3. Anal. Calcd for $C_{24}H_{80}N_{18}S_8Sm_2Sn_2$ (%): C, 20.53; H, 6.10; and N, 17.81. Found (%): C, 20.45; H, 5.94; and N, 17.68.

2.2.4. Synthesis of [Sm(trien)(tren)(Cl)]$_2$Sn$_2$S$_6$ · en (3). Light yellow platelet crystals of **3** were prepared with a procedure similar to the synthesis of **1,** except that mixed trien/en solution (v/v = 3 : 1) (4 mL) was used as a solvent (43% yield based on Sn). The compound is stable in dry air and in C_2H_5OH and CH_3OCH_3. Anal. Calcd for $C_{26}H_{80}N_{18}Cl_2S_6Sm_2Sn_2$ (%): C, 21.59; H, 5.57; and N, 17.43. Found (%): C, 21.41; H, 5.56; and N, 17.27.

2.3. *X-ray structure determination*

The intensity data were collected on a Rigaku Mercury CCD diffractometer at 193(2) K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) with a ω-scan method to a maximum 2θ value of 50.68° for **1**, and 50.70° for **2a**, **2b**, and **3**. An absorption correction was applied for all the compounds using the multiscan method. The structures were solved with direct methods using SHELXS-97 [40], and refinement was performed against F^2 using SHELXL-97 [41]. All non-hydrogen atoms were refined anisotropically. The hydrogens were positioned with idealized geometry and refined with fixed isotropic displacement parameters using a riding model. Technical details of data collections and refinement are summarized in table 1.

3. Results and discussion

3.1. *Synthesis of the compounds*

Hexathiostannate $[Sn_2S_6]^{4-}$ compounds with lanthanide complex cations as the counterions were synthesized under solvothermal conditions. The reaction of $SmCl_3$, Sn, and S in a molar ratio of 1 : 1 : 3 in 4 mL en at 170°C produced the binuclear samarium(III) complex $[Sm_2(en)_6(\mu_2\text{-OH})_2]Sn_2S_6$ (**1**). When the reaction was conducted in dien instead of en as the solvent, the mononuclear samarium(III) complex $[Sm(dien)_3]_2[(Sn_2S_6)Cl_2]$ (**2a**) was obtained. A gray powder amorphous to XRD was formed when the reaction was conducted in trien, but the reaction in the trien–en mixture gave a mixed-coordination samarium(III) compound

Table 1. Crystallographic data and structure refinement details for **1**, **2a**, **2b**, and **3**.

	1	**2a**	**2b**	**3**
CCDC deposit no.	733205	733206	733207	733208
Empirical formula	$C_{12}H_{50}N_{12}O_2S_6Sm_2Sn_2$	$C_{24}H_{78}N_{18}S_6Cl_2Sm_2Sn_2$	$C_{24}H_{80}N_{18}S_8Sm_2Sn_2$	$C_{26}H_{80}N_{18}Cl_2S_6Sm_2Sn_2$
Formula weight	1125.08	1420.38	1415.62	1446.42
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)	$P\bar{1}$ (no.2)
Wavelength (Mo-Kα) (Å)	0.71073	0.71073	0.71073	0.71073
Unit cell dimensions (Å, °)				
a	10.1294(14)	11.6315(11)	11.6981(16)	10.320(3)
b	11.3768(15)	15.0907(13)	15.212(2)	10.491(3)
c	14.962(2)	14.1420(13)	14.2191(19)	13.791(3)
α	90	90	90	100.524(3)
β	98.128(3)	96.202(2)	95.654(3)	91.930(3)
γ	90	90	90	119.083(4)
Volume (Å^3), Z	1706.9(4), 2	2467.8(4), 2	2518.0(6), 2	1269.8(5), 1
Calculated density (g cm^{-3})	2.189	1.912	1.867	1.892
F(000)	1084	1404	1404	716
Absorption coefficient (mm^{-1})	5.235	3.748	3.650	3.644
Reflections collected	16,164	23,470	24,239	12,438
Independent reflections	3110 ($R_{int} = 0.0663$)	4497 ($R_{int} = 0.0264$)	4591 ($R_{int} = 0.0406$)	4620 ($R_{int} = 0.0429$)
Reflections with [$I > 2\sigma(I)$]	2842	4310	4195	3841
Parameters	164	245	249	242
R_1 [$I > 2\sigma(I)$]	0.0746	0.0209	0.0331	0.0559
wR_2 (all data)	0.2175	0.0510	0.0598	0.1170
Goodness-of-fit on F^2	1.173	1.272	1.212	1.105

$[Sm(trien)(tren)(Cl)]_2Sn_2S_6 \cdot en$ (**3**). To investigate the influence of Cl^- in the synthesis, Sm_2O_3 was used instead of $SmCl_3$ in the solvothermal reactions. The reaction of Sm_2O_3, Sn, and S in en produced compound **1**. In dien, Sm_2O_3 resulted in a new samarium(III) complex $[Sm(dien)_3]_2[(Sn_2S_6)(SH)_2]$ (**2b**) which is isostructural to **2a**. But in trien or trien/en, no crystalline compounds were formed when Sm_2O_3 was used. In the syntheses, samarium(III) complex cations with ethylene polyamine ligands were formed *in situ* to act as counterions to $[Sn_2S_6]^{4-}$. Our present and previous work show that the system Ln_2O_3 (or $LnCl_3$)/polyamine (en, dien, or trien) are convenient sources of lanthanide(III)–polyamine complex cations under solvothermal conditions [33–38].

3.2. *Crystal structures*

Compounds **1**–**3** consist of hexathiostannate $[Sn_2S_6]^{4-}$ anions and samarium(III) complexes with different ethylene polyamine ligands. $[Sn_2S_6]^{4-}$ is built up from two tetrahedral SnS_4 sharing a common edge. The structural parameters of $[Sn_2S_6]^{4-}$ (table 2) are in the normal range of literature values [19–24, 27]. In **1**, two $[Sm(en)_3]^{3+}$ moieties are joined by two μ_2-OH bridging ligands resulting in a binuclear complex cation $[Sm_2(en)_6(\mu_2\text{-}OH)_2]^{4+}$, which is isostructural with $[Ln_2(en)_6(\mu_2\text{-}OH)_2]Sn_2S_6$ (Ln = Dy, Er) [38]. Each Sm^{3+} ion is an eight coordinate from six nitrogens of three en and two μ_2-OH bridging ligands. The coordination geometry can be described as a distorted bicapped trigonal prism. The binuclear $[Sm_2(en)_6(\mu_2\text{-}OH)_2]^{4+}$ complex cation is centrosymmetric with a four-membered Sm_2O_2 ring (figure 1). The Sm_2O_2 core has the shape of a rhomboid with O–Sm–O angle of 68.3(5)° and Sm–O–Sm angle of 111.7(5)°. Sm–N bond lengths are between 2.568(16) and 2.635(14) Å, in agreement with those in other samarium (III)-en complexes [35, 36]. The binuclear $Ln_2O_2(\mu_2\text{-}OH)$ core has only been observed once before in $[Ce(tpa)(\mu_2\text{-}OH)(MeCN)(H_2O)]_2I_4$ (tpa = tris(2-pyridylmethyl)amine) [42], although a series of polynuclear lanthanide hydroxyl complexes have been known for a long time [43–46]. The structural evolution of $Ln_2O_2(\mu_2\text{-}OH)$ cores across the lanthanide series are summarized in table 3. The O–Ln–O angle decreases and the Ln–O–Ln angle increases with decreasing Ln–O bond length across the lanthanide series.

In **1**, the terminal sulfurs of $[Sn_2S_6]^{4-}$ have contacts with NH_2 groups of adjacent $[Sm_2(en)_6(\mu_2\text{-}OH)_2]^{4+}$ moieties with N···S separations varying from 3.353(16) to 3.594(14) Å and N–H···S angles between 147.5° and 174.9°, indicating weak

Table 2. Selected bond lengths (Å) and angles (°) for **1**, **2a**, **2b**, and **3**.

	1	**2a**	**2b**	**3**
$Sn-S_t$[a]	2.347(4), 2.327(4)	2.3290(7), 2.3311(7)	2.3292(12), 2.3299(12)	2.344(2), 2.335(3)
$Sn-S_b$[b]	2.462(4), 2.456(4)	2.4442(7), 2.4619(7)	2.4405(11), 2.4661(12)	2.457(3), 2.449(2)
Sm–N	2.568(16) – 2.635(14)	2.597(2) – 2.658(2)	2.592(4) – 2.672(4)	2.552(8) – 2.741(8)
Sm–O(Cl)	2.311(13), 2.329(12)			2.878(2)
S–Sn–S	92.05(14) – 113.89(15)	93.06(2) – 114.83(3)	93.03(4) – 114.63(4)	93.81(8) – 116.90(8)
Sn–S–Sn	87.95(13)	86.94(2)	86.97(4)	86.19(8)
N–Sm–N	65.0(5) – 153.3(5)	62.34(7) – 149.59(8)	63.14(12) – 149.51(12)	63.7(2) – 153.0(2)
N–Sm–O(Cl)	68.3(5) – 153.7(4)			72.93(18) – 145.95(18)

[a] Lengths of terminal Sn–S bonds.
[b] Lengths of bridging Sn–S bonds.

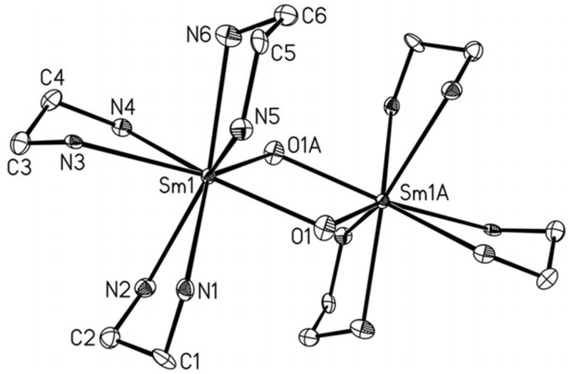

Figure 1. Crystal structure of $[Sm_2(en)_6(\mu_2\text{-}OH)_2]^{4+}$ in **1** with the labeling scheme (30% thermal ellipsoids). Hydrogens are omitted for clarity.

Table 3. Bond lengths (Å) and angles (°) for $Ln_2O_2(\mu_2\text{-}OH)$ rhomboidal cores.

	Ln = Ce [42]	Ln = Sm	Ln = Dy [38]	Ln = Er [38]
Ln–O	2.331(7)	2.320(13)	2.276(3)	2.257(3)
Ln···Ln	3.844(2)	3.8405(16)	3.7821(4)	3.7559(5)
O–Ln–O	69.5(3)	68.3(5)	67.66(11)	67.41(12)
Ln–O–Ln	110.5(3)	111.7(5)	112.34(11)	112.59(12)

intermolecular hydrogen bonds. The $[Sn_2S_6]^{4-}$ and $[Sm_2(en)_6(\mu_2\text{-}OH)_2]^{4+}$ ions are arranged in a layer parallel to the (0 0 1) plane through N–H···S hydrogen bonds (figure 2). The layers are further connected *via* N–H···S bonds resulting in a 3-D network.

Compounds **2a** and **2b** are isostructural, crystallizing in the monoclinic space group *P2₁/n*. They are composed of $[Sm(dien)_3]^{3+}$ and $[Sn_2S_6]^{4-}$ with monovalent anions Cl^- and SH^- as charge compensating ions. Sm(III) is coordinated by nine nitrogens of three tridentate dien ligands, forming a distorted tricapped trigonal prism, which is highlighted by a solid full line in figure 3. Unlike Sm(III) in **1** which forms a binuclear complex, the Sm(III) coordination sphere is saturated by three dien ligands; therefore, a mononuclear complex is formed. The Sm–N bond lengths range from 2.597(2) to 2.658(2) (av. 2.621(2) Å) for **2a** and 2.592(4) to 2.672(4) (av. 2.625(4) Å) for **2b**, and as expected, slightly longer than those found in **1** (Sm–N: av. 2.610(14) Å). Extensive N–H···S and N–H···Cl interactions are observed between $[Sm(dien)_3]^{3+}$ and $[Sn_2S_6]^{4-}$ and Cl^- ions in **2a**. Each $[Sn_2S_6]^{4-}$ interacts with four $[Sm(dien)_3]^{3+}$ cations (figure 4) with N···S separations between 3.322(3) and 3.369(3) Å and N–H···S angles between 145.3° and 172.6°, whereas each free Cl^- contacts three $[Sm(dien)_3]^{3+}$ ions by four N–H···Cl interactions (figure 5) with N···Cl separations between 3.256(3) and 3.452(3) Å and N–H···Cl angles between 138.2° and 174.0°. A 3-D network of $[Sm(dien)_3]^{3+}$, $[Sn_2S_6]^{4-}$, and Cl^- ions is formed *via* N–H···S and N–H···Cl H-bonding. A similar hydrogen-bonding network is observed in **2b**.

In **3**, the Sm(III) is coordinated by a tetradentate trien, a tetradentate tren, and a Cl^- to form a nine-coordinate complex cation $[Sm(trien)(tren)(Cl)]^{2+}$ (figure 6). Triethylenetetraamine (trien) might contain the isomer tris(2-aminoethyl)amine (tren).

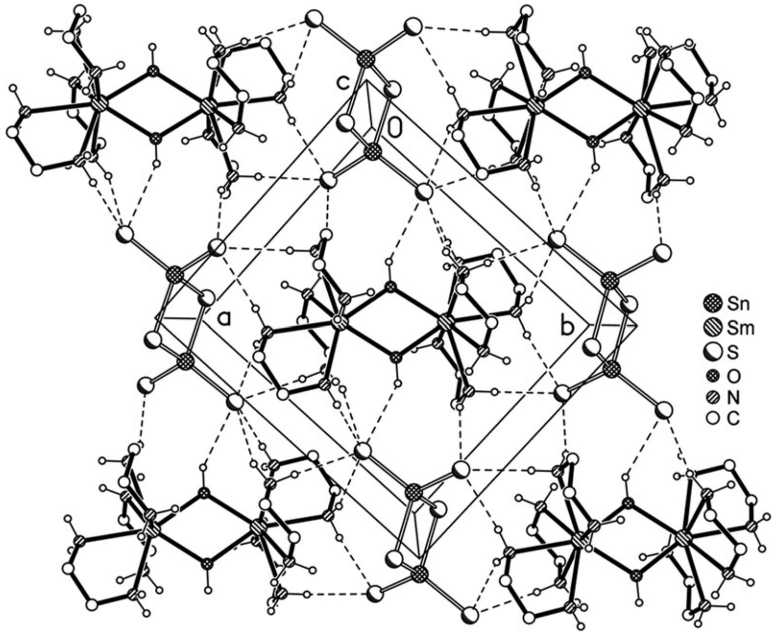

Figure 2. A sectional crystal packing of **1** viewed along the *c*-axis showing N–H···S and O–H···S interactions in dashed lines. Hydrogens of CH_2 are omitted for clarity.

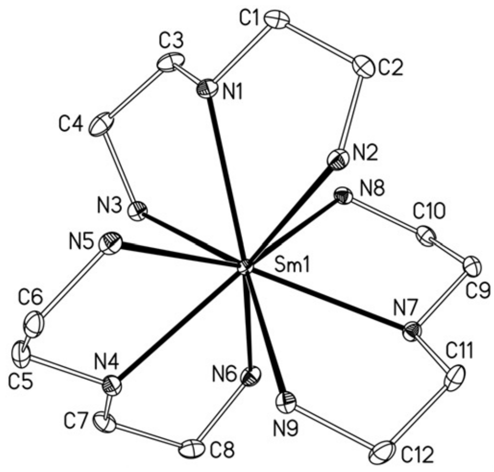

Figure 3. Crystal structure of $[Sm(dien)_3]^{3+}$ in **2a** with the labeling scheme (30% thermal ellipsoids). Hydrogens are omitted for clarity.

Compound **3** was prepared in mixed trien/en solvent, but en does not take part in coordination with Sm(III). This can be interpreted in terms of the stronger chelating effect of the tetradentate ligands trien and tren with respect to en. In $[Sm(trien)(tren)(Cl)]^{2+}$, all nitrogen donors of trien and tren are bound to Sm(III),

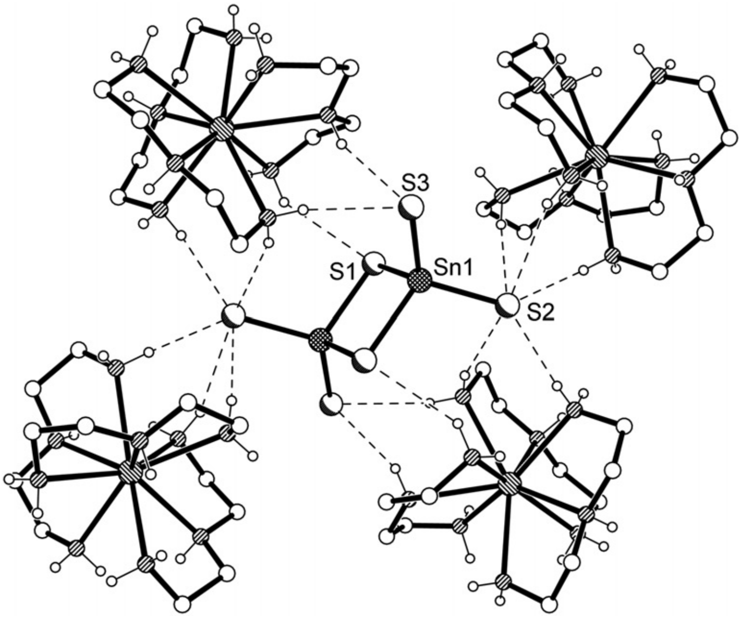

Figure 4. A view of N–H $\cdots$ S interactions between $[Sm(dien)_3]^{3+}$ and $[Sn_2S_6]^{4-}$ in **2a**. Hydrogens of CH_2 are omitted for clarity.

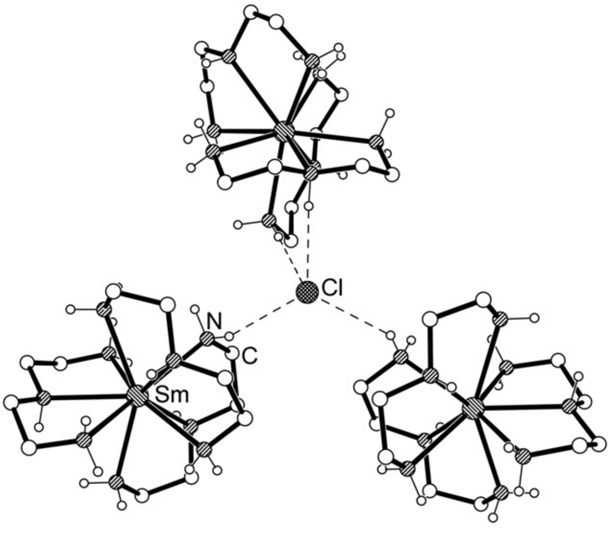

Figure 5. A view of N–H $\cdots$ Cl interactions between $[Sm(dien)_3]^{3+}$ and Cl^- in **2a**. Hydrogens of CH_2 are omitted for clarity.

different from the observation that the tertiary nitrogen of trien and tren is not bound to trivalent lanthanides in DMSO [32]. $[Sm(trien)(tren)(Cl)]^{2+}$ is the first example of a lanthanide complex with mixed ethylene polyamine ligands. The mixed coordination polyhedron SmN_8Cl can be described as a tricapped trigonal prism. The Sm–N bond

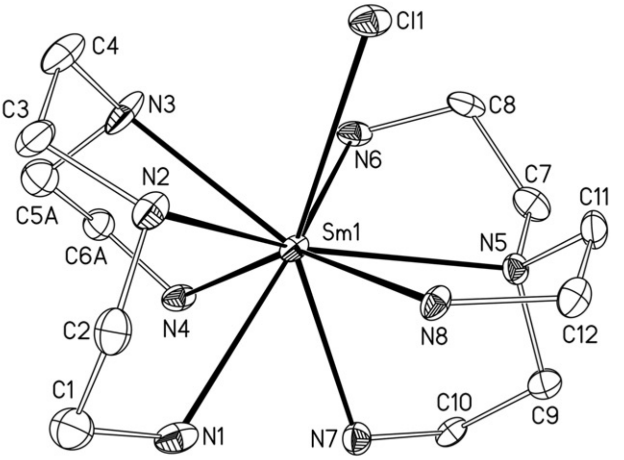

Figure 6. Crystal structure of $[Sm(trien)(tren)(Cl)]^{2+}$ in **3** with the labeling scheme (30% thermal ellipsoids). Hydrogens are omitted for clarity.

lengths from 2.552(8) to 2.742(8) Å with an average of 2.624(8) Å match well with the corresponding bond distances in **2a** and **2b**. In the crystal structure of **3**, $[Sm(trien)(tren)(Cl)]^{2+}$ is coupled *via* N(2)–H(2)···Cl(1) and N(8)–H(8A)···Cl(1) interactions (N···Cl = 3.473(8), 3.471(7) Å, N–H···Cl = 159.0, 177.7°). The $[Sm(trien)(tren)(Cl)]^{2+}$ couples are connected by $[Sn_2S_6]^{4-}$ *via* N–H···S interactions (N···S = 3.355(8)–3.701(9) Å, N–H···S = 149.7–169.9°) and by en molecules *via* N–H···N interactions (N···N = 3.45(3) Å, N–H···N = 173.0°), leading to a layered structure within the (0 1 1) plane of the unit cell (figure 7). The layers are further connected through N–H···S interactions forming a 3-D network structure.

3.3. *Optical properties*

Optical absorption spectra of **1**, **2a**, and **3** show well-defined steep absorption edges from which the band gaps can be estimated as 3.46 eV for **1**, 2.78 eV for **2a**, and 2.51 eV for **3**, respectively (figure 8), which suggests that the small ligands OH^- and Cl^- have significant influence on the band gap of samarium(III) thiostannates. These band gaps are larger than those of tin sulfides free of organic components, such as $EuCu_2SnS_4$ (2.2 eV) [47], $K_2Sn_2S_8$ (2.15 eV), and α-$Rb_2Sn_2S_8$ (2.15 eV) [48]. The band gap of **2a** is comparable with that of zinc thiostannate $[Na_5Zn_{3.5}Sn_{3.5}S_{13}] \cdot 6H_2O$ (2.9 eV) [7].

4. Conclusion

The Sm/Sn/S system was investigated in the ethylene polyamines en, dien, and trien/en under solvothermal conditions, and four new samarium thiostannates, **1**, **2a**, **2b**, and **3**, were synthesized. In en, the Sm(III) ion forms $[Sm_2(en)_6(\mu_2\text{-}OH)_2]^{4+}$, in which Sm(III) is eight coordinate, but it forms mononuclear nine-coordinate complexes $[Sm(dien)_3]^{3+}$

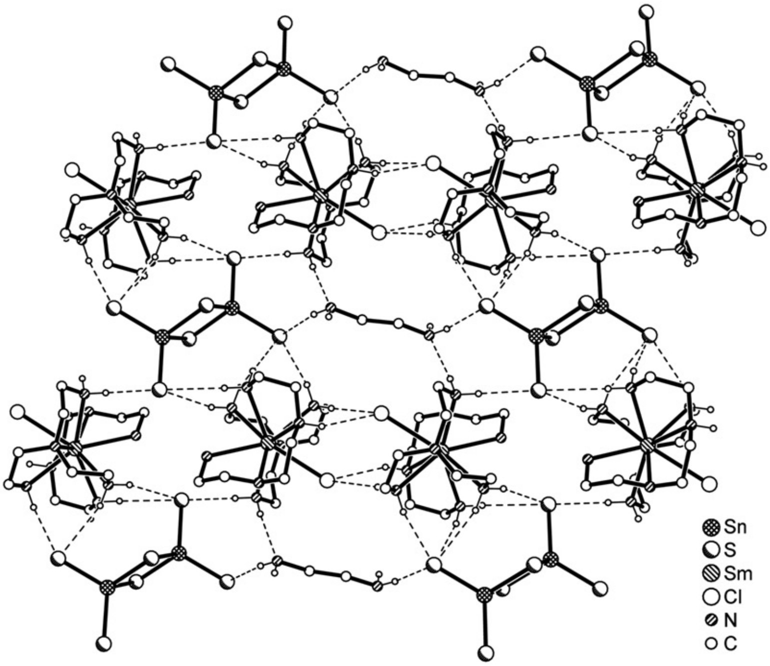

Figure 7. A sectional crystal packing of **3** viewed along the *c*-axis showing N–H $\cdots$ S, N–H$\cdots$Cl, and N–H $\cdots$ N interactions in dashed lines. Hydrogens of CH_2 are omitted for clarity.

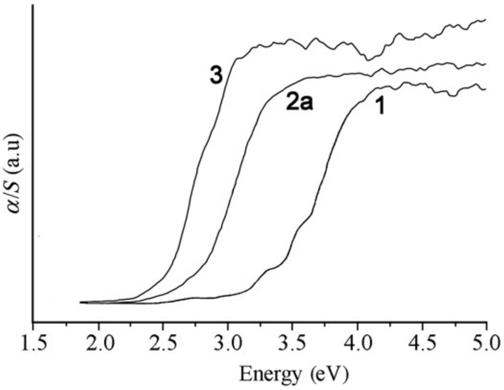

Figure 8. Optical absorption spectra of **1**, **2a**, and **3**.

and $[Sm(trien)(tren)(Cl)]^{2+}$ in dien and trien/en, respectively. The coordination modes of Sm(III) are influenced by the denticity of ethylene polyamines, and the monovalent OH^- and Cl^- ions as well. Besides the alkali metal cations, organic cations and transition metal complex cations, such $[Sm_2(en)_6(\mu_2\text{-}OH)_2]^{4+}$, $[Sm(dien)_3]^{3+}$, and $[Sm(trien)(tren)(Cl)]^{2+}$ lanthanide complex cations, can act as counterions to $[Sn_2S_6]^{4-}$, showing the flexibility of the $[Sn_2S_6]^{4-}$ anion in combination with various counterions. Unlike trien and tren whose tertiary nitrogen is not bound to trivalent lanthanide ions in DMSO, trien and tren coordinate to samarium(III) with all nitrogen donors under solvothermal conditions. Compound **3** is the first example of a lanthanide complex with tetradentate trien and tren ligands, although a number of lanthanide complexes with multidentate carboxylic ligands have been prepared [49, 50].

Supplementary material

Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre as supplementary data, CCDC nos 733205 (**1**), 733206 (**2a**), 733207 (**2b**), and 733208 (**3**). Copies of the data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; or Email: deposit@ccdc.cam.ac.uk

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