

镧(III)系锑硒化合物 $[\text{Ln}(\text{en})_4]\text{SbSe}_4 \cdot 0.5\text{en}$ ($\text{Ln}=\text{Dy}, \text{Ho}$) 的溶剂热合成与晶体结构

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摘要: 本文研究了 $\text{Ln}_2\text{O}_3/\text{Sb}/\text{Se}/\text{en}$ 溶剂热反应体系, 合成了 2 个镧(III)系锑硒化合物 $[\text{Ln}(\text{en})_4]\text{SbSe}_4 \cdot 0.5\text{en}$ ($\text{Ln}=\text{Dy}$ (**1**), Ho (**2**)), 用元素分析和红外光谱对化合物进行了表征, 并用 X-射线单晶衍射测定了化合物的单晶结构, 两者都属于单斜晶系, $P2_1/n$ 空间群。结构对比研究发现, 在 en 溶剂中, SbSe_4^{3-} 离子可以与半径较大的 La^{3+} 和 Nd^{3+} 离子配位, 而不与半径较小的 Dy^{3+} 和 Ho^{3+} 离子配位, 可见镧系收缩效应对 SbSe_4^{3-} 离子与镧系金属离子 Ln^{3+} 的配位有重要影响。

关键词: 溶剂热合成; 镧(III)系配合物; 锑硒化合物; 晶体结构

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Solvothermal Syntheses and Crystal Structures of Lanthanide(III) Selenidoantimonates $[\text{Ln}(\text{en})_4]\text{SbSe}_4 \cdot 0.5\text{en}$ ($\text{Ln}=\text{Dy}, \text{Ho}$)

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Abstract: Organic hybrid lanthanide(III) selenidoantimonates $[\text{Dy}(\text{en})_4]\text{SbSe}_4 \cdot 0.5\text{en}$ (**1**) and $[\text{Ho}(\text{en})_4]\text{SbSe}_4 \cdot 0.5\text{en}$ (**2**) (en = ethylenediamine) were synthesized under mild solvothermal conditions and characterized by elemental analysis, IR spectra and single-crystal X-ray diffraction. **1** and **2** are isostructural-crystallizing in the monoclinic space group $P2_1/n$. Crystallographic data for **1**: $a=1.140\ 69(14)$ nm, $b=1.314\ 19(16)$ nm, $c=1.628\ 3(2)$ nm, $\beta=92.324(3)^\circ$, $V=2.439\ 0(5)$ nm³, $Z=4$, $M_r=870.56$, $D_c=2.371$ g·cm⁻³, $F(000)=1\ 624$, the final $R=0.038\ 6$ and $wR=0.073\ 3$ for observed reflections 3 874 with $I>2\sigma(I)$. For **2**: $a=1.140\ 20(17)$ nm, $b=1.314\ 70(18)$ nm, $c=1.623\ 2(2)$ nm, $\beta=92.358(4)^\circ$, $V=2.431\ 1(6)$ nm³, $Z=4$, $M_r=872.99$, $D_c=2.385$ g·cm⁻³, $F(000)=1\ 628$, the final $R=0.070\ 1$ and $wR=0.121\ 9$ for observed reflections 3 471 with $I>2\sigma(I)$. **1** and **2** consist of tetrahedral anion SbSe_4^{3-} , lanthanide complex cation $[\text{Ln}(\text{en})_4]^{3+}$ ($\text{Ln}=\text{Dy}, \text{Ho}$) and free en molecule. The lanthanide Ln^{3+} ion is in an eight coordinated environment involving in eight N atoms of four en ligands forming a bicapped trigonal prism. In the crystal structure of **1** and **2**, extensive N—H···Se hydrogen bonding interactions lead to a 3-dimensional network structure of the cations and anions. CCDC: 777749, **1**; 777750, **2**.

Key words: solvothermal synthesis; lanthanide(III) complex; selenidoantimonate; crystal structure

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0 Introduction

Lanthanide chalcogenides have attracted increased attention in recent years because of their promising photo-, thermo- and electroluminescence, magnetic and nonlinear optical properties^[1-3]. These compounds are generally prepared by the flux method at high temperature^[4]. Recently, the mild solvothermal synthesis, in which the reaction is performed in the presence of a structure-directing agent such as an organic amine, has been proven to be a versatile route to the preparation of chalcogenides containing such Main Group elements as germanium, tin, arsenic, and antimony^[5-7]. When transition metal (TM) ions were introduced into the amine solution, the transition metal complex cations formed in situ act as space fillers and/or charge compensating ions in the chalcogenometalate compounds and the ternary chalcogenometalates containing transition metals are obtained^[8-12].

Recently, we have developed a solvothermal route to the preparation of lanthanide chalcogenometalates in the light of the solvothermal synthesis of above ternary transition metal chalcogenometalates in amine solution. We introduced lanthanide metals into the solvothermal synthetic system Sb/S/en, and had successfully synthesized two series of lanthanide thioantimonates $[\text{Ln}(\text{en})_3(\text{H}_2\text{O})_x(\mu_{3\rightarrow 3}\text{-SbS}_4)]$ ($x=0, 1$; Ln=La, Nd, Sm) and $[\text{Ln}(\text{en})_4]\text{SbS}_4 \cdot 0.5\text{en}$ (Ln=Eu, Dy, Yb)^[13-14]. The structural types of these lanthanide thioantimonates are related with the entity of the lanthanide (III) series, and the structure dividing point locates at the samarium(III) ion^[14]. Recently, we extended the solvothermal method to the synthesis of lanthanide selenidoantimonates, and the novel compounds $[\text{Ln}(\text{en})_4(\text{SbSe}_4)]$ (Ln=La, Nd) and $[\text{Sm}(\text{en})_4]\text{SbSe}_4 \cdot 0.5\text{en}$ were first prepared by the solvothermal route in en^[15]. Now we study on the synthetic system $\text{Ln}_2\text{O}_3/\text{Sb}/\text{Se}/\text{en}$ under solvothermal conditions in detail to investigate the relationship between the structural feature of the lanthanide selenidometalates and the entity of lanthanide (III) ions across the lanthanide series, and two new lanthanide selenidoantimonates $[\text{Dy}(\text{en})_4]\text{SbSe}_4 \cdot 0.5\text{en}$ and $[\text{Ho}(\text{en})_4]\text{SbSe}_4 \cdot 0.5\text{en}$ were prepared from the synthetic system.

1 Experimental

1.1 Materials and instruments

All reagents were obtained commercially and used without further purification. Elemental analysis was conducted on a MOD 1106 elemental analyzer. FTIR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr discs in the 4 000~400 cm^{-1} range.

1.2 Synthesis

Compound **1** was synthesized by a solvothermal reaction of Dy_2O_3 (187 mg, 0.5 mmol), Sb (122 mg, 1 mmol), and Se (316 mg, 4 mmol) in 6 mL en. The reactant mixture was loaded into a Teflon-lined stainless steel autoclave with an inner volume of 15 mL, and then the sealed autoclave was heated under autogenous pressure at 160 $^\circ\text{C}$ for 6 d. Upon cooling to ambient temperature, orange block crystals of **1** were obtained in *ca.* 48% yield (based on Sb) and stored under a vacuum. Anal. Calcd. for $\text{C}_9\text{H}_{36}\text{N}_9\text{Se}_4\text{DySb}$ (%): C, 12.42; H, 4.17; N, 14.48. Found (%): C, 12.24; H, 4.06; N, 14.31. IR data (KBr pellet, cm^{-1}): 3 328vs, 3 218 vs, 3 088vs, 2 871vs, 1 582s, 1 571vs, 1 490s, 1 380 s, 1 328s, 1 156m, 972s, 826m, 781m, 589m, and 480m. Chip crystals of **2** were prepared with a procedure similar to the synthesis of **1** except that Ho_2O_3 was used instead of Dy_2O_3 with 56% yield (based on Sb). Anal. Calcd. for $\text{C}_9\text{H}_{36}\text{N}_9\text{Se}_4\text{HoSb}$ (%): C, 12.38; H, 4.16; N, 14.44. Found (%): C, 12.25; H, 4.02; N, 14.28. IR data (KBr pellet, cm^{-1}): 3 303vs, 3 282s, 3 245s, 3 132s, 2 930 vs, 2 882s, 1 570vs, 1 511s, 1 386m, 1 331s, 1 007s, 866w, 814w, 776w, 662w, 498m.

1.3 X-ray crystallography

The intensity data were collected on a Rigaku Mercury CCD diffractometer at 293(2) K using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\,073\,\text{nm}$) with a ω -scan method to a maximum 2θ value of 50.70° for **1** and **2**. An absorption correction was applied for all the compounds using multi-scan method. The structures were solved with direct methods using the SHELXS-97 program^[16] and refinement was performed against F^2 using the SHELXL-97 program^[17]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms

were positioned with idealized geometry and refined with fixed isotropic displacement parameters using a riding model. Technical details of the data collection

and refinement are summarized in Table 1.

CCDC: 777749, **1**; 777750, **2**.

Table 1 Crystallographic data collection and structure refinement details for **1** and **2**

	1	2
Empirical formula	$\text{C}_9\text{H}_{36}\text{N}_9\text{Se}_4\text{DySb}$	$\text{C}_9\text{H}_{36}\text{N}_9\text{Se}_4\text{HoSb}$
Formula weight	870.56	872.99
T / K	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a / nm	1.140 69(14)	1.140 20(17)
b / nm	1.314 19(16)	1.314 70(18)
c / nm	1.628 3(2)	1.623 2(2)
$\beta / (^\circ)$	92.324(3)	92.358(4)
V / nm^3	2.439 0(5)	2.431 1(6)
Z	4	4
$D_c / (\text{g} \cdot \text{cm}^{-3})$	2.371	2.385
$F(000)$	1 624	1 628
μ / mm^{-1}	10.129	10.343
Reflns. collected	23 246	23 311
Unique reflns. (R_{int})	4 451 (0.055 6)	4 437 (0.090 6)
Observed reflns. [$I > 2\sigma(I)$]	3 874	3 471
Parameters refined	227	227
Final R indices R_1, wR_2 [$I > 2\sigma(I)$]	0.038 6, 0.073 3	0.070 1, 0.121 9
Goodness-of-fit on F^2	1.201	1.190
Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	711 and -997	1 132 and -1 652

2 Result and discussion

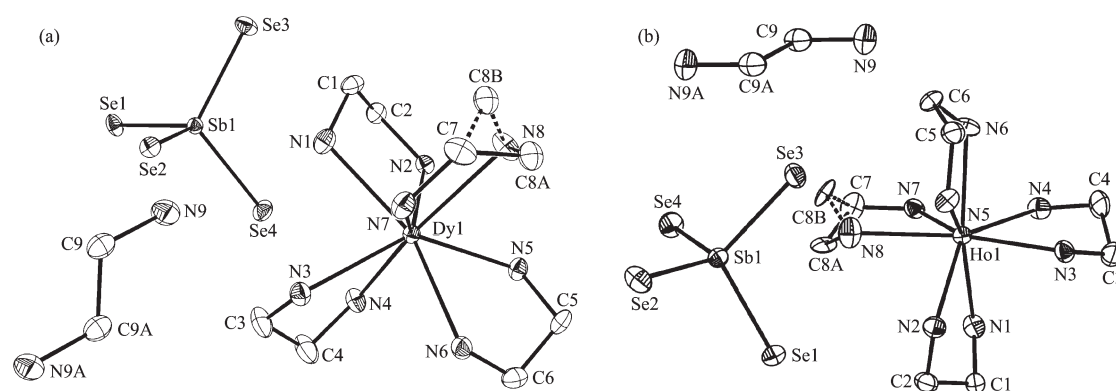
2.1 Synthesis

Compounds **1** and **2** were synthesized with a one-pot process by the reaction of Dy_2O_3 (or Ho_2O_3), Sb and Se in en at 160 °C. In the solvothermal reaction, the lanthanide(III) oxides Ln_2O_3 ($\text{Ln}=\text{Dy}, \text{Ho}$) were transferred to lanthanide(III) complex cations $[\text{Ln}(\text{en})_4]^{3+}$ to act as counter ions of the SbSe_4^{3-} anions. When en- H_2O mixed solution was used instead of en in the synthesis, an unknown amorphous grey powder was obtained. It is well known that lanthanide(III) ions are typically hard acid and preferentially hydrolyze to form hydroxyl precipitate in basic solution. So the waterless en is needed in the solvothermal synthesis to avoid the hydrolysis of lanthanide(III) ion.

2.2 Crystal structure

Compounds **1** and **2** are isostructural crystallizing

in the monoclinic space group $P2_1/n$ with four formula units. They are composed of isolated $[\text{Ln}(\text{en})_4]^{3+}$ ($\text{Ln}=\text{Dy}, \text{Ho}$) and SbSe_4^{3-} ions and free en molecule. The crystal structures of **1** and **2** are depicted in Fig.1. The atom C(8) of **1** and **2** are disordered (Fig.1) and the occupancies of disordered C/C' are assigned as 57% and 43% for **1**, and 59% and 41% for **2**. The lanthanide(III) ion is coordinated by four bidentate en ligands, and the coordination geometry can be described as a distorted bicapped trigonal prism, with three nitrogen atoms N(1), N(7), and N(8) forming one face, and N(4), N(5), and N(6) forming the opposite face. The capping positions are occupied by N(2) and N(3) atoms form DyN_8 (Fig.1 (a)). The Ln-N bond lengths range from 0.249 3 (5) to 0.254 2 (6) nm for Dy-N, and from 0.246 1 (11) to 0.2518 (11) nm for Ho-N (Table 2). Both bond lengths are consistent with those in the reported dysprosium(III) and holmium(III) complex with amino ligand respectively.



30% thermal ellipsoids, hydrogen atoms are omitted for clarity

Fig.1 Crystal structures of **1** (a) and **2** (b) with the labelling scheme

Table 2 Selected bond lengths (nm) and angles ($^{\circ}$) of compounds **1** and **2**

1					
Sb(1)-Se(1)	0.2463 7(9)	Sb(1)-Se(2)	0.247 68(8)	Sb(1)-Se(3)	0.245 25(8)
Sb(1)-Se(4)	0.2459 6(8)	Dy(1)-N(1)	0.247 7(5)	Dy(1)-N(2)	0.250 4(5)
Dy(1)-N(3)	0.252 8(5)	Dy(1)-N(4)	0.251 5(5)	Dy(1)-N(5)	0.251 8(5)
Dy(1)-N(6)	0.249 3(5)	Dy(1)-N(7)	0.253 9(5)	Dy(1)-N(8)	0.254 2(6)
Se(1)-Sb(1)-Se(2)	110.03(3)	Se(1)-Sb(1)-Se(3)	109.16(3)	Se(1)-Sb(1)-Se(4)	109.00(3)
Se(2)-Sb(1)-Se(3)	109.29(3)	Se(2)-Sb(1)-Se(4)	105.32(3)	Se(3)-Sb(1)-Se(4)	113.96(3)
N(1)-Dy(1)-N(2)	68.13(17)	N(1)-Dy(1)-N(3)	77.00(18)	N(1)-Dy(1)-N(4)	93.5(2)
N(1)-Dy(1)-N(5)	139.72(16)	N(1)-Dy(1)-N(6)	152.71(17)	N(1)-Dy(1)-N(7)	81.27(18)
N(1)-Dy(1)-N(8)	90.7(2)	N(2)-Dy(1)-N(3)	128.95(18)	N(2)-Dy(1)-N(4)	78.05(17)
N(2)-Dy(1)-N(5)	72.19(16)	N(2)-Dy(1)-N(6)	138.40(17)	N(2)-Dy(1)-N(7)	133.01(17)
N(2)-Dy(1)-N(8)	78.53(17)	N(3)-Dy(1)-N(4)	67.93(17)	N(3)-Dy(1)-N(5)	136.89(18)
N(3)-Dy(1)-N(6)	78.44(18)	N(3)-Dy(1)-N(7)	72.93(18)	N(3)-Dy(1)-N(8)	139.11(18)
N(4)-Dy(1)-N(5)	84.75(18)	N(4)-Dy(1)-N(6)	88.09(19)	N(4)-Dy(1)-N(7)	140.66(17)
N(4)-Dy(1)-N(8)	152.66(17)	N(5)-Dy(1)-N(6)	67.56(17)	N(5)-Dy(1)-N(7)	123.58(18)
N(5)-Dy(1)-N(8)	74.80(19)	N(6)-Dy(1)-N(7)	80.32(18)	N(6)-Dy(1)-N(8)	100.3(2)
N(7)-Dy(1)-N(8)	66.68(17)				
2					
Sb(1)-Se(1)	0.247 77(16)	Sb(1)-Se(2)	0.245 45(17)	Sb(1)-Se(3)	0.246 10(17)
Sb(1)-Se(4)	0.245 80(17)	Ho(1)-N(1)	0.246 2(11)	Ho(1)-N(2)	0.249 8(11)
Ho(1)-N(3)	0.246 6(11)	Ho(1)-N(4)	0.250 6(10)	Ho(1)-N(5)	0.249 1(9)
Ho(1)-N(6)	0.246 1(11)	Ho(1)-N(7)	0.251 8(11)	Ho(1)-N(8)	0.251 7(12)
Se(1)-Sb(1)-Se(2)	109.32(6)	Se(1)-Sb(1)-Se(3)	110.10(6)	Se(1)-Sb(1)-Se(4)	105.11(6)
Se(2)-Sb(1)-Se(3)	109.08(6)	Se(2)-Sb(1)-Se(4)	114.03(7)	Se(3)-Sb(1)-Se(4)	109.12(7)
N(1)-Ho(1)-N(2)	68.0(4)	N(1)-Ho(1)-N(3)	89.1(4)	N(1)-Ho(1)-N(4)	78.5(4)
N(1)-Ho(1)-N(5)	139.0(4)	N(1)-Ho(1)-N(6)	152.2(4)	N(1)-Ho(1)-N(7)	79.6(4)
N(1)-Ho(1)-N(8)	99.5(4)	N(2)-Ho(1)-N(3)	84.1(4)	N(2)-Ho(1)-N(4)	137.0(4)
N(2)-Ho(1)-N(5)	72.1(4)	N(2)-Ho(1)-N(6)	139.8(4)	N(2)-Ho(1)-N(7)	124.2(4)
N(2)-Ho(1)-N(8)	74.8(4)	N(3)-Ho(1)-N(4)	68.8(4)	N(3)-Ho(1)-N(5)	77.8(4)
N(3)-Ho(1)-N(6)	93.8(4)	N(3)-Ho(1)-N(7)	140.9(4)	N(3)-Ho(1)-N(8)	152.0(4)

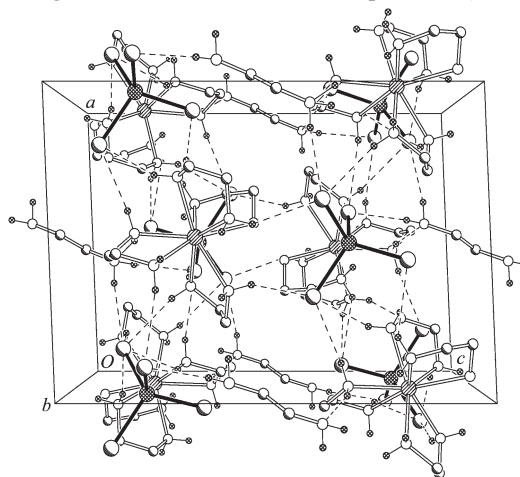
Continued Table 2

N(4)-Ho(1)-N(5)	129.3(4)	N(4)-Ho(1)-N(6)	76.8(4)	N(4)-Ho(1)-N(7)	72.3(4)
N(4)-Ho(1)-N(8)	139.0(4)	N(5)-Ho(1)-N(6)	68.3(4)	N(5)-Ho(1)-N(7)	132.8(4)
N(5)-Ho(1)-N(8)	78.2(4)	N(6)-Ho(1)-N(7)	80.8(4)	N(6)-Ho(1)-N(8)	90.8(4)
N(7)-Ho(1)-N(8)	67.1(4)				

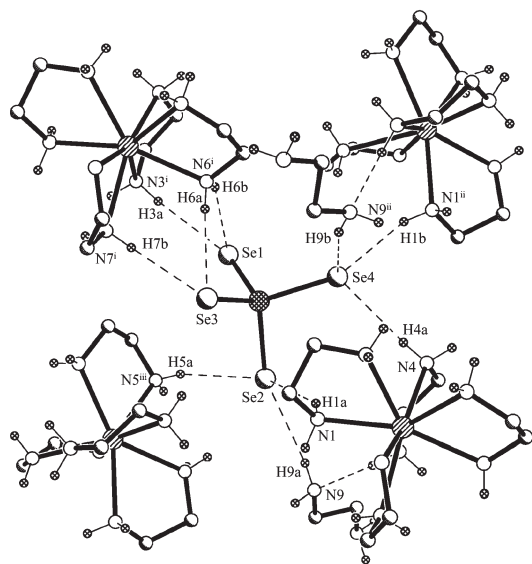
ely^[14,18]. The tetraselenidoantimonate SbSe_4^{3-} anion can be described as a distorted tetrahedron, as evidenced by the Se-Sb-Se angles ranging from $105.32(3)^\circ$ to $113.96(3)^\circ$ for **1**, and from $105.11(6)^\circ$ to $114.03(7)^\circ$ for **2**. The Sb-Se bond lengths are between 0.245 25(8) and 0.247 68(8) nm for **1**, and 0.245 45(17) and 0.247 77(16) nm for **2** (Table 2). Both bond lengths and angles are in the range of those observed in other compounds containing the SbSe_4^{3-} tetrahedral anion^[15,19-20].

In **1**, all Se atoms of SbSe_4^{3-} anion are involved in hydrogen bonding with NH_2 groups of en ligands. Each of the SbSe_4^{3-} anion contacts with four $[\text{Dy}(\text{en})_4]^{3+}$ cations and two en molecules forming $\text{N}-\text{H} \cdots \text{Se}$ hydrogen bonds with $\text{N} \cdots \text{Se}$ lengths ranging from 0.340 4(6) to 0.372 7(6) nm and $\text{N}-\text{H} \cdots \text{Se}$ angles ranging from 141.4° to 171.6° (Fig.2). Between the free en molecule and coordinated en ligand, hydrogen bond $\text{N}(3)-\text{H}(3\text{B}) \cdots \text{N}(9)$ is observed with $\text{N}(3) \cdots \text{N}(9)$ length of 0.311 4(8) nm and $\text{N}(3)-\text{H}(3\text{B}) \cdots \text{N}(9)$ angle of 157.8° (Tabe 3). The lengths and angles of hydrogen bonds are in

agreement with the values reported in literatures^[15,21]. The $\text{N}-\text{H} \cdots \text{Se}$ and $\text{N}-\text{H} \cdots \text{N}$ hydrogen-bonding interactions lead to a 3-dimensional network structure of $[\text{Dy}(\text{en})_4]^{3+}$, SbSe_4^{3-} , and en moieties (Fig.3). A similar H-bonding network is observed in compound **2** (Tabe 3).

Hydrogen atoms of CH_2 are omitted for clarityFig.3 Crystal packing of **1** viewed along b axis

Under the same synthetic conditions, the reactions of La_2O_3 or Nd_2O_3 , Sb, and Se in en produced compounds $[\text{La}(\text{en})_4(\text{SbSe}_4)]$ and $[\text{Nd}(\text{en})_4(\text{SbSe}_4)]$ respectively^[15]. In $[\text{La}(\text{en})_4(\text{SbSe}_4)]$ and $[\text{Nd}(\text{en})_4(\text{SbSe}_4)]$, the SbSe_4^{3-} ion coordinates to $[\text{La}(\text{en})_4]^{3+}$ and $[\text{Nd}(\text{en})_4]^{3+}$ ions as a monodentate ligand. The reaction of Sm_2O_3 , Sb, and Se gave compound $[\text{Sm}(\text{en})_4]\text{SbSe}_4 \cdot 0.5\text{en}$ ^[15] which is isostructural with **1** and **2**. This structural difference can be interpreted in terms of the coordination number of lanthanide(III) ions. It is commonly observed that the lighter lanthanide ions prefer coordination number of nine and heavier ones prefer eight in solution^[22]. Because en is a bidentate ligand, the $[\text{La}(\text{en})_4]^{3+}$ and $[\text{Nd}(\text{en})_4]^{3+}$ ions are bonded to the monodentate ligand of SbSe_4^{3-} to maintain the coordination number of nine for La^{3+} and Nd^{3+} , and $[\text{La}(\text{en})_4(\text{SbSe}_4)]$ and $[\text{Nd}(\text{en})_4(\text{SbSe}_4)]$ are formed. While the coordination number of Sm^{3+} , Dy^{3+} and Ho^{3+} have been saturated by four en ligands, SbSe_4^{3-} anion has no opportunity to coordinate to the metal



Symmetry codes: ⁱ $x-1, y, z$; ⁱⁱ $-x+3/2, y-1/2, -z+1/2$; ⁱⁱⁱ $-x+3/2, y+1/2, -z+1/2$

Showing the $\text{N}-\text{H} \cdots \text{Se}$ and $\text{N}-\text{H} \cdots \text{N}$ interactions in dashed lines, hydrogen atoms of CH_2 are omitted for clarity

Fig.2 Environment of a SbSe_4^{3-} anion in **1**

Table 3 Hydrogen bonding of compounds 1 and 2

D-H...A	$d(\text{H}\cdots\text{A}) /$ nm	$d(\text{D}\cdots\text{A}) /$ nm	$\angle(\text{DHA}) /$ ($^{\circ}$)
1			
N(1)–H(1A) ...Se(2)	0.290	0.370 4(6)	149.7
N(1)–H(1B) ...Se(4) ⁱⁱ	0.254	0.340 4(6)	162.3
N(3)–H(3A) ...Se(1) ⁱ	0.272	0.360 9(6)	171.6
N(3)–H(3B) ...N(9)	0.226	0.311 1(8)	157.8
N(4)–H(4A) ...Se(4)	0.284	0.372 7(6)	168.4
N(5)–H(5A) ...Se(2) ⁱⁱⁱ	0.269	0.355 4(5)	161.3
N(6)–H(6A) ...Se(3) ⁱ	0.265	0.353 1(6)	165.5
N(6)–H(6B) ...Se(1) ⁱ	0.279	0.355 5(5)	143.0
N(7)–H(7B) ...Se(3) ⁱ	0.287	0.362 2(6)	141.4
N(9)–H(9B) ...Se(4) ⁱⁱ	0.277	0.360 5(6)	156.3
N(9)–H(9A) ...Se(2)	0.283	0.366 5(6)	157.8
2			
N(1)–H(1A) ...Se(2) ⁱ	0.264	0.351 3(12)	163.1
N(1)–H(1B) ...Se(3) ⁱ	0.278	0.355 4(11)	145.5
N(2)–H(2A) ...Se(1) ⁱ	0.268	0.354 8(12)	162.9
N(2)–H(2B) ...Se(1)	0.280	0.359 6(12)	147.4
N(3)–H(3A) ...Se(4) ⁱⁱⁱ	0.284	0.372 0(12)	167.3
N(4)–H(4A) ...Se(3) ⁱ	0.272	0.361 1(12)	172.6
N(4)–H(4B) ...N(9)	0.225	0.310 3(17)	157.7
N(5)–H(5A) ...Se(3)	0.263	0.341 6(11)	145.9
N(6)–H(6B) ...Se(4)	0.254	0.340 0(12)	161.1
N(7)–H(7B) ...Se(2) ⁱ	0.291	0.363 9(12)	139.6
N(9)–H(9A) ...Se(1) ⁱⁱ	0.282	0.366 1(13)	157.3
N(9)–H(9B) ...Se(4) ⁱⁱⁱ	0.278	0.361 3(13)	157.3

Symmetry transformations used to generate equivalent atoms: **1**: ⁱ $x-1, y, z$; ⁱⁱ $-x+3/2, y-1/2, -z+1/2$; ⁱⁱⁱ $-x+3/2, y+1/2, -z+1/2$; **2**: ⁱ $x+1/2, -y+3/2, z-1/2$; ⁱⁱ $-x+1, -y+2, -z+1$; ⁱⁱⁱ $x-1/2, -y+3/2, z-1/2$.

centers and the ionic compounds $[\text{Sm}(\text{en})_4]\text{SbSe}_4 \cdot 0.5\text{en}$, $[\text{Dy}(\text{en})_4]\text{SbSe}_4 \cdot 0.5\text{en}$ and $[\text{Ho}(\text{en})_4]\text{SbSe}_4 \cdot 0.5\text{en}$ are formed.

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