**8286** *Inorg. Chem.* **2009**, *48*, 8286–8293
DOI: 10.1021/ic900901t

Inorganic Chemistry
Article

# The Coordination of the Tetraselenidoantimonate $[SbSe_4]^{3-}$ Anion with Trivalent Lanthanide Ions Tuned by Ethylene Polyamines

**Dingxian Jia,* Qinyan Jin, Jiangfang Chen, Yingli Pan, and Yong Zhang**

*College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, People's Republic of China*

Received May 9, 2009

The solvothermal synthetic system Ln/Sb/Se (Ln = La, Eu) was investigated in different ethylene polyamines, and a series of lanthanum and europium selenidoantimonates [La(en)$_2$(dien)($\eta^2$-SbSe$_4$)] (**Ia**), [La(dien)$_2$($\mu$-$\eta^1$,$\eta^2$-SbSe$_4$)] (**Ib**), [La(trien)$_2$(H$_2$O)]SbSe$_4$ (**Ic**), [La(en)(trien)($\mu$-$\eta^1$,$\eta^2$-SbSe$_4$)] (**Id**), [Eu(en)$_2$(dien)(SbSe$_4$)] (**IIa**), [Eu(en)(trien)($\eta^2$-SbSe$_4$)] (**IIb**), and [Eu(dien)$_2$($\eta^2$-SbSe$_4$)] (**IIc**) (en = ethylenediamine, dien = diethylenetriamine, trien = triethylenetetramine) were prepared. A systematic investigation of the crystal structures showed that the soft Lewis basic ligand $[SbSe_4]^{3-}$ can be tuned to coordinate to the hard Lewis acidic lanthanide ions as a monodentate ligand, mono-SbSe$_4$; a bidentate chelating ligand, $\eta^2$-SbSe$_4$; or a tridentate bridging ligand, $\mu$-$\eta^1$,$\eta^2$-SbSe$_4$, by the ethylene polyamines or mixed ethylene polyamines used in the syntheses. The $[SbSe_4]^{3-}$ anion exhibited different coordination modes for La$^{3+}$ and Eu$^{3+}$ ions in the presence of the same ethylene polyamine because of the different coordination numbers of La$^{3+}$ and Eu$^{3+}$ ions.

## Introduction

The mild solvothermal synthesis of main group chalcogenidometalates containing transition-metal (TM) complexes in ethylene polyamines has attracted increasing attention[1] since the cobalt thioantimonate [Co(en)$_3$]CoSb$_4$S$_8$ was prepared in ethylenediamine in 1996,[2] and a number of these chalcogenidometalates including chalcogenido-germanates,[3] -stannates,[4] -arsenates,[5] and -antimonates[6] have been prepared in ethylene polyamines of ethylenediamine (en) and diethylenetriamine (dien). However, the coordinate sites of TM$^{n+}$ ions are prone to being saturated by the bidentate en and tridentate dien ligands due to the formation of octahedral complexes $[TM(en)_3]^{n+}$ and $[TM(dien)_2]^{n+}$. The TM-coordinating chalcogenidometalates are only observed for Cr$^{3+}$ and Mn$^{2+}$ metals, including the limited examples of $[Cr(en)_2(GeS_4)]^-$, $[\{Cr(en)\}_2(GeSe_4)_2]^{2-}$, $[Cr(en)_2(SnSe_4)]^-$,[7] [{Mn(en)$_2$}$_2$(en)(Sn$_2$S$_6$)],[8] $[Mn(dien)(AsS_4)]^-$,[9] Cr(en)$_2$SbS$_3$,[10] [Mn$_2$(en)$_2$(Sb$_2$S$_5$)],[11] [Mn$_2$(dien)(Sb$_2$S$_5$)],[12] $[Mn_4(en)_9(SbSe_4)_4]^{4-}$,[13] and $[Mn_2(SbSe_4)_2(en)_4(H_2O)]^{2-}$.[14] Recently, by adopting a tetradentate polyamine, tris(2-aminoethyl)amine (tren), as a chelating ligand in the solvothermal synthesis,

---

*To whom correspondence should be addressed. E-mail: jiadingxian@suda.edu.cn.

(1) (a) Li, J.; Chen, Z.; Wang, R. J.; Proserpio, D. M. *Coord. Chem. Rev.* **1999**, *190−192*, 707–735. (b) Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **2000**, 3041–3052. (c) Dehnen, S.; Melullis, M. *Coord. Chem. Rev.* **2007**, *251*, 1259–1280.

(2) Stephan, H. O.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1996**, *118*, 12226–12227.

(3) (a) van Almsick, T.; Loose, A.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **2005**, *631*, 21–23. (b) Jia, D. X.; Dai, J.; Zhu, Q. Y.; Cao, L. H.; Lin, H. H. *J. Solid State Chem.* **2005**, *178*, 874–881. (c) Jia, D. X.; Zhu, A. M.; Zhang, Y.; Deng, J. *Monatsh. Chem.* **2007**, *138*, 191–197.

(4) (a) Shreeve-Keyer, J. L.; Warren, C. J.; Dhingra, S. S.; Haushalter, R. C. *Polyhedron* **1997**, *16*, 1193–1199. (b) Li, J.; Chen, Z.; Emge, T. J.; Yuen, T.; Proserpio, D. M. *Inorg. Chim. Acta* **1998**, *273*, 310–315. (c) Jia, D. X.; Zhang, Y.; Dai, J.; Zhu, Q. Y.; Gu, X. M. *Z. Anorg. Allg. Chem.* **2004**, *630*, 313–318. (d) Jia, D. X.; Dai, J.; Zhu, Q. Y.; Zhang, Y.; Gu, X. M. *Polyhedron* **2004**, *23*, 937–942.

(5) (a) Fu, M. L.; Guo, G. C.; Liu, X.; Liu, B.; Cai, L. Z.; Huang, J. S. *Inorg. Chem. Commun.* **2005**, *8*, 18–21. (b) Jia, D. X.; Zhao, Q. X.; Dai, J.; Zhang, Y.; Zhu, Q. Y. *Z. Anorg. Allg. Chem.* **2006**, *632*, 349–353.

(6) (a) Stephan, H. O.; Kanatzidis, M. G. *Inorg. Chem.* **1997**, *36*, 6050–6057. (b) Bensch, W.; Näther, C.; Stähler, R. *Chem. Commun.* **2001**, 477–478. (c) Stähler, R.; Näther, C.; Bensch, W. *Eur. J. Inorg. Chem.* **2001**, 1835–1840. (d) Powell, A. V.; Paniagua, R.; Vaqueiro, P.; Chippindale, A. M. *Chem. Mater.* **2002**, *14*, 1220–1224. (e) Stähler, R.; Mosel, B. D.; Eckert, H.; Bensch, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 4487–4489. (f) Stähler, R.; Näther, C.; Bensch, W. *J. Solid State Chem.* **2003**, *174*, 264–275. (g) Kiebach, R.; Studt, F.; Näther, C.; Bensch, W. *Eur. J. Inorg. Chem.* **2004**, 2553–2556. (h) Vaqueiro, P.; Chippindale, A. M.; Powell, A. V. *Inorg. Chem.* **2004**, *43*, 7963–7965. (i) Vaqueiro, P.; Darlow, D. P.; Powell, A. V.; Chippindale, A. M. *Solid State Ionics* **2004**, *172*, 601–605. (j) Jia, D. X.; Zhang, Y.; Zhao, Q. X.; Deng, J. *Inorg. Chem.* **2006**, *45*, 9812–9817. (k) Puls, A.; Näther, C.; Bensch, W. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1239–1243.

(7) Melullis, M.; Brandmayer, M. K.; Dehnen, S. *Z. Anorg. Allg. Chem.* **2006**, *632*, 64–72.

(8) Gu, X. M.; Dai, J.; Jia, D. X.; Zhang, Y.; Zhu, Q. Y. *Cryst.Growth Design* **2005**, *5*, 1845–1848.

(9) Fu, M. L.; Guo, G. C.; Cai, L. Z.; Zhang, Z. J.; Huang, J. S. *Inorg. Chem.* **2005**, *44*, 184–186.

(10) Schur, M.; Rijnberk, H.; Näther, C.; Bensch, W. *Polyhedron* **1998**, *18*, 101–107.

(11) Schur, M.; Bensch, W. *Z. Naturforsch.* **2002**, *B57*, 1–7.

(12) Engelke, L.; Stähler, R.; Schur, M.; Näther, C.; Bensch, W.; Pöttgen, R.; Möller, M. H. *Z. Naturforsch.* **2004**, *B59*, 869–876.

(13) Bensch, W.; Näther, C.; Schur, M. *Chem. Commun.* **1997**, 1773–1774.

(14) van Almsick, T.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1413–1415.

the Bensch[15] and Sheldrick[16] groups have prepared a number of chalcogenidometalates incorporated with TM complexes of $Mn^{2+}$, $Fe^{2+}$, $Ni^{2+}$, and $Co^{2+}$. It can be seen from the results that the coordination of TM with the chalcogenidometalate anion is much influenced by the denticity of ethylene polyamines.

Unlike the transition metals which exhibit the restricted stereochemistry in coordination complexes, the lanthanide(III) ions are characterized by variable coordination numbers and geometries,[17] which theoretically provides the lanthanide metals with different structural features from the transition metals in the combination with chalcogenidometalates in the presence of ethylene polyamines. A couple of years ago, we started to investigate the solvothermal synthetic systems Ln/M/Q (Ln = lanthanide; M = Sn, As, Sb; Q = S, Se) in en and dien solvents, from which a series of lanthanide-containing chalcogenidometalates were prepared.[18−21] The coordinations of the tetrachalcogenidometalate anions $[SnSe_4]^{4-}$,[18] $[AsSe_4]^{3-}$,[19] $[SbS_4]^{3-}$,[20] and $[SbSe_4]^{3-}$[21] with lanthanide(III)−en and −dien complexes are successfully achieved in these synthetic systems. In the case of system Ln/Sb/Se, two types of compounds were obtained with en as the solvent. Across the lanthanide series, the lighter lanthanide metals form neutral complexes represented by $[La(en)_4(SbSe_4)]$ (**I**), in which the $[SbSe_4]^{3-}$ anion coordinates to the $[La(en)_4]^{3+}$ ion as a monodentate ligand,[21a] while the heavier ones develop ionic complexes represented by $[Eu(en)_4]SbSe_4\cdot 0.5en$ (**II**) in which the $[SbSe_4]^{3-}$ anion exists as a discrete ion.[21b] To examine the effect of amines on the coordination of the $[SbSe_4]^{3-}$ ion to the lanthanide metals, we investigated the La(Eu)/Sb/Se system in different ethylene polyamines and found that not only can the $[SbSe_4]^{3-}$ anion coordinate to the heavier lanthanide metals but also the coordination modes of $[SbSe_4]^{3-}$ can be tuned by the ethylene polyamines. Herein, we report the syntheses and characterizations of a series of lanthanum(III) and europium(III) selenidoantimonates, $[La(en)_2(dien)(\eta^2\text{-}SbSe_4)]$ (**Ia**), $[La(dien)_2(\mu\text{-}\eta^1,\eta^2\text{-}SbSe_4)]$ (**Ib**), $[La(trien)_2(H_2O)]SbSe_4$ (**Ic**), $[La(en)(trien)(\mu\text{-}\eta^1,\eta^2\text{-}SbSe_4)]$ (**Id**), $[Eu(en)_2(dien)(SbSe_4)]$ (**IIa**), $[Eu(en)(trien)(\eta^2\text{-}SbSe_4)]$ (**IIb**), and $[Eu(dien)_2(\eta^2\text{-}SbSe_4)]$ (**IIc**), in which the monodentate, bidentate, and tridentate coordination modes are observed for the $[SbSe_4]^{3-}$ anion.

## Experimental Section

**Materials and Methods.** All starting chemicals were analytical grade and used as purchased. Elemental analyses were conducted on a MOD 1106 elemental analyzer. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr discs in the 4000−400 $cm^{-1}$ range. 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 using the Kubelka−Munk function $\alpha/S = (1 - R)^2/2R$.[22] Thermoanalytical measurements were performed using a thermogravimetric analysis−differential scanning calorimetry (TG-DSC) microanalyzer of SDT 2960, and all of the samples were heated under a nitrogen stream of 100 mL $min^{-1}$ with a heating rate of 5 °C $min^{-1}$.

**Syntheses.** All complexes were synthesized in ethylene polyamines or mixed polyamines under solvothermal conditions. In a typical synthetic procedure, the reactants in a certain molar ratio were dispersed in ethylene polyamine or mixed polyamines under stirring; then, the mixture was loaded into a Teflon-lined stainless steel autoclave with an inner volume of 15 mL. The sealed autoclave was heated at 180 °C for 7 days. After being cooled to ambient temperature, crystals were filtered off, washed with ethanol, and stored under a vacuum.

**Synthesis of $[La(en)_2(dien)(\eta^2\text{-}SbSe_4)]$ (Ia).** Red polyhedron crystals of **Ia** were prepared by the reaction of $La_2O_3$ (82 mg, 0.25 mmol), Sb (61 mg, 0.50 mmol), and Se (158 mg, 2 mmol) in 3 mL of a mixed en/dien (1:1 (v/v)) solvent (53% yield based on Sb). Elem Anal. Calcd for $C_8H_{29}N_7Se_4LaSb$: C, 12.01; H, 3.65; N, 12.26. Found: C, 11.83; H, 3.61; N, 12.07. IR (KBr, $cm^{-1}$): 3730 (w), 3609 (w), 3242 (m), 3206 (m), 3177 (m), 3126 (m), 2945 (m), 2886 (m), 1566 (vs), 1520 (m), 1463 (s), 1413 (m), 1329 (s), 1271 (m), 1154 (m), 1084 (s), 1029 (m), 976 (vs), 897 (m), 863 (w), 813 (w), 764 (w), 688 (s), 609 (m), 584 (m), 495 (m), 479 (s), 446 (s).

**Synthesis of $[La(dien)_2(\mu\text{-}\eta^1,\eta^2\text{-}SbSe_4)]$ (Ib).** Orange block crystals of **Ib** were prepared by the reaction of $La_2O_3$ (82 mg, 0.25 mmol), Sb (61 mg, 0.50 mmol), and Se (158 mg, 2 mmol) in 3 mL of dien (56% yield based on Sb). Elem Anal. Calcd for $C_8H_{26}N_6Se_4LaSb$: C, 12.27; H, 3.35; N, 10.73. Found: C, 12.12; H, 3.31; N, 10.55. IR (KBr, $cm^{-1}$): 3411 (s), 3296 (s), 3201(v), 3172 (vs), 3126 (s), 2909 (s), 2863 (m), 1567 (vs), 1451 (vs), 1397 (m), 1366 (s), 1327 (m), 1258 (m), 1154(m), 1135(m), 1050 (vs), 1019 (s), 965 (vs), 903 (m), 864 (m), 810 (w), 756 (w), 602 (s), 556 (m), 486 (s).

**Synthesis of $[La(trien)_2(H_2O)]SbSe_4$ (Ic).** Orange chip crystals of **Ic** were prepared by the reaction of $La_2O_3$ (82 mg, 0.25 mmol), Sb (61 mg, 0.50 mmol), and Se (158 mg, 2 mmol) in 3 mL of trien (31% yield based on Sb). Elem Anal. Calcd for $C_{12}H_{38}N_8OSe_4LaSb$: C, 16.25; H, 4.32; N, 12.63. Found: C, 16.12; H, 4.26; N, 12.46. IR (KBr, $cm^{-1}$): 3735(s), 3172 (vs), 3110 (vs), 2902 (s), 2863(s), 1574 (s), 1451 (s), 1358 (w), 1312 (s), 1289 (s), 1181 (w), 1134 (m), 1081 (s), 1050 (vs), 965 (s), 903 (m), 872 (s), 826 (m), 810 (m), 605 (s), 663 (w), 594 (w), 540 (m), 440(m).

**Synthesis of $[La(en)(trien)(\mu\text{-}\eta^1,\eta^2\text{-}SbSe_4)]$ (Id).** Red needle crystals of **Id** were prepared by the reaction of $La_2O_3$ (82 mg, 0.25 mmol), Sb (61 mg, 0.50 mmol), and Se (158 mg, 2 mmol) in 3 mL of a mixed en/trien (1:1 (v/v)) solvent (48% yield based on Sb). Elem Anal. Calcd for $C_8H_{26}N_6Se_4LaSb$: C, 12.27; H, 3.35; N, 10.73. Found: C, 12.15; H, 3.34; N, 10.58. IR (KBr, $cm^{-1}$): 3404 (s), 3211 (vs), 3094 (vs), 2917 (vs), 2863 (s), 1568 (vs), 1521 (vs),

---

(15) (a) Behrens, M.; Scherb, S.; Näther, C.; Bensch, W. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1367–1373. (b) Stähler, R.; Bensch, W. *Eur. J. Inorg. Chem.* **2001**, 3073–3078. (c) Stähler, R.; Bensch, W. *J. Chem. Soc., Dalton Trans.* **2001**, 2518–2522. (d) Kiebach, R.; Bensch, W.; Hoffmann, R.-D.; Pöttgen, R. *Z. Anorg. Allg. Chem.* **2003**, *629*, 532–538. (e) Schaefer, M.; Näther, C.; Bensch, W. *Solid State Sci.* **2003**, *5*, 1135–1139. (f) Schaefer, M.; Stähler, R.; Kiebach, W. R.; Näther, C.; Bensch, W. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1816–1822. (g) Schaefer, M.; Näther, C.; Lehnert, N.; Bensch, W. *Inorg. Chem.* **2004**, *43*, 2914–2921. (h) Schaefer, M.; Kurowski, D.; Pfitzner, A.; Näther, C.; Rejai, Z.; Möller, K.; Ziegler, N.; Bensch, W. *Inorg. Chem.* **2006**, *45*, 3726–3731. (i) Möller, K.; Näther, C.; Bannwarth, A.; Bensch, W. *Z. Anorg. Allg. Chem.* **2007**, *633*, 2635–2640. (j) Lühmann, H.; Rejai, Z.; Möller, K.; Leisner, P.; Ordolff, M.-E.; Näther, C.; Bensch, W. *Z. Anorg. Allg. Chem.* **2008**, *634*, 1687–1695. (k) Engelke, L.; Näther, C.; Leisner, P.; Bensch, W. *Z. Anorg. Allg. Chem.* **2008**, *634*, 2959–2965.

(16) (a) Kromm, A.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **2008**, *634*, 121–124. (b) Kromm, A.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **2008**, *634*, 225–227. (c) Kromm, A.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **2009**, *635*, 205–207.

(17) Cassol, A.; Di Bernardo, P.; Portanova, R.; Tolazzi, M.; Tomat, G.; Zanonato, P. *J. Chem. Soc., Dalton Trans.* **1992**, 469–474.

(18) (a) Zhu, A. M.; Jin, Q. Y.; Jia, D. X.; Gu, J. S.; Zhang, Y. *Eur. J. Inorg. Chem.* **2008**, 4756–4761. (b) Jia, D. X.; Zhu, A. M.; Deng, J.; Zhang, Y. *Z. Anorg. Allg. Chem.* **2007**, *633*, 1246–1250.

(19) Jia, D. X.; Zhu, A. M.; Deng, J.; Zhang, Y.; Dai, J. *Dalton Trans.* **2007**, 2083–2086.

(20) (a) Jia, D. X.; Zhu, Q. Y.; Dai, J.; Lu, W.; Guo, W. J. *Inorg. Chem.* **2005**, *44*, 819–821. (b) Jia, D. X.; Zhao, Q. X.; Zhang, Y.; Dai, J.; Zou, J. L. *Inorg. Chem.* **2005**, *44*, 8861–8867.

(21) (a) Jia, D. X.; Zhao, Q. X.; Zhang, Y.; Dai, J.; Zhou, J. *Eur. J. Inorg. Chem.* **2006**, 2760–2765. (b) Jia, D. X.; Zhu, A. M.; Jin, Q. Y.; Zhang, Y.; Jiang, W. Q. *J. Solid State Chem.* **2008**, *181*, 2370–2377.

(22) Wendlandt, W. W.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966.

**Table 1.** Crystal Data and Summary of X-ray Data Collection

| | **Ia** | **Ib** | **Ic** | **Id** |
|---|---|---|---|---|
| empirical formula | $C_8H_{29}N_7Se_4LaSb$ | $C_8H_{26}N_6Se_4LaSb$ | $C_{12}H_{38}N_8OSe_4LaSb$ | $C_8H_{26}N_6Se_4LaSb$ |
| fw | 799.88 | 782.85 | 887.00 | 782.85 |
| color of cryst | red | orange | orange | orange |
| cryst syst | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/n$ (no. 14) | $P2_1/c$ (no. 14) | $P2_1$ (no. 4) | $P2_1/n$ (no. 14) |
| $a$, Å | 8.6554(14) | 8.9753(13) | 10.9619(17) | 14.421(2) |
| $b$, Å | 27.909(4) | 13.4326(18) | 10.5221(15) | 9.0480(12) |
| $c$, Å | 9.3570(16) | 16.600(2) | 11.1483(17) | 15.561(2) |
| α, deg | 90 | 90 | 90 | 90 |
| $\beta$, deg | 109.303(3) | 97.604(4) | 91.611(4) | 100.890(4) |
| $\gamma$, deg | 90 | 90 | 90 | 90 |
| $V$, Å$^3$ | 2133.3(6) | 1983.7(5) | 1285.4(3) | 1993.9(5) |
| $Z$ | 4 | 4 | 2 | 4 |
| $T$, K | 293(2) | 293(2) | 293(2) | 293(2) |
| calcd density, Mg m$^{-3}$ | 2.491 | 2.621 | 2.292 | 2.608 |
| $F$(000) | 1480 | 1440 | 836 | 1440 |
| $2\theta$(max), deg | 50.68 | 50.70 | 50.68 | 50.68 |
| total reflns collected | 20103 | 18933 | 12641 | 18706 |
| unique reflns | 3906 ($R_{int}$ = 0.0522) | 3619 ($R_{int}$ = 0.0771) | 4616 ($R_{int}$ = 0.0510) | 3638 ($R_{int}$ = 0.0820) |
| no. of param | 191 | 182 | 243 | 182 |
| R1 [$I > 2\sigma(I)$] | 0.0412 | 0.0533 | 0.0439 | 0.0589 |
| wR2 (all data) | 0.0829 | 0.1203 | 0.0801 | 0.1159 |
| GOF on $F^2$ | 1.173 | 1.131 | 1.077 | 1.195 |

| | **IIa** | **IIb** | **IIc** |
|---|---|---|---|
| empirical formula | $C_8H_{29}N_7Se_4EuSb$ | $C_8H_{26}N_6Se_4EuSb$ | $C_8H_{26}N_6Se_4EuSb$ |
| fw | 812.93 | 795.90 | 795.90 |
| color of cryst | red | orange | orange |
| cryst syst | triclinic | monoclinic | triclinic |
| space group | $P\bar{1}$ (no. 2) | $P2_1/c$ (no. 14) | $P\bar{1}$ (no. 2) |
| $a$, Å | 10.117(2) | 10.172(4) | 8.2239(15) |
| $b$, Å | 12.104(2) | 13.476(5) | 8.2399(15) |
| $c$, Å | 17.179(3) | 14.791(5) | 16.173(4) |
| α, deg | 89.083(7) | 90 | 93.475(17) |
| $\beta$, deg | 88.431(7) | 98.707(6) | 104.656(17) |
| $\gamma$, deg | 86.795(7) | 90 | 108.89(2) |
| $V$, Å$^3$ | 2099.4(7) | 2004.3(12) | 991.0(3) |
| $Z$ | 4 | 4 | 2 |
| $T$, K | 293(2) | 293(2) | 293(2) |
| calcd density, Mg m$^{-3}$ | 2.572 | 2.638 | 2.667 |
| $F$(000) | 1504 | 1464 | 732 |
| $2\theta$(max), deg | 50.70 | 50.00 | 48.50 |
| total reflns collected | 20392 | 14542 | 8845 |
| unique reflns | 7619 ($R_{int}$ = 0.0555) | 3481 ($R_{int}$ = 0.0643) | 3170 ($R_{int}$ = 0.0902) |
| no. of params | 378 | 182 | 170 |
| R1 [$I > 2\sigma(I)$] | 0.0675 | 0.0416 | 0.0777 |
| wR2 (all data) | 0.1461 | 0.1245 | 0.2074 |
| GOF on $F^2$ | 1.041 | 1.139 | 1.110 |

1466 (s), 1398 (m), 1368 (m), 1335 (m), 1151 (m), 1073 (s), 1011 (s), 973 (s), 903 (s), 826 (m), 756 (m), 595 (w), 586 (w), 471 (w).

**Synthesis of [Eu(en)$_2$(dien)(SbSe$_4$)] (IIa).** Red block crystals of **IIa** were prepared with a procedure similar to that for the synthesis of **Ia**, except that $Eu_2O_3$ was used instead of $La_2O_3$ (45% yield based on Sb). Elem Anal. Calcd for $C_8H_{29}N_7Se_4EuSb$: C, 11.82; H, 3.60; N, 12.06. Found: C, 11.64; H, 3.52; N, 11.85. IR (KBr, cm$^{-1}$): 3728 (w), 3611 (w), 3251 (m), 3206 (m), 3195 (m), 3118 (m), 2941 (m), 2886 (s), 1567 (vs), 1519 (s), 1451 (m), 1328 (s), 1268 (m), 1142 (m), 1081 (s), 1042 (m), 996 (s), 972 (s), 903 (m), 857 (w), 818 (w), 761 (w), 681 (s), 601 (m), 583 (m), 479 (s), 445 (m).

**Synthesis of [Eu(en)(trien)($\eta^2$-SbSe$_4$)] (IIb).** Orange prism crystals of **IIb** were prepared with a procedure similar to that for the synthesis of **Id**, except that $Eu_2O_3$ was used instead of $La_2O_3$ (43% yield based on Sb). Elem Anal. Calcd for $C_8H_{26}N_6Se_4EuSb$: C, 12.07; H, 3.29; N, 10.56. Found: C, 11.94; H, 3.26; N, 10.48. IR (KBr, cm$^{-1}$): 3406 (s), 3209 (vs), 3094 (vs), 2918 (vs), 2866 (s), 1567 (vs), 1518 (vs), 1467 (s), 1398 (m), 1331 (m), 1150 (m), 1078 (s), 1009 (s), 973 (s), 901 (s), 826 (m), 758 (m), 598 (w), 587 (w), 471 (w), 455 (m).

**Synthesis of [Eu(dien)$_2$($\eta^2$-SbSe$_4$)] (IIc).** Orange block crystals of **IIc** were prepared with a procedure similar to that for the synthesis of **Ib** except that $Eu_2O_3$ was used instead of $La_2O_3$ (51% yield based on Sb). Elem Anal. Calcd for $C_8H_{26}N_6Se_4EuSb$: C, 12.07; H, 3.29; N, 10.56. Found: C, 11.88; H, 3.23; N, 10.41. IR (KBr, cm$^{-1}$): 3243 (m), 3203 (s), 3126 (s), 3108 (s), 2925 (s), 2917 (s), 2871 (s), 1580 (vs), 1459 (vs), 1381 (m), 1320 (s), 1056 (s), 965 (vs), 887 (w), 857 (w), 780 (m), 671 (s), 588 (s), 526 (s), 478 (s), 454 (m).

**X-Ray Crystal Structure Determinations.** Data were collected on a Rigaku Mercury CCD diffractometer at 293(2) K using graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) with a $\omega$-scan method to a maximum $2\theta$ value of 50.68° for **Ia**, **Ic**, and **Id**; 50.70° for **Ib** and **IIa**; 50.00° for **IIb**; and 48.50° for **IIc**. An absorption correction was applied for all of the compounds using multiscan. The structures were solved with direct methods using the program SHELXS-97,[23] and the refinement was

---

(23) (a) Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

performed against $F^2$ using SHELXL-97.[23] All of the non-hydrogen atoms were refined anisotropically. The atoms C(11) and C(12) in **Ic** and **IIa** are disordered, and the occupancies of the disordered atoms C/C′ were assigned as 73% and 27% for **Ic** and 66% and 34% for **IIa**. The hydrogen atoms were added geometrically and refined using the riding model. Crystallographic, experimental, and analytical data for the title compounds are listed in Table 1.

## Results and Discussion

**The Coordination of the $[SbSe_4]^{3-}$ Anion with the $La^{3+}$ Ion Influenced by Ethylene Polyamines.** For the purpose of convenient elucidation and comparison, the structure of complex **I** is briefly summarized here. In **I**, the $[SbSe_4]^{3-}$ anion coordinates to the $[La(en)_4]^{3+}$ ion as a monodentate ligand (Figure 1). The $La^{3+}$ ion lies in a nine-fold coordination environment with one Se and eight N atoms.[21a]

The crystal structures of **Ia**−**Id** are depicted in Figure 1. All $La^{3+}$ ions are in nine-fold coordination environments. In **Ia**, $La^{3+}$ is coordinated to two bidentate en ligands, a tridentate dien ligand, and a bidentate $[SbSe_4]^{3-}$ anion, giving the neutral complex $[La(en)_2(dien)(\eta^2\text{-}SbSe_4)]$. In **Ib**, the $La^{3+}$ ion is coordinated by two tridentate dien ligands; then, the $[La(dien)_2]^{3+}$ cations are interconnected by the tridentate bridging ligand $\mu\text{-}\eta^1,\eta^2\text{-}SbSe_4$, whose Se1 and Se2 atoms coordinate to one $[La(dien)_2]^{3+}$ cation and whose Se3 coordinates to another $[La(dien)_2]^{3+}$ cation. The $[La(dien)_2]^{3+}$ and $[SbSe_4]^{3-}$ ions are alternatively interlinked into the neutral chain $[La(dien)_2(\mu\text{-}\eta^1,\eta^2\text{-}SbSe_4)]_\infty$ by the La−Se bonds (Figure 1). The $La^{3+}$ ion in **Ic** is coordinated to eight N atoms of two tetradentate trien ligands and one O atom of a water molecule. The tetrahedron $[SbSe_4]^{3-}$ exists as a discrete anion to compensate the charge of the complex $[La(trien)_2(H_2O)]^{3+}$ cation (Figure 1). Complex **Id** is a structural isomer of **Ib** with the same formula, $C_8H_{26}N_6Se_4LaSb$, since one en and one trien molecule have the same sum formula (en + trien = $C_8H_{26}N_6$) as two dien molecules (2dien = $C_8H_{26}N_6$). In **Id**, the $[SbSe_4]^{3-}$ ion acts as the same $\mu\text{-}\eta^1,\eta^2\text{-}SbSe_4$ bridging ligand as the $[SbSe_4]^{3-}$ ion in **Ib** to connect the $[La(en)(trien)]^{3+}$ cations into the neutral coordination polymer $[La(en)(trien)(\mu\text{-}\eta^1,\eta^2\text{-}SbSe_4)]_\infty$ (Figure 1). The La−N(en) (av. 2.713(6) Å in **Ia**), La−N(dien) (av. 2.716(6) Å in **Ia**, 2.692(9) Å in **Ib**), and La−N(trien) (av. 2.701(8) Å in **Ic**) bond lengths show no significant difference and match well with the values for $La^{3+}$ complexes with en and dien ligands.[20b,21a] The La−Se bond lengths are 3.1944(9) and 3.1573(9) Å in **Ia**, 3.1944(13)−3.3094(12) Å in **Ib**, and 3.2190(13)−3.3260(12) Å in **Id** (Table 2), which are in good agreement with the values reported in the literature.[21a]

In the crystal structures of **Ia**−**Id**, numerous weak N−H···Se hydrogen bonds are observed between the $[SbSe_4]^{3-}$ anion and the $NH_2$ or NH groups of ethylene polyamines. In **Ia**, the $[Ln(en)_2(dien)(\eta^2\text{-}SbSe_4)]$ moieties are arranged end-to-end, forming one-dimensional chains via N−H···Se hydrogen bonds, and the $[Ln(en)_2(dien)(\eta^2\text{-}SbSe_4)]$ moieties show different orientations in the neighbor chains (Figure 2). The $[La(dien)_2(\mu\text{-}\eta^1,\eta^2\text{-}SbSe_4)]_\infty$ chains in **Ib** run parallel along the *a* axis and are connected into a layer perpendicular to the *c* axis (Figure 3) via N−H···Se interactions with N···Se separations of 3.388(8)−3.799(9) Å and N−H···Se angles of 129.8−167.7°. The $[La(en)(trien)(\mu\text{-}\eta^1,\eta^2\text{-}SbSe_4)]_\infty$ chains in **Id** exhibit a packing diagram

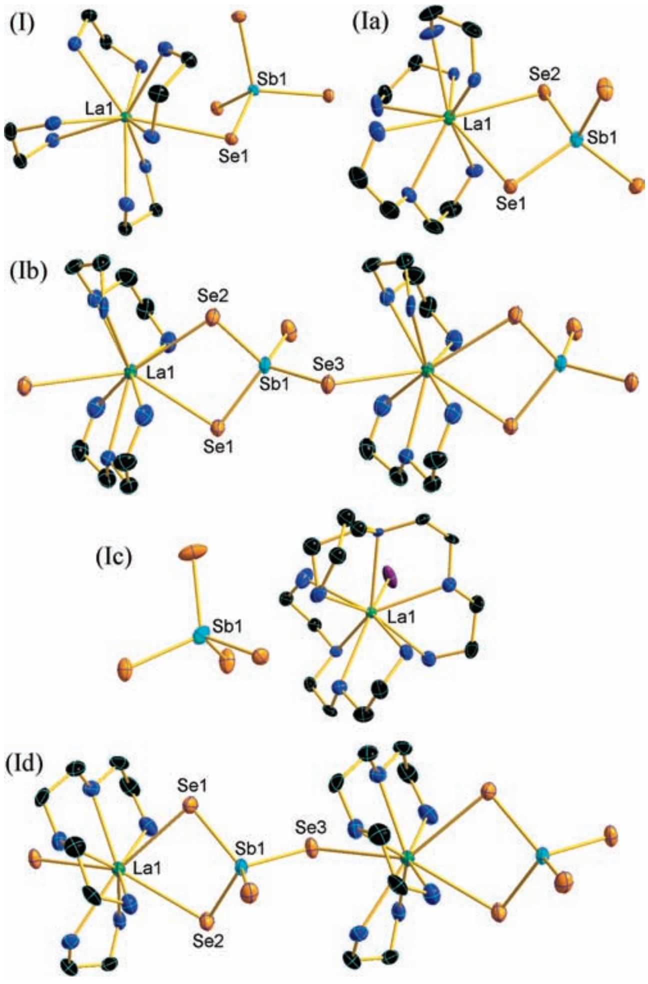

**Figure 1.** Molecular stuctures of **I** (en),[21a] **Ia** (en, dien), **Ib** (dien), **Ic** (trien), and **Id** (en, trien) with labeling (50% probability ellipsoids). The denotation of polyamine in parentheses refers to the amino ligands of the $La^{3+}$ ion in the complex. Hydrogen atoms are omitted for clarity.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **Ia**, **Ib**, **Ic**, and **Id**

| | **Ia** | **Ib** | **Ic** | **Id** |
|---|---|---|---|---|
| Sb−Se | 2.4551(9)−2.4869(9) | 2.4539(14)−2.4735(13) | 2.4566(13)−2.4663(15) | 2.4534(13)−2.4735(14) |
| La−Se | 3.1944(9), 3.1573(9) | 3.1944(13)−3.3094(12) | | 3.2190(13)−3.3260(12) |
| La−N | 2.687(7)−2.753(6) | 2.670(9)−2.714(9) | 2.674(8)−2.742(7) | 2.632(9)−2.715(9) |
| Se−Sb−Se | 102.73(3)−113.42(3) | 101.84(4)−114.11(5) | 107.92(5)−111.62(5) | 103.37(5)−112.78(5) |
| Sb−Se−La | 89.14(2), 90.31(3) | 90.19(4)−116.37(4) | | 89.30(4)−120.69(4) |
| Se−La−Se | 75.11(2) | 73.49(3)−139.87(4) | | 74.06(3)−137.70(4) |
| Se−La−N | 68.43(12)−153.80(15) | 66.15(17)−136.33(17) | | 65.7(2)−148.15(18) |
| N−La−N | 61.0(2)−143.1(2) | 62.2(3)−142.3(3) | 63.0(2)−149.6(3) | 63.3(3)−133.4(3) |

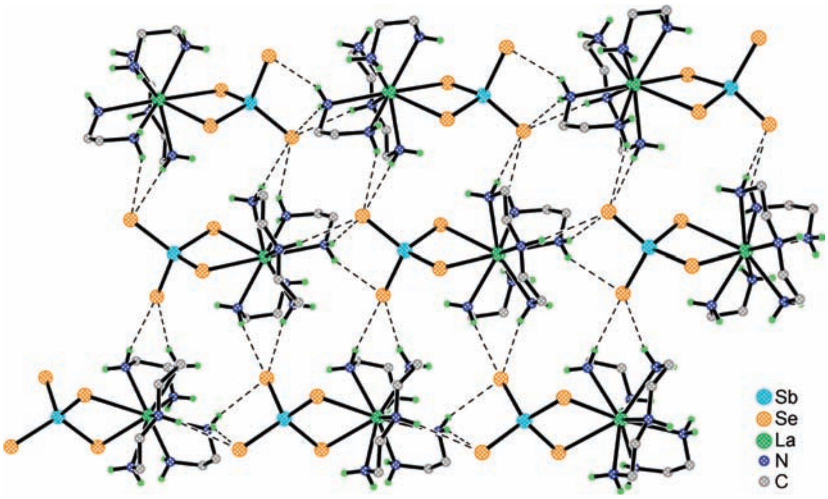

**Figure 2.** A view of the layer constructed by the $[La(en)_2(dien)(\eta^2\text{-}SbSe_4)]$ moieties via N−H···Se interactions (shown in dashed lines) in **Ia**.

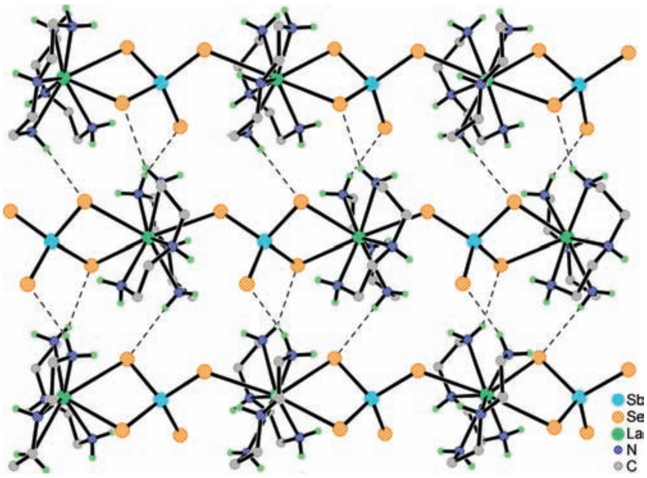

**Figure 3.** A view of the layer constructed by the $[La(dien)_2(\mu\text{-}\eta^1,\eta^2\text{-}SbSe_4)]_\infty$ chains via N−H···Se interactions (shown in dashed lines) in **Ib**.

similar to that of the chains in **Ib**. In **Ic**, all Se atoms of the $[SbSe_4]^{3-}$ anion contact $[La(trien)_2(H_2O)]^{3+}$ via N−H···Se interactions (Figure 4) with N···Se separations of 3.530(8)−3.818(8) Å and N−H···Se angles of 129.6−170.5°. The $[SbSe_4]^{3-}$ anions and $[La(trien)_2(H_2O)]^{3+}$ cations are arranged in rods parallel to the *b* axis. All molecules of **Ia**−**Id** are further connected into three-dimensional networks via the N−H···Se contacts (see Figure S4−S7 in the Supporting Information).

Summarizing the structures of **I** and **Ia**−**Id** (Figure 1), the coordination modes of the $[SbSe_4]^{3-}$ anion with the $La^{3+}$ ion are apparently controlled by the ethylene polyamines as the second ligands. With trien as the ligand to $La^{3+}$, the $[SbSe_4]^{3-}$ anion forms the ionic complex $[La(trien)_2(H_2O)]SbSe_4$ (**Ic**) in which $[SbSe_4]^{3-}$ exists as a free ion. In $[La(en)_4(SbSe_4)]$ (**I**), the $[SbSe_4]^{3-}$ anion binds to the eight-coordinated $[La(en)_4]^{3+}$ ion as a monodentate ligand to a saturated coordination number of nine for the $La^{3+}$ ion. In the presence of the mixed en/dien ligands, the $[SbSe_4]^{3-}$ ion coordinates to the seven-coordinated $[La(en)_2(dien)]^{3+}$ complex as a bidentate chelating ligand $\eta^2\text{-}SbSe_4$, leading to the neutral complex $[La(en)_2(dien)(\eta^2\text{-}SbSe_4)]$ (**Ia**). In dien and en/trien solvents, $La^{3+}$ forms the six-coordinated complexes $[La(dien)_2]^{3+}$ and $[La(en)(trien)]^{3+}$, and the $[SbSe_4]^{3-}$ anion coordinates to the six-coordinated complexes as a tridentate $\mu\text{-}\eta^1,\eta^2\text{-}SbSe_4$ bridging ligand to form the coordination polymers $[La(dien)_2(\mu\text{-}\eta^1,\eta^2\text{-}SbSe_4)]_\infty$ (**Ib**) and $[La(en)(trien)(\mu\text{-}\eta^1,\eta^2\text{-}SbSe_4)]_\infty$ (**Id**), respectively.

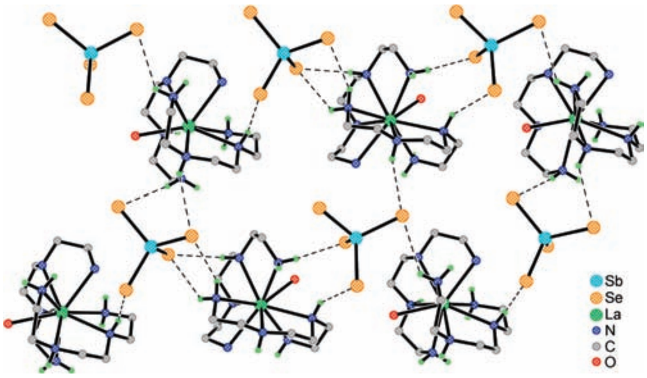

**Figure 4.** A view of the layer constructed by the $[La(trien)_2(H_2O)]^{3+}$ and $[SbSe_4]^{3-}$ ions via N−H···Se interactions (shown in dashed lines) in **Ic**.

**The Coordination of the $[SbSe_4]^{3-}$ Anion with the $Eu^{3+}$ Ion Influenced by Ethylene Polyamines.** Complex **II** is also briefly mentioned here, and its structure is depicted in Figure 5. Complex **II** consists of the $[Eu(en)_4]^{3+}$ and $[SbSe_4]^{3-}$ ions and free en molecules.[21b] $Eu^{3+}$ lies in an eight-fold coordination environment with eight N atoms of four en ligands.

The crystal structures of **IIa**−**IIc** are depicted in Figure 5. All $Eu^{3+}$ ions are in eight-fold coordination environments. In **IIa**, the $Eu^{3+}$ ion is coordinated by two en ligands and a dien ligand, giving a seven-coordinated complex, $[Eu(en)_2(dien)]^{3+}$. The $[SbSe_4]^{3-}$ ion combines with the $[Eu(en)_2(dien)]^{3+}$ ion as a monodentate ligand via the Eu−Se bond. There are two crystallographically independent $[Eu(en)_2(dien)(SbSe_4)]$ moieties in **IIa**, and the structure of $[Eu(1)(en)_2(dien)(Sb(1)Se_4)]$ is presented in Figure 5. $[Eu(1)(en)_2(dien)(Sb(1)Se_4)]$ and $[Eu(2)(en)_2(dien)(Sb(2)Se_4)]$ exhibit very similar molecular structures, except that the former possesses a smaller Eu−Se−Sb angle than the latter (Eu(1)−Se(1)−Sb(1) = 119.76(6)°, Eu(2)−Se(5)−Sb(2) = 124.31(6)°; Table 3).

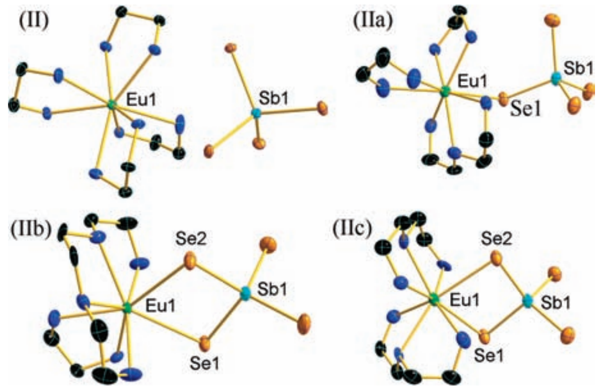

**Figure 5.** Molecular stuctures of **II** (en),[21b] **IIa** (en, dien), **IIb** (en, trien), and **IIc** (dien) with labeling (50% probability ellipsoids). The denotation of polyamine in parentheses refers to the amino ligands of the $Eu^{3+}$ ion in the complex. Hydrogen atoms are omitted for clarity.

In **IIa**, the [Eu(1)(en)$_2$(dien)(Sb(1)Se$_4$)] and [Eu(2)(en)$_2$(dien)(Sb(2)Se$_4$)] moieties stack alternatively and are connected end-to-end through the N−H···Se hydrogen bonds, forming a one-dimensional chain parallel to the *c* axis (Figure 6). The Eu−Se and Eu−N bond lengths are in the range of the literature values, respectively.[18a,20b,21b] The Sb−Se lengths and Se−Sb−Se angles are in agreement with the corresponding values in **Ia**−**Id** (Tables 2 and 3).

Like the relationship between **Ib** and **Id**, [Eu(en)(trien)($\eta^2$-SbSe$_4$)] (**IIb**) and [Eu(dien)$_2$($\eta^2$-SbSe$_4$)] (**IIc**) are also isomeric compounds with the same formula of $C_8H_{26}N_6Se_4EuSb$. But **IIb** and **IIc** crystallize in monoclinic space group $P2_1/c$ and triclinic space group $P\overline{1}$, respectively. The $Eu^{3+}$ ion is coordinated to one bidentate en and one tetradentate trien ligand in **IIb** and to two tridentate dien ligands in **IIc**, forming six-coordinated complexes [Eu(en)(trien)]$^{3+}$ and [Eu(dien)$_2$]$^{3+}$, respectively. The [SbSe$_4$]$^{3-}$ ion coordinated to the [Eu(en)(trien)]$^{3+}$ or [Eu(dien)$_2$]$^{3+}$ ion as a bidentate $\eta^2$-SbSe$_4$ chelating ligand through Se1 and Se2 atoms to give the neutral complexes **IIb** and **IIc** (Figure 5). The Sb−Se, Eu−Se, and Eu−N bond lengths of **IIb** are in agreement with the corresponding bond lengths of **IIc** (Table 3).

The structural difference between **IIb** and **IIc** caused by amine ligands is reflected by bond angles. The angles around Se(1) and Se(2) in **IIb** are 90.40(4) and 91.68(4)°, respectively, which are distinctly larger than the corresponding angles observed in **IIc** (85.96(9) and 86.39(9)°), while the Se−Eu−Se angle (77.31(4)°) in **IIb** is much smaller than the corresponding angle in **IIc** (82.19(8)°). In addition, the tetrahedral [SbSe$_4$]$^{3-}$ ion in **IIb** is more distorted, as evidenced by the Se−Sb−Se angles, which vary from 99.41(5)° to 113.43(5)° for **IIb** and from 105.07(11)° to 113.21(11)° for **IIc** (Table 3). On the other hand, the crystallographic difference between **IIb** and **IIc** is reflected by the molecular packing in the crystals. In **IIb**, the [Eu(en)(trien)($\eta^2$-SbSe$_4$)] moieties are connected end-to-end into one-dimensional chains, and the chains are further connected into a layer parallel to the (001) plane of the unit cell via N−H···Se hydrogen bonds (Figure 7). The orientations of the chains alternate in the same layer (Figure 7). But in **IIc**, the orientations of the [Eu(dien)$_2$($\eta^2$-SbSe$_4$)] moieties are in the same direction in the layer (Figure 8).

Comparing the structures of **II**, **IIa**, **IIb**, and **IIc** (Figure 5), the coordination modes of the [SbSe$_4$]$^{3-}$ anion with the $Eu^{3+}$ ion are influenced by en, dien, and trien polyamines. In **II**, the $Eu^{3+}$ ion is saturated by four en ligands, so [SbSe$_4$]$^{3-}$ exists as a discrete ion. In en/dien solvent, the [SbSe$_4$]$^{3-}$ ion coordinates to the seven-coordinated complex [Eu(en)$_2$(dien)]$^{3+}$ as a monodentate ligand to maintain a coordination number of eight for the $Eu^{3+}$ ion, forming the complex [Eu(en)$_2$(dien)(SbSe$_4$)] (**IIa**). In en/trien and dien solvents, the [SbSe$_4$]$^{3-}$ ions coordinate to the six-coordinated complexes [Eu(en)(trien)]$^{3+}$ and [Eu(dien)$_2$]$^{3+}$ as bidentate chelating ligands to form the neutral compounds [Eu(en)(trien)($\eta^2$-SbSe$_4$)] (**IIb**) and [Eu(dien)$_2$($\eta^2$-SbSe$_4$)] (**IIc**), respectively.

**The Different Effects of Ethylene Polyamines on the $La^{3+}$ and $Eu^{3+}$ Complexes.** In this work, all $La^{3+}$ ions form nine-coordinated complexes, and all $Eu^{3+}$ ions form eight-coordinated complexes. These results are in accord with the observation that the lighter lanthanide ions prefer to form nine-coordinated complexes and heavier ones prefer to form eight-coordinated complexes in solution because of the longer ionic radii of lighter lanthanide ions.[24] Consequently, the ethylene polyamine exhibits different effects on the coordination of the $La^{3+}$ and $Eu^{3+}$ ions with the [SbSe$_4$]$^{3-}$ anion. In en, the [SbSe$_4$]$^{3-}$ anion coordinates to the [La(en)$_4$]$^{3+}$ ion as a monodentate ligand in **I**, but it does not coordinate with the [Eu(en)$_4$]$^{3+}$ ion in **II**. In en/dien, because $La^{3+}$ and $Eu^{3+}$ form the same seven-coordinated complex [Ln(en)$_2$(dien)]$^{3+}$ (Ln = La, Eu), the [SbSe$_4$]$^{3-}$ ion acts as a bidentate $\eta^2$-SbSe$_4$ chelating ligand in **Ia**, and a monodentate ligand in **IIa**, to maintain the coordination numbers of nine and eight for the $La^{3+}$ and $Eu^{3+}$ ions, respectively. Comparing complexes **Ib** and **IIc**, which are synthesized in dien solvent, the [SbSe$_4$]$^{3-}$ ion coordinates to [La(dien)$_2$]$^{3+}$ in **Ib** as a $\eta^1,\eta^2$-SbSe$_4$ bridging ligand to connect the [La(dien)$_2$]$^{3+}$ ions into a polymer, but it acts as a bidentate $\eta^2$-SbSe$_4$ chelating ligand to [Eu(dien)$_2$]$^{3+}$ in **IIc**. Meanwhile, in en/trien, the [SbSe$_4$]$^{3-}$ ion shows a coordination mode of $\mu$-$\eta^1,\eta^2$-SbSe$_4$ with [La(en)(trien)]$^{3+}$ (**Id**) and $\eta^2$-SbSe$_4$ with [Eu(en)(trien)]$^{3+}$ (**IIb**) (Figures 1 and 5). It should be pointed out that the coordination modes of [SbSe$_4$]$^{3-}$ with the $La^{3+}$ and $Eu^{3+}$ lanthanide ions not only are driven by achieving coordination numbers of nine and eight around the metals, respectively, but are also related with the sterical hindrance of the ethylene polyamines. For example, according to HSAB theory, in dien, $La^{3+}$ should form complex [La(dien)$_3$]SbSe$_4$ in which the hard Lewis acidic $La^{3+}$ ion is coordinatively saturated by three hard Lewis basic dien ligands with a coordination number of nine. But actually, in dien, $La^{3+}$ forms complex [La(dien)$_2$($\mu$-SbSe$_4$)]$_\infty$ (**Ib**) in which $La^{3+}$ is six-coordinated by two dien ligands, and then [SbSe$_4$]$^{3-}$ coordinates to $La^{3+}$ as a tridentate $\mu$-$\eta^1,\eta^2$-SbSe$_4$ bridging ligand. The formation of [La(dien)$_2$($\mu$-$\eta^1,\eta^2$-SbSe$_4$)]$_\infty$ (**Ib**), other than the proposed [La(dien)$_3$]SbSe$_4$, is perhaps demanded by the strict sterical hindrance of dien and [SbSe$_4$]$^{3-}$ ligands.

**Optical Properties.** Solid state optical absorption spectra of complexes **Ia**−**IIc** were recorded from powder

---

[24] Cossy, C.; Barnes, A. C.; Enderby, J. E.; Merbach, A. E. *J. Chem. Phys.* **1989**, *90*, 3254–3259.

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for **IIa**−**IIc**

| | **IIa** | **IIb** | **IIc** |
|---|---|---|---|
| Sb−Se | 2.442(2)−2.5008(17) | 2.4295(13)−2.4754(12) | 2.446(3)−2.493(3) |
| Eu−Se | 3.0218(17), 3.0322(17) | 3.0484(14), 2.9951(12) | 3.019(3), 2.993(3) |
| Eu−N | 2.502(12)−2.589(13) | 2.559(4)−2.592(4) | 2.55(2) 2.61(2) |
| Se−Sb−Se | 103.41(6)−114.41(8) | 99.41(5)−113.43(5) | 105.07(11)−113.21(11) |
| Sb−Se−Eu | 119.76(6), 124.31(6) | 90.40(4), 91.68(4) | 85.96(9), 86.39(9) |
| Se−Eu−Se | | 77.31(4) | 82.19(8) |
| Se−Eu−N | 73.2(3)−152.5(3) | 69.31(18)−147.66(18) | 74.2(6)−152.8(5) |
| N−Eu−N | 64.6(4)−145.6(4) | 65.7(3)−159.4(3) | 64.9(7)−144.7(8) |

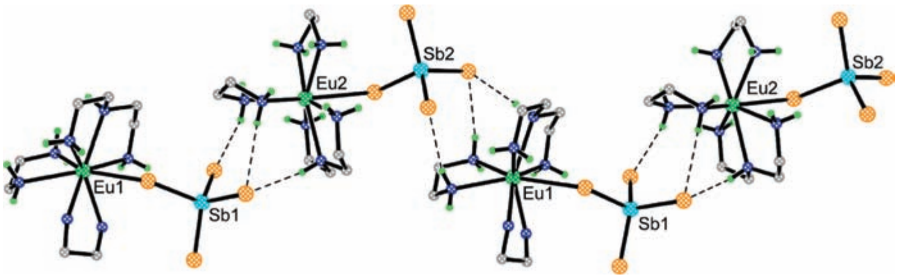

**Figure 6.** A view of the chain constructed by the [Eu(en)$_2$(dien)(SbSe$_4$)] moieties via the N−H···Se interactions (shown in dashed lines) in **IIa**.

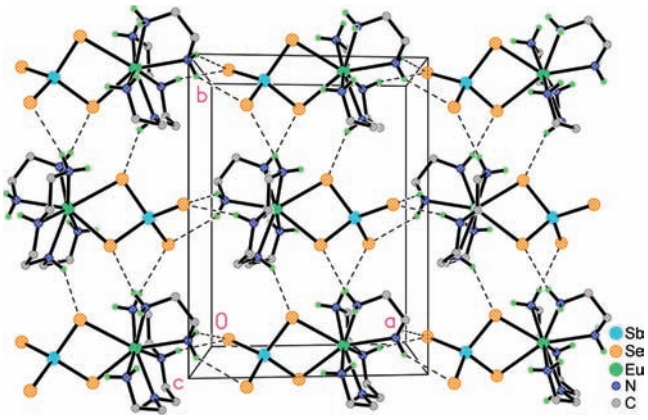

**Figure 7.** A view of the layer constructed by [Eu(en)(trien)($\eta^2$-SbSe$_4$)] moieties via N−H···Se interactions (shown in dashed lines) in complex **IIb**.

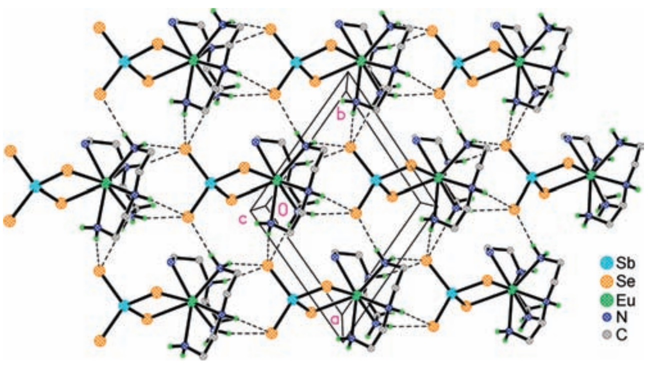

**Figure 8.** A view of the layer constructed by [Eu(dien)$_2$($\eta^2$-SbSe$_4$)] moieties via N−H···Se interactions (shown in dashed lines) in complex **IIc**.

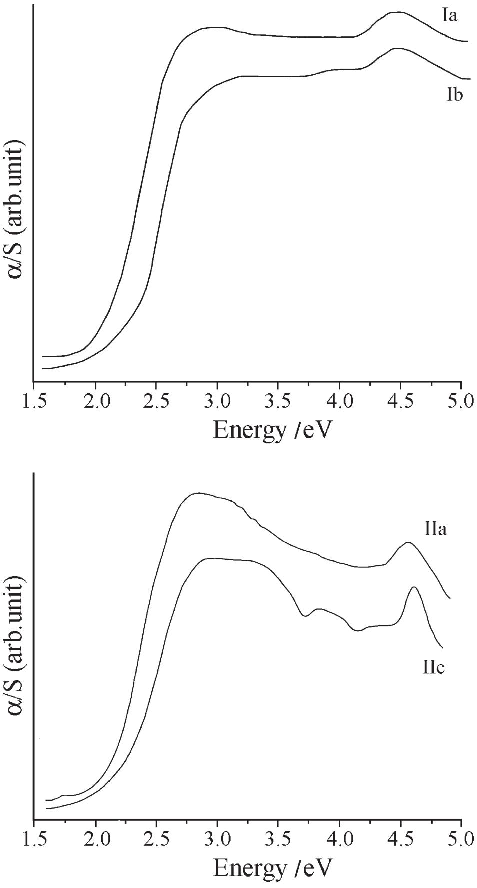

**Figure 9.** Optical absorption spectra of **Ia** and **Ib** (top) and **IIa** and **IIc** (bottom).

samples at room temperature, and the representative spectra of **Ia**, **Ib**, **IIa**, and **IIc** are shown in Figure 9. The absorption spectra of the complexes show well-defined abrupt absorption edges from which the band gaps can be estimated as 2.12 eV for **Ia**, 2.23 eV for **Ib** (Figure 9), 2.29 eV for **Ic**, 2.15 eV for **Id** (Figure S8, Supporting Information), 2.09 eV for **IIa**, 2.24 eV for **IIb** (Figure S9, Supporting Information), and 2.19 eV for **IIc** (Figure 9). The band gaps suggest that the organic hybrid complexes **Ia**−**IIc** are semiconductors. The band gaps are much larger than those of the layered copper selenidoantimonate compounds Cs$_2$Cu$_2$Sb$_2$Se$_5$

(1.2−1.3 eV),[25] $Cu_2SbSe_3\cdot0.5en$ (1.58 eV),[26] and $Cu_2SbSe_3\cdot en$ (1.61 eV).[26]

## Conclusion

The solvothermal synthetic system Ln/Sb/Se (Ln = La, Eu) has been systematically investigated in ethylene polyamines of en, dien, and trien, as well as in the mixtures of en/dien and en/trien. We have shown that the coordination of the soft basic ligand $[SbSe_4]^{3-}$ with the hard acidic $La^{3+}$ and $Eu^{3+}$ lanthanide ions can be tuned by using the different ethylene polyamines as the synthetic solvents. The $[SbSe_4]^{3-}$ anion coordinates with $La^{3+}$ as a monodentate ligand in en, a bidentate chelating ligand in en/dien, and a tridentate bridging ligand in dien or en/trien, while it binds with $Eu^{3+}$ as a monodentate ligand in en/dien and a bidentate chelating ligand in en/trien or dien. On the other hand, the $[SbSe_4]^{3-}$ anion shows different coordination modes with $La^{3+}$ and $Eu^{3+}$ in the presence of the same polyamine ligands because of the different coordination numbers of the $La^{3+}$ and $Eu^{3+}$ ions. The tunable coordination of the $[SbSe_4]^{3-}$ anion with the $La^{3+}$ and $Eu^{3+}$ ions is related with the coordination numbers of the lanthanide metals, and the sterical hindrance of the ethylene polyamine ligands as well. The systematic investigation on the structures of the series of lanthanum and europium selenidoantimonates in this work will contribute to a more complete understanding of the coordination chemistry of lanthanide metals and the designation and preparation of new lanthanide chalcogenidometalates.

**Acknowledgment.** This work was supported by the National Natural Science Foundation of P. R. China (No. 20771077) and the Key Laboratory of Organic Synthesis of Jiangsu Province, Soochow University.

**Supporting Information Available:** Additional tables and structural figures, IR spectra, thermal analyses and TG-DSC curves (PDF) and crytsal data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

---

(25) Chen, Z.; Wang, R. J.; Dilks, K. J.; Li, J. *J. Solid State Chem.* **1999**, *147*, 132–139.

(26) Chen, Z.; Dilks, R. E.; Wang, R. J.; Lu, J. Y.; Li, J. *Chem. Mater.* **1998**, *10*, 3184–3188.