Heterometallic Lanthanide−Group 14 Metal Chalcogenolates

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Heterometallic chalcogenolate compounds containing both lanthanide (Ln) and group 14 metals (M; M = Sn, Pb) form a variety of structures that can be understood in the context of relative metal−chalcogen bond strengths. The compounds $(THF)_2Eu(\mu_2\text{-}SePh)_6Pb_2$ (**1**), $[Yb(THF)_6][Sn(SePh)_3]_2$ (**2**), and $[(py)_2Eu(2\text{-}S\text{-}NC_5H_4)_2Sn(2\text{-}S\text{-}NC_5H_4)_2]_n$ (**3**) have been prepared, and their structures have been established by low-temperature single-crystal X-ray diffraction. Ln−S bonds are found to be relatively insensitive to the presence of a group 14 metal thiolate, whereas Ln−Se bonds are readily distorted upon coordination to $Pb(SePh)_2$, and cleaved by the addition of the stronger Lewis acid $Sn(SePh)_2$. The stereochemically active lone pair of electrons on the group 14 metal influences structure, as does the identity of the chalcogenolate. All three compounds show no interaction between the Ln ion and the group 14 metal lone pair. Crystal data (**1**−**3** Mo Kα; −80 to −100 °C): **1**, triclinic space group $P\bar{1}$, $a = 10.582(3)$ Å, $b = 12.114(2)$ Å, $c = 18.946(6)$ Å, $\alpha = 89.57(2)°$, $\beta = 86.11(4)°$, $\gamma = 75.87(2)°$, $V = 2350(1)$ Å^3, $Z = 2$; **2**, monoclinic space group $P2_1/c$, $a = 12.961(2)$ Å, $b = 22.768(4)$ Å, $c = 22.560(4)$ Å, $\beta = 95.04(2)°$, $V = 6632(2)$ Å^3, $Z = 4$; **3**, monoclinic space group Cc, $a = 20.737(6)$ Å, $b = 9.801(3)$ Å, $c = 18.849(5)$ Å, $\beta = 125.34(2)°$, $V = 3125(2)$ Å^3, $Z = 4$.

Introduction

Heterometallic compounds that contain lanthanide (Ln) ions have been targeted synthetically for both fundamental and applied reasons.[1−3] Fundamentally, the nature of Ln−chalcogen bonding in $Ln(ER)_x$ (E = S, Se, Te; R = organic) complexes is relatively unexplored, and heterometallic coordination complexes represent relatively uncomplicated derivatives that can contribute to our understanding of Ln−E bonding and Ln−E bond reactivity. From a more applied perspective, these molecules serve as models for understanding the photophysical properties of Ln-doped semiconductor materials.[4] Heterometallic Ln/M compounds are also potentially useful in upconversion, the absorption of low-energy radiation, and the subsequent emission of a higher energy photon in a radiative f−f transition.[5]

Heterometallic chalcogenolate compounds containing Ln and group 12 metals have recently been reported.[1] From the descriptions of bi- and tetrametallic compounds and the numerous ionic structures, an understanding of how the covalent metals influence Ln−chalcogen bonds has been emerging. The more covalent metals appear to effectively polarize chalcogenolate electron density away from the lanthanide ion, to the extent that in some compounds the Ln−chalcogen bonds no longer exist. In this paper, we extend lanthanide−main group chalcogenolate chemistry in two directions. First, the interactions between lanthanide benzeneselenolates and group 14 benzeneselenolates were studied in order to assess how the presence of a stereochemically active lone pair on the group 14 metal would influence the structure of heterometallic compounds.[6] Second, the phenyl substituent was replaced by a 2-pyridinechalcogenolate in order to determine whether this sterically undemanding bifunctional ligand would lead to a more extensive network of bridging interactions. The results of each synthetic modification are presented.

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(1) (a) Berardini, M.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 5327. (b) Brewer, M.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 5919. (c) Berardini, M.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1994**, *116*, 6941.

(2) (a) Berardini, M.; Emge, T. J.; Brennan, J. G. *J. Chem. Soc., Chem. Commun.* **1993**, 1537. (b) Khasnis, D. V.; Lee, J.; Brewer, M.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1994**, *116*, 7129.

(3) Wei, P.; Wu, D.; Zhou, Z.; Li, S.; Mak, T. *Polyhedron* **1997**, *16*, 749−763. (b) Wu, L.; Munakata, M.; Yamamoto, M.; Kuroda-Sowa, T.; Maekawa, M. *J. Coord. Chem.* **1996**, *37*, 361−369. (c) Fedushkin, I. L.; Nevodchikov, V. K.; Cherkasov, V. K.; Bochkarev, M. N.; Schumann, H.; Girgsdies, F.; Goerlitz, F. H.; Kociok-Koehn, G.; Pickardt, J. *J. Organomet. Chem.* **1996**, *511*, 157−62. (d) Hogerheide, M. P.; Ringelberg, S. N.; Grove, D. M.; Jastrzebski, J.; Boersma, J.; Smeets, W.; Spek, A.; van Koten, G. *Inorg. Chem.* **1996**, *35*, 1185−94.

(4) (a) Pomrenke, G. S.; Klein, P. B.; Langer, D. W. *Rare Earth Doped Semiconductors*; MRS Symposium 301; Materials Research Society: Pittsburgh, PA, 1993. (b) Singer, K. E.; Rutter, P.; Praker, A. R.; Wright, A. C. *Appl. Phys. Lett.* **1994**, *64*, 707−9. (c) Swiatek, K.; Godlewski, M.; Niinisto, L.; Leskela, M. *J. Appl. Phys.* **1993**, *74*, 3442−6. (d) Taniguchi, M.; Takahei, K. *J. Appl. Phys* **1993,** *73*, 943−7. (e) Jourdan, N.; Yamaguchi, H.; Harikoshi, Y. *Jpn. J. Appl. Phys.* **1993**, *32*, 1784−7. (f) Kalboussi, A.; Moneger, S.; Marrakchi, G.; Guillot, G.; Lambert, B.; Guivarc'h, A. *J. Appl. Phys.* **1994**, *75*, 4171−5. (g) Takahei, K.; Taguchi, A.; Harikoshi, Y.; Nakata, J. *J. Appl. Phys.* **1994**, *76*, 4332−9. (h) Lozykowski, H. J.; Alshawa, A. K.; Brown, I. *J. Appl. Phys.* **1994**, *76*, 4836−46. (i) Kimura, T.; Isshiki, H.; Ishida, H.; Yugo, S.; Saito, R.; Ikoma, T. *J. Appl. Phys.* **1994**, *76*, 3714−9. (j) Charreire, Y.; Marbeuf, A.; Tourillon, G.; Leskela, M.; Niinisto, L.; Nykanen, E.; Soininen, P.; Tolonen, O. *J. Electrochem. Soc.* **1992**, *139*, 619−21. (k) Charreire, Y.; Svoronos, D. R.; Ascone, I.; Tolonen, O.; Niinisto, L.; Leskela, M. *J. Electrochem. Soc.* **1993**, *140*, 2015−9.

(5) For recent references see: (a) Zou, X.; Toratani, H. *J. Non-Cryst. Solids* **1996**, *201*, 37. (b) Lupei, V.; Georgescu, S. *Opt. Eng.* **1996**, *35*, 1265. (c) Noginov, M. A.; Venkateswarlu, P.; Mahdi, M. *J. Opt. Soc. Am. B* **1996**, *13*, 735. (d) Booth, I.; Archambault, J.; Ventrudo, B. *Opt. Lett.* **1996**, *21*, 348. (e) Witte, O.; Stolz, H.; von der Osten, W. *J. Phys. D: App. Phys.* **1996**, *29*, 561. (f) de Arujo, C.; Menezes, L. S.; Aegerter, M. A. *Appl. Phys. Lett.* **1996**, *68*, 602. (g) Komukai, T.; Yamamoto, T.; Miyajima, Y. *IEEE J. Quantum Electron.* **1995**, *31*, 1880. (h) Baney, D. M.; Yang, L.; Chang, K. *Electron. Lett.* **1995**, *31*, 1842. (i) Peng, B.; Izumitani, T. *Opt. Mater.* **1995**, *4*, 701. (j) Mita, Y.; Yamamoto, H.; Shionoya, S. *J. Appl. Phys.* **1995**, *78*, 1219. (k) Kadono, K.; Higuchi, H.; Tanaka, H. *J. Non-Cryst. Solids* **1995**, *184*, 309. (l) Pan, Z.; Morgan, S. H.; Collins, W. E. *J. Appl. Phys.* **1995**, *77*, 4688. (m) Riedener, T.; Gudel, H. U.; McFarlane, R. A. *J. Lumin.* **1995**, *63*, 327. (n) Brodin, A.; Mattsson, B.; Torell, L. M. *Electrochim. Acta* **1995**, *40*, 2393

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Table 1. Summary of Crystallographic Details for **1**−**3**

	1	**2**	**3**
empirical formula	$C_{44}H_{46}EuO_2Pb_2Se_6$	$C_{60}H_{78}O_6Se_6Sn_2Yb$	$C_{30}H_{26}EuN_6S_4Sn$
fw	1646.91	1779.40	869.46
space group	$P\bar{1}$	$P2_1/c$	Cc
a (Å)	10.582(3)	12.961(2)	20.737(6)
b (Å)	12.114(2)	22.768(4)	9.801(3)
c (Å)	18.946(6)	22.560(4)	18.849(5)
α (deg)	89.57(2)	90.00(2)	90.00(2)
β (deg)	86.11(4)	95.04(2)	125.34(2)
γ (deg)	75.87(2)	90.00(2)	90.00(2)
V (Å^3)	2350(1)	6632(2)	3125(2)
Z	2	4	4
d_{calc} (g/cm^{-3})	2.328	1.782	1.848
T (°C)	−120(5)	−80(5)	−120(5)
λ (Å)	0.710 73	0.717 03	0.710 73
abs coeff (cm^{-1})	131.5	54.8	30.9
obsd reflns [$I > 2\sigma(I)$]	4653	3369	2317
$R(F)$ [$I > 2\sigma(I)$]	0.041	0.050	0.033
w$R(F^2)$ [$I > 2\sigma(I)$]	0.101	0.104	0.072

[a] Definitions: $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $wR(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. Additional crystallographic details are given in the Supporting Information.

Experimental Section

General Methods. All syntheses were carried out under ultrapure nitrogen (JWS), using conventional drybox or Schlenk techniques. Solvents (Fisher) were refluxed over molten alkali metals (diethyl ether, THF, pyridine) or P_2O_5 (CH_3CN) and collected immediately prior to use. PhSeSePh and dipyridyl disulfide (PySSPy) were purchased from either Aldrich or Strem and recrystallized prior to use. Eu, Yb, Sn, and Pb were purchased from Strem. Melting points were taken in sealed capillaries and are uncorrected. IR spectra were taken on a Mattus Cygnus 100 FTIR spectrometer and recorded from 4000 to 450 cm^{-1}, as a Nujol mull. Electronic spectra were recorded on a Varian DMS 100S spectrometer with the samples in a 0.10 mm quartz cell attached to a Teflon stopcock. Elemental analyses were performed by Quantitative Technologies, Inc. (Salem, NJ). NMR spectra were obtained on either a Varian Gemini 200 MHz or Varian 400 MHz NMR spectrometer and are reported in δ (ppm).

(THF)$_2$Eu(μ_2-SeC$_6$H$_5$)$_6$Pb$_2$ (1). Pb (0.83 g, 4 mmol), Eu (0.30 g, 2.0 mmol), Hg (55 mg, 0.27 mmol), and diphenyl diselenide (1.9 g, 6 mmol) were added to THF (20 mL) while the mixture was stirred, and a light yellow solution color developed within hours. After days, the bright orange solution was filtered and layered with hexane (50 mL) to give yellow crystals of **1** (2.1 g, 64%; mp 65−80 °C (dec, turns dark brown) that become amorphous within minutes of isolation. Anal. Calcd for $C_{44}H_{46}EuPb_2O_2Se_6$ (calcd for THF-free product in parentheses): C, 32.1 (28.8); H, 2.82 (2.01). Found: C, 30.8; H, 1.90 IR: 2922 (br), 2724 (s), 2672 (s), 2361 (s), 1947 (s), 1872 (s), 1811 (s), 1745 (s), 1568 (m), 1461 (s), 1377 (s), 1297 (s), 1260 (s), 1175 (s), 1018 (s), 1064 (s), 915 (s), 866 (s), 839 (s), 803 (s), 731 (m), 688 (s), 662 (m), 460 (m) cm^{-1}. ^{1}H NMR (20 mg in 0.50 mL of $(CD_3)_2SO$) contained resonances at 7.5, 3.71, and 1.85 ppm which were too broad ($w_{1/2}$ = 188, 78, 156 Hz) for accurate integration.

[Yb(THF)$_6$][Sn(SeC$_6$H$_5$)$_3$]$_2$ (2). Sn (0.35 g, 2.0 mmol), Yb (0.6 g, 3.9 mmol), Hg (55 mg, 0.27 mmol), and diphenyl diselenide (1.3 g, 6.0 mmol) were added to THF (20 mL). The mixture was stirred, and an orange solution color developed within hours. After 3 days, the bright orange solution was filtered and layered with hexane (50 mL) to give yellow crystals of **2** (1.5 g, 42%; mp 90 °C, dec 110 °C) that become amorphous within a few minutes of isolation. Anal. Calcd for $C_{60}H_{78}YbSn_2Se_6O_6$ (calcd for THF-free product in parentheses): C, 40.5 (32.1); H: 4.42 (2.24). Found: C, 37.4; H, 2.64. IR: 2962 (br), 2714 (s), 2591 (s), 2527 (s), 2527 (s), 2350 (s), 2250 (s), 1958 (m), 1870 (m), 1808 (m), 1735 (m), 1637 (s), 1571 (m), 1438 (s), 1366 (s), 1293 (s), 1168 (s), 1022 (s), 730 (m), 667 (m), 615 (m), 577 (m), 468 (m), 405 (m) cm^{-1}. ^{1}H NMR (20 mg in 0.50 mL of $(CD_3)_2SO$) contained resonances at 7.46 (2 H), 7.05(3 H), 3.62 (4 H), 1.74 (4 H).

[(py)$_2$Eu(μ_2-S-2-NC$_5$H$_4$)$_2$Sn(μ_2-S-2-NC$_5$H$_4$)$_2$]$_n$ (3). Sn (0.48 g, 4.0 mmol), Eu (0.30 g, 2.0 mmol), Hg (55 mg, 0.27 mmol), and dipyridyl disulfide (1.32 g, 6.0 mmol) were added to pyridine (20 mL) while the mixture was stirred, and a red solution color developed within hours. After 1 day, the brown red solution was filtered and layered with hexane (50 mL) to give yellow red crystals of **3** (0.86 g, 50%; mp > 400 °C) that desolvate within hours of isolation. Anal. Calcd for $C_{30}H_{26}EuSnN_6S_4$: C, 41.4; H: 3.48; N, 9.66. Found: C, 41.6; H, 3.69; N, 10.1. IR: 3049 (s), 3025 (s), 1515 (m), 1396 (s), 1313 (s), 1232 (s), 1169 (s), 1104 (s), 1042 (s), 990 (s), 875 (s), 744 (s), 633 (s), 489 (s), 430 (s) cm^{-1}. ^{1}H NMR (20 mg in 0.50 mL of $(CD_3)_2SO$) contained a broad set of overlapping resonances centered at 8.57 (4 H), 7.73 (2 H), 7.37 (4 H), and 7.18 (1 H) ppm. UV: λ_{max} (ca. 1 mg/mL of py) = 418 nm.

X-ray Structure Determination of 1−3. Data for **1**−**3** were collected on a CAD4 diffractometer with graphite-monochromatized Mo Kα radiation, λ = 0.710 73 Å, at low temperatures (153−193 K). In all structures, 3 check reflections were measured every 2 h and showed no significant intensity variation. The data were corrected for Lorenz effects and polarization. The absorption corrections were based on a Gaussian grid method (SHELX76).[7] The structures were solved by Patterson methods (SHELXS86).[8] All non-hydrogen atoms were refined (SHELXL93)[9] based upon F_o^2. All hydrogen atom coordinates were calculated with idealized geometries (SHELXL93). Crystallographic data and final R indices are given in Table 1. Complete crystallographic details are given in the Supporting Information.

Results

Heterometallic compounds containing lanthanide ions and the group 14 metals can be prepared in a single step by the direct reduction of chalcogen−chalcogen bonds with Ln(0) and M(0) and a trace amount of mercury which increases the rate of the reaction. Three compounds, (THF)$_2$Eu(μ_2-SePh)$_6$Pb$_2$ (**1**), [Yb(THF)$_6$][Sn(SePh)$_3$]$_2$ (**2**), and [(py)$_2$Eu(2-S-NC$_5$H$_4$)$_2$Pb(2-S-NC$_5$H$_4$)$_2$]$_n$ (**3**), were isolated and characterized by NMR, IR, and UV−visible spectroscopies and by low-temperature single-crystal X-ray diffraction experiments.

Reduction of PhSeSePh with a Eu/Pb mixture leads to the formation of yellow, trimetallic (THF)$_2$Eu(μ_2-SePh)$_6$Pb$_2$ (**1**).

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(6) (a) Teff, D.; Huffman, J.; Caulton, K. *Inorg. Chem.***1996**, *35*, 2981. (b) Caulton, K.; Teff, D.; Huffman, J. *Inorg. Chem.* **1995**, *34*, 2491. (c) Papiernik, R.; Hubert-Pfalzgraf, L.; Daran, J. *J. Chem. Soc., Chem. Commun.* **1990**, 695. (d) Seligson, A. L.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 8214. (e) Cheng, Y.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1996**, *35*, 342. (f) Hitchcock, P. B.; Lappert, M. F.; Samways, B. J.; Weinberg, E. L. *J. Chem. Soc., Chem. Commun.* **1983**, 1492.

(7) Sheldrick, G. M. SHELX76, Program for Crystal Structure Determination, Univ. of Cambridge, England, 1976.

(8) Sheldrick, G. M. SHELXS86, Program for the Solution of Crystal Structures, University of Gottingen, Germany, 1986.

(9) Sheldrick, G. M. SHELXL93, Program for Crystal Structure Refinement, University of Gottingen, Germany, 1993.

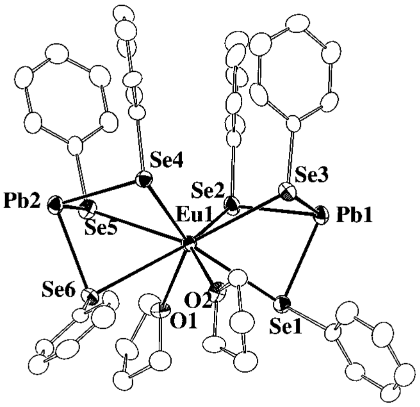

Figure 1. Molecular structure of $(THF)_2Eu(\mu_2\text{-}SePh)_6Pb_2$ (**1**).

Table 2. Significant Bond Lengths (Å) and Angles (deg) for **1**[a]

Pb(1)−Se(1)	2.741(1)	Pb(1)−Se(3)	2.791(2)
Pb(1)−Se(2)	2.800(2)	Pb(2)−Se(6)	2.749(1)
Pb(2)−Se(5)	2.773(2)	Pb(2)−Se(4)	2.821(2)
Eu(1)−O(2)	2.561(7)	Eu(1)−O(1)	2.621(8)
Eu(1)−Se(4)	3.191(2)	Eu(1)−Se(2)	3.265(2)
Eu(1)−Se(3)	3.267(2)	Eu(1)−Se(5)	3.320(2)
Eu(1)−Se(6)	3.328(2)	Eu(1)−Se(1)	3.351(2)
Se(1)−C(1)	1.946(12)	Se(2)−C(7)	1.923(11)
Se(3)−C(13)	1.915(11)	Se(4)−C(19)	1.921(11)
Se(5)−C(25)	1.912(11)	Se(6)−C(31)	1.929(11)
Pb(2)−Eu(1)	4.084(2)		

Se(1)−Pb(1)−Se(3)	88.08(4)	Se(1)−Pb(1)−Se(2)	77.89(4)
Se(3)−Pb(1)−Se(2)	95.13(5)	Se(6)−Pb(2)−Se(5)	78.32(4)
Se(6)−Pb(2)−Se(4)	86.98(4)	Se(5)−Pb(2)−Se(4)	95.36(5)
Se(6)−Pb(2)−Eu(1)	54.11(3)	Se(5)−Pb(2)−Eu(1)	53.89(4)
Se(4)−Pb(2)−Eu(1)	51.15(4)	O(2)−Eu(1)−O(1)	102.4(2)
O(2)−Eu(1)−Se(4)	81.5(2)	O(1)−Eu(1)−Se(4)	138.1(2)
O(2)−Eu(1)−Se(2)	138.1(2)	O(1)−Eu(1)−Se(2)	77.9(2)
Se(4)−Eu(1)−Se(2)	126.23(4)	O(2)−Eu(1)−Se(3)	75.1(2)
O(1)−Eu(1)−Se(3)	139.3(2)	Se(4)−Eu(1)−Se(3)	82.40(4)
Se(2)−Eu(1)−Se(3)	78.35(4)	O(2)−Eu(1)−Se(5)	139.0(2)
O(1)−Eu(1)−Se(5)	71.2(2)	Se(4)−Eu(1)−Se(5)	78.85(4)
Se(2)−Eu(1)−Se(5)	81.52(4)	Se(3)−Eu(1)−Se(5)	136.18(4)
O(2)−Eu(1)−Se(6)	76.6(2)	O(1)−Eu(1)−Se(6)	68.6(2)
Se(4)−Eu(1)−Se(6)	72.00(4)	Se(2)−Eu(1)−Se(6)	137.25(4)
Se(3)−Eu(1)−Se(6)	144.11(4)	Se(5)−Eu(1)−Se(6)	63.27(4)
O(2)−Eu(1)−Se(1)	77.4(2)	O(1)−Eu(1)−Se(1)	68.8(2)
Se(4)−Eu(1)−Se(1)	149.48(4)	Se(2)−Eu(1)−Se(1)	63.53(4)
Se(3)−Eu(1)−Se(1)	71.05(4)	Se(5)−Eu(1)−Se(1)	131.04(4)
Se(6)−Eu(1)−Se(1)	122.95(4)	O(2)−Eu(1)−Pb(2)	101.1(2)
O(1)−Eu(1)−Pb(2)	95.8(2)	Se(4)−Eu(1)−Pb(2)	43.50(3)
Se(2)−Eu(1)−Pb(2)	120.67(4)	Se(3)−Eu(1)−Pb(2)	124.85(4)
Se(5)−Eu(1)−Pb(2)	42.44(3)	Se(6)−Eu(1)−Pb(2)	42.00(3)
Se(1)−Eu(1)−Pb(2)	163.45(3)	C(1)−Se(1)−Pb(1)	98.4(3)
C(1)−Se(1)−Eu(1)	125.3(3)	Pb(1)−Se(1)−Eu(1)	83.99(4)
C(7)−Se(2)−Pb(1)	99.7(4)	C(7)−Se(2)−Eu(1)	121.2(4)
Pb(1)−Se(2)−Eu(1)	84.71(4)	C(13)−Se(3)−Pb(1)	98.5(4)
C(13)−Se(3)−Eu(1)	119.9(3)	Pb(1)−Se(3)−Eu(1)	84.83(4)
C(19)−Se(4)−Pb(2)	94.6(4)	C(19)−Se(4)−Eu(1)	116.5(4)
Pb(2)−Se(4)−Eu(1)	85.35(4)	C(25)−Se(5)−Pb(2)	101.4(4)
C(25)−Se(5)−Eu(1)	124.2(4)	Pb(2)−Se(5)−Eu(1)	83.67(4)
C(31)−Se(6)−Pb(2)	99.2(3)	C(31)−Se(6)−Eu(1)	123.0(3)
Pb(2)−Se(6)−Eu(1)	83.89(4)		

Figure 1 shows an ORTEP diagram for **1**, and Table 2 gives a listing of selected bond lengths and angles for **1**. The compound contains a central Eu(II) ion coordinated to two neutral THF donors and bridged to a pair of Pb(II) ions through sets of three doubly bridging benzeneselenolates. This compound is the only product isolated in a crystalline form when starting with either a 1:1 or a 1:2 Eu:Pb ratio (eq 1).

$$\mathrm{Eu + Pb + 2PhSeSePh} \rightarrow (\mathrm{THF})_2\mathrm{EuPb_2(SePh)_6} \leftarrow \mathrm{Eu + 2Pb + 3PhSeSePh} \quad (1)$$

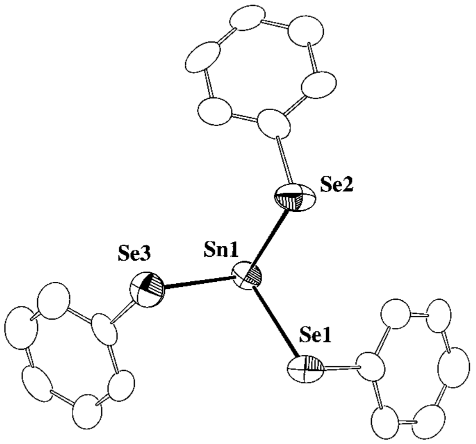

Figure 2. Molecular structure of the pyramidal anions in $[Yb(THF)_6][Sn(SePh)_3]_2$ (**2**).

Table 3. Significant Bond Lengths (Å) and Angles (deg) for **2**[a]

Yb(1)−O(2)	2.354(11)	Yb(2)−O(4)	2.353(10)
Yb(1)−O(3)	2.363(10)	Yb(2)−O(5)	2.365(11)
Yb(1)−O(1)	2.402(11)	Yb(2)−O(6)	2.385(12)
Sn(1)−Se(3)	2.630(2)	Sn(2)−Se(4)	2.651(2)
Sn(1)−Se(2)	2.646(2)	Sn(2)−Se(5)	2.686(3)
Sn(1)−Se(1)	2.668(3)	Sn(2)−Se(6)	2.644(3)
Se(1)−C(25)	1.93(2)	Se(4)−C(43)	1.90(2)
Se(2)−C(31)	1.92(2)	Se(5)−C(49)	1.89(2)
Se(3)−C(37)	1.92(2)	Se(6)−C(55)	1.94(2)

O(2)−Yb(1)−O(3)	92.9(4)	O(2)′−Yb(1)−O(3)	87.1(4)
O(2)−Yb(1)−O(3)′	87.1(4)	O(2)′−Yb(1)−O(3)′	92.9(4)
O(2)−Yb(1)−O(1)	90.1(4)	O(2)′−Yb(1)−O(1)	89.9(4)
O(3)−Yb(1)−O(1)	90.3(4)	O(3)′−Yb(1)−O(1)	89.7(4)
O(2)−Yb(1)−O(1)′	89.9(4)	O(2)′−Yb(1)−O(1)′	90.1(4)
O(3)−Yb(1)−O(1)′	89.7(4)	O(3)′−Yb(1)−O(1)′	90.3(4)
O(4)″−Yb(2)−O(5)″	87.0(4)	O(4)−Yb(2)−O(5)″	93.0(4)
O(4)″−Yb(2)−O(5)	93.0(4)	O(4)−Yb(2)−O(5)	87.0(4)
O(4)″−Yb(2)−O(6)″	88.6(4)	O(5)−Yb(2)−O(6)	90.9(4)
O(4)−Yb(2)−O(6)″	91.4(4)	O(5)″−Yb(2)−O(6)″	90.9(4)
O(5)−Yb(2)−O(6)″	89.1(4)	O(4)″−Yb(2)−O(6)	91.4(4)
O(4)−Yb(2)−O(6)	88.6(4)	O(5)″−Yb(2)−O(6)	89.1(4)
Se(3)−Sn(1)−Se(2)	93.64(8)	Se(3)−Sn(1)−Se(1)	95.47(8)
Se(2)−Sn(1)−Se(1)	92.03(7)	C(25)−Se(1)−Sn(1)	93.7(6)
C(31)−Se(2)−Sn(1)	97.2(5)	C(37)−Se(3)−Sn(1)	93.8(5)
Se(6)−Sn(2)−Se(4)	92.24(8)	Se(6)−Sn(2)−Se(5)	101.08(8)
Se(4)−Sn(2)−Se(5)	96.54(8)	C(43)−Se(4)−Sn(2)	89.9(5)
C(49)−Se(5)−Sn(2)	95.8(6)	C(55)−Se(6)−Sn(2)	92.7(6)

[a] Symmetry transformations used to generate equivalent atoms: ′, $-x-1, -y, -z-1$; ″, $-x, -y, -z$.

The analogous Eu−Sn compound was prepared in a similar fashion but the crystalline product becomes amorphous within minutes of isolation, and so structural characterization was not possible. Synthesis of the related Yb(II) derivative was then attempted, and again only a compound with a 1:2 Yb:Sn ratio could be isolated, regardless of the starting Yb:Sn ratio. This bright orange crystalline compound was also extremely sensitive to desolvation but was stable enough to collect low-temperature single-crystal X-ray diffraction data. The product was identified as $[Yb(THF)_6][Sn(SePh)_3]_2$ (**2**), a heterometallic cation anion pair (see Figure 2). The Yb ion has a well-defined octahedral coordination sphere composed of oxygen atoms from the THF ligands (see Table 3), and the $Sn(SePh)_3$ anions adopt the expected pyramidal geometry with a stereochemically active lone pair on the Sn ion (eq 2)

$$\mathrm{Yb + Sn + 2PhSeSePh} \rightarrow [\mathrm{Yb(THF)_6}][\mathrm{Sn(SePh)_3}]_2 \leftarrow \mathrm{Yb + 2Sn + 3PhSeSePh} \quad (2)$$

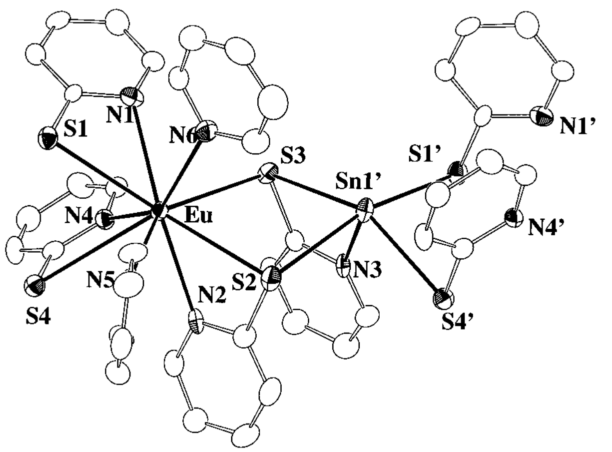

Figure 3. Molecular structure of the repeating unit in polymeric $[(py)_2Eu(2\text{-}S\text{-}NC_5H_4)_2Pb(2\text{-}S\text{-}NC_5H_4)_2]_n$ (**3**).

Table 4. Significant Bond Lengths (Å) and Angles (deg) for **3**[a]

Eu−N(2)	2.679(10)	Eu−N(1)	2.728(10)
Eu−N(5)	2.739(10)	Eu−N(4)	2.756(9)
Eu−N(6)	2.898(11)	Eu−S(1)	3.080(4)
Eu−S(2)	3.110(4)	Eu−S(3)	3.161(3)
Eu−S(4)	3.367(3)	Sn−N(3)′	2.253(9)
Sn−S(4)	2.735(3)	Sn−S(1)	2.795(4)
Sn−S(2)′	2.814(4)	Sn−S(3)′	2.930(3)
S(1)−C(1)	1.729(13)	S(2)−C(6)	1.793(12)
S(2)−Sn″	2.814(4)	S(3)−C(11)	1.737(11)
S(3)−Sn″	2.930(3)	S(4)−C(16)	1.752(13)

N(2)−Eu−N(1)	145.9(3)	N(2)−Eu−N(5)	77.7(3)
N(1)−Eu−N(5)	134.4(3)	N(2)−Eu−N(4)	80.2(3)
N(1)−Eu−N(4)	71.7(3)	N(5)−Eu−N(4)	124.2(3)
N(2)−Eu−N(6)	129.8(3)	N(1)−Eu−N(6)	74.4(3)
N(5)−Eu−N(6)	82.9(3)	N(4)−Eu−N(6)	145.9(3)
N(2)−Eu−S(1)	143.1(2)	N(1)−Eu−S(1)	53.7(2)
N(5)−Eu−S(1)	83.4(2)	N(4)−Eu−S(1)	84.8(2)
N(6)−Eu−S(1)	77.7(2)	N(2)−Eu−S(2)	54.1(2)
N(1)−Eu−S(2)	137.4(2)	N(5)−Eu−S(2)	69.6(2)
N(4)−Eu−S(2)	129.8(2)	N(6)−Eu−S(2)	75.8(2)
S(1)−Eu−S(2)	144.05(8)	N(2)−Eu−S(3)	81.2(2)
N(1)−Eu−S(3)	75.5(2)	N(5)−Eu−S(3)	143.6(2)
N(4)−Eu−S(3)	80.2(2)	N(6)−Eu−S(3)	88.4(2)
S(1)−Eu−S(3)	129.12(9)	S(2)−Eu−S(3)	73.99(9)
N(2)−Eu−S(4)	74.4(2)	N(1)−Eu−S(4)	100.6(2)
N(5)−Eu−S(4)	74.3(2)	N(4)−Eu−S(4)	50.5(2)
N(6)−Eu−S(4)	142.1(2)	S(1)−Eu−S(4)	70.01(9)
S(2)−Eu−S(4)	121.45(9)	S(3)−Eu−S(4)	127.46(9)
N(3)′ −Sn−S(4)	87.3(2)	N(3)′ −Sn−S(1)	79.7(2)
S(4)−Sn−S(1)	84.12(10)	N(3)′ −Sn−S(2)′	83.1(2)
S(4)−Sn−S(2)′	88.79(10)	S(1)−Sn−S(2)′	161.70(12)
N(3)′ −Sn−S(3)′	59.7(2)	S(4)−Sn−S(3)′	146.51(9)
S(1)−Sn−S(3)′	94.56(10)	S(2)′ −Sn−S(3)′	82.12(10)
C(1)−S(1)−Sn	95.2(4)	C(1)−S(1)−Eu	80.8(4)
Sn−S(1)−Eu	103.46(10)	C(6)−S(2)−Sn″	112.1(4)
C(6)−S(2)−Eu	82.1(5)	Sn″ −S(2)−Eu	100.74(11)
C(11)−S(3)−Sn″	75.0(4)	C(11)−S(3)−Eu	104.7(4)
Sn″ −S(3)−Eu	97.04(9)	C(16)−S(4)−Sn	83.4(4)
C(16)−S(4)−Eu	79.0(4)	Sn−S(4)−Eu	97.77(9)

[a] Symmetry transformations used to generate equivalent atoms: ′, $x + {}^1/_2$, $-y + {}^1/_2$, $z + {}^1/_2$; ″, $x - {}^1/_2$, $-y + {}^1/_2$, $z - {}^1/_2$.

Substitution of the benzeneselenolate ligand with a 2-pyridinethiolate group yielded a heterometallic Ln/main group chalcogenolate polymer. Reduction of dipyridyl disulfide with Eu/Sn/Hg, followed by crystallization from pyridine, gives polymeric $[(py)_2Eu(2\text{-}S\text{-}NC_5H_4)_2Sn(2\text{-}S\text{-}NC_5H_4)_2]_n$ (**3**) in high yield. The structure of **3** contains an alternating series of Eu(II) and Sn(II) ions bridged by pairs of sulfur atoms in a linear array, as in Figure 3. The Sn ions have a distorted octahedral coordination sphere composed of four sulfur donors, one nitrogen donor, and a stereochemically active lone pair of electrons trans to the nitrogen (see Table 4). The Eu(II) ions are nine coordinate, with two neutral pyridine donors, three pyridinethiolate nitrogen atoms, and four sulfur atoms comprising the primary coordination sphere. In the structure, the Eu−S distances range from 3.080(3) to 3.365(3) Å and are consistent with the reported Eu−S distances in the divalent europium pyridinethiolates $(bipyridine)(THF)_2Eu(2\text{-}S\text{-}NC_5H_4)_2$ and $(py)_4Eu(2\text{-}S\text{-}NC_5H_4)_2$.[10] The Sn−S distances in **3** (2.735(3)−2.930(3) Å) are also within the range expected for a Sn(II)−S bond. In contrast to the synthesis of **1** and **2**, polymer **3** is isolated as a crystalline product only when starting with a 1:2 Eu:Sn ratio. Attempts to increase the yield of **3** by using a 1:1 Eu:Sn starting ratio did not result in the precipitation of any crystalline product (eq 3).

$$\mathrm{Eu} + \mathrm{Sn} + 2\mathrm{PySSPy} \nrightarrow \\ [(py)_2Eu(SPy)_2Sn(SPy)_2]_n \leftarrow \mathrm{Eu} + 2\mathrm{Sn} + 3\mathrm{PySSPy} \quad (3)$$

Discussion

The structures of **1**−**3** clearly illustrate how both the identity of the softer, more covalent metal ion and the identity of the chalcogenolate substituent can influence heterometallic structure. The differences in structures can be understood by considering the relative metal−chalcogen bond strengths, and we can use diatomic metal chalcogen bond strengths (in kcal/mol: SmS (93),[11] SmSe (79.1 ± 3.5),[12] SnS (111.0 ± 0.8),[13] SnSe (95.9 ± 1.4),[14] PbS (82.7 ± 0.4),[15] and PbSe (72.4 ± 1.0))[15] as a guide for understanding the structures observed in this work. From the diatomic bond strength measurements it is clear, first, that metal−sulfide bonds are stronger than the corresponding metal−selenide bonds and, second, that Sn−chalcogen bonds are stronger than Sm−chalcogen bonds. There is no reason to expect these trends to be any different in molecular chemistry.

Compound **2** crystallizes as a complex cation/anion pair because the more covalent metal essentially polarizes electron density away from the chalcogen[1] to the extent that Ln−neutral donor interactions are preferred. In related group 12 metal chemistry, the same absence of Ln−Se bonds was noted in $[Yb(THF)_6][Hg_5(SePh)_{12}]$ and $[Sm(THF)_7][Zn_4(SePh)_{10}]$.[1a] However, because the group 12 metals need to fill two additional coordination sites, chalcogenolate cleavage tended to result only when there was an excess of $M(EPh)_2$ present, so that complex $M_x(EPh)_{2x+2}$ dianions formed [$M(ER)_3^-$ complexes are known[16] but are scarcer than anions with tetrahedral geometries]. In the absence of excess group 12 $M(EPh)_2$, neutral molecules such as $(THF)_4Eu(\mu\text{-}SePh)_3ZnSePh$ and $(THF)_3EuHg(SePh)_4$ were isolated. With the group 14 metals, the formal $SePh^-$ abstraction from Ln by $M(SePh)_2$ results in the formation of electronically saturated $M(SePh)_3$ anions that do not coordinate additional chalcogenolates.

Missing from the structure of **1** is any direct interaction between the Yb(II) ion and the stereochemically active lone pair of electrons on the Sn(II) ion. Compounds with direct Ln−Sn bonds are known,[17] but the preparation of such a molecule requires the absence of strong donor solvents that would compete effectively for a Ln coordination site.

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(10) Berardini, M.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 6179.
(11) Fenochka, B. V.; Gorkienko, S. P. *Zh. Fiz. Khim.* **1973**, *47*, 2445
(12) Nagai, S.; Shinmei, M.; Yokokawa, T. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1904.
(13) Drowart, J.; Goldfinger, P. *Q. Rev. (London)* **1966**, *20*, 545.
(14) Collin, R.; Drowart, J. *Trans. Faraday Soc.* **1964**, *60*, 673.
(15) Uy, O. M.; Drowart, J. *Trans. Faraday. Soc.* **1969**, *65*, 3221.
(16) Christou, G.; Folting, K.; Huffman, J. C. *Polyhedron* **1984**, *3*, 1247.
(17) Cloke, F. G. N.; Dalby, C.; Hitchcock, P. B. *J. Chem. Soc., Chem. Commun.* **1991**, 779.

Trimetallic **1** crystallizes as a neutral molecule because Pb−Se bonds are weaker than the Sn−Se bonds and so cleavage of the Ln−Se bond is thermodynamically less favorable. In the structure both Pb ions are linked to the Eu ion through a set of three bridging selenolates, similar to the bridging in $(THF)_4Eu(SePh)_3ZnSePh$,[1a] although the range in M−Se bond lengths is not as large. The Pb lone pair in **1** replaces the terminal selenolate of the Zn complex and is not oriented toward any neighboring Eu(II) ions. A similar triple bridge between hard and soft metals is found in heterometallic alkaline earth/Pb alkoxides,[18] although in these compounds it is presumably the harder metal ions that stabilize the alkoxides bound to the softer Pb(II) ion, rather than the softer metal stabilizing the alkoxides coordinated to the alkaline earth ions.

The 1:2 Ln:M ratios found in **1** and **2** represent a significant deviation from earlier Ln/group 12 metal chalcogenolate chemistry, in which 1:1 Ln/M complexes invariably formed in the absence of additional $M(EPh)_2$. This change in Ln:M ratio is due to the stereochemically active lone pair on the group 14 metal. In the Ln/group 12 metal complexes, there were two vacant coordination sites available on the less electropositive metals, and $Ln(ER)_x$ essentially acted as a chelating ligand toward the group 12 ion. With only a single two electron donor needed to complete an octet at the group 14 metal center, heterometallic compounds with a 2:1 M:Ln ratio are produced, with each covalent metal stabilizing only one of the Ln chalcogenolate ligands. Attempts to extend this chemistry to include Ln(III) ions with a 1:3 Ln:M ratio were unsuccessful with metals as large as Sm. The only deviation from this general 1:2 Ln(II):M formula was observed when the phenyl group was substituted by pyridinethiolate (SPy), a ligand system that tends to produce $M(ER)_x$ compounds with unusually high coordination numbers.

Compound **3** is the first lanthanide/main group chalcogenolate complex to crystallize as a polymer. In SPy coordination chemistry, the combination of both strong hard and soft donors, as well as the minimal steric requirements, generally leads to the formation of $M(SPy)_x$ complexes with large coordination numbers. For example, in lanthanide chemistry, the eight-coordinate $Eu(SPy)_4$ anion[10] has the highest coordination number of all reported lanthanide chalcogenolates.[19] Examples in main group chemistry include $Cd(EPy)_2$ (E = S,[20] Se[21]), which crystallize as distorted octahedral polymers, rather than adopt the tetrahedral geometry so characteristic of group 12 metal chalcogenolate structures, or $Pb_3(2\text{-}SC_5H_3NSiMe_3)_6$,[22] which contains an eight-coordinate Pb(II) ion.

Polymer **3** contains a nine-coordinate Eu(II) ion (4S, 5N) and a square pyramidal Sn(II) ion with four S atoms forming the base of the pyramid and a stereochemically active lone pair trans to a single apical SPy nitrogen. The Sn geometry is related to the coordination environment in homoleptic $Sn(SePy)_2$, which can be viewed as a dimer with weak Sn−Se interactions between neighboring dimeric units. The range of Sn−Se bond lengths in the selenolate dimer is considerably broader than the Sn−S bond lengths in **3**. Unlike **2**, compound **3** retains the Ln−chalcogen bonds in the presence of Sn(II) because the Ln−S bonds are considerably stronger than Ln−Se bonds and so are not as readily replaced by neutral donors.

The solution structure of **3** does not necessarily resemble the solid-state structure, but a precise solution structure is unobtainable because only a single set of averaged chalcogenolate resonances are observed in the ^{1}HNMR spectrum. Still, some form of heterometallic structure is maintained in pyridine solution, since the UV−visible spectrum of **3** is completely different from the spectrum of $Eu(SPy)_2$ in pyridine.[10] It is also important to note here that while both **1** and **2** are fractionally crystallized with either a 1:1 or 1:2 Ln:M starting ratio, **3** can be isolated routinely only when a 1:2 Eu:Sn starting ratio is present. A 1:1 Eu/Sn reduction of PySSPy gives small amounts of light yellow powder as the only isolable product. In the successful synthesis of **3**, the second equivalent of $Sn(SPy)_2$ presumably serves to solubilize a heterometallic product or form solution structures similar to **2**, and from these solutions **3** can be isolated by fractional crystallization.

Conclusion

Lanthanide chalcogenolates react with group 14 metal chalcogenolates to form heterometallic molecules or polymers. In both Sn and Pb chemistry, there is a stereochemically active lone pair that does not coordinate to the Ln ion. Complex structures depend significantly on the relative strength of the metal−chalcogen bonds, with Ln−Se bond cleavage occurs in the reaction of $Sn(SePh)_2$ with $Yb(SePh)_2$. If Pb is substituted for Sn, the weaker bonds between the main group element and the chalcogen lead to the formation of a neutral molecular product, rather than a solvated Ln(II) ion.

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Supporting Information Available: For **1**−**3**, tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles and ORTEP diagrams (33 pages). Ordering information is given on any current masthead page.

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(18) Veith, M. *Chem. Rev.* **1990**, *90*, 3.

(19) Strzelecki, A. R.; Timinski, P. A..; Hesel, B. A.; Bianconi, P. A. *J. Am. Chem. Soc.* **1992**, *114*, 3159−3160. (b) Cary, D. R.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 2520−2521. (c) Berardini, M.; Emge, T.; Brennan, J. G. *J. Chem. Soc., Chem. Commun.* **1993**, 1537−8. (d) Berardini, M.; Emge, T.; Brennan, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 8501−2. (e) Khasnis, D. V.; Lee, J.; Brewer, M.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1994**, *116*, 7129−33. (f) Brewer, M.; Khasnis, D.; Buretea, M.; Berardini, M.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1994**, *33*, 2743−7. (g) Carey, D. R.; Arnold, J. *Inorg. Chem.* **1994**, *33*, 1791. (h) Mashima, K.; Nakayama, Y.; Kanehisa, N.; Kai, Y.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1847−8. (i) Strzelecki, A. R.; Likar, C.; Hesel, B. A.; Utz, T.; Lin, M. C.; Bianconi, P. A. *Inorg. Chem.* **1994**, *33*, 5188. (j) Mashima, K.; Nakayama, Y.; Fukumoto, H.; Kanehisa, N.; Kai, Y.; Nakamura, A. *J. Chem. Soc. Chem. Commun.* **1994**, 2523−4. (k) Tatsumi, K.; Amemiya, T.; Kawaguchi, H.; Tani, K. *J. Chem. Soc., Chem. Commun.* **1993**, 773−4. (l) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Smith, R. G. *J. Chem. Soc., Chem. Commun.* **1992**, 932−3. (m) Lee, J.; Brewer, M.; Berardini, M.; Brennan, J. *Inorg. Chem.* **1995**, *34*, 3215. (n) Cary, D.; Ball, G.; Arnold, J. *J. Am. Chem. Soc.* **1995**, *117*, 3492. (o) Mashima, K.; Nakayama, Y.; Shibahara, T.; Fukumoto, H.; Nakamura, A. *Inorg. Chem.* **1996**, *35*, 93.

(20) Hursthouse, M. B.; Khan, O.; Mazid, M.; Motevalli, M.; O'Brian, P. *Polyhedron* **1990**, *9*, 541.

(21) Cheng, Y.; Emge, T.; Brennan, J. *Inorg. Chem.* **1994**, *34*, 3711.

(22) Block, E.; Ofori-Okai, G.; Kang, H.; Wu, J.; Zubieta, J. *Inorg. Chim. Acta* **1991**, *190*, 5.