Octanuclear Lanthanide Sulfido Clusters: Synthesis, Structure, and Coordination Chemistry

Jonathan H. Melman, Thomas J. Emge, and J. G. Brennan*

Department of Chemistry, Rutgers, the State University of New Jersey, 610 Taylor Road,
Piscataway, New Jersey 08854-8087

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Octanuclear $(THF)_8Ln_8S_6(SPh)_{12}\cdot x$THF clusters (Ln = lanthanide ion) can be isolated from the reactions of $Ln(SPh)_3$ with elemental S. Complexes have been isolated successfully for Ln = Ce (**1**), Pr (**2**), Nd (**3**), Sm (**5**), Gd (**6**), Tb (**7**), Dy (**8**), Ho (**9**), and Er (**10**). Only the Ce and Sm compounds are intensely colored, due to a relatively low energy f^1-to-d^1 promotion for **1** and a S^{2-} to Sm charge transfer absorption for **5**. The complexes are all thermally unstable with respect to loss of THF at room temperature. The reaction of $Sm(SPh)_3$ with S in a THF/DME mixture gives thermally unstable $(THF)_8Ln_8S_6(SPh)_{12}\cdot 6$DME (**4**). The analogous pyridine (py) complexes $(py)_8Ln_8S_6(SPh)_{12}\cdot x$py (Ln = Nd (**11**), Sm (**12**), Er (**13**)) were also found to desolvate at room temperature. All compounds have been characterized by conventional methods and by low-temperature single-crystal X-ray diffraction. Complete structural analyses have been obtained for compounds **4**, **7**, **12**, and **13**, and the structures of the rest were confirmed by unit cell determinations. In each case, the same basic octanuclear framework, with a cube of metal atoms connected by S^{2-} ligands capping the faces of the cube, and SPh ligands spanning the edges of the cube, is observed. Differences in the structures originate either in the relative orientation of the Ph moieties or in the number and orientations of the lattice solvent molecules. The Ce cluster is isostructural with $(THF)_8Sm_8Se_6(SePh)_{12}$, compounds **2** and **3** are isostructural with the previously reported structure of **6**, clusters **5** and **8**−**10** are isostructural with **7**, and cluster **11** is isostructural with **12**.

Introduction

The chalcogenido cluster chemistry of the lanthanide (Ln) metals has been invigorated by the recent observation that elemental chalcogen (E; E = S, Se) will displace arylchalcogenolate ligands (EPh; E = S, Se) to form lanthanide chalcogenido compounds (reaction 1).[1−4] Chalcogenido clusters have

$$x\mathrm{Ln(EPh)_3} + y\mathrm{E} \rightarrow \mathrm{Ln}_x\mathrm{E}_y\mathrm{(EPh)}_{3x-2y} \qquad (1)$$

been prepared in high yield from both $Ln(SPh)_3$ and $Ln(SePh)_3$ starting materials, and compounds with four, six, and eight metal ions have been successfully isolated and characterized by spectroscopic and diffraction techniques. With such a general synthetic approach supplementing more traditional but less general approaches to Ln−chalcogenido bonds,[5−7] it is now possible to begin addressing the question of whether the combination of traditionally covalent ligands and highly ionic metals will yield compounds with unusual physical properties or chemical reactivities. For example, in the cubane $Yb_4Se_4(SePh)_4$ and double cubane $Yb_6S_6(SPh)_6$ compounds there were anomalous Yb−E bond length patterns that suggested that covalent bonding interactions between ligand and metal 5d/6p orbitals may influence the physical properties of these cluster compounds.[3] Such bonding descriptions are found in solid state Ln_2E_3 literature[8] but rarely in molecular Ln chemistry.[9]

By far, the most frequently observed Ln cluster structure contains the octanuclear $(L)_8Ln_8E_6(EPh)_{12}$ (L = Lewis base) framework in which a cube of Ln ions is connected by E^{2-} ligands that cap the faces of the cube, with EPh ligands bridging the cube edges. First isolated in a study of the thermal decomposition of $Sm(SePh)_2$,[1] this cubic arrangement of metals was subsequently observed in the displacement reactions of $Ln(SPh)_3$ with elemental S.[2] Further reactivity studies have shown that L, E, and EPh ligands are chemically exchangeable, and the persistence of the Ln_8 core in these reactions suggests that this structure is composed of particularly stable ratios of Ln:E:EPh.[4]

This paper begins to define the scope and limitations of $(L)_8Ln_8S_6(SPh)_{12}$ cluster chemistry. The L = THF complexes for Ln = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, and Er were prepared

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(1) Freedman, D.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1997**, *119*, 11112.
(2) Melman, J. H.; Emge, T. J.; Brennan, J. G. *Chem. Commun.* **1997**, 2269.
(3) Freedman, D.; Melman, J.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1998**, *37*, 4162.
(4) Freedman, D.; Emge, T.; Brennan, J. Submitted
(5) Cary, D.; Ball, G.; Arnold, J. *J. Am. Chem. Soc.* **1995**, *117*, 3492.
(6) (a) Evans, W.; Rabe, G.; Ziller, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2110. (b) Berg, D.; Burns, C.; Andersen, R. A.; Zalkin, A. *Organometallics* **1989**, *8*, 1865. (c) Evans, W.; Rabe, G.; Ziller, J.; Doedens, R. *Inorg. Chem.* **1994**, *33*, 2719.
(7) Pernin, C. G.; Ibers, J. A. *Inorg. Chem.* **1997**, *36*, 3802.
(8) (a) Gerth, G.; Kienle, P.; Luchner, K. *Phys. Lett. A* **1968**, *27*, 557. (b) Eatough, N. L.; Hall, H. T. *Inorg. Chem.* **1970**, *9*, 417. (c) Dagys, R. S.; Anisimov, F. G. *Sov. Phys. Solid State* **1984**, *26*, 547. (d) Wachter, P. *CRC Crit. Rev. Solid State Sci.* **1972**, *3*, 189. (e) Byrom, E.; Ellis, D. E.; Freeman, A. J. *Phys. Rev. B* **1976**, *14*, 3558. (f) Zhukov, V. P.; Gubanov, V. A.; Weber, J. *J. Chem. Phys. Solids* **1981**, *42*, 631.
(9) (a) King, W. A.; Di Bella, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 627. (b) King, W. A.; Marks, T. J.; Anderson, D. M. *J. Am. Chem. Soc.* **1992**, *114*, 9221. (c) Brennan, J.; Cloke, F. G. N.; Sameh, A.; Zalkin, A. *J. Chem. Soc., Chem. Commun.* **1987**, 1668. (d) Anderson, D.; Cloke, F. G. N.; Cox, P.; Edelstein, N.; Green, J.; Pang, T.; Sameh, A.; Shalimoff, G. *J. Chem. Soc., Chem. Commun.* **1989**, 53. (e) Anderson, D.; Cloke, F. G. N.; Cox, P. *J. Chem. Soc., Chem. Commun.* **1990**, 284.

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and characterized by a variety of techniques, including low-temperature single-crystal X-ray diffraction. In an attempt to find a thermally stable system, the analogous L = pyridine complexes (Ln = Pr, Sm, Er) were also successfully isolated and characterized.

Experimental Section

General Methods. All syntheses were carried out under ultrapure nitrogen (JWS), using conventional drybox or Schlenk techniques. Solvents (Fisher) were refluxed continuously over molten alkali metals or K/benzophenone and collected immediately prior to use. Anhydrous pyridine (Aldrich) was purchased and refluxed over KOH. PhSSPh was purchased from either Aldrich or Strem and recrystallized from hexane. Ln and Hg 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 on KBr plates. 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. (Whitehouse, NJ). These compounds are sensitive to the thermal dissociation of lattice solvent and neutral donor ligands at room temperature, and so the experimentally determined elemental analyses are often found to be lower than the computed analyses (lattice solvents are excluded in the calculated percentages for all but one product). Products appear homogeneous, and for every sample several crystals of each compound were examined by single-crystal X-ray diffraction in an attempt to find a crystal suitable for a complete structural determination. The same unit cell was obtained consistently for each compound. NMR spectra were obtained, but the only signals observed were attributable to uncoordinated THF, pyridine, or DME.

Synthesis of $Ce_8S_6(SPh)_{12}(THF)_8$·2THF (1). Ce (0.370 g, 2.64 mmol), PhSSPh (0.865 g, 3.96 mmol), and Hg (0.030 g, 0.15 mmol) were combined in THF (25 mL), and the mixture was stirred until the Ce was consumed (2 days). Elemental S (0.063 g, 2.0 mmol) was added to the cloudy green solution, and the color turned reddish-brown within minutes. Additional THF (25 mL) was added, and after 24 h the solution was filtered, concentrated to ca. 40 mL, and layered with hexane (15 mL) to give orange hexagonal prismatic crystals (0.224 g, 21%), which became slightly opaque at 84 °C, began to darken at 137 °C, and were brown by 189 °C and black by 295 °C. IR: 2957 (s), 2853 (s), 2726 (w), 2669 (w), 1576 (w), 1461 (s), 1377 (s), 1261 (m), 1171 (w), 1152 (w), 1099 (w), 1080 (m), 1023 (m), 912 (w), 862 (w), 801 (w), 737 (m), 693 (m), 664 (w), 615 (w), 483 (w) cm^{-1}. UV−vis (py): 367 nm. Unit cell: monoclinic space group $P2_1/c$, a = 13.242(8) Å, b = 30.164(14) Å, c = 16.338(7) Å, β = 91.77(5)°, Z = 2, V = 6523(6) Å^3. Anal. Calcd for $C_{104}H_{124}Ce_8O_8S_{18}$: C, 39.0; H, 3.91. Found: C, 37.7; H, 3.92.

Synthesis of $Pr_8S_6(SPh)_{12}(THF)_8$·3THF (2). Pr (0.396 g, 2.81 mmol), PhSSPh (0.920 g, 4.21 mmol), and Hg (30 mg, 0.15 mmol) were combined in THF (30 mL), and the mixture was stirred until the metal was consumed. Elemental S (68 mg, 2.1 mmol) was added to the cloudy gray solution, and the color instantly changed to greenish-brown. After 4 days the solution was filtered, the volume was reduced in vacuo to ca. 20 mL, and the yellow-green solution was layered with hexane (15 mL) to give pale green crystals (0.73 g, 61%), which turned pasty yellow at 165 °C but did not melt below 325 °C. IR: 2924 (s), 2872 (s), 2724 (w), 2672 (w), 1571 (w), 1461 (s), 1377 (s), 1305 (w), 1262 (w), 1169 (w), 1154 (w), 1113 (w), 1075 (w), 1022 (w), 973 (w), 917 (w), 863 (w), 803 (w), 736 (m), 724 (m), 691 (w), 662 (w), 481 (w) cm^{-1}. Unit cell: triclinic space group $P\bar{1}$, a = 17.661(5) Å, b = 18.297(5) Å, c = 20.490(5) Å, α = 102.82(2)°, β = 94.56(2)°, γ = 94.17(2)°, Z = 2, V = 6407(3) Å^3. UV−vis (4-*tert*-butylpyridine): 497, 457 nm. Anal. Calcd for $C_{104}H_{124}O_8Pr_8S_{18}$: C, 38.9; H, 3.90. Found: C, 39.3; H, 4.12.

Synthesis of $Nd_8S_6(SPh)_{12}(THF)_8$·3THF (3). Nd (0.406 g, 2.82 mmol), PhSSPh (0.922 g, 4.22 mmol), and Hg (20 mg, 0.1 mmol) were combined in THF (20 mL), and the mixture was stirred for 5 days. Because Nd was still present in the reaction mixture, the solution was heated to 55 °C for an additional 3 days until the reaction appeared to be complete. To this cloudy blue solution was added elemental S (0.068 g, 2.1 mmol), and the color quickly changed to green. After 3 days the solution was filtered, the volume was reduced to ca. 20 mL, and the solution was layered with hexane to give green crystals (0.55 g, 45%), which began to lose solvent at 139 °C and began to darken at 203 °C. The compound precipitated in two different morphologies: triclinic space group $P\bar{1}$, a = 17.632(4) Å, b = 18.236(3) Å, c = 20.441(2) Å, α = 102.92(1)°, β = 94.65(1)°, γ = 94.21(2)°, Z = 2, V = 6353(2) Å^3; monoclinic space group $C2/c$, a = 26.826(5) Å, b = 20.822(6) Å, c = 47.515(8) Å, β = 90.12(1)°, Z = 8, V = 26541(10) Å^3. IR: 2924 (s), 2860 (s), 2342 (w), 1655 (w), 1461 (s), 1378 (s), 1306 (w), 1261 (w), 1168 (w), 1154 (w), 1094 (w), 1080 (w), 1022 (w), 973 (w), 892 (w), 868 (w), 801 (w), 723 (w), 669 (w), 617 (w) cm^{-1}. Anal. Calcd for $C_{104}H_{124}Nd_8O_8S_{18}$: C, 38.6; H, 3.87. Found: C, 37.4; H, 3.91.

Synthesis of $Sm_8S_6(SPh)_{12}(THF)_8$·6DME (4). Sm (0.529 g, 3.52 mmol), PhSSPh (1.156 g, 5.294 mmol), and Hg (0.06 g, 0.3 mmol) were combined in DME (30 mL). After 24 h, no apparent reaction had taken place, and THF (30 mL) was added to the mixture. After 1 day the Sm metal had been consumed, and to this cloudy yellow-green solution was added elemental S (0.086 g, 2.7 mmol), to give a more intensely green color. An additional 30 mL of THF was added to dissolve the remaining precipitate, the solution was filtered, and the volume was reduced to ca. 50 mL. Upon standing overnight yellow crystals (0.34 g, 21%) precipitated from the yellow-green solution. The compound began to darken at 175 °C and turned completely brown by 380 °C. IR: 2952 (s), 2923 (s), 2854 (s), 2726 (w), 2670 (w), 1641 (w), 1573 (w), 1461 (s), 1378 (s), 1262 (w), 1197 (w), 1155 (w), 1137 (w), 1108 (m), 1082 (m), 1067 (w), 1024 (m), 965 (w), 923 (w), 902 (w), 872 (m), 853 (w), 800 (w), 746 (m), 722 (w), 692 (m), 669 (w), 617 (w), 526 (w), 483 (w), 455 (w), 421 (w) cm^{-1}. Anal. Calcd for $C_{104}H_{124}O_8S_{18}Sm_8$: C, 38.0; H, 3.90. Found: C, 39.0; H, 4.49.

Synthesis of $Sm_8S_6(SPh)_{12}(THF)_8$·3THF (5). Sm (0.383 g, 2.55 mmol), PhSSPh (0.835 g, 3.82 mmol), and Hg (0.048 g, 0.24 mmol) were combined in THF (40 mL). The mixture was stirred for 6 days until the metal was consumed, and then elemental S (0.061 g, 1.9 mmol) was added to the cloudy yellow solution. After 4 days, the cloudy solution was filtered, the volume was reduced under vacuum, and the yellow solution was layered with hexane to give yellow crystals (0.444 g 42%), which appeared to darken at 204 °C, were brown by 247 °C, and melted at 281 °C. UV−vis (py): 233.6 nm. IR: 2952 (s), 2924 (s), 2855 (s), 2726 (w), 2672 (w), 1639 (w), 1573 (w), 1461 (s), 1378 (s), 1311 (w), 1260 (m), 1216 (w), 1091 (m), 1021 (m), 910 (w), 873 (w), 799 (m), 741 (w), 722 (w), 693 (w), 662 (w), 542 (w), 483 (w) cm^{-1}. Unit cell: monoclinic space group $C2/c$, a = 26.75(3) Å, b = 20.77(1) Å, c = 47.29(5) Å, β = 90.2(1)°, Z = 8, V = 26275(38) Å^3; triclinic space group $P\bar{1}$, a = 17.609(6) Å, b = 18.224(7) Å, c = 20.423(6) Å, α = 102.74(3)°, β = 94.50(3)°, γ = 93.94(3)°, Z = 2, V = 6348(4) Å^3. Anal. Calcd for $C_{104}H_{124}O_8S_{18}Sm_8$: C, 38.1; H, 3.81. Found: C, 37.6; H, 3.99.

Synthesis of $Gd_8S_6(SPh)_{12}(THF)_8$·3THF (6). Gd (0.380 g, 2.42 mmol), PhSSPh (0.791 g, 3.62 mmol), and Hg (0.06 g, 0.3 mmol) were combined in THF (35 mL), and the mixture was stirred for 24 h until Gd was consumed. Elemental S (0.058 g, 1.8 mmol) was added to this reaction mixture, and after 2 days the solution was filtered, concentrated to ca. 20 mL, and layered with hexane (15 mL) to give colorless crystals (0.384 g, 38%), which appeared to lose solvent at ca. 175 °C but did not decompose below 325 °C. IR: 2923 (s), 2856 (s), 2724 (w), 2671 (w), 1462 (s), 1377 (s), 1305 (w), 1262 (w), 1208 (w), 1168 (w), 1154 (w), 1076 (w), 1022 (w), 973 (w), 919 (w), 892 (w), 864 (w), 850 (w), 801 (w), 773 (w), 723 (m), 691 (w), 662 (w), 564 (w), 482 (w) cm^{-1}. Unit cell: triclinic space group $P\bar{1}$, a = 17.513(4) Å, b = 18.136(4) Å, c = 20.382(4) Å, α = 102.94(2)°, β = 94.39(2)°, γ = 93.72(2)°, Z = 2, V = 6268(3) Å^3. Anal. Calcd for $C_{104}H_{124}Gd_8O_8S_{18}$: C, 37.4; H, 3.75. Found: C, 37.3; H, 4.11.

Synthesis of $Tb_8S_6(SPh)_{12}(THF)_8$·3THF (7). Tb (0.346 g, 2.18 mmol), PhSSPh (0.713 g, 3.27 mmol), and Hg (0.029 g, 0.14 mmol) were combined in THF (35 mL). The mixture was stirred for 2 days until metal was consumed, and then elemental S (0.052 g, 1.62 mmol) was added to the colorless mixture. After a day, the solution was filtered, and the volume was reduced to ca. 30 mL and layered with hexane

(30 mL) to give pale yellow crystals (0.563 g, 61%), which began to lose solvent at 133 °C and appeared to melt at 275 °C. IR: 3442 (w), 3145 (w), 2919 (s), 2857 (s), 2725 (w), 2672 (w), 1643 (w), 1573 (w), 1462 (s), 1377 (s), 1261 (w), 1196 (w), 1152 (w), 1080 (w), 1023 (m), 912 (w), 886 (w), 863 (w), 800 (m), 760 (w), 733 (m), 690 (m), 662 (w), 515 (w), 484 (w), 464 (w), 420 (w), 404 (w) cm^{-1}. Unit cell: monoclinic space group $C2/c$, $a = 26.706(8)$ Å, $b = 20.751(5)$ Å, $c = 46.954(10)$ Å, $\beta = 90.21(2)°$, $Z = 8$, $V = 26021(8)$ Å^3. Anal. Calcd for $C_{104}H_{124}O_8S_{18}Tb_8$: C, 37.3; H, 3.73. Found: C, 37.5; H, 3.81.

Synthesis of $Dy_8S_6(SPh)_{12}(THF)_8$·3THF (8). Dy (0.316 g, 1.94 mmol), PhSSPh (0.637 g, 2.92 mmol), and Hg (0.021 g, 0.10 mmol) were combined in THF (40 mL), and the solution was stirred for 2 days until the metal was consumed. Elemental S (0.062 g, 1.9 mmol) was added to this gray-black mixture, and after 2 weeks the reaction product was filtered and the resulting pale gold solution was layered with hexane (20 mL) to give colorless crystals (0.490 g, 59%), which began to turn brown at 125 °C and continued to darken without melting up to 325 °C. IR: 2952 (s), 2859 (s), 2723 (w), 2669 (w), 2400 (w), 1767 (w), 1575 (w), 1455 (s), 1377 (s), 1261 (m), 1093 (m), 1020 (m), 865 (w), 800 (m), 740 (w), 722 (w), 699 (w), 661 (w), 545 (w), 486 (w), 465 (w), 454 (w), 404 (w) cm^{-1}. Unit cell: monoclinic space group $C2/c$, $a = 26.758(8)$ Å, $b = 20.757(9)$ Å, $c = 46.896(23)$ Å, $\beta = 90.38(3)°$, $Z = 8$, $V = 26046(19)$ Å^3. Anal. Calcd for $C_{104}H_{124}Dy_8O_8S_{18}$: C, 37.0; H, 3.70. Found: C, 36.1; H, 3.86.

Synthesis of $Ho_8S_6(SPh)_{12}(THF)_8$·3THF (9). Ho (0.400 g, 2.43 mmol), PhSSPh (0.793 g, 3.63 mmol), and Hg (0.029 g, 0.14 mmol) were combined in THF (30 mL), and the solution was stirred for 4 days until the metal was consumed and an orange-pink color developed. Elemental S was added (0.058 g, 1.8 mmol), and after 2 days the solution was filtered and layered with hexane to give pink crystals (0.492 g, 48%), which appeared yellow in sunlight. The compound appeared to lose color at 115 °C and melted at 278 °C. IR: 2921 (s), 2863 (s), 2725 (w), 2673 (w), 2360 (m), 2342 (w), 1654 (w), 1573 (w), 1462 (s), 1377 (s), 1310 (w), 1261 (w), 1168 (w), 1075 (m), 1023 (m), 974 (w), 915 (w), 873 (w), 801 (w), 738 (m), 724 (m), 691 (w), 669 (w), 617 (w), 485 (w) cm^{-1}. Unit cell: monoclinic space group $C2/c$, $a = 26.667(4)$ Å, $b = 20.693(3)$ Å, $c = 46.782(6)$ Å, $\beta = 90.15(1)°$, $Z = 8$, $V = 25815(7)$ Å^3. UV−vis (THF): 649, 544, 456, 423 nm. Anal. Calcd for $C_{104}H_{124}Ho_8O_8S_{18}$: C, 36.7; H, 3.68. Found: C, 34.7; H, 3.61.

Synthesis of $Er_8S_6(SPh)_{12}(THF)_8$·3THF (10). Er (0.362 g, 2.16 mmol), PhSSPh (0.709 g, 3.25 mmol), and Hg (0.031 g, 0.15 mmol) were combined in THF (40 mL), and the solution was stirred for 2 days until the metal was consumed. Elemental S (0.052 g, 1.6 mmol) was added to the cloudy orange mixture, and after 7 days the orange solution was filtered, the volume was reduced to ca. 25 mL, and the solution was layered with hexane to give pink crystals (0.372 g, 40%), which did not appear to change visibly up to 325 °C. IR: 2952 (s), 2924 (s), 2854 (s), 2724 (w), 2672 (w), 1752 (w), 1639 (w), 1575 (w), 1462 (s), 1383 (s), 1261 (m), 1081 (m), 1024 (m), 927 (w), 873 (w), 802 (w), 741 (m), 693 (w), 540 (w), 485 (w), 467 (w) cm^{-1}. Unit cell: monoclinic space group $C2/c$, $a = 26.631(8)$ Å, $b = 20.684(6)$ Å, $c = 46.708(16)$ Å, $\beta = 90.23(3)°$, $Z = 8$, $V = 25729(14)$ Å^3. UV−vis (py): 524, 381 nm. Anal. Calcd for $C_{104}H_{124}Er_8O_8S_{18}$: C, 36.6; H, 3.66. Found: C, 36.4; H, 3.50.

Synthesis of $Nd_8S_6(SPh)_{12}(py)_8$·6py (11). Nd (0.407 g, 2.82 mmol), PhSSPh (0.924 g, 4.23 mmol), and Hg (0.026 g, 0.13 mmol) were combined in pyridine (40 mL), and the solution was stirred for 5 days until the metal was consumed. Elemental sulfur (0.068 g, 2.1 mmol) was added to the blue-green solution, and after 11 days the solution was filtered, the volume was reduced to ca. 25 mL, and the blue-green solution was layered with hexane (20 mL) to give blue crystals (0.142 g, 11%), which became opaque at 76 °C and light yellow at 302 °C but did not appear to melt below 350 °C. IR: 3440 (w), 2953 (s), 2924 (s), 2854 (s), 2725 (w), 2669 (w), 1461 (s), 1383 (s), 1261 (m), 1092 (m), 1023 (m), 911 (w), 873 (w), 853 (w), 800 (m), 740 (w), 722 (w), 699 (w), 662 (w), 619 (w), 601 (w), 527 (w), 479 (w), 468 (w), 432 (w), 405 (w) cm^{-1}. Unit cell: rhombohedral space group $R\bar{3}$, $a = 27.966(5)$ Å, $c = 16.222(6)$ Å, $Z = 3$, $V = 10986(5)$ Å^3. UV−vis (4-tert-butylpyridine): 598 nm. Anal. Calcd for $C_{137}H_{130}Nd_8N_{14}S_{18}$: C, 45.3; H, 3.48; N, 5.21. Found: C, 44.8; H, 3.48; N, 5.51.

Synthesis of $Sm_8S_6(SPh)_{12}(py)_8$·6py (12). Sm (0.368 g, 2.45 mmol), PhSSPh (0.801 g, 3.66 mmol), and Hg (0.011 g, 0.055 mmol) were combined in pyridine (50 mL), and the solution was stirred for 1 day until the metal was consumed. Elemental S (0.056 g, 1.75 mmol) was added to the dark green-yellow solution, which was filtered after 7 days, concentrated to ca. 30 mL, and layered with hexane (20 mL) to give yellow crystals (0.390 g, 31%), which appeared to desolvate at 150 °C and to turn light brown at 266 °C but did not decompose below 325 °C. IR: 2924 (s), 2854 (s), 2727 (w), 2666 (w), 1634 (w), 1463 (s), 1378 (s), 1260 (m), 1091 (m), 1021 (m), 873 (w), 800 (m), 736 (w), 722 (w) cm^{-1}. Anal. Calcd for $C_{112}H_{100}N_8S_{18}Sm_8$: C, 40.3; H, 3.02; N, 3.41. Found: C, 38.6; H, 3.82; N, 3.44.

Synthesis of $Er_8S_6(SPh)_{12}(py)_8$·1py (13). Er (0.313 g, 1.87 mmol), PhSSPh (0.613 g, 2.81 mmol), and Hg (0.027 g, 0.13 mmol) were combined in THF (35 mL) and stirred until the metal was consumed. Elemental S (0.045 g, 1.4 mmol) was added to the pink solution, which was filtered after 2 days. Pyridine (2 mL, 25 mmol) was added to the solution, and layering with hexane gave pink crystals (0.383 g, 46%), which appeared to lose solvent at 142 °C but did not decompose below 350 °C. IR: 2921 (s), 2856 (s), 2724 (w), 2672 (w), 1638 (w), 1598 (w), 1573 (w), 1461 (s), 1378 (s), 1308 (w), 1263 (w), 1222 (w), 1150 (w), 1116 (w), 1081 (m), 1066 (m), 1036 (m), 1023 (m), 1000 (m), 895 (w), 874 (w), 838 (w), 802 (w), 739 (m), 689 (m) cm^{-1}. Anal. Calcd for $C_{112}H_{100}N_8Er_8S_{18}$: C, 38.7; H, 2.90; N, 3.23. Found: C, 39.5; H, 3.18; N, 2.80.

X-ray Structure Determination of 4, 7, 12, and 13. Data for **4**, **7**, **12**, and **13** were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å) at −120 °C. The check reflections measured every hour showed less than 2% intensity variation. The data were corrected for Lorentz effects and polarization, and absorption, the latter by a numerical (SHELX76)[10] method. The structures were solved by direct methods (SHELXS86).[11] All non-hydrogen atoms were refined (SHELXL97) on the basis of $F_{obs}{}^2$. All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97).[12] Scattering factors (f_o, f', f'') are as described in SHELXL97. Crystallographic data and final R indices for **4**, **7**, **12**, and **13** are given in Table 1. Significant bond distances and angles for **4**, **7**, **12**, and **13** are given in Tables 2, 3, 4, and 5, respectively. Complete crystallographic details are given in the Supporting Information. An ORTEP diagram[13] of the basic $L_8Ln_8S_6(SPh)_{12}$ unit common to **4**, **7**, **12**, and **13** is shown in Figure 1.

Results and Discussion

Octanuclear cluster compounds of the formula $(THF)_8Ln_8S_6(SPh)_{12}$ (Ln = Ce (**1**), Pr (**2**), Nd (**3**), Sm (**5**), Gd (**6**), Tb (**7**), Dy (**8**), Ho (**9**), and Er (**10**)) can be prepared from the reactions of $Ln(SPh)_3$ with elemental S in THF at room temperature (reaction 2). The Ce cluster **1** crystallizes in a unit cell that is isostructural with the previously reported Se analogue $(THF)_8Sm_8Se_6SePh_{12}$,[1] the Pr and Nd clusters **2** and **3** crystallize in unit cells that are isostructural with the previously reported triclinic structure of the Gd complex **6**,[2] and clusters **5** and **8**−**10** crystallize in unit cells that are isostructural with the monoclinic structure of **7**, which has been characterized fully by low-temperature single-crystal X-ray diffraction in this work. The same basic structural motif, with a cube of eight Ln ions

$$8Ln(SPh)_3 + 6S \rightarrow (THF)_8Ln_8S_6(SPh)_{12} + PhSSPh \quad (2)$$

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(10) Sheldrick, G. M. *SHELX76, Program for Crystal Structure Determination*, University of Cambridge: Cambridge, England, 1976.

(11) Sheldrick, G. M. *SHELXS86, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1986.

(12) Sheldrick, G. M. *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(13) (a) Johnson, C. K. ORTEP II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976. (b) Zsolnai, L. *XPMA and ZORTEP, Programs for Interactive ORTEP Drawings*; University of Heidelberg: Heidelberg, Germany, 1997.

Table 1. Summary of Crystallographic Details for $(THF)_8Sm_8S_6(SPh)_{12}\cdot 6DME$ (**4**), $(THF)_8Tb_8S_6(SPh)_{12}\cdot 3THF$ (**7**), $(py)_8Sm_8S_6(SPh)_{12}\cdot 6py$ (**12**), and $(py)_8Er_8S_6(SPh)_{12}\cdot py$ (**13**)

	4	7	12	13
empirical formula	$C_{30.81}H_{43.12}O_{4.5}S_{4.5}Sm_2$	$C_{116}H_{148}O_{11}S_{18}Tb_8$	$C_{23.67}H_{21.67}N_{2.33}S_3Sm_{1.33}$	$C_{7.31}H_{6.56}Er_{0.5}N_{0.56}S_{1.13}$
fw	930.50	3566.78	635.41	222.02
space group	tetragonal $I4/m$	monoclinic $C2/c$	rhombohedral $R\bar{3}$	tetragonal $I4/mmm$
a (Å)	18.256(8)	26.706(8)	27.946(8)	18.261(5)
b (Å)	18.256(8)	20.751(5)	27.946(8)	18.261(5)
c (Å)	21.482(16)	46.954(10)	16.158(8)	20.938(3)
α (deg)	90.00(5)	90.00(2)	90.00(3)	90.00(2)
β (deg)	90.00(5)	90.24(2)	90.00(3)	90.00(2)
γ (deg)	90.00(5)	90.00(2)	120.00(3)	90.00(2)
V (Å^3)	7160(7)	26021(11)	10928(7)	7260(3)
Z	8	8	18	32
D(calcd) (g/cm^{-3})	1.727	1.821	1.738	1.625
temp (°C)	−120	−120	−120	−120
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
abs coeff (mm^{-1})	3.545	4.629	3.480	4.869
$R(F)^a$ [$I > 2\sigma(I)$]	0.050	0.063	0.083	0.066
$R_w(F^2)^a$ [$I > 2\sigma(I)$]	0.116	0.154	0.157	0.160

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

Table 2. Significant Bond Lengths (Å) and Angles (deg) for **4**[a]

Sm(1)−O(1)	2.501(6)	Sm(1)−S(1)′	2.786(3)
Sm(1)−S(2)	2.822(2)	Sm(1)−S(3)	2.828(3)
Sm(1)−S(4)″	2.831(3)	Sm(1)−S(1)	2.854(3)
Sm(1)−S(4)	2.890(3)	S(1)−Sm(1)″	2.786(3)
S(3)−C(1)	1.782(13)	S(4)−C(7)	1.772(11)
C(1)−S(3)−Sm(1)	113.7(4)	C(7)−S(4)−Sm(1)‴	104.6(3)
C(7)−S(4)−Sm(1)	121.1(2)		

[a] Sulfido ligands: S(1,2). Thiolate ligands: S(3,4). Symmetry transformations used to generate equivalent atoms: (′) $y + 1, -x + 1, -z$; (″) $-y + 1, x - 1, z$; (‴) $y + 1, -x + 1, z$.

connected by S^{2-} capping the faces of the cube, and SPh bridging the edges of the cube, is found for all compounds (Figure 1).

Such an extended series of structurally identical lanthanide compounds is unusual and is found primarily in compounds with sterically demanding ligands such as in the $(C_5H_5)_3Ln-THF$ series,[14] rather than in compounds containing ligands with single donor atoms. Such persistence suggests that the octanuclear core is particularly stable and not just particularly insoluble. The increasingly smaller metal sizes are reflected in the average Ln−S bond lengths and thus in the average Ln−Ln distances (for **4** and **12**, 3.85 Å; for **7**, 3.80 Å; for **13**, 3.73 Å).

Both Eu and the smaller Ln (Tm−Yb) have not yet been isolated in this Ln_8 core. In Eu chemistry, the trivalent oxidation state is relatively unstable, and while sulfido,[15] resonance-stabilized thiolate,[16] and thiocarbamate[17] ligands will form stable Eu(III) compounds, aryl thiolates[18] apparently do not. There is a distinct color change upon addition of S to solutions of $Eu(SPh)_2$, but no reaction products have been isolated. The smaller $Ln(SPh)_n$ also react with elemental S, but the resulting sulfido clusters have been shown, at least for Yb, to contain metal ions with octahedral coordination geometries rather than the seven-coordinate structures of **1**−**13**. Product identity appears to depend on metal size rather than reaction stoichiometry: $Yb(SPh)_3$ reacts with either $^3/_4$ or 1.0 S to give the cubane derivative $Yb_6S_6SPh_6$ and not a Yb_8 product, while the reaction of $Dy(SPh)_3$ with either $^3/_4$ or 1.0 S in THF gives only the Dy_8 cluster.

In an attempt to form a thermally stable Sm_8 cube with a chelating ligand capping the Sm ion, $Sm(SPh)_3$ was prepared in DME, and the addition of THF was necessary for the reaction to go to completion. Saturation of the solution did not produce a DME coordination complex, but instead cluster **4** was isolated and characterized by low-temperature single-crystal X-ray diffraction. The complex was found to crystallize as a THF coordination complex, with lattice DME ligands totally uninvolved in coordination to the metal. Table 2 gives a list of significant bond lengths and angles for cluster **4**. The compound is also thermally sensitive at room temperature.

The more basic pyridine ligand was next examined as a potential source of thermal stability. Clusters of Nd and Sm were prepared by the reaction of $Ln(SPh)_3$ with elemental S in pyridine, and saturation of these solutions gave the pyridine complexes **11** and **12** in high yields; the Er compound **13** was also prepared by first forming the Er_8 cube in THF and then adding pyridine. Structural characterization of both compounds revealed that while pyridine readily coordinates to the Ln(III) center, it leaves the cubic arrangement intact. Significant bond lengths for **12** and **13** are given in Tables 4 and 5, respectively. In both **12** and **13** there is still only one N donor coordinated to the metal, and the benzenethiolates still bridge the edges of the cube. Unfortunately, in both cases the cluster crystallizes with lattice pyridine ligands that dissociate once the cluster is isolated at room temperature.

The major differences in molecular structure for the six structural types observed here (exemplified by **1**, **4**, **6**, **7**, **12**, and **13**) are based not on the metal coordination geometry of the Ln_8S_{18} core but rather on the subtle dihedral angle differences among the eight Lewis base ligands (py or THF), 12 sites of thiolate ligands, and the entrained solvent molecules.

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(14) (a) Rogers, R. D.; Atwood, J. L.; Emad, A.; Sikora, D. J.; Rausch, M. D. *J. Organomet. Chem.* **1981**, *216*, 383. (b) Wasserman, H. J.; Zozulin, A. J.; Moody, D. C.; Ryan, R. R.; Salazar, K. V. *J. Organomet. Chem.* **1983**, *254*, 305. (c) Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Organomet. Chem.* **1980**, *192*, 65.

(15) Grizik, A. A.; Eliseev, A. A.; Borodulenko, G. P.; Tolstova, V. A. *Russ. J. Inorg. Chem.* **1977**, *22* (2), 309.

(16) Berardini, M.; Lee, J.; Freedman, D.; Lee, J.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1997**, *36*, 5772.

(17) (a) Brown, D.; Holah, D. G.; Rickard, C. E. F. *J. Chem. Soc. A* **1970**, 786. (b) Ciaopolini, M.; Nardi, N.; Colamarino, P.; Orioli, P. *J. Chem. Soc., Dalton Trans.* **1977**, 379. (c) Pinkerton, A. A.; Meseri, Y.; Rieder, C. *J. Chem. Soc., Dalton Trans.* **1978**, 85. (d) Pinkerton, A. A.; Schwartzenback, D. *J. Chem. Soc., Dalton Trans.* **1976**, 2466.

(18) Mashima, K.; Nakayama, Y.; Fukumoto, H.; Kanehisa, N.; Kai, Y.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2523.

Table 3. Significant Bond Lengths (Å) and Angles (deg) for **7**[a]

Tb(1)−O(1A)	2.488(12)	Tb(1)−S(3)	2.714(5)	Tb(1)−S(7)	2.785(6)
Tb(1)−S(2)	2.805(6)	Tb(1)−S(9)	2.826(7)	Tb(1)−S(8)	2.833(6)
Tb(1)−S(1)	2.839(5)	Tb(2)−O(2A)	2.472(13)	Tb(2)−S(1)	2.755(6)
Tb(2)−S(2)′	2.790(5)	Tb(2)−S(3)	2.796(6)	Tb(2)−S(9)	2.811(6)
Tb(2)−S(6)	2.817(6)	Tb(2)−S(4)	2.844(6)	Tb(3)−O(3)	2.451(11)
Tb(3)−S(2)	2.748(5)	Tb(3)−S(1)	2.760(6)	Tb(3)−S(5)	2.797(6)
Tb(3)−S(6)′	2.816(6)	Tb(3)−S(3)′	2.826(5)	Tb(3)−S(7)	2.862(6)
Tb(4)−O(4)	2.448(11)	Tb(4)−S(1)′	2.761(6)	Tb(4)−S(8)	2.784(6)
Tb(4)−S(2)	2.796(5)	Tb(4)−S(3)	2.796(6)	Tb(4)−S(4)′	2.805(6)
Tb(4)−S(5)′	2.838(6)	Tb(5)−O(5)	2.429(11)	Tb(5)−S(13)	2.737(2)
Tb(5)−S(11)	2.760(6)	Tb(5)−S(10)	2.785(6)	Tb(5)−S(17)	2.786(6)
Tb(5)−S(14)	2.833(6)	Tb(5)−S(15)	2.837(6)	Tb(6)−O(6)	2.465(12)
Tb(6)−S(11)	2.767(6)	Tb(6)−S(19)	2.774(6)	Tb(6)−S(10)	2.775(5)
Tb(6)−S(14)	2.806(6)	Tb(6)−S(12)	2.819(2)	Tb(6)−S(16)	2.858(6)
Tb(7)−O(7)	2.420(12)	Tb(7)−S(10)″	2.744(6)	Tb(7)−S(11)	2.778(6)
Tb(7)−S(18)	2.809(6)	Tb(7)−S(13)	2.810(2)	Tb(7)−S(15)″	2.810(6)
Tb(7)−S(17)	2.839(6)	Tb(8)−O(8)	2.447(11)	Tb(8)−S(10)″	2.759(6)
Tb(8)−S(12)	2.764(2)	Tb(8)−S(18)	2.789(6)	Tb(8)−S(16)	2.795(6)
Tb(8)−S(11)	2.822(5)	Tb(8)−S(19)″	2.865(6)		
C(1)−S(4)−Tb(2)	116.3(8)	C(7)−S(5)−Tb(3)	106.8(8)	C(13)−S(6)−Tb(2)	118.5(9)
C(19)−S(7)−Tb(1)	110.7(7)	C(19)−S(7)−Tb(3)	119.4(8)	C(25)−S(8)−Tb(4)	109.4(8)
C(25)−S(8)−Tb(1)	115.1(8)	C(31A)−S(9)−Tb(2)	119.0(15)	C(31B)−S(9)−Tb(2)	106.6(14)
C(31A)-S(9)−Tb(1)	105.7(16)	C(31B)−S(9)−Tb(1)	117.9(14)		
C(37)−S(14)−Tb(6)	106.6(8)	C(37)−S(14)−Tb(5)	119.4(8)	C(43)−S(15)−Tb(7)″	107.5(8)
C(43)−S(15)−Tb(5)	119.8(8)	C(49)−S(16)−Tb(8)	105.9(8)	C(49)−S(16)−Tb(6)	120.7(8)
C(55)−S(17)−Tb(5)	106.2(9)	C(55)−S(17)−Tb(7)	118.3(8)	C(61)−S(18)−Tb(8)	107.6(8)
C(61)−S(18)−Tb(7)	114.1(8)	C(67)−S(19)−Tb(6)	103.1(7)	C(67)−S(19)−Tb(8)″	121.3(8)

[a] Sulfido ligands: S(1−3,10−13). Thiolate ligands: S(4−9,14−19). Symmetry transformations used to generate equivalent atoms: (′) $-x+1, -y+1, -z$; (″) $-x+1, y, -z-{}^{1}/_{2}$.

Table 4. Significant Bond Lengths (Å) and Angles (deg) for **12**

Sm(1)−N(1A)	2.634(13)	Sm(1)−N(1B)	2.72(2)
Sm(1)−S(1)′	2.784(3)	Sm(1)−S(1)	2.794(4)
Sm(1)−S(2)	2.795(4)	Sm(1)−S(2)′	2.855(5)
Sm(1)−S(3)	2.863(6)	Sm(1)−S(1)″	2.874(3)
Sm(2)−N(2)	2.70(3)	Sm(2)−S(1)′	2.803(4)
Sm(2)−S(3)	2.860(6)	S(2)−C(1)	1.783(15)
S(3)−C(7)	1.789(17)		
C(1)−S(2)−Sm(1)	109.5(4)	C(1)−S(2)−Sm(1)″	116.7(5)
C(7)−S(3)−Sm(2)	113.5(6)	C(7)−S(3)−Sm(1)	113.1(5)

[a] Sulfido ligand: S(1). Thiolate Ligands: S(2,3). Symmetry transformations used to generate equivalent atoms: (′) $y, -x+y, -z$; (″) $x-y, x, -z$.

Table 5. Significant Bond Lengths (Å) and Angles (deg) for **13**

Er(1)−S(2)	2.735(2)	Er(1)−N(1)	2.59(2)
Er(1)−S(1)	2.752(3)	Er(1)−S(4)	2.773(5)
S(3)−C(1)	1.782(10)	Er(1)−S(3)	2.734(7)
S(4)−C(7)	1.795(9)		
C(1)−S(3)−Er(1)	125.9(10)	C(7)−S(4)−Er(1)′	102.1(10)
C(7)−S(4)−Er(1)	125.8(10)		

[a] Sulfido ligands: S(1,2). Thiolate ligands: S(3,4). Symmetry transformations used to generate equivalent atoms: (′) $-y, x, z$.

With respect to the Ln_8S_6 capped cube, the overall molecular site symmetry may be less than cubic. It is reasonable, therefore, that substituent disorder of the bonded L and SPh ligands within a given lattice symmetry is possible in the crystal. Such disorder was in fact prevalent in the highest symmetry cases **12** and **13**.

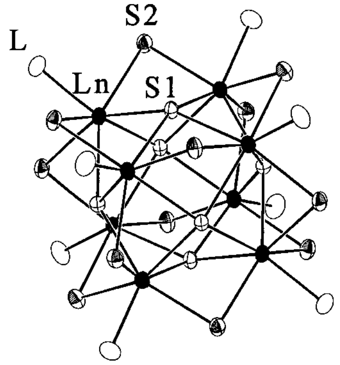

Figure 1. ORTEP diagram of the common core Ln_8 region for $(L)_8Ln_8S_6(SPh)_{12}$ (C and H atoms removed). The filled atoms are Ln, the shaded atoms (S2) are thiolate S, the crossed atoms (S1) are sulfido ligands, and the open atoms represent the donor atom from the neutral THF (O) or pyridine (N) ligand.

Because ligand orbitals do not generally overlap with the valence f orbitals of the lanthanides, compounds containing lanthanide ions usually adopt the characteristic color of forbidden f−f transitions with well-defined energies that are independent of temperature, pressure, or the identity of the ligands surrounding the metal.[19] Exceptions to this rule occur when the redox active lanthanides (i.e., Sm, Eu, Yb) exhibit charge transfer (CT) excitations, or when an $f^n \rightarrow f^{n-1}d^1$ promotion is energetically feasible (i.e., Ce(III), Sm(II), Yb(II)). Cluster colors follow these trends: the compounds of Pr, Nd, Gd, Tb, Dy, Ho, and Er exhibit colors that are characteristic of each Ln ion, while the Ce and Sm compounds are more intensely colored. For the Sm clusters, the CT assignment is based on analogy with the intensely colored $Ln(EPh)_3$ compounds[16,20] and the spectroscopic assignment of these transitions by the use of resonance Raman spectroscopy,[21] although it is not possible to determine unequivocally whether the color involves SPh or S^{2-} ligands. Still, the red color of $Sm_8Se_6(SePh)_{12}$ was assigned as

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(19) *Lanthanide Probes in Life, Chemical, and Earth Sciences: Theory and Practice*; Bunzli, J.-C. G., Choppin, G. R., Eds.; Elsevier: Amsterdam, 1989; pp 11−13.

(20) (a) Berardini, M.; Emge, T.; Brennan, J. G. *J. Chem. Soc., Chem. Commun.* **1993**, 1537. (b) Berardini, M.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 6179. (c) Lee, J.; Brewer, M.; Berardini, M.; Brennan, J. *Inorg. Chem.* **1995**, *34*, 3215.

(21) Lee, J.; Freedman, D.; Melman, J.; Brewer, M.; Sun, L.; Emge, T. J.; Long, F. H.; Brennan, J. G. *Inorg. Chem.* **1998**, *37*, 2512.

a Se^{2-} to Sm CT absorption, on the basis of the colors of $Sm_8S_6(SePh)_{12}$ (yellow) and $Sm_8Se_6(SPh)_{12}$ (red),[4] and so the lowest energy CT absorptions in **4**−**5** are tentatively assigned as S^{2-} to Sm CT transitions.

Compounds with Ce−S bonds are interesting because of the utility of red Ce_2S_3 as a replacement for Hg-based pigments.[22] The cerium cluster **1** is a yellow orange crystalline compound with an absorption maximum of 367 nm in pyridine. The color of this neutral cluster appears considerably less red than the reported anionic Ce compounds with sulfur-based ligands, i.e., $Ce(S_2CNEt_2)_4^-$ ($\lambda_{max} = 439$ nm)[23] or $Ce(S\text{-}2\text{-}NC_5H_4)_4^-$ ($\lambda_{max} = 447$ nm),[16] and further derivatives are currently being pursued in order to establish whether this shift results from some form of covalent interaction between the Ce d and sulfur-based orbitals or if purely electrostatic models[24] can account for the behavior.

Conclusion

The $Ln_8S_6(SPh)_{12}$ cluster framework remains invariant throughout most of the lanthanide series. Clusters with all of the lanthanides from Ce through Er can be prepared in high yield and isolated from a number of solvent systems, including monodentate ethers, chelating ligands, and donor solvents as basic as pyridine. The persistent crystallization of this structure in six different unit cells that differ in the orientation of the SPh groups or in the identity/number of the lattice solvent molecules is an indication that the octanuclear framework is a particularly stable combination of Ln:E:EPh.

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Supporting Information Available: X-ray crystallographic files in CIF format for the crystal structures of $(THF)_8Sm_8S_6(SPh)_{12}\cdot 6DME$, $(THF)_8Tb_8S_6(SPh)_{12}\cdot 3THF$, $(py)_8Sm_8S_6(SPh)_{12}\cdot 6py$, and $(py)_8Er_8S_6(SPh)_{12}\cdot py$ are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) (a) Chopin, T.; Guichon, H.; Touret, O. US Patent 5,348,581, 1994. (b) Chopin, T.; Dupuis, D. US Patent 5,401,309, 1995.

(23) Ciampolini, M.; Nardi, N.; Colamarino, P.; Orioli, P. *J. Chem. Soc., Dalton Trans.* **1976**, 379.

(24) (a) Mauricot, R.; Gressier, P.; Evain, M.; Brec, R. *J. Alloys Compd.* **1995**, *223*, 130. (b) Perrin M. A.; Wimmer, E. *Phys. Rev. B, Condens. Matter* **1996**, *54*, 2428. (c) Zhukov, V.; Mauricot, R.; Gressier, P.; Evain, M. *J. Solid State Chem.* **1997**, *128*, 197.