

# (THF)<sub>8</sub>Ln<sub>8</sub>E<sub>6</sub>(EPh)<sub>12</sub> Cluster Reactivity: Systematic Control of Ln, E, EPh, and Neutral Donor Ligands

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Octametallic (L)<sub>8</sub>Ln<sub>8</sub>E<sub>6</sub>(EPh)<sub>12</sub> clusters (L = Lewis base; Ln = lanthanide ion; E = S, Se; EPh = SPh, SePh) can be prepared either by the reduction of Se–C bonds with low-valent Ln or by the reaction of Ln(SePh)<sub>3</sub> with elemental E. Because all possible ligand sites (i.e., L, E, EPh) are reactive, the ligands can be varied systematically to further the understanding of structure/property relationships. Chalcogenolate ligands can be selectively varied, as in the reaction of (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub> with PhSSPh to form (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SPh)<sub>12</sub>. Neutral L can be altered without disrupting structure, as in the replacement of THF with pyridine to give (py)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub>. Even chalcogenido ligands can be chemically replaced: the reaction of (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SPh)<sub>12</sub> with elemental S gives the all-sulfur cluster (THF)<sub>8</sub>Sm<sub>8</sub>S<sub>6</sub>(SPh)<sub>12</sub>. All compounds were isolated and characterized by IR and UV–visible spectroscopy and by low-temperature single-crystal X-ray diffraction to confirm that the structures contain cubes of Ln(III) ions with E<sup>2-</sup> capping the faces and EPh bridging the edges of the cube. The Sm<sub>8</sub>Se<sub>6</sub>(EPh)<sub>12</sub> clusters are intensely colored because of a Se<sup>2-</sup> to Sm(III) charge transfer absorption, while the sulfido clusters exhibit the light yellow color characteristic of Sm(III) complexes. The light green Nd complex (py)<sub>8</sub>Nd<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub> was isolated from the reaction of Nd(SePh)<sub>3</sub> with Se to confirm that chalcogenolate displacement is general to the redox-inactive lanthanides and that the intense colors of the Sm selenido clusters are related to the redox activity of the Ln. The two pyridine complexes (py)<sub>8</sub>LnSe<sub>6</sub>(SePh)<sub>12</sub> (Ln = Nd, Sm) are isostructural. Crystal data (Mo K $\alpha$ , 153(2) K) are as follows. (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SPh)<sub>12</sub>: triclinic space group  $P\bar{1}$ ,  $a = 17.637(7)$  Å,  $b = 18.337(5)$  Å,  $c = 20.466(12)$  Å,  $\alpha = 103.04(4)^\circ$ ,  $\beta = 94.71(4)^\circ$ ,  $\gamma = 94.28(3)^\circ$ ,  $Z = 2$ . (py)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub>: monoclinic space group  $C2/m$ ,  $a = 18.770(2)$  Å,  $b = 28.113(4)$  Å,  $c = 16.461(3)$  Å,  $\beta = 120.65(1)^\circ$ ,  $Z = 2$ . (THF)<sub>8</sub>Sm<sub>8</sub>S<sub>6</sub>(SePh)<sub>12</sub>: orthorhombic space group  $Pcab$ ,  $a = 19.803(3)$  Å,  $b = 22.446(3)$  Å,  $c = 26.072(4)$  Å,  $Z = 8$ .

## Introduction

Cluster chemistry is generally viewed as the bridge connecting molecular and solid state inorganic chemistry. While the metal chalcogenido (ME<sub>x</sub>; E = S, Se, Te) cluster chemistry of the main group<sup>1</sup> and transition elements<sup>2</sup> has received considerable attention, the chemistry of the corresponding lanthanides<sup>3–6</sup> (Ln) is just beginning to emerge. Given that molecular Ln chemistry

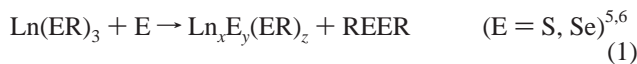
is described almost<sup>5b,7</sup> exclusively in ionic terms, and that covalent bonding descriptions are often used to describe solid state lanthanide chalcogenides,<sup>8</sup> a systematic investigation of lanthanide chalcogenido clusters would be fundamentally important to the goal of outlining the relationships between these disparate bonding descriptions.

Two new and general synthetic approaches to Ln cluster materials have recently been described. Low-valent Ln ions will cleave Se–C bonds<sup>5a</sup> to give selenido clusters, and elemental chalcogen has been shown to displace ER (reaction 1) from

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Ln(ER)<sub>3</sub> to give lanthanide chalcogenido clusters, often in greater than 70% isolated yield. These two new synthetic



approaches complement the previously reported thermal decomposition<sup>4</sup> of Ln(TeSi(SiMe<sub>3</sub>)<sub>3</sub>)<sub>3</sub> (Ln = La, Ce) and the reduction of elemental E by divalent Ln compounds.<sup>3,9</sup> Importantly, these new synthetic routes are potentially general for the entire lanthanide series. Cluster reactivity can now be examined, macroscopic properties can be correlated with structure, the influence of Ln and E on cluster structure and physical properties can be established, and questions regarding the relationships between molecular and solid state properties can be addressed.

This paper presents initial studies on the chemical reactivity of (L)<sub>8</sub>Ln<sub>8</sub>E<sub>6</sub>(EPh)<sub>12</sub> clusters. All of the different ligand types, i.e., E<sup>2-</sup>, ER<sup>-</sup>, and L, are shown to be chemically reactive. Further, the reaction of Nd(SePh)<sub>3</sub> with elemental Se to give a neodymium selenido cluster illustrates the generality of this synthetic route to the redox-inactive lanthanides. The implications of these various reactivities on general cluster chemistry and on the ability to tailor cluster properties are discussed.

## 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. PhSeSePh and PhSSPh were 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<sup>-1</sup> as a Nujol mull on KBr plates. Electronic spectra were recorded on a Varian DMS 100S spectrometer with the samples in a 1.0 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 neutral donor ligands at room temperature, and so the experimentally determined elemental analyses are often found to be lower than the computed analyses. 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 on either a Varian Gemini 200 MHz or a Varian 400 MHz NMR spectrometer, and chemical shifts are reported in δ (ppm).

**Synthesis of (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub> (1).** Sm (0.30 g, 2.0 mmol) was added to a mixture of diphenyl diselenide (0.93 g, 3.0 mmol) and Hg (0.05 g, 0.25 mmol) in THF (40 mL). After 5 h of stirring, the metal had dissolved. Sulfur was added (0.056 g, 1.75 mmol), and the solution color changed from red to olive. After 3 days the solution was filtered, concentrated to ca. 30 mL, and layered with hexanes (15 mL) to give light yellow crystals (0.050 g, 5.2%; the compound does not melt but slowly turns dark orange, brown, and finally black by 320 °C). Anal. Calcd for C<sub>104</sub>H<sub>124</sub>O<sub>8</sub>Se<sub>12</sub>S<sub>6</sub>Sm<sub>8</sub>: C, 32.4; H, 3.26. Found: C, 30.9; H, 3.29. The <sup>1</sup>H NMR spectrum (C<sub>5</sub>D<sub>5</sub>N, 20 °C) contained resonances from uncoordinated THF (3.64 and 1.60 ppm). IR: 2895 (s), 2727 (w), 2361 (w), 2340 (w), 1572 (m), 1463 (s), 1378 (s), 1261 (w), 1170 (w), 1152 (w), 1071 (s), 1021 (s), 913 (m), 863 (m), 730 (s), 692 (m), 664 (m), 466 (m) cm<sup>-1</sup>.

**Synthesis of (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SPh)<sub>12</sub>·3THF (2).** Sm (0.30 g, 2.0 mmol) was added to a mixture of PhSeSePh (0.625 g, 2.00 mmol) and Hg (0.05 g, 0.25 mmol) in THF (40 mL). After 3 weeks PhSSPh (0.357

g, 1.6 mmol) was added to the dark brown mixture. Within 1 h the solution color had turned orange. After 2 days the solution was filtered, concentrated (ca. 25 mL), and layered with hexanes (25 mL) to give orange crystals (0.40 g, 42%), which gradually turned dark brown above 250 °C but did not melt below 320 °C. Anal. Calcd for C<sub>116</sub>H<sub>148</sub>O<sub>11</sub>S<sub>12</sub>-Se<sub>6</sub>Sm<sub>8</sub>: C, 36.9; H, 3.95. Found: C, 35.5; H, 3.50. <sup>1</sup>H NMR (C<sub>5</sub>D<sub>5</sub>N, 20 °C): only the protons from uncoordinated THF (3.64, 1.59) were observed. The compound did not show an absorption maximum in THF from 320 to 800 nm. IR: 2899 (s), 2724 (w), 2672 (w), 2530 (w), 1945 (m), 1872 (m), 1811 (w), 1765 (w), 1571 (s), 1460 (s), 1378 (s), 1297 (w), 1262 (m), 1174 (m), 1154 (w), 1111 (m), 1078 (s), 1066 (s), 1019 (s), 911 (m), 858 (s), 738 (s), 690 (s), 664 (s), 614 (w), 483 (s), 416 (s) cm<sup>-1</sup>.

**Synthesis of (py)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub>·3py (3).** Sm (0.30 g, 2.0 mmol), diphenyl diselenide (0.94 g, 3.0 mmol), and Hg (0.05 g, 0.25 mmol) were added to pyridine (40 mL), and the mixture was stirred for 2 days at room temperature. Elemental Se (0.10 g, 1.25 mmol) was added to the light brown solution, and after 10 days the bright orange solution was filtered, concentrated to 30 mL, and layered with hexanes. The orange crystals (0.24 g, 24%, based on elemental Se) did not melt but gradually turned dark red until 165 °C and then slowly turned dark brown up to 300 °C. Anal. Calcd for C<sub>127</sub>H<sub>115</sub>N<sub>11</sub>Se<sub>18</sub>Sm<sub>8</sub>: C, 34.5; H, 2.62; N, 3.49. Found: C, 33.6; H, 2.74; N, 3.28. The <sup>1</sup>H NMR (OC<sub>4</sub>D<sub>8</sub>, 20 °C) spectrum contained resonances from pyridine (8.54 (d, 2H), 7.65 (m, 1H), 7.24 (t, 2H)) and resonances from the phenyl ring (6.60 (t, 1H), 6.25 (t, 2H), 5.68 (s, 2H)). The relative ratios of py:Ph integrations vary with the length of time the crystals are isolated. λ<sub>max</sub> (py): 450 nm. IR: 3077 (m), 2925 (s), 2723 (w), 1912 (w), 1862 (w), 1679 (w), 1631 (w), 1596 (m), 1579 (s), 1461 (s), 1377 (s), 1261 (m), 1216 (w), 1144 (w), 1067 (w), 1030 (m), 803 (m), 744 (s), 702 (s), 620 (w), 601 (m), 464 (m), 405 (m) cm<sup>-1</sup>.

**Synthesis of (py)<sub>8</sub>Nd<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub>·3py (4).** Nd (0.28 g, 2.0 mmol), diphenyl diselenide (0.94 g, 3.0 mmol), and Hg (0.05 g, 0.025 mmol) were added to pyridine (40 mL), and the mixture was stirred for 2 days. Elemental Se (0.12 g, 1.5 mmol) was added to the light green solution, which was stirred for 5 days and then filtered to separate the green/gray precipitate. The solution was concentrated to ca. 30 mL and layered with hexanes (20 mL) to give pale green blocks (0.10 g, 10%) of **4**, which turned gold around 235 °C and steadily turned darker orange without melting up to 300 °C. Anal. Calcd for C<sub>127</sub>H<sub>115</sub>N<sub>11</sub>Se<sub>18</sub>-Nd<sub>8</sub>: C, 34.9; H, 2.65; N, 3.53. Found: C, 32.7; H, 2.62; N, 2.92. <sup>1</sup>H NMR (C<sub>4</sub>D<sub>8</sub>O, 20 °C): 8.54 (d, 2H), 7.66 (t, 1H), 7.26 (t, 2H). IR: 3076 (m), 2908 (s), 2722 (w), 1596 (m), 1579 (s), 1463 (s), 1377 (s), 1216 (m), 1144 (m), 1067 (m), 1030 (m), 990 (m), 743 (s), 701 (s), 620 (w), 602 (w), 465 (m), 405 (m) cm<sup>-1</sup>. Unit cell (Mo Kα, -120 °C): space group C2/m; a = 18.788(5) Å; b = 28.140(8) Å; c = 16.501(3) Å; β = 120.73(2)°; V = 7499(3) Å<sup>3</sup>.

**Chalcogenido Replacement of Se<sup>2-</sup> with S<sup>2-</sup>.** Sm (0.30 g, 2.0 mmol), diphenyl diselenide (625 mg, 2.0 mmol), and Hg (0.50 g, 0.025 mmol) were added to THF (40 mL) and put under an atmosphere of H<sub>2</sub>. After stirring of the mixture for 3 days, the H<sub>2</sub> was replaced with N<sub>2</sub>. Diphenyl disulfide (0.35 g, 1.6 mmol) was added to the dark brown solution, and 3 days later elemental sulfur (0.48 g, 1.5 mmol) was added to the light brown solution. After 2 days the brown mixture was filtered to remove an insoluble brown precipitate, concentrated to ca. 25 mL, and layered with hexane to give yellow crystals (0.14 g, 16%) of the all-sulfur cluster, which were identified by the characteristic light yellow color and by single-crystal X-ray diffraction data (unit cell determination) at -120 °C.<sup>6</sup>

**X-ray Structure Determination of 1–3.** Data for 1–3 were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) at room temperature. The check reflections measured every 1 h showed less than 2% intensity variation. The data were corrected for Lorentz effects and polarization, and absorption, the latter by a numerical (SHELX76)<sup>10</sup> method. The structures were solved by direct methods (SHELXS86).<sup>11</sup>

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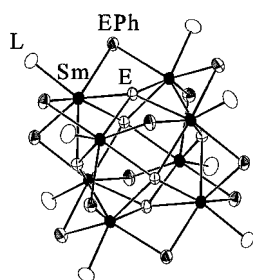
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**Table 1.** Summary of Crystallographic Details for (THF)<sub>8</sub>Sm<sub>8</sub>S<sub>6</sub>(SePh)<sub>12</sub> (**1**), (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SPh)<sub>12</sub> (**2**), and (py)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub> (**3**)

	<b>1</b>	<b>2</b>	<b>3</b>
empirical formula	C <sub>52</sub> H <sub>62</sub> O <sub>4</sub> S <sub>3</sub> Se <sub>6</sub> Sm <sub>4</sub>	C <sub>116</sub> H <sub>148</sub> O <sub>11</sub> S <sub>12</sub> Se <sub>6</sub> Sm <sub>8</sub>	C <sub>127</sub> H <sub>115</sub> N <sub>11</sub> Se <sub>18</sub> Sm <sub>8</sub>
fw	1922.36	3779.62	4419.38
space group (No.)	<i>Pcab</i> (61)	<i>P</i> $\bar{1}$ (2)	<i>C2/m</i> (12)
<i>a</i> (Å)	19.803(3)	17.637(7)	18.770(2)
<i>b</i> (Å)	22.446(3)	18.337(5)	28.113(4)
<i>c</i> (Å)	26.072(4)	20.466(12)	16.461(3)
$\alpha$ (deg)	90.00(1)	103.04(4)	90.00(1)
$\beta$ (deg)	90.00(1)	94.71(4)	120.65(1)
$\gamma$ (deg)	90.00(1)	94.28(3)	90.00(1)
<i>V</i> (Å <sup>3</sup> )	11 589(3)	6397(5)	7472(1)
<i>Z</i>	8	2	2
<i>D</i> (calcd) (g/cm <sup>-3</sup> )	2.204	1.962	1.964
temp (°C)	-120	-120	-120
$\lambda$ (Å)	0.710 73	0.710 73	0.710 73
abs coeff (mm <sup>-1</sup> )	7.913	5.566	7.519
<i>R</i> ( <i>F</i> ) <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.044	0.035	0.059
<i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> ) <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.106	0.085	0.129

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



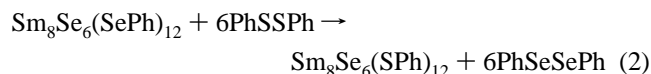
**Figure 1.** Molecular structure of generic (L)<sub>8</sub>Sm<sub>8</sub>E<sub>6</sub>(E'Ph)<sub>12</sub> cluster, with the C and H atoms removed. The filled atoms are Sm, the crossed atoms are E<sup>2-</sup>, the shaded atoms are E(Ph), and the unfilled atoms represent the neutral donor. Compound **1**: L = O(C<sub>4</sub>H<sub>8</sub>), E = S, E' = Se. Compound **2**: L = O(C<sub>4</sub>H<sub>8</sub>), E = Se, E' = S. Compound **3**: L = N(C<sub>5</sub>H<sub>4</sub>), E = E' = Se.

All non-hydrogen atoms were refined (SHELXL97) on the basis of  $F_{obs}^2$ . All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97).<sup>12</sup> Scattering factors ( $f_o$ ,  $f'$ ,  $f''$ ) are as described in SHELXL97. Crystallographic data and final *R* indices for **1–3** are given in Table 1. Significant bond distances and angles for **1–3** and complete crystallographic details are given in the Supporting Information. An ORTEP diagram<sup>13</sup> that illustrates the main structural framework of **1–3** is shown in Figure 1.

## Results

Chalcogenido, chalcogenolate, and neutral donor ligands are all reactive sites in L<sub>8</sub>Ln<sub>8</sub>E<sub>6</sub>(E'Ph)<sub>12</sub> cluster compounds. The octametallic structure can be isolated for most Ln, with various combinations of E<sup>2-</sup>, EPh<sup>-</sup>, and neutral monodentate Lewis bases. In this work, the synthesis and characterization of (THF)<sub>8</sub>Sm<sub>8</sub>S<sub>6</sub>(SePh)<sub>12</sub>, (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SPh)<sub>12</sub>, (py)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub>, and (py)<sub>8</sub>Nd<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub> are described.

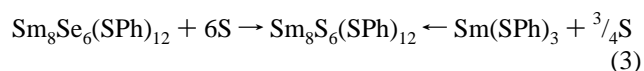
The displacement of PhSe by PhS on the edges of the cubic (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub> cluster is facile at room temperature (reaction 2). Addition of PhSSPh to a solution of (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>-



(SePh)<sub>12</sub>, prepared from the thermal decomposition of “(THF)<sub>x</sub>Sm(SePh)<sub>2</sub>” in THF, gives deep orange crystals of (THF)<sub>8</sub>Sm<sub>8</sub>-

Se<sub>6</sub>(SPh)<sub>12</sub> (**2**), which were isolated in 42% yield and characterized by conventional methods and low-temperature single-crystal X-ray diffraction (space group *P* $\bar{1}$ ). Cluster **2** contains the same structural framework (see Figure 1) as the all-sulfur analogue but crystallizes in a different unit cell (space group *I4/m*).

The Se<sup>2-</sup> ligands in (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SPh)<sub>12</sub> can be replaced with S<sup>2-</sup> by the reaction of the selenido clusters with S to give (THF)<sub>8</sub>Sm<sub>8</sub>S<sub>6</sub>(SPh)<sub>12</sub>, a cluster that has also been prepared<sup>6</sup> by the reaction of Sm(SPh)<sub>3</sub> with elemental S in the presence of trace Hg (reaction 3). This substitution appears complete within



minutes at room temperature, and the isolated compound was identical to the product isolated from the Sm(SPh)<sub>3</sub>/S reaction. The related reaction of the selenolate cluster Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub> with S did not give an isolable product.

The sulfido/selenolate complex can be prepared by the reaction of Sm(SePh)<sub>3</sub> with elemental S in THF. The isolated product, (THF)<sub>8</sub>Sm<sub>8</sub>S<sub>6</sub>(SePh)<sub>12</sub> (**1**), was characterized by low-temperature single-crystal X-ray diffraction. Cluster **1** contains the same octametallic framework and crystallizes in the same unit cell (space group *Pcab*) as the all-Se compound. The light yellow color of both the all-sulfur cluster and this S<sup>2-</sup>/SePh compound indicates that the deep orange color of the all-Se compound and the mixed Se<sup>2-</sup>/SPh clusters most likely results from Se<sup>2-</sup> to Sm charge transfer (CT) absorptions.

Neutral donors are also potential variables in tuning the chemical or physical properties of these cluster compounds. The octametallic Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub> cluster can be crystallized from solvents as strongly basic as pyridine with no apparent disruption of cluster structure. The reaction of Sm(SePh)<sub>3</sub> with Se in pyridine gives (py)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub> (**3**) in 4 times the yield of the analogous THF derivative. The pyridine cluster contains the same heavy-atom framework in which the SePh ligands still occupy bridging positions along the edges of the cube.

This chemistry can be extended to the non-redox-active lanthanides with an appropriate synthetic entry to selenido clusters. The reaction of Nd(SePh)<sub>3</sub> with elemental Se in

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**Table 2.** Summary of Average Bond Lengths (Å) in (L)<sub>8</sub>Sm<sub>8</sub>E<sub>6</sub>(E'Ph)<sub>12</sub> Clusters (Ranges in Parentheses)

compd	Sm–Sm	Sm–E <sup>2-</sup>	Sm–E(Ph)	D <sup>a</sup>
(THF) <sub>8</sub> Sm <sub>8</sub> S <sub>6</sub> (SePh) <sub>12</sub>	3.88 (3.83–3.93)	2.83 (2.74–2.89)	2.96 (2.93–3.00)	0.71 (0.67–0.77)
(THF) <sub>8</sub> Sm <sub>8</sub> S <sub>6</sub> (SPh) <sub>12</sub>	3.86 (3.85–3.86)	2.82 (2.79–2.86)	2.85 (2.83–2.89)	0.72 (0.72–0.72)
(THF) <sub>8</sub> Sm <sub>8</sub> Se <sub>6</sub> (SPh) <sub>12</sub>	3.98 (3.93–4.01)	2.88 (2.83–2.93)	2.92 (2.88–2.94)	0.79 (0.73–0.85)
(THF) <sub>8</sub> Sm <sub>8</sub> Se <sub>6</sub> (SePh) <sub>12</sub>	3.98 (3.93–4.03)	2.93 (2.85–2.97)	2.98 (2.92–3.02)	0.79 (0.73–0.86)
(py) <sub>8</sub> Sm <sub>8</sub> Se <sub>6</sub> (SePh) <sub>12</sub>	4.00 (4.00–4.01)	2.94 (2.91–2.95)	2.99 (2.86–3.19)	0.79 (0.77–0.80)

<sup>a</sup> Distance of E<sup>2-</sup> above the corresponding Sm<sub>4</sub> plane that it caps.

pyridine gives the analogous selenido cluster (py)<sub>8</sub>Nd<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub> (**4**), which was identified by low-temperature single-crystal X-ray diffraction. The light green-blue color of **4** is characteristic of Nd complexes, and the absence of any visible CT absorptions is additional proof of the Se<sup>2-</sup> to Sm CT assignment for **2** and **3** stated above.

## Discussion

The present work illustrates how neutral, anionic, and dianionic ligands can be systematically varied in chalcogenido cluster synthesis. The ability to selectively vary each ligand type is crucial to the goal of understanding the origin of cluster physical properties and, ultimately, the ability to selectively tailor such properties to deliver materials with specific characteristics. While these reactions have been studied in “ionic” systems, the general synthetic methodology should also apply to the more covalent metals.

The room temperature reaction of S with (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SPh)<sub>12</sub> to give the sulfido cluster (THF)<sub>8</sub>Sm<sub>8</sub>S<sub>6</sub>(SPh)<sub>12</sub> can be understood in terms of relative metal–chalcogen bond strengths. Replacement of Se<sup>2-</sup> by S<sup>2-</sup> creates four stronger Ln–S bonds and one weak Se–Se bond at the thermodynamic cost of breaking four weaker Ln–Se bonds and one stronger S–S bond (gas phase diatomic bond strengths in kcal/mol: SmS (93);<sup>15</sup> SmSe(79);<sup>16</sup> SS (102);<sup>17</sup> SeSe (80)<sup>18</sup>). From the relative magnitudes of M–E bond strengths, it is clear that this reaction should be extendable to the chalcogenido clusters of the more covalent metals, even when the surface chalcogenido ligands coordinate as few as one or two metal ions. Apparently edge bridging SPh ligands in Sm<sub>8</sub> clusters are relatively inert with respect to subsequent displacement by the elemental Se byproduct. The same reactivity is not observed when less stable SePh ligands span the cube corners: there is a clear reaction of SmSe<sub>6</sub>(SePh)<sub>12</sub> with elemental S, but no cluster products could be isolated from the reaction mixture. This chalcogenolate replacement reaction may also be useful in semiconductor cluster chemistry, when layered heterogeneous cluster structures (i.e., ZnS deposited on a CdS cluster core) are targeted in efforts to control cluster excited state lifetimes.<sup>14</sup>

Changing the steric and/or electronic properties of the ligands present in a solution cluster synthesis can effectively change the nature of an isolated product by influencing relative cluster solubilities.<sup>2,19</sup> In the present system, substitution of THF by pyridine was attempted in order to determine whether strongly

basic neutral donors could fragment or distort the Ln<sub>8</sub>E<sub>6</sub> core.<sup>20</sup> While “Sm(SePh)<sub>2</sub>” decomposes thermally in pyridine (as judged by the disappearance of the intense Sm(II) to pyridine charge transfer absorption), the reaction did not give an isolable product. Instead, the (py)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub> cluster was isolated in 24% yield from the reaction of Sm(SePh)<sub>3</sub> with excess Se in pyridine. A precise structural analysis of **3** was not possible because of a twinning-like disorder in the overall structure, but the derived results clearly indicate that all six Sm<sub>4</sub> faces are capped by Se<sup>2-</sup> ligands, that in the solid state the bridging selenolates still span the edges of the cube, and that there is only one py ligand coordinating to each Sm atom. While THF and pyridine may have similar steric properties, the greater base strength of the pyridine could have disrupted cluster structure by displacing μ<sub>2</sub>-SePh ligands, i.e., in the structures of dimeric [(py)<sub>2</sub>Sm(μ<sub>2</sub>-SePh)(SePh)<sub>2</sub>]<sub>2</sub> and polymeric [(THF)<sub>4/3</sub>Sm(μ<sub>2</sub>-SePh)<sub>3</sub>]<sub>n</sub>, where the stronger pyridine donor clearly displaces μ<sub>2</sub>-SePh more effectively than THF from the inner coordination sphere of a lanthanide ion (a similar but less dramatic effect is noted in the structures of polymeric [(THF)Sm(μ<sub>2</sub>-SPh)<sub>3</sub>]<sub>n</sub> and tetrameric (py)<sub>8</sub>Sm<sub>4</sub>(μ<sub>2</sub>-SPh)<sub>8</sub>(SPh)<sub>4</sub>).<sup>21</sup> The ability to incorporate pyridine ligands without disrupting cluster structure creates the possibility of preparing multidimensional cluster arrays by linking clusters with the multitude of commercially available 4-substituted pyridine ligands.

A comparison of the heterochalcogen compounds **1** and **2** with the all-sulfur and all-selenium compounds (THF)<sub>8</sub>Sm<sub>8</sub>S<sub>6</sub>(SPh)<sub>12</sub><sup>6</sup> and (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub><sup>5a</sup> provides an unprecedented opportunity to evaluate the relative influence of anionic ligands on structural properties, summarized in Table 2. From the table, three trends emerge. Most noticeably, bond geometries about the E<sup>2-</sup> ligands appear to be relatively insensitive to the identity of EPh, particularly for S<sup>2-</sup>, where there is virtually no change in average Sm–S bond length or the distance of E<sup>2-</sup> above the Sm<sub>4</sub> plane upon substitution of SPh for SePh. The size of the E<sup>2-</sup> ligand also appears to determine the distances between Sm(III) ions. Finally, there are significant variations in Sm–E<sup>2-</sup> bond lengths and Sm–EPh bond lengths within a given molecule, even though these bonds are chemically indistinguishable.

These significant variations in chemically equivalent Sm–E bond geometries indicate that bonding information based on structural data should be treated cautiously. For example, in the cubane cluster [(py)<sub>2</sub>YbSe(SePh)<sub>4</sub>] and the double cubane [(py)<sub>5</sub>Yb<sub>6</sub>S<sub>6</sub>(SPh)<sub>6</sub>] clusters each octahedral metal ion exhibited variations in Yb–E bond lengths that could be rationalized in terms of a trans influence. Still, the variations in Yb–E bond lengths (ca 0.04 Å) for the cubane clusters are smaller than the variations in Sm–E bond lengths in the present cluster compounds. While covalent effects should be less evident in a

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seven-coordinate structure (assuming involvement of metal p and d orbitals), the 0.10 Å range in chemically equivalent bond lengths found in the present work implies that Ln–E bond geometries are susceptible to lattice effects. This is not to say that the early or middle lanthanides cannot bond in a covalent fashion—the bis-arene Ln complexes<sup>7</sup> are examples in which covalent bonding is clearly important—but only that both chemical reactivity and spectroscopic properties should be evaluated when addressing the nature of the Ln–E bond. In this sense, the reactions reported here are consistent with predominantly ionic bonding.

The synthesis of cluster **4** by displacement of SePh with Se<sup>2-</sup> provides a reliable entry into the selenido cluster chemistry of the non-redox-active lanthanides. With this displacement reaction, all Ln<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub> clusters become viable synthetic targets, and subsequent reaction chemistry is plausible. Cluster **4** is also important for confirming the origin of the intense colors of **2** and **3**. In early chalcogenolate work, the colors of the redox-active Ln(EPh)<sub>3</sub> were first assigned by measuring the energy of the transition as a function of Ln and E.<sup>22</sup> The isostructural redox-inactive complexes were useful for establishing that the

transitions were metal dependent. Subsequent resonance Raman experiments on Ln(EPh)<sub>3</sub> (Ln = Sm, Yb; E = S, Se)<sup>21</sup> confirmed that LMCT absorptions were responsible for the intense red colors of Sm(SePh)<sub>3</sub>, Yb(SePh)<sub>3</sub>, and Yb(SPh)<sub>3</sub>. In the same fashion, given the intense colors of **2** and **3** and the characteristic light colors of **1**, **4**, and **5**, the visible color of the Sm selenido compounds can be assigned as a Se<sup>2-</sup> to Sm CT excitation.

### Conclusion

Every component of a Ln<sub>8</sub>E<sub>6</sub>EPh<sub>12</sub> cluster is a potential variable: chalcogenido, chalcogenolate, and neutral donors can be systematically varied to give cluster derivatives with the same octametallate core, and this versatility is useful for identifying the origins of cluster physical properties, i.e., the lowest energy electronic transitions are E<sup>2-</sup> (and not EPh) to Ln CT absorptions. The reactivity appears to be dominated by ionic considerations with smaller, highly charged ligands coordinating preferentially to the Ln(III) ion.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for the crystal structures of (py)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub>, (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SPh)<sub>12</sub>, and (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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