

## Lanthanide–Transition Metal Chalcogenido Cluster Materials

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[(THF)<sub>3</sub>Sm(SePh)<sub>2</sub>Zn(SePh)<sub>2</sub>]<sub>n</sub> decomposes to give a variety of products, including [(THF)<sub>8</sub>Sm<sub>4</sub>Se(SePh)<sub>8</sub>]<sup>2+</sup>[Zn<sub>8</sub>Se(SePh)<sub>16</sub>]<sup>2-</sup>, an ionic cluster that can also be prepared in more than 60% yield by stoichiometric addition of Se to a mixture of Sm(SePh)<sub>3</sub> and Zn(SePh)<sub>2</sub>. The isostructural Nd compound [(THF)<sub>8</sub>Nd<sub>4</sub>Se(SePh)<sub>8</sub>]<sup>2+</sup>[Zn<sub>8</sub>Se(SePh)<sub>16</sub>]<sup>2-</sup> was also prepared by the stoichiometric route to establish the viability of this cluster type with redox-inactive Ln. In addition, the salt [Yb(THF)<sub>6</sub>]<sup>3+</sup>[Fe<sub>4</sub>Se<sub>4</sub>(SePh)<sub>4</sub>]<sup>3-</sup> was isolated and structurally characterized. These ionic cluster materials illustrate the difficulties associated with doping Ln ions into covalent metal chalcogenido matrices.

## Introduction

Doping of lanthanide (Ln) ions into ME matrixes (M = main group or transition metal; E = S, Se, Te) is a challenging materials synthesis goal inspired by the potential utility of such doped products as light emitting devices<sup>1</sup> or optical fibers.<sup>2</sup> Such Ln-doped materials are viable synthetic targets, but a detailed understanding of the problems associated with this preparative work remains unclear. While it is certainly known that chalcogenido matrixes do not readily incorporate Ln ions, the manner by which Ln interacts with a ME matrix, or the mechanisms by which Ln ions manage to avoid these interactions, is ambiguous on a molecular level.

In simple heterometallic chalcogenolate chemistry, the tendency for Ln–E bonds to cleave has already been

established. EPh can be displaced by “weaker” Lewis bases from Ln coordination spheres, if there is a material present that can coordinate to and thus stabilize the displaced EPh; i.e., Ln(SePh)<sub>2</sub> will react with group 12 metal selenolates to form ionic compounds such as [Yb(THF)<sub>6</sub>][Hg<sub>5</sub>(SePh)<sub>12</sub>] or [Sm(THF)<sub>7</sub>][Zn<sub>4</sub>(SePh)<sub>10</sub>].<sup>3</sup> The relative strengths of the different metal–chalcogen bonds were thought to be important factors governing a product’s molecular structure, with Ln–S bonds cleaving less readily<sup>4,5</sup> than Ln–Se bonds, and Zn(II) extracting EPh more effectively than Hg(II). In this series of compounds, only Ln(II)–SePh bonds were found to cleave, with stronger LnSe bonds to Ln(III) remaining intact.<sup>6</sup>

Recent experiments show that Ln(EPh)<sub>3</sub> react readily with EE bonds to reduce the EE bond and oxidatively eliminate PhEPh.<sup>7</sup> The only products of these reactions thus far obtained have been lanthanide chalcogenido clusters or solid-state LnE<sub>x</sub>. The utility of this reactivity for doping Ln into main group or transition metal chalcogenido materials has yet to be explored in detail.

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Presented here are our initial experiments illustrating the challenges associated with heterometallic Ln/ME syntheses. We outline the preparation and characterization of two different types of heterometallic Ln/M ( $M = \text{Zn}, \text{Fe}$ ) compounds, and from the observed reactivity we propose conditions that should be useful in the synthesis of heterometallic materials.

## 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 were collected immediately prior to use. Anhydrous pyridine (Aldrich) was purchased and refluxed over KOH. Nd, Sm, Yb, Se, Hg, and Zn were purchased from Strem. PhSeSePh was purchased from Acros and recrystallized from hexane. Melting points were taken in sealed capillaries and are uncorrected. IR spectra were taken on a Mattus Cygnus 100 FTIR or Thermo Nicolet Avatar 360 FT-IR spectrometer, and were recorded from 4000 to 500  $\text{cm}^{-1}$  as a Nujol mull on NaCl 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 thermally sensitive and when isolated will lose both lattice and coordinated tetrahydrofuran (THF) molecules.

**Synthesis of  $[(\text{THF})_8\text{Sm}_4\text{Se}(\text{SePh})_8][\text{Zn}_8\text{Se}(\text{SePh})_{16}] \cdot 6\text{THF}$  (1).** Method A, from thermal decomposition of  $[(\text{THF})_3\text{Sm}(\text{SePh})_2\text{Zn}(\text{SePh})_2]_n$ : Zn (0.13 g, 2.0 mmol) and  $(\text{SePh})_2$  (0.94 g, 3.0 mmol) were combined in THF (50 mL) with a catalytic amount of Hg (0.035 g). The mixture was stirred until all the metal was consumed to give an opaque yellow solution. Sm (0.150 g, 1.0 mmol) was then added and the mixture was stirred until the Sm dissolved (4 days), resulting in a black-brown solution. The solution was allowed to settle for 1 week and a tiny amount of black precipitate fell out. The black-brown solution was filtered (50 mL) and layered with hexanes (5 mL) to give yellow needles (0.69 g, 46%) of **1**. Method B, by reduction of Se with  $\text{Sm}(\text{SePh})_3/\text{Zn}(\text{SePh})_2$ : Zn (0.13 g, 2.0 mmol), PhSeSePh (1.09 g, 3.5 mmol), and Hg (0.05 g, 0.25 mmol) were combined in THF (60 mL). The mixture was stirred until all the metal was consumed to give a yellow solution and white precipitate. Metallic Sm (0.15 g, 1.0 mmol) was added and the mixture was stirred until all Sm metal was consumed, giving a deep orange-brown solution. Powdered Se (0.04 g, 0.5 mmol) was then added, and within 10 min the solution became bright orange and all the Se was consumed. The mixture was filtered as soon as the Se was no longer visible, after which yellow needles of **1** precipitated (3.9 g, 64%; mp 292 °C (dec)). Anal. Calcd for  $\text{C}_{200}\text{H}_{232}\text{O}_{14}\text{Se}_{34}\text{Sm}_4\text{Zn}_8$ : C, 39.9; H, 3.87. Found: C, 40.3; H, 4.13. Once isolated, the compound is insoluble in THF and does not have a resolved UV-visible absorption maximum in pyridine. IR (Nujol): 2927 (w), 2724 (s), 1784 (s), 1571 (s), 1461 (m), 1377 (m), 1261 (s), 1198 (s), 1168 (m), 1018 (m), 971 (s), 800 (s), 723 (m), 688 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{C}_5\text{D}_5\text{N}$ , 20 °C): 8.05 (6H), 7.00 (9H), 3.60 (7H), 1.58 (7H). These integrations depend on the length of time the compound has been isolated from the mother liquor, with the THF intensities decreasing as the isolation time increases, presumably due to loss of lattice THF.

**Synthesis of  $[(\text{THF})_8\text{Nd}_4\text{Se}(\text{SePh})_8][\text{Zn}_8\text{Se}(\text{SePh})_{16}] \cdot 6\text{THF}$  (2).** Zn (0.262 g, 4.0 mmol) and  $(\text{SePh})_2$  (1.249 g, 4.0 mmol) were combined in THF (40 mL) with a catalytic amount of Hg (0.032 g). The mixture was stirred until all the metal was consumed (5

days) to give an opaque white solution. Nd (0.288 g, 2.0 mmol) and  $(\text{SePh})_2$  (0.936 g, 3.0 mmol) were then added to the solution, and the mixture was stirred until the Nd dissolved (1 day), resulting in a transparent teal solution. Elemental Se (0.080 g, 1.0 mmol) was added and the mixture was stirred for 5 min. The solution turned translucent lime green and some black precipitate was noted. The lime green solution was filtered (40 mL) and cooled (5 °C, 1 month; -15 °C, 1 month). Returning the sample to room temperature resulted in the formation of thin blue lathes (1.1 g, 37%) that turn yellow-green and melt at 248 °C. Anal. Calcd for  $\text{C}_{200}\text{H}_{232}\text{O}_{14}\text{Nd}_4\text{Se}_2\text{Zn}_8$ : C, 39.9; H, 3.89. Found: C, 38.0; H, 3.83. The compound shows an optical absorption maximum at 593 nm in pyridine and is insoluble in THF. IR: 2927 (w), 2856 (w), 1784 (s), 1573 (s), 1467 (m), 1377 (s), 1260 (s), 1097 (s), 1068 (s), 1020 (m), 851 (s), 801 (s), 732 (s), 689 (s), 665 (s)  $\text{cm}^{-1}$ .

**Synthesis of  $[\text{Yb}(\text{THF})_6][\text{Fe}_4\text{Se}_4(\text{SePh})_4]$  (3).** Yb (346 mg, 2.0 mmol), iron(II) iodide (310 mg, 1.0 mmol), and PhSeSePh (936 mg, 3.0 mmol) were stirred in THF (50 mL) for 20 h to give a black/brown solution. Elemental Se (237 mg, 3.0 mmol) was added, and after 3 h the resultant black/red mixture was filtered. The filtrate was concentrated to 43 mL and layered with hexanes (15 mL) to give black hexagonal crystals (1.3 g, 37%) that melted at 174 °C. Anal. Calcd for  $\text{C}_{48}\text{H}_{68}\text{Fe}_4\text{O}_6\text{Se}_8\text{Yb}$ : C, 32.6; H, 3.87. Found: C, 31.4; H, 3.81. UV-vis (pyr): 487 (3.89  $\times 10^2$ ) nm. The compound is not soluble in THF. IR: 3658 (s), 3583 (s), 2727 (s), 2285 (s), 1788 (s), 1642 (m), 1571 (s), 1463 (w), 1377 (w), 1366 (m), 1357 (m), 1261 (s), 1169 (s), 1065 (m), 1017 (s), 859 (s), 803 (s), 775 (s), 722 (s)  $\text{cm}^{-1}$ .

**X-ray Structure Determinations of 1, 2, and 3.** Data for **1**, **2**, and **3** were collected on a Bruker Smart APEX CCD diffractometer with graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 100 K. The data were corrected for Lorentz effects and polarization, and absorption, the latter by a multiscan (SADABS)<sup>8</sup> method. The structures were solved by Patterson or direct methods (SHELXS86).<sup>9</sup> All non-hydrogen atoms were refined (SHELXL97)<sup>10</sup> based upon  $F_{\text{obs}}^2$ . All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97). Scattering factors ( $f_o, f', f''$ ) were as described in SHELXL97. Crystallographic data and final  $R$  indices for **1**, **2**, and **3** are given in Table 1. ORTEP diagrams<sup>11</sup> for **1** and **3** are shown in Figures 1 and 2, respectively. Significant bond geometries for **1** and **3** are given in the figure captions. Complete crystallographic details for **1–3** are given in the Supporting Information.

## Results

The complex cluster  $[(\text{THF})_8\text{Sm}_4\text{Se}(\text{SePh})_8][\text{Zn}_8\text{Se}(\text{SePh})_{16}]$  (**1**) can be isolated from two different synthetic approaches. In the first method, thermal decomposition of  $[(\text{THF})_3\text{Sm}(\text{SePh})_2\text{Zn}(\text{SePh})_2]_n$ <sup>12</sup> results in reductive cleavage of C–Se bonds to give two isolable Sm(III) products. The major product was isolated manually and identified by low-temperature single-crystal X-ray diffraction as  $(\text{THF})_8\text{Sm}_8$ -

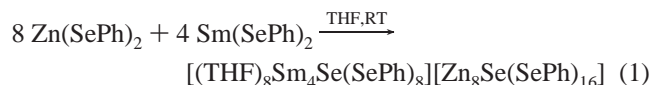
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**Table 1.** Summary of Crystallographic Details for **1**, **2**, and **3**

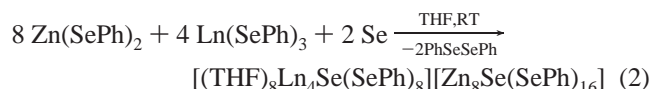
	<b>1</b>	<b>2</b>	<b>3</b>
empirical formula	C <sub>200</sub> H <sub>232</sub> Sm <sub>4</sub> -O <sub>14</sub> Se <sub>26</sub> Zn <sub>8</sub>	C <sub>200</sub> H <sub>232</sub> Nd <sub>4</sub> -O <sub>14</sub> Se <sub>26</sub> Zn <sub>8</sub>	C <sub>48</sub> H <sub>68</sub> Fe <sub>4</sub> -O <sub>6</sub> Se <sub>8</sub> Yb
fw	6037.18	6012.74	1769.14
space group	P $\bar{1}$	P $\bar{1}$	Cc
<i>a</i> (Å)	18.8341(8)	18.8674(15)	13.8219(7)
<i>b</i> (Å)	20.1465(8)	20.2111(16)	19.975(1)
<i>c</i> (Å)	28.455(1)	28.431(2)	21.508(1)
$\alpha$ (deg)	76.388(1)	76.455(2)	90.00
$\beta$ (deg)	87.251(1)	87.358(2)	100.724(1)
$\gamma$ (deg)	86.481(1)	86.445(2)	90.00
<i>V</i> (Å <sup>3</sup> )	10468(1)	10514(1)	5834.5(5)
<i>Z</i>	2	2	4
<i>D</i> (calcd) (g/cm <sup>-3</sup> )	1.915	1.899	2.014
temperature (K)	100(2)	100(2)	100(2)
$\lambda$ (Å)	0.71073	0.71073	0.71073
abs coeff (mm <sup>-1</sup> )	6.577	6.419	7.591
<i>R</i> ( <i>F</i> ) <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.054	0.050	0.038
<i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> ) <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.107	0.117	0.071

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

Se<sub>6</sub>(SePh)<sub>12</sub>,<sup>7a</sup> a cluster originally isolated from the thermal decomposition of “Sm(SePh)<sub>2</sub>”. A second product was also isolated by hand, subjected to a low-temperature single-crystal X-ray diffraction experiment, and identified as **1**, an ionic compound with a 4 Sm dication and an 8 Zn dianion. Figure 1 shows an ORTEP diagram of **1**, and significant bond lengths are given in the figure caption. In this C–Se bond cleavage reaction the isolation of pure **1** in higher yield can be accomplished by starting with a 1:2 Sm(SePh)<sub>2</sub>:Zn(SePh)<sub>2</sub> ratio (reaction 1).



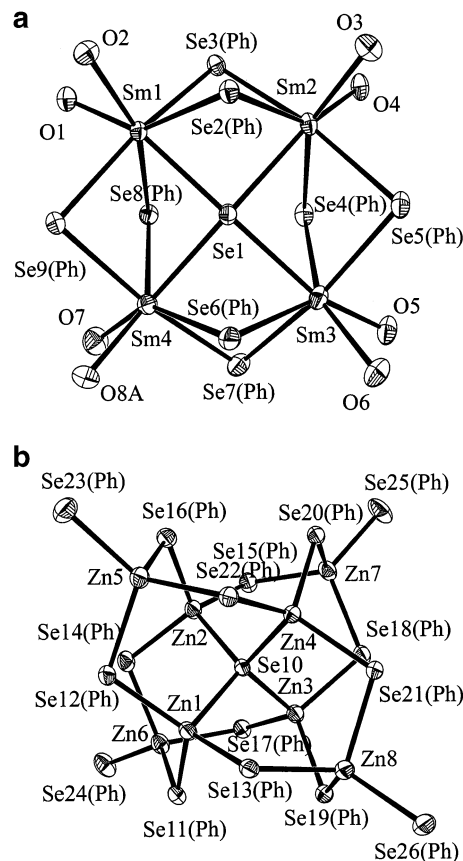
The same heterometallic product can also be prepared by the reaction of a stoichiometric mixture of Zn(SePh)<sub>2</sub>/Sm(SePh)<sub>3</sub> with Se in THF at room temperature (reaction 2).



The compound reacts with water or oxygen and loses coordinated THF within minutes of isolation.

The isostructural Nd compound [(THF)<sub>8</sub>Nd<sub>4</sub>Se(SePh)<sub>8</sub>]-[Zn<sub>8</sub>Se(SePh)<sub>16</sub>] (**2**) was also prepared by stoichiometric combination of Nd/Zn/Se/SePh and isolated as pale blue crystals in 37% yield. Structural analysis of this compound established the identity of the product and demonstrated the viability of this product class with redox-inactive Ln. The light blue color of **2** confirms that the deep yellow color of **1** is in some way associated with the redox activity of Sm [i.e., Se to Sm charge transfer (CT)].

In a separate but similar vein, attempts to produce heterometallic cubane clusters containing Ln and Fe led to the isolation and characterization of [Yb(THF)<sub>6</sub>][Fe<sub>4</sub>Se<sub>4</sub>(SePh)<sub>4</sub>] (**3**). In this synthesis, Yb metal reduces PhSeSePh in the presence of FeI<sub>2</sub>, and the resultant mixture is then used to reduce elemental Se. There is no iodide in the final

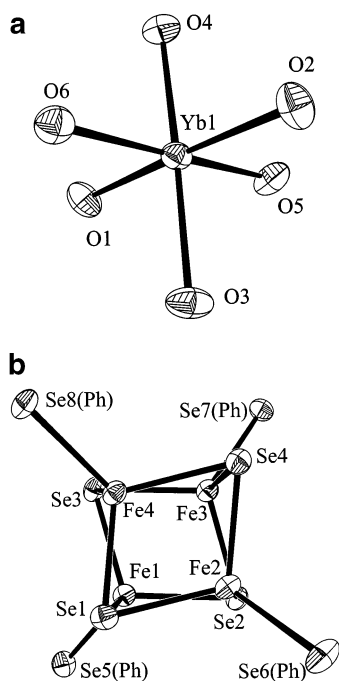


**Figure 1.** Core molecular structure of the cation (a) and anion (b) in [(THF)<sub>8</sub>Ln<sub>4</sub>Se(SePh)<sub>8</sub>][Zn<sub>8</sub>Se(SePh)<sub>16</sub>] (Ln = Sm, Nd), with the C and H atoms removed for clarity. Thermal ellipsoids are drawn at the 50% probability level for the Sm compound. Significant distances (Å) for **1**: Sm(1)–O(2), 2.415(6); Sm(1)–O(1), 2.419(6); Sm(1)–Se(1), 2.9123(11); Sm(1)–Se(3), 2.9400(11); Sm(1)–Se(9), 2.9514(11); Sm(1)–Se(8), 2.9907(11); Sm(1)–Se(2), 2.9908(11); Sm(1)–Sm(2), 4.0810(7); Sm(2)–O(4), 2.391(6); Sm(2)–O(3), 2.438(7); Sm(2)–Se(4), 2.9499(11); Sm(2)–Se(1), 2.9532(11); Sm(2)–Se(2), 2.9551(11); Sm(2)–Se(5), 2.9856(12); Sm(2)–Se(3), 2.9929(11); Sm(3)–O(5), 2.419(6); Sm(3)–O(6), 2.425(7); Sm(3)–Se(1), 2.9355(11); Sm(3)–Se(5), 2.9360(12); Sm(3)–Se(7), 2.9519(11); Sm(3)–Se(6), 2.9692(11); Sm(3)–Se(4), 3.0011(12); Sm(3)–Sm(4), 4.0959(7); Sm(4)–O(7), 2.385(7); Sm(4)–O(8A), 2.389(5); Sm(4)–Se(1), 2.9243(11); Sm(4)–Se(8), 2.9489(12); Sm(4)–Se(7), 2.9761(12); Sm(4)–Se(6), 2.9831(11); Sm(4)–Se(9), 2.9958(11).

product, which was identified by low-temperature single-crystal X-ray diffraction as **3**. Figure 2 shows an ORTEP diagram of **3**, and significant bond lengths are given in the figure caption. This ionic product contains an octahedral Yb(THF)<sub>6</sub> ion that is clearly trivalent, as judged by the average 2.38 Å Yb–O bond length that is approximately 0.15 Å shorter than the examples of Yb(THF)<sub>6</sub><sup>2+</sup> that have average Yb–O bond lengths of 2.53 Å.<sup>3,13</sup> The cation in **3** is totally unconnected with the heterovalent selenido cubane anion, which contains four chemically equivalent Fe ions with an average oxidation state of 2.25.

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**Figure 2.** Core molecular structure of the cation (a) and anion (b) in  $[\text{Yb}(\text{THF})_6][\text{Fe}_4\text{Se}_4(\text{SePh})_4]$  with thermal parameters shown at the 50% probability level, and the C/H atoms removed for clarity. Significant distances (Å): Yb(1)–O(6), 2.358(5); Yb(1)–O(2), 2.374(5); Yb(1)–O(1), 2.372(5); Yb(1)–O(4), 2.381(5); Yb(1)–O(3), 2.387(5); Yb(1)–O(5), 2.390(5); Fe(1)–Se(3), 2.3573(12); Fe(1)–Se(5), 2.3843(12); Fe(1)–Se(1), 2.4235(12); Fe(1)–Se(2), 2.4240(12); Fe(1)–Fe(3), 2.7741(14); Fe(1)–Fe(4), 2.7873(14); Fe(1)–Fe(2), 2.7918(14); Fe(2)–Se(4), 2.3754(12); Fe(2)–Se(6), 2.4055(12); Fe(2)–Se(1), 2.4295(12); Fe(2)–Se(2), 2.4340(12); Fe(2)–Fe(3), 2.7769(13); Fe(2)–Fe(4), 2.7928(14); Fe(3)–Se(2), 2.3783(12); Fe(3)–Se(7), 2.3942(12); Fe(3)–Se(3), 2.4144(12); Fe(3)–Se(4), 2.4391(12); Fe(3)–Fe(4), 2.7275(14); Fe(4)–Se(1), 2.3659(12); Fe(4)–Se(8), 2.4009(12); Fe(4)–Se(4), 2.4243(12); Fe(4)–Se(3), 2.4341(12).

## Discussion

Clusters **1**–**3** clearly exemplify the chalcophobic nature of Ln ions and the disparate behavior of ionic and covalent metals. In **1** and **2**, selenium-based anionic charge is separated from the Sm core by the cluster of Zn(II) ions, in chemistry that parallels heterometallic Ln/M chalcogenolate reactivity.<sup>3</sup> The Sm fragment is structurally related to the heterovalent (two  $\text{Sm}^{2+}$ , two  $\text{Sm}^{3+}$ ) cluster compound  $(\text{DME})_4\text{Sm}_4\text{Se}(\text{SePh})_8$  (**4**).<sup>14</sup> One significant structural difference between **1** and **4** is the change in average Sm–L bond lengths (Sm– $\text{Se}^{2-} = 2.93$  (**1**), 2.93 (**4**); Sm–Se(Ph) = 2.97 (**1**), 3.04 (**4**); Sm–O = 2.41 (**1**), 2.52 (**4**)) that result from complete oxidation of all the Sm's and the accompanying contraction of ionic radii. The smaller Sm(III) ions in **1** have a most noticeable influence on the readily distorted (and chemically inequivalent) Sm–O bonds and a significant, but less dramatic, impact on the Sm–Se(Ph) bonds. There is virtually no difference in the Sm– $\text{Se}^{2-}$  bond lengths.

The absence of divalent Sm in **1** also has a significant influence on the color of the cluster fragment (black (**4**) and yellow (**1**)), due to the elimination of all electronic transitions associated with the presence of Sm(II) ions (i.e.,  $f^6 \rightarrow f^5d^1$

or Sm(II)–Sm(III) CT). In **1**, the only allowed electronic transition that falls in the visible spectrum is a Se to Sm(III) CT absorption.<sup>15</sup> This absorption is not resolved in the spectrum of **1** in pyridine, but from the pale blue color of the Nd(III) analogue **2** it is clear that the more intense color in **1** is in some way associated with redox activity.

The Zn anion is structurally related to a series of  $\text{Zn}_8\text{Se}$  clusters,<sup>16</sup> including  $[\text{Zn}_8\text{Cl}_4\text{Se}(\text{SePh})_{12}]^{2-}$  and charge neutral  $\text{Zn}_8\text{Se}(\text{SePh})_{14}(\text{PPR}_3)_2$ . As is almost always the case, the Zn ions adopt clearly tetrahedral geometries, maximizing the number of metals with four bonds to Se.

Clusters **1** and **2** represent a plausible visualization of the process by which heterometallic precursors decompose to give separate metal chalcogenide solids, as noted in the synthesis of  $\text{EuS/MS}$  ( $M = \text{Zn}, \text{Cd}$ ) from the thermal decomposition of  $\text{Eu}_2\text{M}_2(\text{SPh})_8$  ( $M = \text{Zn}, \text{Cd}, \text{Hg}$ ) molecules.<sup>4</sup> Heterometallic **1** and **2** clearly demonstrate that phase separation can commence at an early stage of solid-state lattice construction.

Just as the individual cluster components in **1** and **2** have related structures in the literature, so too have the anion and cation in **3**. Tri-anion  $[\text{FeSe}(\text{SePh})]^{3-}$  is the only structurally characterized all-selenium cluster within the well-established iron cubane series, but analogous  $[\text{FeS}(\text{SR})]_4^{3-}$ ,<sup>17</sup>  $[\text{FeSe}(\text{SR})]_4^{3-}$ ,<sup>18</sup> and  $[\text{FeTe}(\text{SR})]_4^{3-}$  tri-anions<sup>19</sup> have all been characterized by diffraction methods. For the cationic fragment, there are a number of structurally characterized compounds with  $\text{Yb}(\text{THF})_6^{2+}$  cations,<sup>3,13</sup> but this is the first example of a trivalent Yb that is stable as a THF solvate. Isolation of totally solvated Ln ions is not unprecedented in trivalent lanthanide coordination chemistry, i.e., in solution when  $\text{YbI}_3$  is dissolved in particularly strong donor solvents to form 1:3 electrolytes.<sup>20</sup>

With the structure of **1**, **2**, and **3** we can define important guidelines for the development of successful synthetic approaches to Ln-doped main group chalcogenido cluster and solid-state materials. First, high donor strength solvents should be avoided in order to decrease the relative stability of solvated Ln cations.<sup>3,13,21</sup> Second, the use of more electronegative ancillary ligands (i.e., I or SPh rather than SePh) should favor the formation of charge-neutral heterometallic compounds, because ligands having the stronger Ln–I or Ln–S bonds are not as readily abstracted by main group metals. Finally, excess main group metal chalcogeno-

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late should be avoided, so that anionic charge cannot be delocalized over a number of covalent metal centers. Investigations along these lines are currently in progress.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for the crystal structures of **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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