

## Divalent Samarium Compounds with Heavier Chalcogenolate (EPh; E = Se, Te) Ligands

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Crystalline coordination complexes of Sm(EPh)<sub>2</sub> (E = Se, Te) are described. The selenolate compound Sm(SePh)<sub>2</sub> is unstable in solution, but a divalent selenolate can be prepared and isolated when precisely 1 equiv of Zn(SePh)<sub>2</sub> is present to form heterometallic [(THF)<sub>3</sub>Sm(μ<sub>2</sub>-SePh)<sub>3</sub>Zn(μ<sub>2</sub>-SePh)]<sub>n</sub> (**1**). This compound is a 1D coordination polymer with alternating Sm(II) and Zn(II) ions connected by an alternating (1,3) number of bridging selenolate ligands and three THF ligands bound to each Sm(II) ion. The tellurolate Sm(TePh)<sub>2</sub> forms a stable pyridine coordination compound (py)<sub>5</sub>Sm(TePh)<sub>2</sub> (**2**) that is isostructural with known Eu and Yb benzenetellurolates. Both compounds were characterized by conventional spectroscopic methods. Polymer **1** was characterized by low-temperature single-crystal X-ray diffraction, and the unit cell of the tellurolate was determined. Crystal data (Mo Kα, 153(5) K) are as follows. **1**: monoclinic space group *P2*<sub>1</sub>, *a* = 10.666(2) Å, *b* = 16.270(3) Å, *c* = 12.002(3) Å, β = 114.81(2)°, *Z* = 2. **2**: orthorhombic space group *Pbca*, with *a* = 13.865(3) Å, *b* = 16.453(5) Å, *c* = 31.952(7) Å, *Z* = 8.

### Introduction

Lanthanide (Ln) chalcogenolate (Ln(ER)<sub>x</sub>; E = S, Se, Te; *x* = 2, 3; R = Ph,<sup>1–11</sup> aryl,<sup>12–17</sup> SiR<sub>3</sub>,<sup>18–20</sup> 2-E-NC<sub>5</sub>H<sub>4</sub>,<sup>21–23</sup> alkyl<sup>24,25</sup>) chemistry has developed rapidly in the past few years, motivated by the potential utility of such compounds for doping

Ln ions into chalcogenido matrices. These molecules are also excellent subjects for probing the nature of the Ln–E bond. In addition to the relatively straightforward trivalent chalcogenolate chemistry of the redox active and inactive Ln(ER)<sub>3</sub> compounds,<sup>7–11,14–19,21–25</sup> considerable effort has been devoted toward determining the chemistry of Ln(ER)<sub>2</sub> (Ln = Sm, Eu, Yb).<sup>1–8,12–14,20–22</sup> The simple benzenechalcogenolate (R = Ph) ligands have been particularly useful for the synthesis of well-defined Ln(II) coordination compounds, but while compounds of Eu(EPh)<sub>2</sub><sup>1,2</sup> and Yb(EPh)<sub>2</sub><sup>2,3</sup> were among the first crystallographically characterized Ln(II) chalcogenolates to be described, the corresponding compounds of Sm have been more elusive.

Initial attempts to prepare simple coordination complexes of Sm(SePh)<sub>2</sub> in either THF or pyridine were unsuccessful. Related Lewis base adducts of Sm(SeR)<sub>2</sub> (R = Si(SiMe<sub>3</sub>)<sub>3</sub>;<sup>20</sup> 2,4,6-tri-*i*-prC<sub>6</sub>H<sub>2</sub><sup>13</sup>) have been isolated successfully, but the analogous Sm(SePh)<sub>2</sub> was found to decompose thermally (at room temperature) to give selenido clusters,<sup>26,27</sup> presumably by reduction of the Se–C(Ph) bond and oxidation of the Sm(II) ion. In weakly basic DME, the mixed valent, tetranuclear cluster (DME)<sub>4</sub>Sm<sub>4</sub>(Se)(SePh)<sub>8</sub> has been isolated, while in more basic solvents, the larger octanuclear cluster (THF)<sub>8</sub>Sm<sub>8</sub>Se<sub>6</sub>(SePh)<sub>12</sub> has been isolated. There is no information related to the stability of the analogous SPh and TePh compounds.

Given the utility of Sm(II) compounds as one-electron reducing agents in organic syntheses<sup>28–36</sup> or as redox active

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precursors to Ln chalcogenido clusters,<sup>37–41</sup> the Sm(EPh)<sub>2</sub> compounds are desirable synthetic targets. In this work we describe the high-yield synthesis of crystalline coordination compounds containing Sm(II) ions coordinated to the heavier benzenechalcogenolate EPh (E = Se, Te) ligands.

### 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 was purchased from either Aldrich or Strem and recrystallized from hexane. PhTeTePh was prepared according to literature procedures.<sup>42,43</sup> 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 each compound, several crystals were examined by single-crystal X-ray diffraction and consistently gave the same unit cell.

**Synthesis of [(THF)<sub>3</sub>Sm(μ<sub>2</sub>-SePh)<sub>3</sub>Zn(μ<sub>2</sub>-SePh)]<sub>n</sub> (1).** Zinc metal (0.13 g, 2.0 mmol), diphenyl diselenide (1.25 g, 4.0 mmol), and mercury (0.05 g, 0.25 mmol) were combined in THF (50 mL). After all the zinc had reacted (ca. 1 day) to give a pale-yellow solution/precipitate, samarium metal (0.30 g, 2 mmol) was added. After 2 days the resultant dark-green solution was filtered, concentrated (35 mL), and allowed to sit at room temperature (RT) to give dark-green crystals (1.0 g, 47%; the compound melts with decomposition and turns red at ca. 183 °C, then slowly turns orange at 220 °C). Anal. Calcd for C<sub>36</sub>H<sub>44</sub>O<sub>3</sub>Se<sub>4</sub>SmZn: C, 40.9; H, 4.21. Found: C, 40.1; H, 4.06. <sup>1</sup>H NMR (OC<sub>4</sub>D<sub>8</sub>, 20 °C) revealed phenyl resonances at 9.03 (2H), 7.50 (1H), and 6.83 ppm (2H). IR: 2924 (s), 2861 (s), 2361 (w), 1571(m), 1464 (s), 1382 (s), 1262 (w), 1069 (m), 1033 (m), 1020 (m), 875 (w), 825 (w), 800 (w), 739 (m), 729 (m), 691 (m), 665 (w) cm<sup>-1</sup>. λ<sub>max</sub> (THF): 612 (w<sub>1/2</sub> = 153 nm), 398 (w<sub>1/2</sub> = 125 nm). Reliable molar absorptivities were not obtainable because the compound does not redissolve readily.

**Synthesis of (py)<sub>5</sub>Sm(TePh)<sub>2</sub> (2).** Sm (0.30 g, 2.0 mmol) and diphenylditelluride (0.82 g, 2.0 mmol) were added to pyridine (50 mL), and the mixture was stirred for 2 days. The resultant black-orange solution was filtered and cooled (-6 °C) to give black (orange) crystals of **3** (1.27 g, 67%; mp 130 °C). Anal. Calcd for C<sub>37</sub>H<sub>35</sub>N<sub>5</sub>SmTe<sub>2</sub>: C, 46.5; H, 3.74; N, 7.33. Found: C, 46.1; H, 3.47; N, 7.60. <sup>1</sup>H NMR (OC<sub>4</sub>D<sub>8</sub>, 20 °C) showed only the pyridine resonances at 8.54 (2H), 7.65 (1H), 7.26 (2H) ppm. IR: 2932 (s), 2724 (w), 2673 (w), 2361

**Table 1.** Summary of Crystallographic Details for [(THF)<sub>3</sub>Sm(μ<sub>2</sub>-SePh)<sub>3</sub>Zn(μ<sub>2</sub>-SePh)]<sub>n</sub> (1)

empirical formula	C <sub>36</sub> H <sub>44</sub> O <sub>3</sub> Se <sub>4</sub> SmZn
fw	1056.27
space group (No.)	P2 <sub>1</sub> (4)
a (Å)	10.666(2)
b (Å)	16.270(3)
c (Å)	12.002(3)
α (deg)	90.00(2)
β (deg)	114.81(2)
γ (deg)	90.00(2)
V (Å <sup>3</sup> )	1891(1)
Z	2
D(calcd) (g/cm <sup>-3</sup> )	1.856
temp (K)	153
λ (Å)	0.710 73
abs coeff (mm <sup>-1</sup> )	6.056
R(F) <sup>a</sup> [I > 2σ(I)]	0.037
R <sub>w</sub> (F <sup>2</sup> ) <sup>a</sup> [I > 2σ(I)]	0.081

<sup>a</sup> R(F) = Σ||F<sub>o</sub> - |F<sub>c</sub>||/Σ|F<sub>o</sub>|; R<sub>w</sub>(F<sup>2</sup>) = {Σ[w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ[w(F<sub>o</sub><sup>2</sup>)<sup>2</sup>]}<sup>1/2</sup>. Additional crystallographic details are given in the Supporting Information.

(m), 2342 (w), 1579 (m), 1461 (s), 1378 (s), 1314 (w), 1261 (w), 1216 (m), 1145 (w), 1067 (w), 1031 (m), 801 (w), 732 (m), 701 (s), 634 (s) cm<sup>-1</sup>. λ<sub>max</sub> (THF): 614 (w<sub>1/2</sub> = 292 nm, ε = 550 L mol<sup>-1</sup> cm<sup>-1</sup>), 307 nm. Unit cell (Mo Kα, -120 °C): space group *Pbca*, with a = 13.865(3) Å, b = 16.453(5) Å, c = 31.952(7) Å, V = 7289(3) Å<sup>3</sup>. Addition of 0.5 equiv of PhTeTePh to a solution of **2** results in no color change, and extraction of the reaction mixture with hexane followed by evaporation of the hexane reclaims the 0.5PhTeTePh.

**X-ray Structure Determination of 1.** Data for **1** were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.710 73 Å) at -120 °C. The check reflections measured every hour showed less than 3% intensity variation. The data were corrected for Lorentz effects and polarization, and absorption, the latter by a numerical (SHELX76)<sup>44</sup> method. The structure was solved by direct methods (SHELXS86).<sup>45</sup> All non-hydrogen atoms were refined (SHELXL97) on the basis of F<sub>obs</sub><sup>2</sup>. All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97).<sup>46</sup> Scattering factors (f<sub>o</sub>, f', f'') are as described in SHELXL97. Crystallographic data and final R indices for **1** are given in Table 1. Significant bond distances and angles for **1** are given in Table 2. Complete crystallographic details are given in the Supporting Information. An ORTEP diagram<sup>47</sup> for the common repeating unit of **1** is shown in Figure 1.

### Results

The divalent selenolate Sm(SePh)<sub>2</sub> can be stabilized by coordination of Zn(SePh)<sub>2</sub>. Whereas solutions of green Sm(SePh)<sub>2</sub> turn red-brown within days at room temperature (reaction 1),<sup>26</sup> when Sm metal is oxidized by PhSeSePh in the presence of Zn(SePh)<sub>2</sub>, the resultant green solution color that is characteristic of Sm(II) chalcogenolates<sup>13,20</sup> is maintained for extended periods. Saturation of this green solution gives the heterometallic polymer [(THF)<sub>3</sub>Sm(μ<sub>2</sub>-SePh)<sub>3</sub>Zn(μ<sub>2</sub>-SePh)]<sub>n</sub> (**1**) (reaction 2) that was characterized by conventional spectroscopic methods and low-temperature single-crystal X-ray diffraction. Figure 1 is an ORTEP diagram of the repeating polymeric unit, and Table 2 gives a listing of significant bond lengths and angles for the compound. The compound contains an alternating

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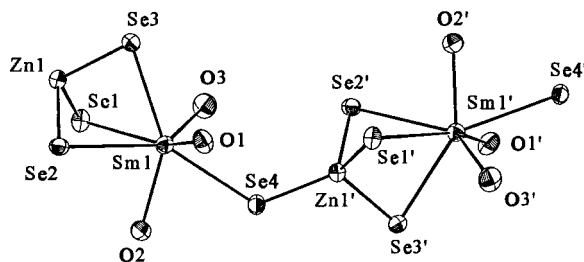
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**Table 2.** Significant Distances (Å) and Angles (deg) for **1**

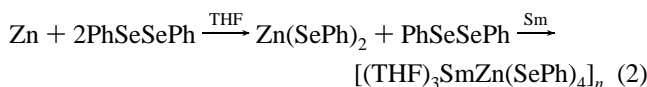
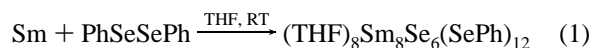
Sm(1)–O(1)	2.504(8)	Sm(1)–O(2)	2.505(7)
Sm(1)–O(3)	2.526(8)	Sm(1)–Se(3)	3.1898(13)
Sm(1)–Se(1)	3.1923(13)	Sm(1)–Se(4)	3.2010(13)
Sm(1)–Se(2)	3.4470(13)	Zn(1)–Se(4)'	2.4299(17)
Zn(1)–Se(2)	2.4725(17)	Zn(1)–Se(3)	2.4749(16)
Zn(1)–Se(1)	2.4942(17)	Se(1)–C(1)	1.942(12)
Se(2)–C(7)	1.934(11)	Se(3)–C(13)	1.897(13)
Se(4)–C(19)	1.940(11)	Se(4)–Zn(1)''	2.4299(17)
O(1)–Sm(1)–O(2)	95.5(2)	O(1)–Sm(1)–O(3)	120.2(3)
O(2)–Sm(1)–O(3)	125.1(3)	O(1)–Sm(1)–Se(3)	79.2(2)
O(2)–Sm(1)–Se(3)	140.00(17)	O(3)–Sm(1)–Se(3)	90.0(2)
O(1)–Sm(1)–Se(1)	151.7(2)	O(2)–Sm(1)–Se(1)	92.65(17)
O(3)–Sm(1)–Se(1)	75.2(2)	Se(3)–Sm(1)–Se(1)	77.22(3)
O(1)–Sm(1)–Se(4)	85.6(2)	O(2)–Sm(1)–Se(4)	73.66(17)
O(3)–Sm(1)–Se(4)	69.7(2)	Se(3)–Sm(1)–Se(4)	143.80(3)
Se(1)–Sm(1)–Se(4)	122.68(3)	O(1)–Sm(1)–Se(2)	85.64(19)
O(2)–Sm(1)–Se(2)	74.41(17)	O(3)–Sm(1)–Se(2)	141.4(2)
Se(3)–Sm(1)–Se(2)	65.69(3)	Se(1)–Sm(1)–Se(2)	70.56(3)
Se(4)–Sm(1)–Se(2)	145.83(3)	Se(4)–Zn(1)–Se(2)	117.96(6)
Se(4)–Zn(1)–Se(3)	117.47(6)	Se(2)–Zn(1)–Se(3)	93.59(6)
Se(4)–Zn(1)–Se(1)	116.60(6)	Se(2)–Zn(1)–Se(1)	101.29(6)
Se(3)–Zn(1)–Se(1)	106.53(6)	C(1)–Se(1)–Zn(1)	106.3(3)
C(1)–Se(1)–Sm(1)	106.4(4)	Zn(1)–Se(1)–Sm(1)	76.14(4)
C(7)–Se(2)–Zn(1)	108.9(3)	C(7)–Se(2)–Sm(1)	119.4(3)
Zn(1)–Se(2)–Sm(1)	71.53(4)	C(13)–Se(3)–Zn(1)	112.9(4)
C(13)–Se(3)–Sm(1)	119.5(4)	Zn(1)–Se(3)–Sm(1)	76.44(4)
C(19)–Se(4)–Zn(1)''	104.4(3)	C(19)–Se(4)–Sm(1)	103.4(3)
Zn(1)''–Se(4)–Sm(1)	124.86(5)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms. ' indicates  $-x, y + 1/2, -z$ , and '' indicates  $-x, y - 1/2, -z$ .

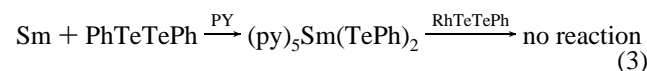


**Figure 1.** ORTEP diagram of the repeating unit of  $[(\text{THF})_3\text{Sm}(\mu_2\text{-SePh})_3\text{Zn}(\text{SePh})]_n$ , with the thermal ellipsoids drawn at the 50% probability level and the C/H atoms removed for clarity.

number (1,3) of doubly bridging SePh ligands connecting the alternating series of Sm(II) and Zn(II) ions. The tetrahedral Zn coordination sphere is comprised entirely of Se atoms, while the larger seven-coordinate Sm(II) ion coordinates to four Se(Ph) and three additional THF ligands. The green color of **1** results from a broad, intense electronic absorption centered at 612 nm that is tentatively assigned as an  $f^6\text{-to-}f^5d^1$  promotion. When the compound is dissolved in pyridine, no absorption maxima are noted from 350 to 750 nm.



The tellurolate compound  $(\text{py})_5\text{Sm}(\text{TePh})_2$  (**2**) can be prepared in high yield from the reduction of PhTeTePh with elemental Sm in pyridine (reaction 3). The product crystallizes in a unit



cell that is isostructural with the pyridine complexes of

$\text{Eu}(\text{TePh})_2$  and  $\text{Yb}(\text{TePh})_2$ .<sup>3</sup> Molecule **2** is considerably more soluble than the selenolate polymer, redissolves readily in pyridine, does not react further with additional PhTeTePh, and is thermally unstable in THF. The compound is intensely colored because of two intense electronic absorptions at 307 and 614 nm that have tentatively been assigned as an  $f^6\text{-to-}f^5d^1$  promotion and a Sm(II)-to-pyridine charge-transfer absorption, respectively. The presence of additional PhTeTePh does not result in further oxidation of the Sm(II) ion.

## Discussion

Measurements of electronic spectra in previous heterometallic Ln/main group chalcogenolate chemistry led to the conclusion that the interaction of  $\text{Ln}(\text{ER})_x$  with the more covalent  $\text{M}(\text{ER})_2$  of the group 12 ( $\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$ )<sup>4,6,7</sup> and group 14 ( $\text{M} = \text{Sn}, \text{Pb}$ )<sup>5</sup> metals resulted in polarization of electron density away from the Ln ion. This polarization prompted the preparation of  $\text{Sm}(\text{SePh})_2$  in the presence of  $\text{Zn}(\text{SePh})_2$ . If the Sm ion were electron-depleted, then any reductive cleavage process involving oxidation of the Sm would be less favorable. While an excess of  $\text{Zn}(\text{SePh})_2$  in solution leads to the formation of the salt  $[\text{Sm}(\text{THF})_7]^{2+}[\text{Zn}_4(\mu_2\text{-SePh})_{10}]^{2-}$  that does not contain Sm–Se(Ph) bonds,<sup>7</sup> the use of a 1:1 Zn:Sm ratio gives the 1:1 heterometallic polymer **1** in high yield. Such 1D polymers are important reference points for understanding the fundamental physical properties of Ln ions doped into chalcogenido-based matrixes<sup>48</sup> and because Ln-doped polymeric materials have potential applications in upconversion processes.<sup>49–54</sup>

Surprisingly, the structure of heterometallic **1** differs from the analogous Eu derivative  $(\text{THF})_4\text{Eu}(\mu_2\text{-SePh})_3\text{Zn}(\text{SePh})$ ,<sup>7</sup> which crystallizes as a molecular bimetallic product with a terminal SePh ligand coordinated to the Zn and an additional THF ligand bound to the Eu. These differences in structure could in theory be explained by the slightly larger (0.01 Å) Sm(II) ion increasing the tendency of chalcogenolate ligands to bridge Ln ions,<sup>11</sup> but there are also changes in the synthetic strategies that are far more likely to account for the difference. Changes in concentration or the presence of trace Hg,  $\text{Hg}(\text{SePh})_2$ , or  $\text{Sm}(\text{SePh})_2$  thermolysis products could conceivably have a significant influence on the structure of the final isolated product. Regardless, the principal Sm(II) species in solution is likely to resemble the structure of the Eu–Zn complex.

From the Sm–Se bond length distribution in **1** it is clear that there are significant steric interactions that influence the length of the Sm–Se bond and thus possibly the solid-state structure. Polymer **1** has three nearly equal Sm–Se bonds (Sm–Se(1), 3.192(1) Å; Sm–Se(3), 3.190(1) Å; Sm–Se(4), 3.201(1) Å) and a fourth bond (Sm–Se(2), 3.447(1) Å) that differs considerably. A similar bond length inequivalence was found in the structure of  $(\text{THF})_4\text{Eu}(\mu_2\text{-SePh})_3\text{Zn}(\text{SePh})$ , although the differences (Eu–Se = 3.162(1) Å, 3.176(1) Å, 3.282(1) Å) were less pronounced. There is only one other structurally characterized Sm(II) compound with a bond to Se in the literature<sup>55</sup>  $[(\text{THF})_2\text{-}$

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Sm(Ph<sub>2</sub>P(Se)NP(Se)Ph<sub>2</sub>)<sub>2</sub>; Sm–Se = 3.14 Å], but the different ligand resonance description and inequivalent Sm coordination numbers preclude a significant comparison of Sm–Se bond lengths.

This compound is not stable indefinitely in solution, and at elevated temperatures it decomposes to give a variety of products, including heterometallic selenido clusters.<sup>56</sup> The compound also appears to be unstable in stronger Lewis base solvents such as pyridine. When pyridine is added to crystalline **1** to give a red-brown solution, there is no absorption maximum in the visible spectrum. The absence of both the f-to-d promotion and an anticipated Sm(II)-to-pyridine charge transfer implies that Sm(II) ions are no longer present in solution. Decomposition in the presence of a stronger base can be rationalized easily because the stronger pyridine donor both increases electron density on the Sm(II) ion and is more likely to fragment the heterometallic product. Both effects will increase the tendency of the Sm(II) ion to oxidize<sup>7</sup> and reduce the C–Se bond.<sup>26,27</sup>

Molecule **2** is isostructural with (py)<sub>5</sub>Yb(TePh)<sub>2</sub>,<sup>3</sup> with a larger unit cell [7289 Å<sup>3</sup> (Sm) vs 7178 Å<sup>3</sup> (Yb)] that is a reflection of larger Sm(II) ionic radius. The stability of the telluroate compound can be attributed to both the instability of the tellurido ligands that would result from any reductive Te–C(Ph) bond cleavage and the inability of Te ligands to stabilize redox active Ln(III) ions. While tellurido clusters of the Ln elements are viable synthetic targets,<sup>18,19,56</sup> they are considerably more difficult to isolate than are their S<sup>2–</sup> or Se<sup>2–</sup> analogues,<sup>26,27,37–41</sup> and presumably the relative instability of Te<sup>2–</sup> coordinated only to Ln(III) ions is a major factor contributing to the isolability of **2**. The instability of **2** in THF can be rationalized either by noting that reductive cleavage of a C–Te bond would presumably be facilitated by the tendency of Sm(TePh)<sub>2</sub> to form oligomeric structures in THF or by considering that Sm(II) can react with THF to form an alkoxide compound.<sup>57</sup>

Along these lines, the thermal instability of Sm(SePh)<sub>2</sub> and the thermal stability of both Sm(Si(SiMe<sub>3</sub>)<sub>3</sub>)<sub>2</sub> and Sm(Se-2,4,6, tri-*i*-prC<sub>6</sub>H<sub>2</sub>)<sub>2</sub> coordination complexes are readily rationalized; reductive Se–C(Ph) bond cleavage would give Sm–Se<sup>2–</sup> and Sm–Ph bonds, whereas cleavage reactions with other ligand systems are less favorable either because they would form rare examples of compounds with Ln–Si bonds<sup>58–61</sup> or sterically congested Ln–C bonds with diorthosubstituted aryl ligands.

In the UV–visible spectrum, the lowest energy electronic absorption for **2** is tentatively assigned as a Sm(II)-to-pyridine

charge-transfer excitation by establishing the influence of both pyridine and Ln on Ln(EPh)<sub>2</sub> electronic spectra. To date, addition of pyridine to THF solutions of Ln(EPh)<sub>2</sub> compounds leads to the formation of significantly more intensely colored products. This effect is most notable in Eu(II) chemistry,<sup>1,2</sup> where Eu(EPh)<sub>2</sub> compounds are essentially colorless because the f<sup>*n*</sup>-to f<sup>*n*–1</sup>d<sup>1</sup> promotion is not found in the visible spectrum. As for the dependence of color on the identity of Ln, differences in the aqueous Ln(II)/Ln(III) redox potentials (Sm, –1.40 V; Yb, –1.04 V; Eu, –0.34 V)<sup>62</sup> are nearly identical to the differences in energy of the lowest electronic transition found for (py)<sub>5</sub>Sm(TePh)<sub>2</sub> (614 nm, 2.03 eV), (py)<sub>5</sub>Yb(TePh)<sub>2</sub> (525 nm, 2.37 eV),<sup>3</sup> and (py)<sub>5</sub>Eu(TePh)<sub>2</sub> (398 nm, 3.12 eV).<sup>2</sup> If this transition is assigned correctly, then the higher energy absorption is presumably an f<sup>6</sup>-to-f<sup>5</sup>d<sup>1</sup> promotion. The significant shift in this absorption position relative to the analogous transition in **1** would certainly be consistent with the extreme sensitivity of these electronic transitions to the composition of the primary coordination sphere.

## Conclusion

Under the appropriate conditions, Sm(EPh)<sub>2</sub> compounds of the heavier chalcogens (E = Se, Te) can be isolated in high yield. The choice of solvent is crucial; the selenolate compound Sm(SePh)<sub>2</sub> can be stabilized by coordination to Zn(SePh)<sub>2</sub> in THF. The covalent Zn ion effectively reduces the tendency of the Sm(II) ion to oxidize further, but this heterometallic product is unstable in pyridine. In contrast, the telluroate compound Sm(TePh)<sub>2</sub> is stable in pyridine but not in THF. As such, they are potentially useful as one-electron reducing agents for organic synthesis or Ln cluster chemistry.

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

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