

## Chalcogen-Rich Lanthanide Clusters from Lanthanide Halide Starting Materials: A New Approach to the Low-Temperature Synthesis of LnS<sub>x</sub> Solids from Molecular Precursors

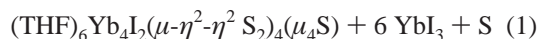
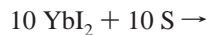
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Chalcogenido (E<sup>2-</sup>; E = S, Se) cluster chemistry<sup>1–3</sup> of the lanthanide (Ln) elements is developing at an extraordinary rate.<sup>4–9</sup> This contribution presents a surprising new dimension in Ln cluster chemistry, one that leads to a completely new approach to the low-temperature synthesis of LnE<sub>x</sub> solids: sterically undemanding halides are useful supporting ligands in the synthesis of stable, soluble, chalcogen-rich lanthanide clusters, and these clusters decompose to give LnE<sub>x</sub> solid-state materials.

Initially we looked at the oxidation of YbI<sub>2</sub> with 1 equiv of elemental S. From the large quantity of colorless YbI<sub>3</sub>(THF)<sub>x</sub> that precipitated from the deep red solution, it was clear that ligand redistribution had occurred. Low-temperature X-ray analysis of the fractionally crystallized red product<sup>10</sup> identified the compound as (THF)<sub>6</sub>Yb<sub>4</sub>I<sub>2</sub>(μ-η<sup>2</sup>-η<sup>2</sup> S<sub>2</sub>)<sub>4</sub>(μ<sub>4</sub>S) (**1**).<sup>11</sup>



Cluster **1** contains a square array of seven coordinate Yb(III) ions connected to adjacent metals by μ-η<sup>2</sup>-η<sup>2</sup> (S–S) ligands, with a single S<sup>2-</sup> ligand capping the Yb<sub>4</sub> plane (Figure 1). Two iodide ligands coordinate on the same side of the Yb<sub>4</sub> plane to opposite Yb ions, and THF ligands fill the available surface of the Yb coordination sphere. The S<sup>2-</sup> atom resides 0.87 Å above the other side of the Yb<sub>4</sub> plane, with Yb–S–Yb<sub>(opposite)</sub> angles of 142° and 143°.

(1) (a) Berg, D.; Burns, C.; Andersen, R. A.; Zalkin, A. *Organometallics* **1989**, *8*, 1865. (b) Evans, W.; Rabe, G.; Ziller, J.; Doedens, R. *Inorg. Chem.* **1994**, *33*, 2719. (c) Zalkin, A.; Berg, D. *Acta Crystallogr.* **1988**, *C44*, 1488.

(2) Evans, W.; Rabe, G.; Ziller, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2110.

(3) Cary, D. R.; Ball, G. E.; Arnold, J. *J. Am. Chem. Soc.* **1995**, *117*, 3492.

(4) Freedman, D.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1997**, *119*, 11112.

(5) Freedman, D.; Melman, J.; Emge, T.; Brennan, J. G. *Inorg. Chem.* **1998**, *37*, 4162.

(6) Melman, J.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1999**, *38*, 2117.

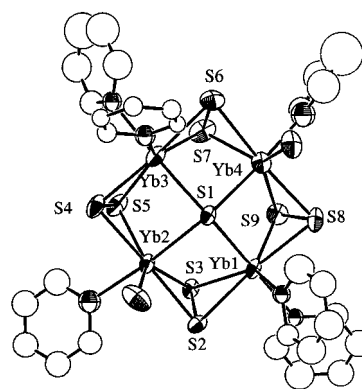
(7) Melman, J. H.; Emge, T. J.; Brennan, J. G. *Chem. Commun.* **1997**, 2269.

(8) Freedman, D.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1999**, *38*, 4400.

(9) Freedman, D.; Sayan, S.; Emge, T.; Croft, M.; Brennan, J. G., manuscript submitted.

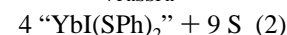
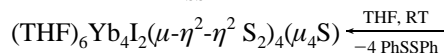
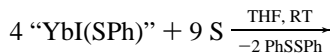
(10) From YbI<sub>2</sub>: Yb (0.345 g, 1.99 mmol) and I (0.507 g, 4.00 mmol) were combined in THF (40 mL). The mixture was stirred until all of the metal was consumed to give a pale orange solution with a large amount of orange-brown precipitate. To this mixture, elemental S (0.064 g, 2.0 mmol) was added. After 1 week of stirring, the solution was red, and a large amount of precipitate had deposited. Filtration and concentration (~20 mL), followed by layering the filtrate with hexane, gave ~20 mg of red crystals that were separated by hand from additional lightly colored precipitate. The compound was identified by UV–visible spectroscopy,<sup>12</sup> mp,<sup>12</sup> and unit cell determination.<sup>11</sup>

(11) **1** crystallizes in the monoclinic space group C2/c, with *a* = 19.380(7) Å, *b* = 12.901(5) Å, *c* = 38.777(11) Å, α = 90.00(4)°, β = 91.24(5)°, γ = 90.00(4)°, *V* = 9639(6) Å<sup>3</sup>, *Z* = 8, ρ<sub>calc</sub> = 2.384 g cm<sup>-3</sup>, (Mo Kα radiation at -120 °C); the crystals are amorphous within an hour of isolation at room temperature). Full-matrix least-squares refinement of 452 parameters and 280 restraints with 6651 unique observations [*F* > 2 σ(*F*)] gave R(*F*) = 0.082, wR(*F*<sup>2</sup>) = 0.213. Complete crystallographic details are given in the Supporting Information.



**Figure 1.** Molecular structure of (THF)<sub>6</sub>Yb<sub>4</sub>I<sub>2</sub>(μ-η<sup>2</sup>-η<sup>2</sup> S<sub>2</sub>)<sub>4</sub>(μ<sub>4</sub>S). Thermal ellipsoids are shown at the 50% probability level. Selected bond length ranges (Å), with average values in [ ]: Yb–S<sup>2-</sup>, 2.676(7)–2.748(7) [2.714]; Yb–S<sub>2</sub>, 2.648(7)–2.722(10) [2.676]; Yb–I, 2.977(2), 2.972(3); Yb–O, 2.26(2)–2.36(2) [2.31]; S–S, 2.08(1) – 2.12(1) [2.10]; Yb–Yb, 3.610(2) – 3.654(2) [3.637].

Because separation of **1** from the YbI<sub>3</sub> major product was problematic, alternative synthetic approaches to **1** were explored. Direct combination of the elements results only in passivation of the Ln surface upon addition of S, and metathesis reactions of Na<sub>2</sub>S/Na<sub>2</sub>S<sub>2</sub> with YbI<sub>3</sub> do not yield significant quantities of NaI. A superior route to this molecule capitalizes on the recent Ln cluster syntheses in which elemental chalcogen displaces chalcogenolates:<sup>4–7</sup> cluster **1** was prepared in ~40% isolated yield by the reaction of 2.25 S with either “YbI(SPh)” or “YbI(SPh)<sub>2</sub>” (reaction 2). The yield does not appear to improve dramatically when a 2:1 Yb:I ratio is employed.<sup>12</sup>



In the structure of **1**, the S–S bond lengths in the disulfide ligand are consistent with a sulfur–sulfur single bond,<sup>13</sup> and the Yb–S bond lengths are within the range of Yb–S bond lengths found

(12) Synthesis of **1** from “YbI(SPh)<sub>2</sub>”: Using standard Schlenk techniques, Yb (0.380 g, 2.20 mmol), PhSSPh (0.479 g, 2.19 mmol), and I<sub>2</sub> (0.279 g, 1.10 mmol) were combined in THF (20 mL). The solution was stirred until all of the metal was consumed. To the resultant deep red solution, S (0.159 g, 4.96 mmol) was added. Within 1 h the mixture turned cloudy brown. After a day the mixture was filtered to remove a small amount of brown precipitate; the red filtrate was reduced in volume (~10 mL) and layered with hexane to give red crystals (0.372 g, 39%) that appear to lose THF at 100 °C, darken at 175 °C, and eliminate a yellow oil at 225 °C. Anal. Calcd for C<sub>28</sub>H<sub>56</sub>O<sub>7</sub>I<sub>2</sub>S<sub>9</sub>Yb<sub>4</sub>: C, 19.3; H, 3.25. Found: C, 19.7; H, 3.31. IR (KBr, Nujol): 2955 (s), 2855 (s), 2726 (w), 2672 (w), 1457 (s), 1377 (s), 1261 (m), 1094 (m), 1019 (m), 915 (w), 873 (w), 801 (m), 752 (w), 722 (w), 668 (w) cm<sup>-1</sup>. UV–vis (THF): λ<sub>max</sub> = 402 nm (ε = 420 L mol<sup>-1</sup> cm<sup>-1</sup>), 457 nm (ε = 410 L mol<sup>-1</sup> cm<sup>-1</sup>). Thermolysis: **1** was sealed in a quartz tube under vacuum, and the temperature was raised to 750 °C over a period of 4 h, while a portion of the tube was kept submerged in liquid nitrogen. At 100 °C a small amount of colorless liquid condensed; at 200 °C yellow solid condensed; a brown solid condensed at 350 °C. The nonvolatile black product was analyzed by X-ray powder diffraction.<sup>21</sup> From “YbI(SPh)”: As above, Yb (0.343 g, 1.98 mmol), PhSSPh (0.216 g, 0.989 mmol), I<sub>2</sub> (0.251 g, 0.99 mmol) and S (0.143 g, 4.46 mmol) gave a similar yield of **1** that was identified by mp. and visible spectroscopy. From YbI<sub>0.5</sub>(SPh)<sub>1.5</sub>: As above, Yb (0.310 g, 1.79 mmol), PhSSPh (0.586 g, 2.69 mmol), I<sub>2</sub> (0.114 g, 0.45 mmol), THF (30 mL) and S (0.129 g, 4.03 mmol) gives **1** (0.30 g, 38%).

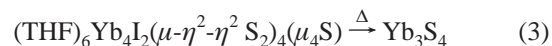
(13) (a) Young, C. G.; Stiefel, E. I.; Kocaba, T. O. *Inorg. Chem.* **1994**, *33*, 6252 (b) Hidai, M.; Nishio, M.; Matsuzaka, H. *Angew. Chem.* **1996**, *35*, 872. (c) Sokolov, M. N.; Hernandez-Molina, R.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1997**, 2059. (d) Ryu, S.; Whang, D.; Tatsumi, K. *Inorg. Chem.* **1997**, *36*, 4607. (e) Heck, J.; Gal, A. W.; van den Berg, W. *Inorg. Chem.* **1997**, *36*, 1821.

in octahedral Yb(III) chalcogenolate complexes<sup>14</sup> and the “double” cubane cluster (py)<sub>10</sub>Yb<sub>6</sub>S<sub>6</sub>(SPh)<sub>6</sub>.<sup>5</sup> Parallel experiments with redox inactive Ln gave crystalline (THF)<sub>6</sub>Ln<sub>4</sub>I<sub>2</sub>(μ-η<sup>2</sup>-η<sup>2</sup> S<sub>2</sub>)<sub>4</sub>(μ<sub>4</sub>-S) (Ln = Tm (**2**), Er (**3**)).<sup>15</sup> These products are useful both for demonstrating that the chemistry applies equally to the redox inactive Ln, and for understanding the absorption spectrum of **1**. Because there is minimal vibrational broadening, these compounds have unusually sharp visible spectra, and the Yb compound dissolved in THF exhibits two absorption maxima at 404 and 460 nm. These bands are absent in the spectra of **2** and **3**, and thus the absorptions in the spectrum of **1** are assigned<sup>14a,16</sup> as (S–S)<sup>2-</sup> and S<sup>2-</sup> to Yb(III) CT excitations.

Disulfido compounds of the lanthanides are unprecedented, and related dichalcogenide compounds of the entire f-block metals are limited to solid-state K<sub>2</sub>U(Se<sub>2</sub>)<sub>4</sub>,<sup>17</sup> molecular UO<sub>2</sub>(S<sub>2</sub>)(R<sub>2</sub>-NCOS)<sub>2</sub><sup>2+</sup>,<sup>18</sup> [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ln]<sub>2</sub>(Te<sub>2</sub>) (Ln = Sm, Yb),<sup>1b</sup> and the (C<sub>5</sub>-Me<sub>5</sub>)<sub>6</sub>Sm<sub>6</sub>Se<sub>11</sub> cluster.<sup>2</sup> The present compounds are, in many ways, unique: derivatives are readily accessed by either halide or Ln substitution, the chemistry is not restricted to redox active metals, and the compounds are stable in solution.

The clusters reported here are also the first molecular “precursors” to Ln<sub>x</sub>E<sub>y</sub> solid-state materials that do not require thermal or photochemical elimination of organic groups bound to E.<sup>3,14a,19</sup> As such, they are particularly attractive sources for doping Ln into sulfide-based semiconductors or optical fibers.<sup>20</sup> When heated in a sealed tube, cluster **1** decomposes in a stepwise fashion. At 100 °C a colorless liquid (THF) is eliminated, and above 300 °C

a yellow-red oil is extruded. An X-ray powder diffraction profile of the resultant solid-state product identifies Yb<sub>3</sub>S<sub>4</sub> as the only crystalline product of the reaction (reaction 3).<sup>21</sup> X-ray fluorescence measurements on the final solid state product indicate that most of the iodine is lost in the thermolysis process. Presumably the iodine is removed as YbI<sub>3</sub>, but volatile Yb<sub>a</sub>S<sub>b</sub>I<sub>c</sub> clusters are also possible thermolysis products.



These halogenated clusters present a number of interesting synthetic possibilities. First, halide ligands might be derivatized metathetically with LiR or NaR reagents (R = CR<sub>x</sub>, NR<sub>2</sub>, OR, SR, naphthalide, ...) to systematically tailor the chemical or physical properties of cluster compounds. Second, because the (S–S)<sup>2-</sup> ligands are potentially reducible to S<sup>2-</sup> ligands (i.e. reaction with elemental Hg gives a product with only a single UV–visible absorption at 460 nm) this class of compound is an attractive entry to the systematic preparation of Ln or heterometallic cluster compounds of higher nuclearity. Finally, the solution-phase stability of this compound suggests that soluble, halide-free Ln<sub>x</sub>S<sub>y</sub> clusters will be viable synthetic targets, that is, a preliminary reaction of Yb(SePh)<sub>3</sub> with 3 S gives an organosoluble product. These avenues are currently under investigation.

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**Supporting Information Available:** Complete tables of crystallographic details, atomic positions and displacement parameters, bond geometries, and a fully labeled ORTEP diagram for **1** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(14) (a) Lee, J.; Brewer, M.; Berardini, M.; Brennan, J. *Inorg. Chem.* **1995**, *34*, 3215. (b) Mashima, K.; Nakayama, Y.; Fukumoto, H.; Kanehisa, N.; Kai, Y.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2523.

(15) Synthesis of **2**: Cluster **2** is prepared identically to **1**. Tm (0.340 g, 2.01 mmol), PhSSPh (0.549 g, 2.51 mmol), I<sub>2</sub> (0.127 g, 0.50 mmol), and Hg (0.030 g, 0.15 mmol) were mixed in THF (30 mL). To the resultant pale green solution, S (0.165 g, 5.03 mmol) was added. Filtration and saturation gave colorless crystals (0.179 g, 21%) that begin to turn red at 205 °C, were dark brown by 230 °C, and showed no further change up to 330 °C. Anal. Calcd for C<sub>28</sub>H<sub>56</sub>O<sub>7</sub>I<sub>2</sub>S<sub>8</sub>Tm<sub>4</sub>: C, 19.5; H, 3.28. Found: C, 18.7; H, 2.76. The IR spectrum is identical to **1**. Unit cell (Mo Kα, –120 °C): monoclinic space group C2/c, *a* = 19.392(9) Å, *b* = 12.921(5) Å, *c* = 38.80(2) Å, β = 91.16(5)°, *V* = 9720(9) Å<sup>3</sup>. Cluster **3**: In an identical fashion, the Er cluster **3** gives light pink crystals in similar yield. This compound has spectroscopic and melting properties that are indistinguishable from the Tm compound, with the exception of the principal Ln(III) f–f electronic absorptions. Unit cell (Mo Kα, –120 °C): monoclinic, C2/c, *a* = 19.325(8) Å, *b* = 12.960(4) Å, *c* = 38.741(15) Å, β = 91.20(3)°, *V* = 9700(6) Å<sup>3</sup>.

(16) (a) Lee, J.; Freedman, D.; Melman, J.; Brewer, M.; Sun, L.; Emge, T. J.; Long, F. H.; Brennan, J. G. *Inorg. Chem.* **1998**, *37*, 2512. (b) Berardini, M.; Lee, J.; Freedman, D.; Lee, J.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1997**, *36*, 5772.

(17) Sutork, A. C.; Katzanadis, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 7754.

(18) Perry, D. L.; Zalkin, A.; Ruben, H.; Templeton, D. L. *Inorg. Chem.* **1982**, *21*, 237.

(19) (a) Berardini, M.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 6179. (b) Brewer, M.; Lee, J.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 5919. (c) Strzelecki, A. R.; Timinski, P. A.; Helsel, B. A.; Bianconi, P. A. *J. Am. Chem. Soc.* **1992**, *114*, 3159. (d) Strzelecki, A. R.; Likar, C. L.; Helsel, B. A.; Utz, T.; Lin, M. C.; Bianconi, P. A. *Inorg. Chem.* **1994**, *33*, 5188. (e) Kuzmina, N. P.; Ivanov, R. A.; Paramonov, S. E.; Martynenko, L. I. *Electrochem. Soc.* **1997**, 880.

(20) For recent examples: (a) Brady, D. J.; Schweizer, T.; Wang, J.; Hewak, D. W. *J. Non-Cryst. Solids* **1998**, *242*, 92. (b) Schweizer, T.; Mober, P.; Hector, J. R.; Hewak, D. W.; Brocklesby, W. S.; Payne, D. N.; Huber, G. *Phys. Rev. Lett.* **1998**, *80*, 1537. (c) Schweizer, T.; Samson, B. N.; Hector, J. R.; Brocklesby, W. S.; Hewak, D. W.; Payne, D. N. *J. Opt. Soc. Am. B* **1999**, *16*, 308. (d) Yun, S. J.; Dey, S.; Nam, K. *J. Korean Phys. Soc.* **1998**, *33*, S-454. (e) Krasteva, V.; Machewirth, D.; Sigel, G. H. *J. Non-Cryst. Solids* **1997**, *213–4*, 304. (f) Saanila, V.; Ihanus, J.; Ritala, M.; Leskela, M. *Chem. Vapor Deposition* **1998**, *4*, 227. (g) Heikkinen, H.; Johansson, L.-S.; Nykanen, E.; Niinisto, L. *Appl. Surf. Sci.* **1998**, *133*, 205.

(21) Flahaut, J.; Domange, L.; Guittard, M.; Lories, J. *Bull. Soc. Chim. Fr.* **1961**, 102.