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Chalcogen-Rich Lanthanide Clusters with Fluorinated Thiolate Ligands

Mark Fitzgerald, Thomas J. Emge, and John G. Brennan*

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

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Mixtures of $Ln(SC_6F_5)_3$ and $Ln(EPh)_3$ (E = S, Se) react with elemental E to give chalcogen-rich clusters with fluorinated thiolate ancillary ligands. The structures of both $(THF)_6Yb_4S(SS)_4(SC_6F_5)_2$ and $(THF)_6Yb_4Se(SeSe)_4(SC_6F_5)_2$ have been established by low-temperature single-crystal X-ray diffraction. Both compounds contain a square array of Yb(III) ions connected by a central μ_4-E^{2-} ligand. The edges of the square Yb_4 array are bridged by four μ_2(EE) ligands, and two terminal SC_6F_5 are on the same side of the Ln_4 plane that is capped by the μ_4-E^{2-} ion. Redox inactive $(THF)_6Tm_4Se(SeSe)_4(SC_6F_5)_2$ was also prepared to establish the extension of this chemistry to the redox inactive Ln. These clusters are soluble in toluene.

Introduction

The finding that lanthanide chalcogenolate complexes react with elemental chalcogen to give lanthanide chalcogenido clusters has led to a series of reports describing the isolation, characterization, and chemical reactivity of these previously elusive species.[1−6] Two prevalent LnE_x structural motifs have been identified: a cubic array of eight Ln ions that have E^{2-} ligands capping the faces of the cube and EPh ligands bridging the edges of the cube,[1−5] and, for the smaller Ln, derivatives of the well-known transition metal cubane clusters,[6,7] in which four Ln and four E occupy alternating vertices of a cube.

A more recent series of chalcogen-rich Ln clusters with $(EE)^{2-}$ ligands have also been described.[7−10] While the structures of these compounds depend on the identity of the ancillary ligands present, the most prevalent structural motif remains a square array of Ln(III) ions connected at the center by an E^{2-} ligand and along the edges by $(EE)^{2-}$ ligands.

A feature common to all isolable LnE and Ln(EE) clusters is the coordination of at least one highly electronegative Lewis base (L: L = pyridine, THF, DME) to every Ln. This tendency of Ln to coordinate L, rather than adopt primary coordination spheres composed entirely of chalcogen donors, is a major impediment to one eventual goal of this field, namely, the synthesis and characterization of increasingly large Ln_xE_y particles. Such clusters are a prerequisite for evaluating how LnE properties evolve as a function of size, and thus how molecular properties are related to solid-state properties. While size dependent physical properties are well documented in transition[11] and main group[12] metal systems, analogous Ln compounds do not yet exist, primarily because the need to use Lewis base solvents appears to favor the coordination of L to Ln, rather than encapsulation of Ln by E.

Recently, we have started looking at how fluorinated thiolate ligands[13,14] might be useful for overcoming this

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* Author to whom correspondence should be addressed. E-mail: bren@rutchem.rutgers.edu.

(1) Freedman, D.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1997**, *119*, 11112.
(2) Melman, J. H.; Emge, T. J.; Brennan, J. G. *Chem. Commun.* **1997**, 2269.
(3) Melman, J. H.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1999**, *38*, 2117.
(4) Freedman, D.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1999**, *38*, 4400.
(5) Freedman, D.; Sayan, S.; Emge, T. J.; Croft, M.; Brennan, J. G. *J. Am. Chem. Soc.* **1999**, *121*, 11713.
(6) Freedman, D.; Melman, J. H.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1998**, *37*, 4162.
(7) Kornienko, A.; Melman, J.; Emge, T.; Hall, G.; Brennan, J. G. *Inorg. Chem.* **2002**, *41*, 121.
(8) Melman, J. H.; Fitzgerald, M.; Freedman, D.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1999**, *121*, 10247.
(9) Kornienko, A. Y.; T. Emge, T.; Brennan, J. G. *J. Am. Chem. Soc*. **2001**, *123*, 11933.
(10) Freedman, D.; T. Emge, T.; Brennan, J. G. *Inorg. Chem.* **2002**, *41*, 492.
(11) (a) Eichhofer, A.; Beckmann, E.; Fenske, D.; Herein, D.; Krautscheid, H.; Schloegl, R. *Isr. J. Chem.* **2001**, *41*, 31. (b) Corrigan, J. F.; Fenske, D. *Chem. Commun.* **1997**, 1837.
(12) (a) Li, H.; Kim, J.; Groy, T. L.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 4867. (b) Nowak, C.; Dollefeld, H.; Eychmuller, A.; Friedrich, J.; Kolmakov, A.; Lofken, J. O.; Riedler, M.; Wark, A.; Weller, H.; Wolff, M.; Moller, T. *J. Chem. Phys.* **2001**, *114*, 489. (c) Soloviev, V. N.; Eichhoefer, A.; Fenske, D.; Banin, U. *J. Am. Chem. Soc.* **2000**, *122*, 2673. (d) Behrens, S.; Bettenhausen, M.; Eichhofer, A.; Fenske, D. *Angew. Chem., Int. Ed.* **1998**, *36*, 2797. (e) Behrens, S.; Fenske, D. *Ber. Bunsen-Ges.* **1997**, *101*, 1588.

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tendency of lanthanides to preferentially coordinate L. The SC_6F_5 ligand imparts a number of useful and interesting physical properties to lanthanide compounds. Most importantly, compounds with fluorinated thiolates are considerably more soluble than are their C_6H_5 counterparts,[15-20] to the extent that NMR spectra of $Ln(SC_6F_5)_x$ compounds[13,14] can be obtained in toluene solution. If these solubility properties extend to Ln cluster compounds, then the synthesis of larger Ln clusters with chalcogen-encapsulated Ln ions becomes more feasible. For this reason, we have investigated the synthesis and characterization of lanthanide chalcogenido clusters with fluorinated thiolate ancillary ligands, and describe here our initial results.

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, PhSSPh, and HSC_6F_5 were purchased from Aldrich and recrystallized from hexane. Ln and Hg were purchased from Strem. $Hg(SC_6F_5)_2$ was prepared according to literature procedure.[17] 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 600 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. Molar absorptivities (M^{-1} cm^{-1}) are given in ( ). 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 lose lattice solvents within minutes. ^{19}F NMR spectra were featureless.

Synthesis of $(THF)_6Yb_4Se(SeSe)_4(SC_6F_5)_2\cdot 1.5THF$ (1). Yb (0.100 g, 0.58 mmol) and $Hg(SC_6F_5)_3$ (0.52 g, 0.87 mmol) were combined in THF (20 mL), and the mixture was stirred until all the Yb was consumed (1 h). The red solution was filtered into a solution of $(THF)_3Yb(SeC_6H_5)_3$ (2.9 mmol in 40 mL of THF). The resulting dark red solution containing some red precipitate was stirred for 12 h before Se was added (0.62 g, 7.80 mmol). This dark red solution was filtered, concentrated in vacuo to 40 mL, and layered with hexane (60 mL) to give dark red crystals (1.1 g, 55%) of **1** that continuously darken and appear to lose solvent at 150 °C and again at 255 °C. IR: 2925(s), 2856(s), 1619(w), 1501(s), 1467(s), 1379(m), 1070(m), 1006(m), 970(m), 855(s) cm^{-1}. UV/vis (THF): 377 (1×10^3), 448 (6×10^2); 520 (4×10^2). Anal. Calcd for $C_{42}H_{60}F_{10}O_{7.5}S_2Se_9Yb_4$: C, 21.5; H, 2.58. Found: C, 21.1; H, 2.57.

Synthesis of $(THF)_6Tm_4Se(SeSe)_4(SC_6F_5)_2\cdot 1.5THF$ (2). Tm (0.10 g, 0.59 mmol) and $Hg(SC_6F_5)_2$ (0.53 g, 0.89 mmol) were combined in THF (20 mL), and the mixture was stirred until all the Tm was consumed (1.5 h). The colorless solution was filtered into a light green solution of $(THF)_3Tm(SeC_6H_5)_3$ (2.96 mmol in 40 mL of THF). After 12 h Se was added (0.63 g, 7.99 mmol), and the resulting dark brown/green solution was filtered, reduced to a volume of 40 mL under vacuum, and layered with hexane (60 mL) to give orange crystals of **3** (0.70 g, 34%) that begin to darken at 85 °C and are brown by 200 °C. IR: 2926(s), 2871(s), 1501(m), 1463(s), 1378(s), 1080(m), 1007(m), 970(m), 855(s) cm^{-1}. UV/vis (THF): only weak f−f transitions (799, 699 nm) were resolved. Anal. Calcd for $C_{42}H_{60}F_{10}O_{7.5}S_2Se_9Tm_4$: C, 21.7; H, 2.60. Found: C, 21.4; H, 2.45. Unit cell (Mo Kα, −100 °C): space group $P\bar{1}$, with $a = 12.065(4)$ Å, $b = 16.091(3)$ Å, $c = 17.586(5)$ Å, $\alpha = 63.70(2)°$, $\beta = 87.04(2)°$, $\gamma = 89.90(2)°$, $V = 3056(2)$ Å^3 based on 25 reflections with $7.3° < \Theta < 17.8°$.

Synthesis of $(THF)_6Yb_4S(SS)_4(SC_6F_5)_2\cdot THF$ (3). Yb (0.10 g, 0.58 mmol) and $Hg(SC_6F_5)_2$ (0.52 g, 0.87 mmol) were combined in THF (20 mL), and the mixture was stirred until all the Yb was consumed (1 h). The red solution was filtered into a solution of $(THF)_3Yb(SC_6H_5)_3$ (2.9 mmol in 40 mL of THF), and the mixture was stirred for 3 h before S was added (0.25 g, 7.8 mmol). The resulting dark red solution (ca. 60 mL) was filtered, concentrated in vacuo to 40 mL, and layered with hexane (60 mL) to give red crystals (0.65 g, 40%) that turn brown by 150 °C. IR: 2924(s), 2860(s), 1501(s), 1463(s), 1377(s), 1070(m), 1010(m), 968(m), 855(s) cm^{-1}. UV/vis (THF): 455 (7×10^2), 415 (6×10^2). Anal. Calcd for $C_{40}H_{56}F_{10}O_7S_{11}Yb_4$: C, 24.7; H, 2.84. Found: C, 25.4; H, 3.01. This compound is soluble in toluene: 70 mg of **3** will dissolve in 2 mL of toluene, and there is no significant change in the visible spectrum.

X-ray Structure Determination of 1 and 3. Data for **1** and **3** were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ 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 for absorption, the latter by a numerical (SHELX76)[22] method. The structures were solved by Patterson or direct methods (SHELXS86).[23] All non-hydrogen atoms were refined (SHELXL97) based upon F_{obs}^2. All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97).[24] Scattering factors (f_o, f', f'') are as described in SHELXL97. Crystallographic data and final *R* indices for **1** and **3** are given in Table 1. Significant bond distances for **1** and **3** are given in the captions to Figures 1 and 2, respectively. Complete crystallographic details are given in the Supporting Information. ORTEP diagrams[25] for **1** and **3** are shown in Figures 1 and 2, respectively.

Results

Chalcogen-rich clusters with fluorinated thiolate ancillary ligands can be isolated in a two-step procedure by first preparing a mixture of lanthanide fluorothiolates and benzenechalcogenolates and subsequently displacing the EPh

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(13) Melman, J.; Emge, T.; Brennan, J. G. *Inorg. Chem.* **2001**, *40*, 1078.
(14) Melman, J.; Rhode, C.; Emge, T.; Brennan, J. G. *Inorg. Chem.* **2002**, *41*, 28.
(15) Peach, M. E. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1046.
(16) Peach, M. E. *Can. J. Chem.* **1968**, *46*, 2769.
(17) Peach, M. E. *Can. J. Chem.* **1968**, *46*, 2699.
(18) Chadwick, S.; Englich, U.; Noll, B.; Ruhlandt-Seng, K. *Inorg. Chem.* **1998**, *37*, 4718.
(19) De Mel, V. S. J.; Kumar, R.; Oliver, J. P. *Organometallics* **1990**, *9*, 1303.
(20) Hendershot, D. G.; Kumar, R.; Barber, M.; Oliver, J. P. *Organometallics* **1991**, *10*, 1917.
(21) Delgado, E.; Hernandez, E.; Hedayat, A.; Tornero, J.; Torre, R. *J. Organomet. Chem.* **1994**, *466*, 119.
(22) Sheldrick, G. M. *SHELX76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.
(23) Sheldrick, G. M. *SHELXS86, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1986.
(24) Sheldrick, G. M. *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.
(25) (a) Johnson, C. K. *ORTEP II*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976. (b) Zsolnai, L. *XPMA and ZORTEP, Programs for Interactive ORTEP Drawings*; University of Heidelberg: Heidelberg, Germany, 1997.

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

	1	**3**
empirical formula	$C_{42}H_{60}F_{10}O_{7.5}S_2Se_9Yb_4$	$C_{38.50}H_{53}F_{10}O_{6.63}S_{11}Yb_4$
fw	2341.82	1856.63
space group (No.)	$P\bar{1}$ (2)	$P2_1/n$ (14)
a (Å)	12.082(8)	12.252(2)
b (Å)	16.018(5)	17.763(6)
c (Å)	17.528(8)	27.199(5)
α (deg)	63.60(4)	90
β (deg)	87.42(4)	91.52(2)
γ (deg)	89.94(4)	90
V (Å$^{3)}$	3035(3)	5917(2)
Z	2	4
D(calcd) (g/cm^{-3})	2.563	2.084
temp (°C)	−120	−120
λ (Å)	0.71073	0.71073
abs coeff (mm^{-1})	11.648	6.723
$R(F)^a$ [$I > 2\sigma(I)$]	0.039	0.055
$R_w(F^2)^a$ [$I > 2\sigma(I)$]	0.099	0.137

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

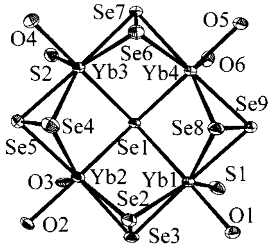

Figure 1. Core bonding region of the molecular structure of $(THF)_6Yb_4Se(SeSe)_4(SC_6F_5)_2$ (**1**) with the C, F, and H atoms removed. Thermal ellipsoids are drawn at the 50% probability level. Significant distances (Å) for **1**: Yb(1)−O(1), 2.306(6); Yb(1)−S(1), 2.658(3); Yb(1)−Se(3), 2.8094(17); Yb(1)−Se(2), 2.810(2); Yb(1)−Se(9), 2.8151(18); Yb(1)−Se(8), 2.8294(17); Yb(1)−Se(1), 2.8915(15); Yb(2)−O(3), 2.286(6); Yb(2)−O(2), 2.308(6); Yb(2)−Se(2), 2.7845(18); Yb(2)−Se(4), 2.8053(16); Yb(2)−Se(5), 2.8065(15); Yb(2)−Se(1), 2.8067(18); Yb(2)−Se(3), 2.8182(14); Yb(3)−O(4), 2.326(6); Yb(3)−S(2), 2.676(3); Yb(3)−Se(5), 2.7840(18); Yb(3)−Se(7), 2.7997(18); Yb(3)−Se(6), 2.8188(19); Yb(3)−Se(4), 2.8220(19); Yb(3)−Se(1), 2.8790(15); Yb(4)−O(6), 2.298(6); Yb(4)−O(5), 2.324(6); Yb(4)−Se(6), 2.7598(18); Yb(4)−Se(9), 2.7931(15); Yb(4)−Se(1), 2.8118(17); Yb(4)−Se(8), 2.8207(18); Yb(4)−Se(7), 2.8429(14); Se(2)−Se(3), 2.3974(19); Se(4)−Se(5), 2.374(2); Se(6)−Se(7), 2.378(2); Se(8)−Se(9), 2.383(2); S(1)−C(1), 1.753(10); S(2)−C(7), 1.764(10).

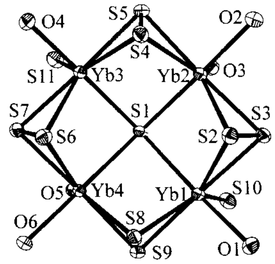

Figure 2. Core bonding region of the molecular structure of $(THF)_6Yb_4S(SS)_4(SC_6F_5)_2$ (**3**) with the C, F, and H atoms removed. Thermal ellipsoids are drawn at the 50% probability level. Significant distances (Å) for **3**: Yb(1)−O(1), 2.317(6); Yb(1)−S(8), 2.679(3); Yb(1)−S(9), 2.680(3); Yb(1)−S(10), 2.683(3); Yb(1)−S(3), 2.686(3); Yb(1)−S(2), 2.724(3); Yb(1)−S(1), 2.730(3); Yb(2)−O(3), 2.289(7); Yb(2)−O(2), 2.316(7); Yb(2)−S(4), 2.653(3); Yb(2)−S(2), 2.656(3); Yb(2)−S(5), 2675(3); Yb(2)−S(3), 2.677(3); Yb(2)−S(1), 2.695(3); Yb(3)−O(4), 2.332(7); Yb(3)−S(11), 2.667(3); Yb(3)−S(7), 2.670(3); Yb(3)−S(5), 2.675(3); Yb(3)−S(4), 2.682(3); Yb(3)−S(6), 2.712(3); Yb(3)−S(1), 2.727(3); Yb(4)−O(5), 2.281(7); Yb(4)−O(6), 2.307(8); Yb(4)−S(6), 2.659(3); Yb(4)−S(8), 2.667(3); Yb(4)−S(9), 2.669(3); Yb(4)−S(7), 2.686(3); Yb(4)−S(1), 2.689(3); S(2)−S(3), 2.102(4); S(4)−S(5), 2.113(4); S(6)−S(7), 2.107(4); S(8)−S(9), 2.116(4).

ligands by reaction with elemental chalcogen (reaction 1).

$$10Ln(EPh)_3 + 2Ln(SC_6F_5)_3 \xrightarrow{27E/THF} 3(THF)_6Ln_4E(EE)_4(SC_6F_5)_2 + 15PhEEPh \quad (1)$$

In this manner, both sulfur- and selenium-rich compounds of redox active Yb were isolated. A Tm_4Se_9 derivative was also prepared to demonstrate the utility of this chemistry for the redox inactive Ln. Benzenechalcogenolates are a crucial component of the cluster synthesis, because the fluorinated thiolate anion is not oxidized to the disulfide in reactions of $Ln(SC_6F_5)_3$ with E.

The selenido compounds $(THF)_6Ln_4Se(SeSe)_4(SC_6F_5)_2$ [Ln = Yb(**1**), Tm(**2**)] were isolated from THF solution in 55% and 34% yields, respectively. The Yb compound was analyzed by low-temperature single-crystal X-ray diffraction and was found to be a tetrametallic product, with a square array of Yb(III) ions connected by $SeSe^{2-}$ ligands that bridge all four edges of the square, and by a central Se^{2-} ligand that sits 0.99 Å above the Ln_4 plane. There are two terminal SC_6F_5 ligands coordinated to nonadjacent Yb ions that sit on the same face of the Ln_4 plane as does the μ_4 selenido ligand. The Tm compound **2** was found to be isostructural with **1**, as established by a determination of the unit cell of **2** at −100 °C.

A sulfur-rich compound of Yb was isolated similarly from THF, and the compound was fully characterized by low-temperature X-ray diffraction and identified as $(THF)_6Yb_4S(SS)_4(SC_6F_5)_2$ (**3**). This sulfur derivative has the same structural motif as **1**, with the central S^{2-} ligand 0.80 Å above the mean Yb_4 plane. One of the SC_6F_5 ligands in **1** is slightly rotated away from the center of the Yb_4Se_9 core [and from Se(1)], whereas all the other SC_6F_5 ligands have corresponding torsion angles near 90°: C(25)−S(11)−Yb(3)−S(1) and C(31)−S(10)−Yb(1)−S(1) at 89° and 93°, respectively, and C(1)−S(1)−Yb(1)−(Se1) and C(7)−S(2)−Yb(3)−Se(1) at 94° and 67°, respectively. Perhaps the largest conformational difference between **1** and **3** is that the THF ligands adjacent to the SC_6F_5 ligands at Yb(1) and Yb(3) are rotated about 110° (or −70°) for **3** versus **1**, as shown by the torsion angles of C(4)−O(1)−Yb(1)−S(1) and C(13)−O(4)−Yb(3)−S(1) at −18° and 6°, respectively, versus Se(1)−Yb(1)−O(1)−C(13) and Se(1)−Yb(3)−O(4)−C(28) at 104° and 114°, respectively.

The crystal packing of **1** and that of **3** differ markedly, as the latter is characterized by a 3D lattice network of ring-to-ring interactions which isolate individual molecules, whereas the former is characterized by isolated dimers of molecules (e.g., the Se_2 ligands of one molecule are in contact with the Se_2 ligands of the inversion-related nearest neighbor molecule), and these are separated by layers of ring-to-ring interactions (Figure 3).

Both Yb compounds show well-defined absorption spectra, with a series of characteristic absorption spectra that can be assigned as E to Yb charge transfer excitations, based on earlier work and by comparison with the redox inactive derivative **2**. The spectrum of the selenido derivative **1** is particularly rich, with three well-defined absorption maxima

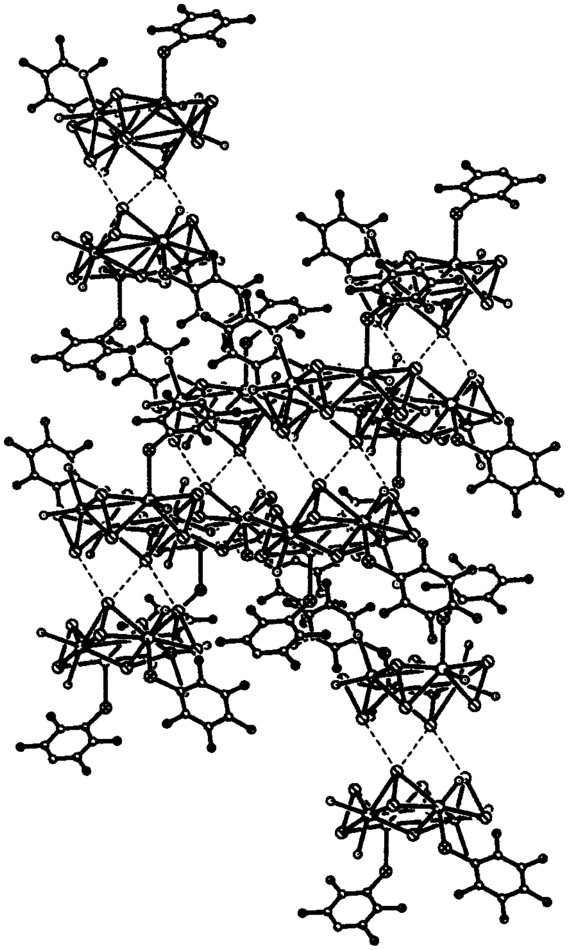

Figure 3. Unit cell packing diagram of **1**. Note the relatively isolated pairs of $(THF)_6Yb_4Se(SeSe)_4(SC_6F_5)_2$ molecules that contain close SeSe···SeSe contacts.

at 377, 448, and 520 nm that are clearly some form of E to Yb charge transfer excitations, by comparison with the visibly transparent Tm compound **2**. The sulfur derivative **3** has diagnostic absorption maxima at 415 and 455 nm that do not shift dramatically (417, 454 nm) when the compound is dissolved in toluene.

Discussion

Both sulfur-rich and selenium-rich lanthanide clusters with fluorinated thiolate ligands are synthetically viable targets. The fluorothiolate imparts considerable solubility in hydrocarbon solvents, and, as such, clusters incorporating these ligands represent an entirely new starting point in the systematic preparation of larger LnE cluster compounds.

The synthesis of **1** leads to the conclusion that basicity of the ancillary ligand donor atom is of paramount importance in determining overall cluster structure, and steric effects are a secondary concern. Cluster **1** is structurally similar to the analogous iodide $(THF)_6Yb_4Se(SeSe)_4I_2$,[7] which has two terminal iodides coordinating to nonadjacent Ln(III) ions. Structures of **1** and the iodide differ from the variety of selenium-rich compounds with ancillary benzenechalcogenolate ligands that have recently been reported. Unlike the selenolate or tellurolate compounds $(py)_8Yb_4Se(SeSe)_2(SeSeE(Ph)SeSe)$ (E = Se, Te), there is no displacement of SC_6F_5 by neutral donor in the title compounds, presumably because the Ln−S bond is stronger than either Ln−Se(Ph) or Ln−Te(Ph) bonds. This interpretation is consistent with the observation that elemental E does not displace SC_6F_5 coordinated to Ln. A direct comparison of **1** with a related selenium-rich thiolate is hampered by two facts: first, reaction of $Yb(SPh)_3$ with Se gives only $(py)_8Yb_4(SeSe)_2Se_2(SPh)_4$,[9] and second, we have not yet isolated chalcogen-depleted $[LnE(SC_6F_5)]_n$ derivatives of **1**. Still, the different structures of **1** and $(py)_8Yb_4(SeSe)_2Se_2(SPh)_4$ can be understood in terms of the different S atom basicities, with the more basic SPh ligands bridging Yb(III) centers even in the presence of basic pyridine donors, and the SC_6F_5 ligands coordinating to Ln only in a terminal fashion.

For the two inequivalent seven-coordinate Ln coordination spheres of **1** and **3**, the Ln−E and Ln−O bonds are usually longer for the Ln that coordinates SC_6F_5, although the differences are sometimes not statistically significant. In **1**, average Yb−O, Yb−Se^{2-}, and Yb−SeSe bond lengths for Yb(1) and Yb(3) are longer than the corresponding average distances for Yb(2) and Yb(4) by 0.012, 0.075, and 0.007 Å, respectively while in **3**, average Yb−O, Yb−S^{2-}, and Yb−SS bond lengths for Yb(1) and Yb(3) are longer than the corresponding average distances for Yb(2) and Yb(4) by 0.027, 0.037, and 0.023 Å, respectively.

Within these structures, Ln−E bond lengths appear to be relatively independent of the Ln coordination environment. A comparison of average Ln−μ_4-E distances between the selenido compounds **1** (2.847 Å) and $(THF)_6Yb_4Se(SeSe)_4I_2$ (2.835 Å),[7] or between the sulfido compounds **3** (2.711 Å) and $(THF)_6Yb_4S(SS)_4I_2$ (2.714 Å),[8] indicates that substitution of iodide by SC_6F_5 has no significant impact on the Ln−μ_4-E bond length. Similarly, a comparison of the Yb−$S(C_6F_5)$ bond lengths in **1** (2.667 Å) and **3** (2.675 Å) indicates that S/Se substitution of the E and EE ligands also has no measurable impact on the length of the Ln−$S(C_6F_5)$ bond.

There is a plethora of allowed E to Yb charge transfer absorptions[26] that may contribute to the electronic spectra of compounds **1** and **3**. Excitations involving CT from E^{2-}, $(EE)^{2-}$, or SC_6F_5 to Yb all potentially fall in the visible spectrum, as has been noted previously for resolved absorptions in the spectra of $(py)_3Yb(SC_6F_5)_3$ (440 nm),[14] $(THF)_6Yb_4S(SS)_4I_2$ (402, 457 nm),[8] and $(THF)_6Yb_4Se(SeSe)_4I_2$ (387 nm).[7] The fact that the chemically inequivalent sets of Yb [Yb(1)/Yb(3) versus Yb(2)/Yb(4)] in **1** and **3** have different bond lengths as noted above also leads us to consider that CT absorptions to different Yb in different coordination environments may also be resolvable. Unfortunately such an abundance of variables make assignment of the visible spectra for **1** and **3** impossible. Even the most likely assignment of the low-energy absorption for **1** (520 nm) as a Se to Yb CT excitation is complicated by the absence of similarly resolved low-energy absorptions in $(THF)_6Yb_4Se(SeSe)_4I_2$ or $(THF)_{10}Yb_6Se_6I_6$.

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

Clearly defined $\pi-\pi$ interactions are present in the structure of **1** and **3**, although these interactions are not as pervasive as the $\pi-\pi$ interactions found in molecular Ln(SC_6F_5)$_x$ compounds (cf. the structure of [(THF)$_3$Eu(SC_6F_5)$_2$]$_n$, in which pairs of thiolates bridge Eu(II) ions in a one-dimensional array[13] with infinitely stacked C_6F_5 rings). In **1** the S(1) thiolate interacts clearly with an adjacent ring, and similarly in **3**, the closest $\pi-\pi$ contact is depicted by the C32···C32″ separation of 3.41 Å. Both π interactions span an inversion center that is a symmetry operation that maintains the coplanarity of the rings. In **1**, the unit cell packing is actually defined by a clustering of polar chalcogen and areas of fluorocarbon concentration, as shown in Figure 3. Within this chalcogen-rich region the shortest intermolecular head-to-head contact between diselenide ligands is at the pair Se(2)···Se(8)‴ and Se(8)···Se(2)‴ at 3.34 Å, a distance considerably shorter than the 3.8 Å van der Waals radius sum expected for Se.[27]

Conclusion

Chalcogen-rich lanthanide clusters with fluorinated thiolate ancillary ligands can be prepared by reactions of elemental E with “Ln(EPh)$_x$(SCF)$_{3-x}$”. The structural and electronic properties of these fluorinated thiolate compounds are similar to those of analogous iodide compounds and differ significantly from those of related chalcogenolate compounds. As toluene soluble sources of LnE$_x$, these compounds represent a new class of starting materials for the synthesis of larger LnE$_x$ clusters with chalcogen-encapsulated Ln.

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

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(27) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1945.