

Fluorinated Thiolates of Divalent and Trivalent Lanthanides. Ln–F Bonds and the Synthesis of LnF₃

Jonathan H. Melman, Thomas J. Emge, and John G. Brennan*

Department of Chemistry, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, New Jersey 08854-8087

Received June 23, 2000

Introduction

While the thiolate chemistry of the lanthanide (Ln) elements has expanded dramatically in the past decade,¹ relatively little is known about how variations in the steric and electronic properties of the organic substituent bound to S influence the physical or chemical properties of lanthanide derivatives. Compounds with SR (R = Ph,^{2–5} trialkyl-substituted Ph,^{5–8} alkyl),^{9,10} are well documented, but unfortunately such vastly different substituents preclude an understanding of how steric and electronic forces influence the Ln–S bond. Because Ln thiolate compounds are sensitive to water and oxygen, isolation via fractional crystallization is the only routine method of purification. As a result, Hammett-like analyses of compounds with Ln–S bonds are essentially impossible.

Substitution of F for H in organic systems perturbs electronic structure with minimal changes in steric properties.¹¹ While numerous 2,4,6-trialkyl-substituted arylthiolate derivatives of Ln compounds have been investigated, the corresponding fluorinated analogues are unknown even though HSC₆F₅ is commercially available. Complexes of SC₆F₅ with the covalent main group metals have been known for decades,^{12,13} while more recently complexes with electropositive metals (i.e., Ca,¹⁴ Al,¹⁵ Ga,¹⁶ Ti¹⁷) have been synthesized and structurally characterized.

The successful synthesis of Ln compounds with SC₆F₅ ligands would have three important chemical consequences. First, fluorinated Ln thiolates are potentially volatile single-source precursors to either LnS_x or LnF₃. Second, because the steric characteristics of the SC₆F₅ group so closely resemble those of SC₆H₅, the properties of molecules or clusters with SC₆F₅ ligands can be compared with their Ph derivatives and differences can be interpreted in terms of the electronic influence of the F substitutions. Finally, C–H bonds often quench photoemission in Ln systems, and so the elimination of C–H bonds is important in the synthesis of Ln coordination complexes with efficient photoemission properties.^{18–23} This manuscript describes the synthesis, structure, and thermal decomposition of the first Ln(SC₆F₅)_x (x = 2, 3) compounds.

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. Hg(SC₆F₅)₂ was prepared in a variation of literature procedures.²⁴ HSC₆F₅ was purchased from Aldrich. Sm and Eu 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 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. Elemental analyses were performed by Quantitative Technologies, Inc. (Whitehouse NJ). ¹⁹F NMR spectra were obtained on a 400 MHz NMR spectrometer with an external HSC₆F₅ reference, and chemical shifts are reported in δ (ppm). Direct probe-EI mass spectra were obtained at the Rutgers University Department of Food Science.

Synthesis of Hg(SC₆F₅)₂. In a modification of the original literature procedure, Hg(CH₃COO)₂ (1.169 g, 3.676 mmol) and HSC₆F₅ (1.468 g, 7.335 mmol) were combined in deionized water (~100 mL). The solution was stirred overnight, and the white precipitate was collected by vacuum filtration and recrystallized by slowly cooling a saturated hot toluene solution to give white crystals (3.194 g, 87%) that were identified by IR and melting point.¹²

Synthesis of [(THF)₂Sm(μ₂-SC₆F₅)(SC₆F₅)₂]₂ (1). Sm (0.150 g, 0.997 mmol) and Hg(SC₆F₅)₂ (0.895 g, 1.50 mmol) were combined in THF (25 mL), and the mixture was stirred until all the Sm was consumed (1 h). The solution was filtered to separate the elemental Hg (0.25 g, 78%), the volume was reduced (ca. 15 mL), and the solution was layered with hexane (12 mL) and then cooled slowly (-20 °C) to give yellow-orange (0.293 g, 33%) crystals that turn darker orange at 74 °C, start becoming lighter yellow at 150–185 °C, and melt at 252–254 °C. Anal. Calcd for C₂₆H₁₆O₂F₁₅S₃Sm: C, 35.0; H, 1.81. Found: C, 34.6; H, 1.84. IR: 2931 (s), 2854 (s), 1506 (m), 1458 (s), 1378 (s), 1343 (m), 1264 (m), 1179 (w), 1170 (w), 1156 (w), 1139 (w), 1122 (w), 1097 (w), 1084 (m), 1065 (m), 1042 (w), 1006 (m), 974 (m), 957 (m), 866 (m), 686 (w) cm⁻¹. The compound does not exhibit a well-defined visible absorption maximum in either pyridine or THF. When heated at 220 °C under vacuum, the compound eliminates white crystalline material that was identified as a mixture of (C₆F₄S)_n (M⁺ =

- (1) Nief, F. *Coord. Chem. Rev.* **1998**, 178–180, 13.
- (2) Brewer, M.; Khasnis, D.; Buretea, M.; Berardini, M.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1994**, 33, 2743.
- (3) Lee, J.; Brewer, M.; Berardini, M.; Brennan, J. *Inorg. Chem.* **1995**, 34, 3215.
- (4) Lee, J.; Freedman, D.; Melman, J.; Brewer, M.; Sun, L.; Emge, T. J.; Long, F. H.; Brennan, J. G. *Inorg. Chem.* **1998**, 37, 2512.
- (5) Mashima, K.; Nakayama, Y.; Shibahara, T.; Fukumoto, H.; Nakamura, A. *Inorg. Chem.* **1996**, 35, 93.
- (6) Mashima, K.; Nakayama, Y.; Fukumoto, H.; Kanehisa, N.; Kai, Y.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2523.
- (7) Strzelecki, A. R.; Lihar, C. L.; Helsel, B. A.; Bianconi, P. A. *Inorg. Chem.* **1994**, 33, 5188.
- (8) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Smith, R. G. *J. Chem. Soc., Chem. Commun.* **1992**, 932.
- (9) Tatsumi, K.; Amemiya, T.; Kawaguchi, H.; Tank, K. *J. Chem. Soc., Chem. Commun.* **1993**, 773.
- (10) Aspinall, H.; Cunningham, S. A.; Maestro, P.; Macaudiere, P. *Inorg. Chem.* **1998**, 37, 5396.
- (11) Carey, F. A.; Sundberg, R. J. In *Advanced Organic Chemistry*, 3rd ed.; Plenum Press: New York, 1990; pp 397–402.
- (12) Peach, M. E. *J. Inorg. Nucl. Chem.* **1973**, 35, 1046.
- (13) Peach, M. E. *Can. J. Chem.* **1968**, 46, 2769.
- (14) Chadwick, S.; Englich, U.; Noll, B.; Ruhlandt-Seng, K. *Inorg. Chem.* **1998**, 37, 4718.
- (15) De Mel, V. S. J.; Kumar, R.; Oliver, J. P. *Organometallics* **1990**, 9, 1303.
- (16) Hendershot, D. G.; Kumar, R.; Barber, M.; Oliver, J. P. *Organometallics* **1991**, 10, 1917.
- (17) Delgado, E.; Hernandez, E.; Hedayat, A.; Tornero, J.; Torre, R. J. *Organomet. Chem.* **1994**, 466, 119.

- (18) Lee, J.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1997**, 36, 5064.
- (19) Piguet, C.; Bünzli, J. G.; Bernardinelli, G.; Hopfgartner, G.; Petoud, S.; Schaad, O. *J. Am. Chem. Soc.* **1996**, 118, 6681.
- (20) Bunzli, J.-C. G.; Petoud, S.; Renaud, F. *J. Alloys Compd.* **1997**, 249, 14.
- (21) Knoepfel, D. W.; Liu, J.; Shore, S. G. *Inorg. Chem.* **1998**, 37, 4828.
- (22) Decurtins, S.; Gross, M.; Ferlay, S. *Inorg. Chem.* **1998**, 37, 2443.
- (23) Cui, Y.; Zheng, F.; Huang, J. *Chem. Lett* **1999**, 4, 281.
- (24) Peach, M. E. *Can. J. Chem.* **1968**, 46, 2699.

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

| | 1 | 2 |
|--|--|---|
| empirical formula | C ₂₆ H ₁₆ F ₁₅ O ₂ S ₃ Sm | C ₂₀ H ₁₆ EuF ₁₀ O ₂ S ₂ |
| fw | 891.92 | 694.41 |
| space group | <i>P</i> 2 ₁ / <i>c</i> (No. 14) | <i>C</i> 2/ <i>c</i> (No. 15) |
| <i>a</i> (Å) | 11.923(10) | 30.049(19) |
| <i>b</i> (Å) | 12.404(7) | 4.936(2) |
| <i>c</i> (Å) | 19.869(14) | 19.077(9) |
| α (deg) | 90.00(6) | 90.00(4) |
| β (deg) | 92.27(7) | 128.61(5) |
| γ (deg) | 90.00(6) | 90.00(3) |
| <i>V</i> (Å ³) | 2936(4) | 2211(2) |
| <i>Z</i> | 4 | 4 |
| <i>D</i> _{calcd} (g/cm ⁻³) | 2.018 | 2.086 |
| temp (°C) | -120 | -120 |
| λ (Å) | 0.710 73 | 0.710 73 |
| abs coeff (mm ⁻¹) | 2.335 | 3.127 |
| <i>R</i> (<i>F</i>) ^a [<i>I</i> > 2 σ (<i>I</i>)] | 0.062 | 0.038 |
| <i>R</i> _w (<i>F</i> ²) ^a [<i>I</i> > 2 σ (<i>I</i>)] | 0.129 | 0.106 |

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

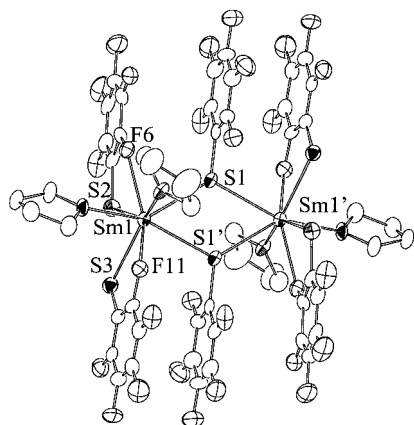


Figure 1. Molecular structure of [(THF)₂Sm(SC₆F₅)₂(μ -SC₆F₅)₂]. Thermal ellipsoids are drawn at the 50% probability level. Significant distances (Å) for **1** are the following: Sm(1)–O(1), 2.396(8); Sm(1)–O(2), 2.427(7); Sm(1)–F(6), 2.582(7); Sm(1)–F(11), 2.641(6); Sm(1)–S(2), 2.740(4); Sm(1)–S(3), 2.771(4); Sm(1)–S(1)', 2.852(4); Sm(1)–S(1), 2.929(4); S(1)–C(1), 1.764(13).

360, 539, 719 for *n* = 2, 3, 4, respectively) by DP-EI-MS. ¹⁹F NMR (24 °C): -136 (*w*_{1/2} = 180 Hz), -164.8 (*w*_{1/2} = 60 Hz), -165.2 (*w*_{1/2} = 75 Hz).

Synthesis of [(THF)₂Eu(μ -SC₆F₅)₂]_{*n*} (2**).** Eu (0.115 g, 0.757 mmol) and Hg(SC₆F₅)₂ (0.678 g, 1.13 mmol) were combined in THF (25 mL), and the solution was stirred until the Eu was consumed. Elemental Hg was not found to precipitate from the yellow solution, suggesting that the product was divalent. Additional Eu was added (0.108 g, 0.711 mmol), and the mixture was stirred for 3 days. The yellow solution was filtered, reduced in volume (ca. 10 mL), and layered with hexane (30 mL) to give pale-yellow needles of **2** (0.425 g, 54%). Anal. Calcd for C₂₀H₁₆O₂EuF₁₀S₂: C, 34.6; H, 2.32. Found: C, 33.7; H, 2.36. IR: 2933 (s), 2849 (s), 1506 (m), 1458 (s), 1377 (s), 1351 (m), 1301 (w), 1254 (m), 1083 (m), 1029 (m), 1014 (w), 993 (w), 962 (m), 921 (w), 867 (m), 740 (m), 621 (w) cm⁻¹. The compound becomes increasingly red up to 288 °C, with no further change up to 350 °C. UV-vis (pyridine): λ_{\max} 340 nm (ϵ = 90 M⁻¹ cm⁻¹). ¹⁹F NMR (24 °C): -131.3 (d, *J* = 22 Hz), -148.3 (t, *J* = 20 Hz), -159.9 (t, *J* = 20 Hz).

X-ray Structure Determinations of **1 and **2**.** Data for **1** and **2** were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromatized Mo K α radiation (λ = 0.710 73 Å) at -120 °C. The check reflections measured every hour showed less than 2% intensity variation. The data were corrected for Lorentz effects, polarization, and

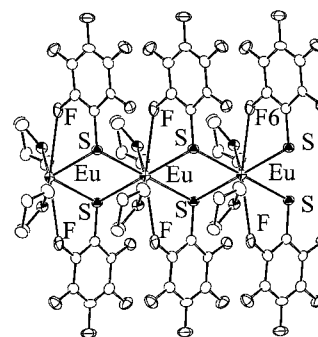
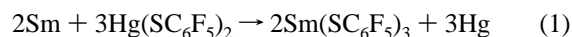


Figure 2. Molecular structure of [(THF)₂Eu(μ -SC₆F₅)₂]_{*n*}. Thermal ellipsoids are drawn at the 50% probability level. Significant distances (Å) for **2** are the following: Eu(1)–O(1), 2.554(5); Eu(1)–F(6), 3.006(6); Eu(1)–S(1), 3.014(3); Eu(1)–S(1)', 3.035(3); S(1)–C(1), 1.750(7).

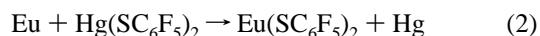
absorption, the last by a numerical (SHELX76)²⁵ method. The structures were solved by direct methods (SHELXS86).²⁶ All non-hydrogen atoms were refined (SHELXL97)²⁷ on the basis of *F*_{obs}². All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97). Scattering factors (*f*_o, *f*' , *f*'') are as described in SHELXL97. Crystallographic data and final *R* indices for **1** and **2** are given in Table 1. Complete crystallographic details are given in the Supporting Information. ORTEP diagrams²⁸ for **1** and **2** are shown in Figures 1 and 2, respectively. A packing diagram for **2** is shown in Figure 3.

Results

Transmetalation reactions of Hg(SC₆F₅)₂ with Sm,



and Eu,



in THF give [(THF)₂Sm(SC₆F₅)₂(μ -SC₆F₅)₂]_{*n*} (**1**) and [(THF)₂Eu(μ -SC₆F₅)₂]_{*n*} (**2**), respectively. Both compounds are extremely soluble in 1:1 THF/hexane mixtures, from which they can be crystallized in high yield. The structure of the Sm compound **1** was determined by low-temperature single-crystal X-ray diffraction and shown to be dimeric, with a pair of thiolates bridging the eight-coordinate Sm(III) ions. Both terminal thiolates chelate to each metal via both Ln–S and Ln–F bonds, while the bridging thiolates do not interact through the fluoride. Two THF ligands complete the inner coordination sphere. Figure 1 gives an ORTEP diagram of **1**. The compound is light-yellow in solution and in the solid state and is considerably more stable than the SPh analogue both thermally and with respect to reactions with water and oxygen. Dimeric **1** decomposes above 220 °C in vacuo by abstracting F to give SmF₃ and a mixture of three F products based on the oligomerization of (C₆F₄S)_{*n*} (*n* = 2, 3, 4).

The Eu compound **2** was also characterized by low-temperature single-crystal X-ray diffraction and shown to be a 1D polymer in the solid state with each Eu ion connected to adjacent

(25) Sheldrick, G. M. *SHELX76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

(26) Sheldrick, G. M. *SHELXS86, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1986.

(27) Sheldrick, G. M. *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(28) (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.

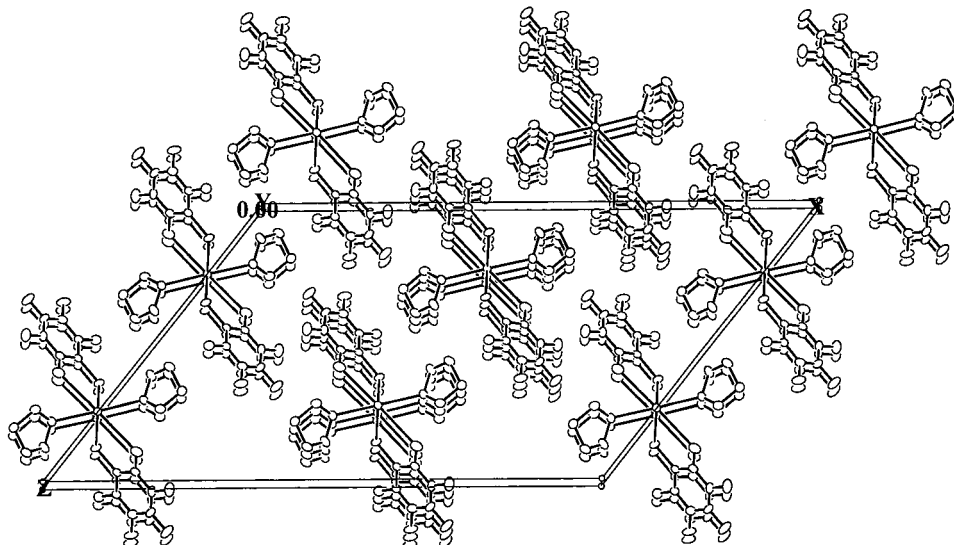


Figure 3. Packing diagram for polymeric **2** along the short axis, which illustrates the stacking of the fluorinated arene rings along the 1D chain.

metals by a pair of thiolates. Figure 2 gives an ORTEP diagram of three repeating polymeric units. In contrast to **1**, the bridging thiolates in **2** interact with the metal through Eu–F bonds (Figure 2) to give an eight-coordinate (4S, 2F, 2O) Eu(II) ion. While essentially colorless in crystalline form and in THF solutions, **2** forms an orange solution with a well-defined absorption maximum ($\lambda_{\text{max}} = 340$ nm) in pyridine that is tentatively assigned as a metal to pyridine charge-transfer absorption. Polymer **2** does not melt but becomes increasingly red up to 280 °C.

Discussion

Fluorinated thiolates of the lanthanides differ substantially from their hydrocarbon analogues in both chemical and physical properties. Most striking is the relative stability of the fluorinated compounds, which decompose only slowly in air and are thus similar to Ln complexes with the chelating, resonance-stabilized pyridinethiolate (2-S–NC₅H₄, or SPy) ligands.^{29,30} The stability of the fluorinated compounds can be attributed to the ability of F to inductively stabilize the thiolate anionic charge, and to the coordination of F to the Ln in a chelating interaction. While the SC₆F₅ compounds are more thermally stable than their Ph counterparts, these ligands are no better than Ph for stabilizing higher oxidation states, in distinct contrast to the SPy ligand. For example, SPy forms stable complexes with Eu(III), while the SC₆F₅ ligand will only oxidize Eu to the divalent state, as determined in earlier Eu–SR (R = Ph, 2,4,6-ⁱPrC₆H₂) synthetic investigations.

Unlike the SPy and SPh compounds, these fluorinated thiolates are extremely soluble, dissolving in 1:1 THF/hexane mixtures. For comparison, the SPy compounds of the middle lanthanides are soluble in pyridine only upon addition of additional SPy anion, which forms Ln(SP₄)[−] salts, while the middle Ln(SPh)₃ compounds are sparingly soluble in refluxing THF from which they crystallize as 1D coordination polymers with sets of three thiolates connecting adjacent metal ions.⁴ In contrast **1** dissolves in THF and recrystallizes readily upon addition of an equal volume of hexane. Solubility is presumably related to the facility with which thiolate ligands bridge Ln(III)

ions, and the F substituents, by polarizing electron density away from the S, reduce the tendency of SC₆F₅ to form oligomeric products.

This presumed polarization has a negligible effect on Sm–S bond lengths. Compound **1** has terminal Ln–S bond lengths of 2.746(4) and 2.772(4) Å that are not significantly different from the terminal Sm–S bond lengths (2.785(3) and 2.752(3) Å) in the pyridine coordination complex⁴ (py)₈Sm₄(SPh)₁₂. Both terminal and bridging Sm–S bonds are within the normal values defined by the diverse array of compounds with Sm–S bonds, i.e., terminal Sm–S bonds in Sm(S–Mes)₃ (2.643(9) Å)⁸ and Sm(S^tBu)₆^{3−} (2.829(3) Å)⁹ and bridging Sm–μ-S bonds in [(THF)Sm(SPh)₃]_n (2.863(8) Å),⁴ [(THF)₃Sm(SAr)₃]₂ (3.017(6) Å),⁵ or [(COT)Sm(THF)(SAr)]₂ (2.883(6) Å).³¹ Similarly, in the divalent polymer **2** there is a complete insensitivity of Eu–S bond length to the fluoro substituents. Distances of 3.014(3) and 3.035(3) Å for the bridging Eu–S bond lengths in **2** are essentially equivalent to the bridging thiolate–Eu(II) distances in the literature, i.e., 2.987(2)–3.014(3) Å in [EuM(SPh)₄]₂ (M = Zn, Cd, Hg)³² or 3.015(6) Å in [(THF)₃Eu(SAr)₂]₂.⁶ Distances from Ln to the O(THF) atoms are also in the normal range for Ln–O bonds for both **1** and **2**.

Coordination of fluoride as a neutral donor has relatively little precedent in lanthanide chemistry. Early investigations of the reactions between fluorinated compounds and organolanthanide(II) compounds resulted in reductive C–F bond cleavage and the isolation of Ln(III) products with F[−] ligands.^{33–37} More recently, a structural investigation of fluorinated arylamido Ln(III) compounds³⁸ revealed dative Ln–F bonds that are similar to the dative interactions found in **1** and **2**. In the report of these amido complexes, both a homoleptic compound

(29) Berardini, M.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 6179.

(30) Berardini, M.; Lee, J.; Freedman, D.; Lee, J.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1997**, *36*, 5772.

(31) Mashima, K.; Nakayama, Y.; Kanehisa, N.; Kai, Y.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1847.

(32) Brewer, M.; Lee, J.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 5919.

(33) Watson, P. L.; Tulip, T. H.; Williams, I. *Organometallics* **1990**, *9*, 1999.

(34) Burns, C. J.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 272.

(35) Burns, C. J.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1989**, 136.

(36) Schumann, H.; Keitsch, M. R.; Winterfeld, J.; Demtschuk, J. *J. Organomet. Chem.* **1996**, *525*, 279.

(37) Finke, R. G.; Keenan, S. R.; Schiraldi, D. A.; Watson, P. L. *Organometallics* **1987**, *6*, 1356.

(38) Click, D. R.; Scott, B. L.; Watkin, J. G. *Chem. Commun.* **1999**, 633.

$\text{Sm}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{F}_5)]_3$ and two heteroleptic derivatives $(\text{THF})_3\text{Sm}(\text{NHC}_6\text{F}_5)_3$ and $(\text{toluene})\text{Nd}(\text{N}(\text{C}_6\text{F}_5)_2)_3$ were described, with the shortest Ln–F interactions found in the homoleptic compound (2.556(6)–2.587(6) Å) and in the arene derivative (2.572(5), 2.616(5), and 2.940(5) Å). With the more strongly donating THF present in the primary coordination sphere, the Sm–F bonds were all lengthened significantly, with Sm–F distances of 2.847(4)–2.876(3) Å.

Both the amido and thiolate ligand systems have similar $[\text{Ln}-\text{X}-\text{C}-\text{C}-\text{F}-\text{Ln}]$ ($\text{X} = \text{N}, \text{S}$) connectivity, but the tendency of the thiolate to form right angle bonds at the heteroatom center certainly enhances the relative ability of the SC_6F_5 ligand to coordinate through a Ln–F bond. This is reflected in the relative Ln–F bond lengths of $(\text{THF})_3\text{Sm}(\text{NHC}_6\text{F}_5)_3$ and eight-coordinate **1** (2.580(8) and 2.645(7) Å). Presumably, basicity at the F is also enhanced in compounds with the charge centered on the more electropositive heteroatom. It is interesting to note that in the related octahedral Ca(II) derivative¹⁴ $(\text{py})_4\text{Ca}(\text{SC}_6\text{F}_5)_2$ there are no Ca–F interactions, presumably because F is displaced by the stronger pyridine donor.

Ionic radii³⁹ are not reliable predictors of Ln–F bond lengths most likely because these bonds should be particularly susceptible to external forces such as ligand–ligand repulsive interactions or the impositions of the crystal lattice. While both the Sm–O and Eu–O bond lengths fall within the expected range of values, with Eu–O being larger by ca. 0.13 Å because of the greater size of the Eu(II) ion relative to Sm(III), the Ln–F bonds are ca. 0.30 Å greater in the Eu compound. Coordination of F to Ln does not have a significant effect on the C–F bond length in either **1** or **2**.

Fluorination of the arene ligand has a moderate effect on the electronic structure of these compounds. The yellow color of trivalent **1** is tentatively attributed to a near-visible S to Sm(III) charge-transfer absorption.^{3,4,40} The conflicting σ -withdrawing and π -donor influences of perfluoro substitution do not produce a dramatic change in electronic structure, with the color of **1** appearing to be indistinguishable, by eye, from the SPh analogue, but an unambiguous assessment is precluded by the inability to identify an absorption maximum for this transition. Fortunately, the electronic properties of polymer **2** are measurably perturbed by the F substituents. When dissolved in pyridine, **2** has a tentatively assigned metal-to-pyridine charge-transfer absorption at 340 nm that, when compared with $\text{Eu}(\text{SPh})_2$ in pyridine ($\lambda_{\text{max}} = 380 \text{ nm}$),⁴¹ suggests that the net effect of the 10 fluoro substituents is a reduction of the electron density at the Eu(II) center. Because SC_6F_5 and SPh coordinate differently (and because $\text{Eu}(\text{SPh})_2$ has been isolated only as part of a heterovalent polymer), it is impossible to confidently attribute the differences solely to differences in electronic structure. Still, the change in absorption energy is greater than the change

produced by replacing the chalcogen (i.e., $\text{Eu}(\text{SePh})_2$ ($\lambda_{\text{max}} = 392 \text{ nm}$)⁴² vs $\text{Eu}(\text{TePh})_2$, ($\lambda_{\text{max}} = 382 \text{ nm}$)⁴³).

A feature common to the structures of both **1** and **2** is a distinctive arrangement of aromatic rings. This is particularly noticeable in polymeric **2**, which, from the unit cell packing diagram in Figure 3, clearly shows that the thiolate rings in **2** are orientated for maximum π – π interactions, and dimeric **1** (Figure 1) also clearly has a stacked arrangement of the three arene ligands (two terminal and one bridging) on the top and bottom of the molecule in the figure. While there are no clearly oriented C_6F_5 groups in the previously mentioned amido compounds, in $(\text{py})_4\text{Ca}(\text{SC}_6\text{F}_5)_2$ the two arenethiolates are aligned with two of the pyridine ligands.

Early investigations into the thermolysis of fluorobenzenethiolates revealed that these compounds were potential single-source precursors to metals, metal fluorides, or metal sulfides, depending on the identity of the metal.¹² Only the noble metals Au and Pt reductively eliminated disulfide. Of the remaining compounds studied, SC_6F_5 compounds of more covalent metals Ag, Tl, Cu, Ni, Pb, and Hg gave MS_x thermolysis products. Both MS and MF_2 were noted in the thermolysis of $\text{Zn}(\text{SC}_6\text{F}_5)_2$ and $\text{Cd}(\text{SC}_6\text{F}_5)_2$, while in Li chemistry, thermal decomposition of LiSC_6F_5 gave LiF. Given that even the thermal decomposition of the relatively chalcophilic metals Zn and Cd formed predominantly metal fluorides, it was reasonable to expect that the analogous chemistry with considerably more electropositive Ln metals would also yield fluoride solids. An analysis of the thermal decomposition of **1** confirms this supposition; XRPD of the nonvolatile products revealed SmF_3 was the only crystalline phase present, while a GC–MS analysis of the volatile products indicated a mixture of products, all oligomers of the F-abstracted SC_6F_4 ligand. The presence of higher order products in addition to the predictable dimer octafluorodithiathrene $(\text{SC}_6\text{F}_4)_2$ suggests these thermolyses may be an interesting synthetic approach to novel fluorinated thiocrown compounds.

Conclusion

Lanthanide compounds with the fluorinated benzenethiolate ligand have a number of attractive physical properties. These compounds are considerably more stable than their hydrocarbon analogues presumably because of inductive stabilization of the sulfur based anion, as well as the ability of F to coordinate to the Ln. They are more soluble than their SPh analogues, and they decompose to give LnF_3 . Further synthetic investigations of thermally stable derivatives are currently underway.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-9982625.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0006908

(39) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

(40) Berardini, M.; Emge, T.; Brennan, J. G. *J. Chem. Soc., Chem. Commun.* **1993**, 1537.

(41) Melman, J.; Croft, M.; Freedman, D.; Emge, T. J.; Brennan, J. G. Manuscript submitted.

(42) Berardini, M.; Emge, T.; Brennan, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 8501.

(43) Khasnis, D. V.; Lee, J.; Brewer, M.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **1994**, *116*, 7129.