Heterometallic Ln/Hg Compounds with Fluorinated Thiolate Ligands

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The early lanthanide benzenefluorothiolates \((\text{Ln}(\text{SC}_6\text{F}_5)_3); \text{Ln} = \text{La, Ce, Pr, Nd, Sm, Gd}\) react with \(\text{Hg}(\text{SC}_6\text{F}_5)_2\) in DME to form ionic heterometallic compounds with Ln cations and Hg anions. X-ray diffraction analyses of all compounds reveal an isostructural series with the general formula \([\text{DME}]_3\text{Ln}(\text{SC}_6\text{F}_5)_2\text{Hg}_2(\text{SC}_6\text{F}_5)_3\]. In the structures, a fluorothiolate ligand has been extracted from the Ln coordination sphere that is saturated with three neutral DME donor ligands and a dative interaction between one ortho fluorine and the Ln. Distances between Ln and F do not vary simply with Ln ionic radius. There are two Ln cations with charge balanced by a \(\text{Hg}_2(\text{SC}_6\text{F}_5)_3\) dianion composed of two distinctly nonideal Hg(II) tetrahedra, all connected through a series of \(\pi-\pi\) interactions that link cations with anions in a one-dimensional array and anions to anions in a more complex 2D network.

Introduction

Heterometallic compounds containing lanthanides (Ln) and transition metals (M) continue to be investigated as potentially useful electronic materials with readily tailored electronic or magnetic properties.\(^{1-6}\) There is an extensive litera-

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inated organic ring imparts useful solubility properties. For example, (solvent)₃LnE(EE)(SC₆F₅)₂ dissolve readily in toluene, whereas (solvent)₃LnE(EE)(EPH)₂ (E = S, Se, Te) are soluble only in Lewis base solvents. The fluorocarbon moiety also imparts curious structural features, including extensive π–π stacking interactions, and in lanthanide chemistry there exists a distinct tendency to exhibit dative Ln–F interactions. In redox reactions of Ln(SC₆F₅)₃ with elemental E, the fluorothiolate ligand did not react, thus presenting an opportunity to prepare the aforementioned toluene soluble clusters.

While displacement chemistry (or the lack thereof) with SC₆F₅⁺ have been examined, heterometallic Ln compounds incorporating SC₆F₅⁻ have not yet been described. Because hydrocarbon soluble heterometallic compounds could be useful for doping Ln/M into a variety of organic based optoelectronic devices, we set out to establish whether Ln(SC₆F₅)₃ would react with Hg(SC₆F₅)₂ to form discrete products. This work outlines the first successful preparation of heterometallic fluorothiolate compounds containing both Ln and Hg, the first structural characterization of heterometallic compounds containing SC₆F₅⁻ ligands, and the first attempt to evaluate how Ln ionic radius influences the length of dative Ln–F bonds.

Experimental Section

**General Methods.** All syntheses were carried out under high purity nitrogen (Airgas), using conventional drybox or Schlenk techniques. Solvents (Aldrich) were refluxed continuously over molten alkali metals or K/benzophenone and collected immediately prior to use, or purified with a dual column Solv-Tek solvent purification system. Lanthanides were purchased from Strem. Hg(SC₆F₅)₂ was prepared according to the modified literature procedure. Melting points were taken in sealed capillaries and are uncorrected. IR spectra were taken on a Thermo Nicolet Avatar 360 FTIR spectrometer, and recorded from 4000 to 600 cm⁻¹ as a Nujol mull on NaCl plates. Mass spectra were recorded on a Finnigan LCQ-DUO mass spectrometer using acetoniitrile as a solvent. 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). The compounds are slightly air sensitive and will eventually lose lattice DME when exposed to air.

**Synthesis of [(DME)₃La(SC₆F₅)₂][Hg(μ-SC₆F₅)₂(SC₆F₅)La]·DME (1).** Method A follows: La (0.14 g, 1.0 mmol) and Hg(SC₆F₅)₂ (1.50 g, 2.5 mmol) were combined in DME (ca. 20 mL), and the mixture was stirred until all the metal was consumed (1 day) to give a colorless solution with a gray powdery precipitate at the bottom of the flask. The colorless solution was filtered away from the mercury (0.25 g, 82%), and Hg(SC6 F5)2 (0.60 g, 1.0 mmol) was added to the solution and stirred overnight to give a colorless solution with a gray powder precipitate at the bottom of the flask. The colorless solution was filtered, reduced in volume under vacuum to ca. 10 mL, and layered with 10 mL of hexane to give colorless plate-shaped crystals upon cooling at 15 °C (0.30 g, 88%).

**Synthesis of [(DME)₃Ce(SC₆F₅)₂][Hg(μ-SC₆F₅)₂(SC₆F₅)Ce]·DME (2).** As for 1 above, Ce (0.14 g, 1.0 mmol) and Hg(SC₆F₅)₂ (1.50 g, 2.5 mmol) in DME (ca. 20 mL) gave colorless small rod-shaped crystals (0.28 g, 82%). The crystals melt (colorless liquid) between 80 and 82 °C; the liquid then turns pale yellow at 120 °C, and then dark brown around 220 °C. IR: 2925 (w), 2725 (s), 2593 (s), 2396 (s), 2351 (s), 1622 (m), 1575 (s), 1463 (w), 1385 (w), 1296 (m), 1261 (w), 1085 (w), 970 (w), 857 (w), 712 (s), 622 (s) cm⁻¹. UV–vis: no absorption maximum from 300 to 750 nm in either THF or pyridine. Anal. Calcd for C₉₂H₈₀F₅₀Hg₂O₁₆S₁₀Pr₂: C, 32.6; H, 2.36. Found: C, 32.2; H, 2.50.

**Synthesis of [(DME)₃Pr(SC₆F₅)₂][Hg(μ-SC₆F₅)₂(SC₆F₅)Pr]·DME (3).** As for 1 above, Pr (0.14 g, 1.0 mmol) and Hg(SC₆F₅)₂ (1.50 g, 2.5 mmol) in DME (ca. 20 mL) gave pale green plate-shaped crystals (0.33 g, 97%) that melt between 72 and 75 °C. The liquid turns deeper green at 140 °C and changes from light brown to dark brown between 245 and 350 °C. IR: 2926 (w), 2729 (w), 2397 (s), 2255 (s), 1711 (s), 1659 (s), 1622 (s), 1579 (w), 1456 (w), 1386 (w), 1257 (w), 1089 (w), 824 (w), 721 (m), 623 (s) cm⁻¹. UV–vis: no absorption maximum from 300 to 750 nm in either THF or pyridine. Anal. Calcd for C₉₂H₈₀F₅₀Hg₂O₁₆S₁₀Nd₂: C, 32.5; H, 2.35. Found: C, 31.7; H, 2.19. NMR (CD3CN, 24 °C): −162.69 (1F, w₁/₂ = 91 Hz); −161.56 (2F, w₁/₂ = 136 Hz); −131.2 (2F, w₁/₂ = 90 Hz). There was no change in line shape as a function of temperature. Method B follows: As for 1 above, Ce (0.14 g, 1.0 mmol) and sequential additions of Hg(SC₆F₅)₂ (0.90 g, 1.5 mmol) and Hg(SC₆F₅)₂ (0.60 g, 1.0 mmol) was added to the solution and stirred overnight to give a colorless solution with a gray powder precipitate at the bottom of the flask. The colorless solution was filtered, reduced in volume under vacuum (10 mL), and layered with 10 mL of hexane to give colorless plate-shaped crystals upon cooling at 15 °C (0.30 g, 88%).

**Synthesis of [(DME)₃Nd(SC₆F₅)₂][Hg(μ-SC₆F₅)₂(SC₆F₅)Nd]·DME (4).** As for 1 above, Nd (0.14 g, 1.0 mmol) and Hg(SC₆F₅)₂ (1.50 g, 2.5 mmol) in DME (ca. 20 mL) gave, upon cooling to 5 °C, colorless crystals (0.27 g, 79%) that melt between 70 and 74 °C.

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Table 1. Summary of Crystallographic Details for 1–6

<table>
<thead>
<tr>
<th>Ln in empirical formula</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Gd</th>
</tr>
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<tr>
<td>( {\text{Ca}_2\text{H}_2\text{F}_6\text{G}<em>3\text{O}</em>{10}\text{S}_0\text{Sn}_2} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>( f_w )</td>
<td>3391.16</td>
<td>3393.58</td>
<td>3395.16</td>
<td>3401.82</td>
<td>3414.04</td>
<td>3427.84</td>
</tr>
<tr>
<td>space group</td>
<td>( P1 )</td>
<td>( P1 )</td>
<td>( P1 )</td>
<td>( P1 )</td>
<td>( P1 )</td>
<td>( P1 )</td>
</tr>
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<td>( a (\AA) )</td>
<td>12.6352(7)</td>
<td>12.6701(7)</td>
<td>12.6591(6)</td>
<td>12.6488(7)</td>
<td>12.6499(10)</td>
<td>12.6757(6)</td>
</tr>
<tr>
<td>( c (\AA) )</td>
<td>19.6962(10)</td>
<td>19.6719(11)</td>
<td>19.5725(10)</td>
<td>19.5108(10)</td>
<td>19.4412(16)</td>
<td>19.4107(9)</td>
</tr>
<tr>
<td>( \alpha (\text{deg}) )</td>
<td>87.021(1)</td>
<td>87.041(1)</td>
<td>87.046(1)</td>
<td>87.149(1)</td>
<td>87.170(2)</td>
<td>87.270(1)</td>
</tr>
<tr>
<td>( \beta (\text{deg}) )</td>
<td>71.86(1)</td>
<td>71.91(1)</td>
<td>71.86(1)</td>
<td>71.86(1)</td>
<td>71.86(1)</td>
<td>71.86(1)</td>
</tr>
<tr>
<td>( \gamma (\text{deg}) )</td>
<td>87.021(1)</td>
<td>87.041(1)</td>
<td>87.046(1)</td>
<td>87.149(1)</td>
<td>87.170(2)</td>
<td>87.270(1)</td>
</tr>
<tr>
<td>( V(\text{Å}^3) )</td>
<td>2933.5(3)</td>
<td>2943.1(3)</td>
<td>2918.2(3)</td>
<td>2914.8(3)</td>
<td>2895.9(4)</td>
<td>2898.2(2)</td>
</tr>
</tbody>
</table>

\( a_{\text{i}} \) and \( c_{\text{i}} \) for \( \text{Ca}_2\text{H}_2\text{F}_6\text{G}_3\text{O}_{10}\text{S}_0\text{Sn}_2 \): (a) Johnson, C. K. ORTEP II; Report ORNL-5138; Oak Ridge National Laboratory, Oak Ridge, TN, 1976. (b) Zsolnai, L. Z. Inorganic Chemistry, Vol. 43, No. 20, 2004 6309.
The Ln through a dative bond to the ortho fluoride F(1). The thiolates on the other side, one of which also coordinates to Ln ions are each chelated by three bidentate DME ligands lengths and angles in the complexes. In all compounds, the treatment of 

![Figure 1](image_url)  
Figure 1. Molecular structure of the cation (a) and dianion (b) in [(DME)₃Ln(SC₆F₅)₂][Hg₂(SC₆F₅)₆]. Thermal ellipsoids are drawn at the 50% probability level for the Pr compound.

Compounds can be prepared either by combining solutions of Ln and Hg reagents or by in situ generation of the Ln reagent in the presence of excess Hg(SC₆F₅)₂ (reaction 1). They are insoluble in apolar solvents (i.e., hexane, toluene) but redissolve in Lewis bases such as pyridine, acetonitrile, or THF. Once isolated, they are relatively stable in air and can be handled briefly with no immediate loss of crystallinity. Attempts to prepare the analogous Eu(III) derivative led only to the isolation of divalent [Eu(SC₆F₅)₂]₁₀⁺ and the later (heavier) lanthanides do not appear to form isolable compounds.

\[
\text{Ln(SC}_6\text{F}_5)_3 + \text{Hg(SC}_6\text{F}_5)_2 \xrightleftharpoons{\text{DME}} \quad \frac{(\text{DME})_3\text{Ln(SC}_6\text{F}_5)_2}{2\text{Ln} + 5\text{Hg(SC}_6\text{F}_5)_2} \quad (1)
\]

Low-temperature single-crystal X-ray diffraction analyses of 1–6 were obtained, revealing an isostructural series of solvated Ln cations with mercury dianions. Figure 1 gives an ORTEP diagram for the Pr derivative as a generic structure of 1–6, and Table 2 gives a listing of significant bond lengths and angles in the complexes. In all compounds, the Ln ions are each chelated by three bidentate DME ligands distributed on one side of the metal. There are two terminal thiolates on the other side, one of which also coordinates to the Ln through a dative bond to the ortho fluoride F(1). The Ln–S and Ln–O bond lengths vary with Ln ionic radius, with the lanthanide contraction accounting for the decrease upon traversing the series from La to Gd (Table 2). In contrast, Ln–F bonds vary in a discontinuous fashion: there is at first a statistically equal set of distances noted from La to Ce to Nd, before a small but steady increase in Ln–F(1) bond length from Nd to Sm, and finally a more dramatic increase at Gd. Pure compounds with lanthanides heavier than Gd were not obtained.

Both cations and anions have intermolecular π−π interactions for adjacent pairs of SC₆F₅ ligands that generate an anion that is flattened on two sides. For the cations, this placement of ligands results in a rather polar molecular species, in contrast to the anion, which contains near inversion symmetry. The flattened molecular shape lends itself to low-dimensional stacking of ions in the crystal structure. For the [(DME)₃Ln(SC₆F₅)₂][Hg₂(SC₆F₅)₆] salts, as in other molecular salts, this also gives rise to segregated 2D sheets of cations that alternate with sheets of anions in the solid state. Further, the anions form infinite chains of directly overlapping pairs of SC₆F₅ ligands between adjacent ions. These chains criss-cross along the crystallographic a and b directions for the inversion-related pairs of SC₆F₅ ligands in the anion to yield a tightly woven 2D sheet of closely interacting anions. Although the a and b axes differ significantly in length, there is no crystallographic distinction between pairs of terminal SC₆F₅ ligands of the anion, since inversion symmetry is imposed on the anion by the space group. As a result, the geometry of the intermolecular π−π interactions along the a versus b directions is approximately the same. This situation accommodates the 50:50 disorder for two sites for each of these terminal SC₆F₅ ligands in the anion, in contrast to the ordered cation. The packing motif for the cations leads to an ordered, but lower dimensional, stacking array, as the cations pair up to form discrete dimers with one intramolecular and two intermolecular π−π interactions. The one DME solvate molecule per Ln is found in the cation sheet, filling a void between cation pairs at the interface to the anion sheet.

**Discussion**

While the SC₆F₅ moiety has, until now, provided an entry into hydrocarbon soluble molecular and cluster chemistry of the lanthanides, compounds 1–6 are soluble only in Lewis base solvents. Molecular Ln(II) and Ln(III) compounds routinely dissolved in aromatic solvents such as toluene, and even the chalcogen rich (THF)₆ LnE(EE)₄ (SC₆F₅)₂ clusters, which had only two SC₆F₅ ligands to solubilize four Ln centers, were toluene soluble. Presumably, the unusual insolubilities of 1–6 originate from the ionic nature of the products. Previously, 1D structures had been noted, i.e., Eu(SC₆F₅)₂, where pairs of bridging thiolates connected adjacent Eu ions and π−π interactions connecting neighboring sets of SC₆F₅ ligands. Even though Eu(SC₆F₅)₂ formed a polymeric lattice, the compound itself dissolved in apolar solvents. Compounds 1–6, with 2D sheets of anions isolating the layers of Ln containing cations, represent the first set of Ln compounds with SC₆F₅ ligands that are totally insoluble in hydrocarbon solvents. The large molecular dipole of the...
Ln/Hg Compounds with Fluorinated Thiolate Ligands

Table 2. Significant Distances (Å) and Angles (deg) for 1–6

<table>
<thead>
<tr>
<th></th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Gd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ln(1)–O(2)</td>
<td>2.563(3)</td>
<td>2.547(3)</td>
<td>2.528(2)</td>
<td>2.512(4)</td>
<td>2.475(4)</td>
<td>2.459(3)</td>
</tr>
<tr>
<td>Ln(1)–O(6)</td>
<td>2.578(2)</td>
<td>2.548(3)</td>
<td>2.536(2)</td>
<td>2.524(4)</td>
<td>2.486(4)</td>
<td>2.465(3)</td>
</tr>
<tr>
<td>Ln(1)–O(4)</td>
<td>2.617(3)</td>
<td>2.590(4)</td>
<td>2.552(3)</td>
<td>2.545(5)</td>
<td>2.496(5)</td>
<td>2.483(3)</td>
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<tr>
<td>Ln(1)–O(1)</td>
<td>2.586(2)</td>
<td>2.570(3)</td>
<td>2.546(4)</td>
<td>2.526(4)</td>
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<td>Ln(1)–O(3)</td>
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<td>2.598(3)</td>
<td>2.569(2)</td>
<td>2.554(5)</td>
<td>2.535(4)</td>
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<tr>
<td>Ln(1)–O(5)</td>
<td>2.640(3)</td>
<td>2.626(3)</td>
<td>2.604(3)</td>
<td>2.592(5)</td>
<td>2.562(4)</td>
<td>2.553(4)</td>
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<tr>
<td>Ln(1)–F(1)</td>
<td>2.797(2)</td>
<td>2.811(3)</td>
<td>2.799(2)</td>
<td>2.801(4)</td>
<td>2.813(3)</td>
<td>2.837(3)</td>
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<tr>
<td>Ln(1)–S(2)</td>
<td>2.8935(10)</td>
<td>2.8692(12)</td>
<td>2.8431(8)</td>
<td>2.8316(15)</td>
<td>2.8011(15)</td>
<td>2.7990(10)</td>
</tr>
<tr>
<td>Ln(1)–S(1)</td>
<td>2.9277(9)</td>
<td>2.9034(11)</td>
<td>2.8807(8)</td>
<td>2.8656(17)</td>
<td>2.8307(14)</td>
<td>2.8171(10)</td>
</tr>
</tbody>
</table>

The Ln containing cations must also play a role in the insolubility of 1–6.

Still, solid-state structure is not necessarily identical to solution structure. $^{19}$F NMR analyses in THF and acetonitrile give some information regarding structure in solution. In acetonitrile, the compounds show only a single set of ortho, meta, and para F resonances, suggesting either that the solution state contains only a single type of SC$_6$F$_5$ environment, or that there is fast site exchange that averages the inequivalent mercury bonding environments (terminal and bridging) with those of the terminal and chelating lanthanide thiolates. In THF, the La compound again shows only a single resonance for the meta and para fluorides, but the ortho resonance is split 3:1, which suggests that there are different Ln versus Hg containing molecular ions in THF solution, and that site exchange between Ln and Hg thiolates is slow on the NMR time scale. The molecular form of the anions is not defined by the NMR experiment, but the tendency of $\text{LnF}_3$ compounds to decompose thermally to give LnF$_3$, it was unclear whether the ionic configurations of 1–6 would have any impact on the identity of the thermolysis products, and so an analysis of the thermal decomposition of 4 was undertaken. In contrast to the thermolysis of heterometallic Ln/Hg SPh compounds, which gave mixtures of LnS and HgS, decomposition of 4 gave only solid-state NdF$_3$, with the mercury fluorothiolate subliming into the cold zone of the thermolysis experiment prior to decomposition (reaction 2).

$\text{[(DME)}_3\text{Nd(SC}_6\text{F}_5)_2\text{]}_2\text{[Hg}_2\text{(SC}_6\text{F}_5)_6\text{]} \xrightarrow{\Delta} \text{NdF}_3 + \text{Hg(SC}_6\text{F}_5)_2 + \text{(SC}_6\text{F}_4)_n $ (2)

The mercury dianion is distinctly distorted from ideal tetrahedral Hg(II) geometries. Although the inner Hg$_2$S$_2$ cores are crystallographically required to be planar (which still allows for tetrahedral symmetry), the bridging ligands show no evidence of disorder, the average S–Hg–S’ angles and average Hg–S–Hg’ angles are within a degree of 90° and sum to approximately 180° for 1–6. This distortion from tetrahedral geometry (i.e., 109.5° angles) and planarity is observed also in the related Hg$_2$(SMe)$_2$ (89.5° and 90.5°, respectively, for S–Hg–S and Hg–S–Hg), even though the latter compound does not display significant inter- or intramolecular $\pi$–$\pi$ interactions between SPh ligands. A related anion, Hg$_2$(SMe)$_2$, contains a mercury–sulfur core that also has Hg geometries that are far from tetrahedral (S–Hg–S, 94.2°), Disorder within the dianion in 1–6 complicates an analysis of the Hg–S bond lengths beyond the above, but all refined to values within the normal range of Hg–S interactions.

Within a given cation, interplanar distances increase slightly on going from the more interior contacts, at 3.2 Å, and for the more exterior contacts, at 3.8 Å. This increase in contact distances is consistent with the inflexibility associated with the bidentate [e.g., $S(1)\cdots Ln\cdots F(1)$] ligand and the flexibility of the adjacent monodentate [e.g., $S(2)\cdots Ln$] ligand. Within the anions, the dihedral angle between adjacent terminal $C_6F_5$ rings is also not zero. However, the contact distances decrease on going from the more interior 3.6 Å contacts to the more exterior 3.2 Å contacts. This decrease in contact distances is consistent with the type of nontetrahedral disorder observed for the Hg coordination. These distances, 3.6 Å on the interior and 3.2 Å on the exterior, are observed for the entire series here, $1-6$. As for intermolecular ring–ring contacts, there are none for the isolated cations, but the disorder in the terminal ligands of the anion allows for two sets of contact distances between parallel rings that are crystallographically equivalent, namely, A•••B and B•••A. For all anions in complexes $1-6$, the intermolecular separation between nearest neighbor rings is parallel at a 3.5 Å separation. This is expected for closely stacking rings that are related by a symmetry center, as found in the 2D array of anions here.

Finally, this isostructural series presents a unique opportunity to evaluate the manner by which steric demands impact dative Ln–F bond lengths. From the distances in Table 2, it becomes clear that these Ln–F interactions are influenced by more than just the ionic radii of Ln and F. The six Ln–O and two Ln–S bonds all behave as expected, gradually contracting as the size of Ln decreases with the lanthanide contraction. This gradual decrease serves to increase interligand repulsive interactions, and the bond most sensitive to these repulsions is Ln–F, the weakest bond within the primary Ln coordination sphere. In the early compounds $1-3$, there are no significant differences in Ln–F bond lengths, which range from La–F (2.797(2) Å) to Nd–F (2.801(4) Å) and are compared to distances noted, for example, in [(THF)$_3$Ce(SC$_6$F$_5$)$_3$]$_2$ (2.749(2) Å) and (py)$_3$Sm(SC$_6$F$_5$)$_3$ (2.703(5) Å). As the series progresses, there is a small but constant increase in the distance separating Ln and F. With Ln ionic radii decreasing from $1$ to $6$ (La = 1.30 Å; Gd = 1.19 Å), the increase in Ln–F separation from Nd (2.801(4) Å) to Gd (2.837(3) Å) must be originating from interligand repulsive interactions that increase as the entire Ln coordination sphere contracts.

Support for this steric interpretation is found in the series of Ln–S–C angles, which increase as the series progresses from La to Gd (see Table 2). The nonchelating S(2) ligand is affected more, with Ln–S(2)–C(7) increasing from 110.1(1)° (La) to 114.0(1)° (Gd). In the chelating thiolate, this opening of Ln–S(1)–C(1) is significant only for Gd, much as was found in the series of Ln–F distances. The inability to isolate compounds with Ln smaller than Gd could be resulting from a change in molecular conformation as the Ln–F interaction becomes unsustainable.

**Conclusion**

Lanthanide and mercury benzenefluorothiolates react to form stable, relatively insoluble heterometallic compounds with transfer of thiolate from Ln to Hg. This anion transfer persists in solution. Contributing to the stability of the observed solid-state structure is an extensive network of $\pi-\pi$ interactions that connect anions with both cations and neighboring anions. The dative Ln–F bond lengths in the structures do not vary with Ln ionic radius.

**Acknowledgment.** This work was supported by the National Science Foundation under Grant CHE-0303075.

**Supporting Information Available:** X-ray crystallographic files in CIF format for the crystal structures of $1-6$. This material is available free of charge via the Internet at http://pubs.acs.org.

—Banerjee et al.