NOVEL LANTHANIDE STRUCTURES: FLUORINATED ALKOXIDES, 
CHALCOGENIDO ALKOXIDES, FLUORIDES, AND OXYCHALCOGENIDES

by

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ABSTRACT OF THE DISSERTATION

Novel Lanthanide Structures: Fluorinated Alkoxides, Chalcogenido Alkoxides, Fluorides, and Oxychalcogenido Clusters

By KIERAN JAMES NORTON

Dissertation Director:
John G. Brennan

A number of novel lanthanide alkoxide species were synthesized with fluorinated ligands. This includes monomers with pentafluorophenol, (DME)$_2$Ln(OC$_6$F$_5$)$_3$ (Ln = Nd, Er, Tm, Eu, and Yb), (py)$_4$Ln(OC$_6$F$_5$)$_3$ (Ln = Eu, Tb, Er, Tm, Yb), and (THF)$_3$Yb(OC$_6$F$_5$)$_3$. Unique europium species, ((py)$_3$Eu(CF$_3$SO$_3$)$_2$)$_n$, (DME)$_2$Eu(µ-OC$_6$F$_5$)$_3$Eu(µ-OC$_6$F$_5$)$_3$Eu(µ-OC$_6$F$_5$)$_3$Eu(DME)$_2$, and (DME)($C_6F_5O$)$_2$Eu(µ-OC$_6$F$_5$)$_3$Eu(DME)$_2$, were also produced. Most reactions proceeded by metathesis of lanthanide chalcogenolates, but direct redox reaction of elemental lanthanide with C$_6$F$_5$OH or CF$_3$SO$_3$H catalyzed by Hg also proved to be viable routes. The Eu(II) trimer was only synthesized through direct oxidation of the metal with the alcohol. Photoluminescence of (DME)$_2$Ln(OC$_6$F$_5$)$_3$ (Ln = Nd, Er, Tm) was tested, and they exhibited high quantum efficiency for lanthanide monomers.

Two series of dimers, (py)$_6$Ln$_2$(OC$_6$F$_5$)$_2$(µ-η$_3$-SS)$_2$ (Ln = Sm, Eu, and Gd) and (py)$_6$Ln$_2$(CF$_3$SO$_3$)$_2$(Se)$_x$ (Ln = Sm, Tm, Yb, and Lu; x = 3 or 4), were synthesized via
substitution of EPh⁻. The europium dimer is the first example of a Eu(III) molecular sulfido species which is extremely dark due to strong, broad LMCT from the sulfido. The selenidos display a conspicuous coordination change resulting from the relatively small difference in Ln ionic radii forming (py)₆Ln₂(CF₃SO₃)₂(µ-η²-SeSe)(µ-Se) for small late lanthanides and (py)₆Ln₂(CF₃SO₃)₂(µ-η²-Se)₂ for larger early lanthanides.

Three fluorido clusters were synthesized without the use of traditional fluoride sources. (DME)₆(py)₆Nd₁₈(C₆F₅O)₁₈F₂₄O₃S₃ was produced from a reaction of neodymium phenylselenolate with C₆F₅OH and sulfur. (py)₈Yb₄F₈(CF₃SO₃)₄ and (DME)₄Tb₄(CF₃SO₃)₆F₂S₂ were synthesized from lanthanide chalcogenolates, elemental chalcogens, and CF₃SO₃H. Cleavage of C-F bonds to form these clusters appears to be a slow reaction. Most reactions producing them took several months.

Lanthanide oxychalcogenido clusters were produced from reacting lanthanide chalcogenolates with pySO₃ or TeO₂ and Te. (THF)₈Ln₈O₂S₂(SePh)₁₆ (Ln = Ce, Nd) clusters were synthesized from “Ln(SePh)₃” and pySO₃. Reactions of “Ln(TePh)₃”, TeO₂ and Te produced [(py)₅Ln₃O(Te₂)₃(TePh)][(py)₇Ln₄Te(Te₂)₂(Te₂Te(Ph)Te₂)(TePh)] (Ln = Ho, Er), [(etpy)₁₁Ho₆O₄Te₄TePh] [Hg(TePh)₃] and [(4etpy)₁₂Yb₆O₄Te₄][Hg(TePh)₃][(TePh)₃].
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<th>Description</th>
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Introduction

Bonding between the seemingly incompatible lanthanide metals and chalcogen atoms has been of particular interest over the past few decades. One motivation for the synthesis of new compounds of this class has been to examine the nature of the bonding between lanthanides and chalcogens. The other reason is investigation into new potential compounds for technological uses.

The valence 4f orbitals in lanthanides are radially contracted with respect to the filled 5s and 5p orbitals. While the f orbitals are frontier orbitals of lanthanide ions, their limited extension prevents them from overlapping well with orbitals of surrounding atoms thereby preventing strong covalent interactions. The poor overlap of lanthanide and ligand orbitals makes the bonds ionic in nature. Lanthanides typically assume a 3+ oxidation state, and only a few commonly take other states (Ce^{4+}, Sm^{2+}, Eu^{2+}, and Yb^{2+}). All are hard cations, cations of high oxidation states contracting the ionic radius, so they are capable of strong electrostatic forces. As a result, solid state structures of lanthanides with hard anions, those with high electronegativity and therefore tightly bound electrons such as oxide and fluoride, have high lattice energies and are very stable. In molecular chemistry, the geometry around a lanthanide metal center is dictated by maximizing the energy of electrostatic attractions and minimizing repulsive steric interactions. As a result, small hard anions are the thermodynamically stable ligands, and the literature is replete with structures containing hydroxo and aqua ligands. Without an importance of directionality in ionic bonding, coordination typically surpasses octahedral geometries with lanthanide ions commonly coordinating 7- 9 ligands with coordination numbers reaching 12 in rare cases.
Chalcogens, conversely, tend to bond covalently with orbital shapes dictating geometries. Molecular geometries are typically derived from tetrahedral (sulfate), octahedral (SF₆, H₂S), or trigonal bipyramidal (SF₄) fundamental shapes. The oxidation states range from +6 in compounds like SF₆ and SO₄²⁻ to -2 in H₂S. Whether in formally positive or negative oxidation states, bond angles around chalcogens have covalent nature and follow standard geometries unlike lanthanides. In addition to adherence to orbital dictated geometries in small molecules, the importance of covalent character is manifested in the solid state structure of tellurium. Ionic bonding would predict equidistant neighboring atoms in the hexagonal lattice, but the crystal structure deviates from hcp packing. Each tellurium atom has two shortened bonds creating a preferred direction resulting in higher conductivity along that screw axis. Sulfur and selenium have multiple allotropes. The most common sulfur structure is composed of S₈ rings similar to a molecular solid. Gray selenium, like tellurium, forms a hexagonal lattice with one dimensional chains, while other phases arrange atoms in rings.

Structures of solid state compounds are typically dictated by packing based largely on the relative sizes of the ionic radii of the ions involved. Even in structures composed of hard ions with extreme electronegativity differences, cations fill tetrahedral, octahedral, or cubic holes in a packed lattice of anions which have ideal orbital alignment to maximize covalent character. Bonding between the highly electropositive lanthanides and soft chalcogens in solid state structures are still described in covalent terms. Moving from oxygen to larger chalcogens, covalent character decreases along with electronegativity. The low ionic character of the larger chalcogens results in relatively weaker bonding with lanthanides.
Molecular lanthanide-chalcogen chemistry is a relatively young field. Metal–chalcogen bonds have been well understood for main group and transition metals for decades. Relative instability of lanthanide–chalcogen bonds has made studying their bonding more difficult, and it has been a slow, lengthy investigation. Molecular lanthanide alkoxide species such as triflate salts can be stable in air and water in hydrated form and are commercially available, but poor bonding between the lanthanides and the larger chalcogens makes lanthanide chalcogenolate molecules relatively unstable. A molecular compound with an Ln–S bond, Ln(S$_2$CN(CH$_2$CH$_3$)$_2$)$_3$, was not isolated until 1968. Early examples of Ln–E (E = S, Se, Te) containing molecular species were simple monomers and salts of dithiocarbamates. More complicated structures were achieved utilizing the steric hindrance of pentamethylcyclopentadienyl ligands to only allow intended reactions. Reaction of Ln(Cp$^*$)$_2$ with chalcogen sources led to monomers and clusters containing Ln–E bonds, but products included the bulky cyclopentadiene that impacted the lengths and angles of other bonds in the structures. Following work used substituted silyl groups and 2,4,6 isopropyl phenyl chalcogenolates to protect the Ln–E bonds.

In an attempt to get a better perspective on the nature of the Ln–E bonds, later work used ligands with smaller cone angles such as EPh$^-$ in dry solvents to produce Ln molecules with less hindered coordination spheres. The ligand cone angle is an estimate of steric demands of a ligand measured as the area around a metal atom if the ligand is rotated around the M–L bond. It is most commonly used to describe phosphine ligands and the dependent reactivity of a catalyst containing such ligands but is a useful steric quantification for other uses. Since lanthanide ions commonly coordinate 7 or
more ligands, cone angle can be used in this area of chemistry to help explain relative stability and reactivity of specific species. Cp has an effective cone angle of 83°, and Cp* coordinating on its face has an effective cone angle of 146°. Since chalcogens can adopt different geometries, unsubstituted EPh ligand cone angles vary. A 90° Ln–S–C angle produces a cone angle of approximately 120° while an Ln–S–C angle of 109° is very similar to a benzyl group, closer to 90°. They provide much more space for reactivity or additional coordination. Without the overwhelming driving force of the steric bulk, this allowed a fuller investigation into Ln–E chemistry driven more by bond energies. Neutral solvent molecules possessing lone electron pairs such as pyridine, tetrahydrofuran and 1,2 dimethoxyethane could act as Lewis bases and filled in around the formally anionic ligands. The strengths of the Ln–S and Ln–Se bonds appear to be greater than the bonds between metal and neutral ligands. This is evidenced in trans effects where bonds trans to chalcogenolate ligands are longer than those trans to pyridine. This has been shown for Ln–S bonds for 2, 4, 6 – triisopropylphenylthiolate and Ln–Se bonds with phenylselenolate ligands among other structures. These solvents, therefore, help stabilize products containing small ligands which bond weakly to lanthanide ions without dominating the structures. After isolation and characterization of (py)₃Ln(EPh)₂ and (py)₃Ln(EPh)₃, in situ preparations of “Ln(EPh)₂” and “Ln(EPh)₃” have been regularly used to prepare other structures in various coordinating solvents.

When considering the strength of Ln–ER bonds for a series of related ligands with different chalcogens, the larger radii in the later periods causes a twofold problem. First is the inverse relationship between radius and electrostatic potential directly weakening the bonds. Second is the decreased Ln–E–R angle, which increases ligand cone angle
and steric repulsion. This angle is not the only factor of steric bulk, but it is important. Hybridization of oxygen orbitals does not include d orbitals which bestows smaller relative bond angles e.g. H₂O at 104.5° and H₂S at 90°. Also, the lower electronegativity of S, Se, and Te compared to O leads to decreased electron density around the chalcogen in isostructural ligands. This results in a lower effective charge which is directly proportional to the electrostatic potential. Chalcogenolates will not substitute for alkoxides in available molecular lanthanide species, so creation of Ln–E bonds must proceed through addition to a lanthanide species in a lower oxidation state or through substitution of other weakly coordinated ligands.

**Scheme 1.**

\[ \text{Ln} + 1.5 \ (\text{EPh})_2 \xrightarrow{\text{cat. Hg}} \text{Ln(EPh)}_3 \]

\[ \text{Ln} + (\text{EPh})_2 \xrightarrow{\text{cat. Hg}} \text{Ln(EPh)}_2 \]

The first reactions employing these chalcogenolate ligands in Ln(EPh)_3 preparations in common organic solvents employed the use of metal amalgams. Solid lanthanide was mixed with excess liquid mercury to dissolve, and to this alloy organic solvent and diphenyldichalcogenide (PhEEPh) was added. Later work employed stoichiometric reaction of (PhEEPh) with lanthanide metals using Hg in catalytic quantities.¹⁴b,c,¹⁵ There are two possible mechanisms for this reaction. Either the Hg inserts into the E–E bond followed by transmetalation with the lanthanide, or the Hg forms an amalgam with the lanthanide that activates direct reaction of the lanthanide with the chalcogen. Lanthanide metals were oxidized to trivalent or divalent states via
reaction Scheme 1. This reaction is a common first step in essentially all successive work.

Lanthanide chalcogenido chalcogenolate clusters were subsequently synthesized by replacing some chalcogenolate ligands in the aforementioned molecules with elemental chalcogen, oxidizing the chalcogenolate back to neutral PhEEPh, and reducing the E to $E^{2-}$. Simple examples include $(\text{py})_8\text{Yb}_4\text{Se}_4(\text{SePh})_4$ and $(\text{py})_{10}\text{Yb}_6\text{S}_6(\text{SPh})_6$. The metal:chalcogen ratio is identical in both cases with excess solvent, but the difference in the identity of the chalcogen gives dissimilar results. Small changes in reaction conditions yield structures with vastly different sizes, shapes, and coordination numbers. Related products with fluorinated thiolate ligands have also been synthesized in an effort to make molecules with stronger emission intensities and increased solubility in fluorinated polymers. Both $(\text{THF})_6\text{Yb}_4\text{S}([[\text{SS}])_4(\text{SC}_6\text{F}_5)_2$ and $(\text{THF})_6\text{Yb}_4\text{Se}[[[\text{SeSe}])_4(\text{SC}_6\text{F}_5)_2$ have been produced. While related to the simple chalcogenido chalcogenolate clusters, they contain dichalcogenido dianions ($E_2^{2-}$) in addition to $E^{2-}$ monatomic ions. This is common when elemental chalcogen is used in excess. Having multiple chalcogen oxidation states gives more possible structures from a given set of reactants. This selenido cluster is also one of numerous species that contain different chalcogens isolated in one cluster. Isolation of lanthanide chalcogenido clusters in which the internal chalcogens differ from the terminal ligands supports the possibility of intentionally synthesizing core-shell clusters with other classes of ligands.

**Scheme 2.**

$$\text{Ln}(\text{EPh})_3 + E' \rightarrow \text{LnE'}_x(\text{EPh})_y + \text{PhEEPh}$$
Related clusters have been synthesized with halides capping a lanthanide-chalcogenido cluster. Iodine has been especially useful due to ease of delivery. As a soft anion it is competitive with the chalcogens as opposed to smaller halides which were originally expected to be more likely to disproportionate into LnX₃ (X = F, Cl). At room temperature I₂ was able to react directly with the metal and (EPh)₂ in solution. Addition of elemental chalcogen replaced all chalcogenolate to give chalcogenido clusters with terminal iodide. Isolated products include (THF)₁₀Yb₆Se₆I₆, a symmetrical cubane structure with one iodine capping each ytterbium atom that was synthesized in yields greater than 10%, and (THF)₆Yb₄I₂(SeSe)₄Se·THF. These types of clusters lack

![Ortep view of (THF)₁₀Yb₆Se₆I₆](image)

Figure 1. Ortep view of (THF)₁₀Yb₆Se₆I₆
chalcogenolate ligands in the final product, but it is still necessary in the reaction mechanism. EPh⁻ or alternative temporary ligands are necessary to dissolve the metal for reaction with elemental chalcogen and halides. Direct reaction of lanthanide metals with chalcogen simply passivates the metal surface.

Complexes of lanthanide ions with alkoxides and other oxygen based ligands have been extensively investigated. Alkali alkoxide salts can be reacted with lanthanide chlorides via metathesis to produce lanthanide alkoxides.¹⁹ To avoid halide contamination and incomplete reactions, commercially available lanthanide halides have been reacted with alkali metal amides, MN(SiMe₃)₂. The resulting lanthanide amides can be purified before reacting with alcohols to synthesize lanthanide alkoxides.²⁰ Alternatively alcohols can undergo redox reactions with solid lanthanide metals using catalytic HgCl₂ or Hg(C₆F₅)₂ to produce lanthanide alkoxides and H₂.²¹ Aryloxyde ligands primarily coordinate through the oxygen with limited examples of secondary intramolecular η⁵ bonding.²² Various Ln(OAr)₃ monomers have been studied primarily focusing on substitution in the ortho positions due to the steric effects. Increasing the size of the ortho substituents is accompanied by a decrease in the coordination number of the metal from seven for the methylated (py)₄Ce(OC₆H₄(CH₃)₂ – 2,6)₃ to five for the t-butyl substituted (py)₂Er(OC₆H₄(t-but)₂ – 2,6)₃.²³²⁴

Lanthanide molecules with oxygen based ligands have commercial uses. Lanthanide triflates are used as Lewis acid catalysts in organic synthesis.²⁵ Lanthanide acetylacetonates are used as NMR shift reagents to resolve overlapping proton signals.²⁶ Gadolinium based MRI contrast reagents similarly work by coordinating the metal with stable oxygen-based polydentate ligands.²⁷ These uses rely on the air and water stability
of these compounds. Lanthanide oxo clusters are also typically stable in air and water. As with chalcogenolate clusters, available neutral electron donors fill the coordination sphere of the metal around the anionic ligands. Aqua ligands are typical, and hydroxo ligands are commonly found on lanthanide oxo clusters.

Molecular lanthanide chalcogenide species are potentially useful for optical and near infrared emission applications. The relative isolation of lanthanide ion electronic states from ligand field effects allows emissions from excited lanthanide ions to reliably peak at the same frequencies regardless of the coordination environment. Theoretically molecular species could accomplish the same function as solid state structures, but they would not be restricted to the delivery methods that work for solid state materials. Solubility in organic media would be a huge advantage if a molecular species could match the emission properties of lanthanide doped solids. Efficiencies of emissive processes and emission intensity are strongly dependent on environment. Fluorinated ligands were investigated for dual reason. First, compounds with fluorinated ligands tend to be more soluble than their hydrogenated counterparts in organic solvents and polymers increasing their potential usefulness. Second, C–H bonds reduce the intensity of some IR emission bands specifically used for fiber optic communication, and replacing C–H bonds with C–F bonds in the phenylchalcogenolates reduced these losses. Harmonics of C–H and O–H vibrational frequencies overlap with some of the bands, so energy of excited state electrons in some lanthanide ions is lost to the ligands in a non-radiative transfer, and the energy is lost as heat thereby dropping efficiency. Emission intensity is also reduced through instances of the photons produced in a radiative pathway being reabsorbed by the ligands before leaving the material.
Fluorinated lanthanide chalcogenolates, \((L)_x\text{Ln}(SC_6F_5)_3\) (\(L = \text{THF, py, DME}\)) (\(\text{Ln} = \text{Nd, Er, Tm}\)), have been previously reported to have the highest emission efficiencies for monomeric lanthanide compounds.\(^{28}\) Clusters exhibit higher efficiency than monomers as a general rule due to the higher concentration of lanthanide ions in solid samples, a trend that holds for fluorinated ligands.\(^{29}\) One of the first lanthanide chalcogenido clusters with fluorinated ligands synthesized, \((\text{THF})_6\text{Tm}_4\text{Se}_9(\text{SC}_6\text{F}_5)_2\)

proved a more fluorescent compound than a thulium monomer with the same fluorinated chalcogenolate, \((\text{DME})_2\text{Tm}(\text{SC}_6\text{F}_5)_3\). While increasing the size of clusters can increase the emission efficiency, oxo cluster emissions decreased as the cluster size continued to grow beyond eight metal atoms. The larger cluster, \((\text{py})_{18}\text{Nd}_{12}\text{O}_6\text{Se}_4(\text{Se}_2)_4(\text{SePh})_4(\text{Se}_2\text{Ph})_2\text{Hg}_2(\text{SePh})_4\)

exhibited less intensity than the similar \((\text{THF})_8\text{Nd}_8\text{O}_2\text{Se}_2(\text{SePh})_{16}\). This reduced efficiency was attributed to phononic relaxation of excited states.

Lanthanide complexes with fluorinated alkoxides are an interesting target for multiple reasons. Comparing the properties of theoretical alkoxides similar to chalcogenolates would be informative about the nature of the bonding. The mixture of lanthanide, oxygen, and sulfur in single molecules has potential use for precursors of low temperatures solid state lanthanide oxysulfide formation. Clusters containing lanthanide chalcogenido cores and terminal fluorinated alkoxide ligands are a target, because if they possess the efficient photoemissive properties displayed by fluorinated chalcogenolates but with greater stability in the presence of oxygen based molecules, they would have greater potential for application.
In this thesis, Chapter 1 discusses the synthesis and properties of fluorinated lanthanide alkoxides. Relatively simple structures were synthesized through substitution reactions between lanthanide chalcogenolates and alkoxides. We also used direct redox reactions between lanthanide metal and either pentafluorophenol or triflic acid to produce the same structures as the original substitution reaction as well as synthesizing a trimer that was not produced by substitution. Monomers of emissive lanthanides (Ln = Nd, Er, and Tm) were tested and compared to isomorphous thiolates.

Chapter 2 outlines the synthesis and properties of lanthanide chalcogenido alkoxides. Three structures, \((py)_6\text{Ln}_2(OC_6F_5)_2(SS)_2\) (Ln = Sm, Eu, and Gd), \((py)_6\text{Ln}_2(CF_3\text{SO}_3)_2(SeSe)_2\) (Ln = Sm and Tm), and \((py)_6\text{Ln}_2(CF_3\text{SO}_3)_2(SeSe)Se\) (Ln = Tm, Yb, and Lu), were produced. Due to insolubility of the sulfido dimer, the synthesis involved slow diffusion of solutions containing the reactants resulting in immediate crystallization upon reaction. The other structures were produced through more traditional techniques of separate reaction and crystallization steps. The spectroscopic properties of the Eu(II) sulfide molecule are dominated by MLCT absorbing strongly and broadly across the optical region.

The Third chapter focuses on lanthanide fluorides first produced accidentally through abstraction of fluorides from ligand molecules by the metal and later attempts to intentionally synthesize such structures. Contrary to belief that molecules created through surprising and unintended reaction pathways would be easy to reproduce, they were surprisingly elusive. This is not altogether surprising considering the complexity of one structure, \((\text{DME})_6(py)_6\text{Nd}_{18}(C_6F_5\text{O})_{18}F_{24}\text{O}_3\text{S}_3\).
Chapter 4 is concerned with lanthanide oxychalcogenido clusters. A series of cluster compounds have been isolated and fully characterized, and a new structure of the same class, [(4etpy)$_{12}$Ho$_6$O$_4$Te$_4$]$^{2+}$ has been identified. Isolation of uniform samples of this class of structures is difficult. Some structures have partial occupancy of different elements, and tellurides have flexibility in their bonding and oxidation states leading to subtle variety in structures.
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(a) Berardini, M.; Emge, T. J.; Brennan, J. G. One-Dimensional Coordination Polymers: \([\{(pyridine)_2Eu(µ-SeC_6H_5)_2\}_4\}_∞\) and \([\{(THF)_3Eu(µ-SeC_6H_5)_2\}_∞\]. *J. Am. Chem. Soc.* 1993, 115, 8501-8502.  


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Chapter 1. Lanthanide Complexes with Fluorinated Alkoxide Ligands

Fluorinated alkoxides are an interesting class of ligands for designing lanthanide clusters that are more stable than lanthanide chalcogenolates and are soluble in organic media. The first step towards synthesizing lanthanide chalcogenido alkoxide clusters is to make simple compounds with such ligands to probe their bonding and solubility properties. Although properties could vary significantly from alkoxide monomers to clusters, knowing chemistry of Ln(OR)_x compounds is essential for planning cluster reaction and crystallization conditions. Even simple binary lanthanide systems can coordinate in multiple motifs including discrete neutral molecules, polymers, and ions.\(^1\)

When lanthanides form ionic complexes, the charge can be balanced with alkali metal cations, mercury complexes, or acidic cations which are commonly used to introduce ligands into reaction solutions.\(^2\)

Two fluorinated alkoxide ligands were chosen for this research. First was pentafluorophenoxide. This ligand lends itself well to comparison with previously investigated systems containing pentafluorophenylthiolate ligands. The identical structure of these ligands should provide similar steric effects possibly taking up slightly less space due to the tendency of oxygen to have wider bond angles than sulfur. The similarities made analogs of known lanthanide thiolate complexes obvious targets. Differences in the expected length and stability of the Ln–O bonds compared to Ln–S bonds created interest in the possibility of novel motifs as well. It is commercially available as an alcohol, requiring a different mechanism than the disulfides used in the syntheses this work is compared with.
Trifluoromethylsulfonic (triflic) acid was the second fluorinated ligand investigated with the intention to synthesize lanthanide chalcogenido alkoxide clusters. Similar to the work with perfluorophenoxide, the first step was to identify potential lanthanide alkoxide monomers, polymers or salts that could be produced as side products in pursuit of chalcogenido clusters. There are two major differences between the bonding of these two ligands. The obvious difference is the shared charge across multiple oxygen atoms in the sulfonate group through resonance theoretically allowing the possibility of it to act as a bidentate or tridentate ligand. The second key difference is its basicity. Triflic acid is a super acid with a pKₐ around -15. While pentafluorophenol is acidic for an alcohol, it only has a pKₐ of 5.5. The increased acidity should allow fast reaction between triflic acid and either neutral lanthanide metals through oxidation or with chalcogenolates through metathesis. The high acidity also makes triflate a weaker conjugate base and a hard anion. Hydrated lanthanide triflates monomers, Ln(CF₃SO₃)₃, are commercially available, and they are useful Lewis acid catalysts in aqueous solutions. Their weak basicity allows the temporary breaking of Ln–O bonds to form a complex between the metal and a Lewis basic site on an organic molecule promoting reaction of the molecule. However, these cleavages are temporary and do not result in permanent substitution for triflate. The facile ligand exchange does not affect the stability of Ln-CF₃SO₃ bonding making it a strong candidate as a ligand in stable lanthanide complexes.

Lanthanide triflates can be isolated in multiple forms. In addition to commercially available trivalent hydrated forms, an anhydrous polymer, (Sm₂(CF₃SO₃)₄(THF)₃)ₙ, has been reported.³ As in the case of the aryloxides, investigation of solubility of potential side products like this was a prudent first step.
Though commercially available lanthanide triflates are useful at times, the coordinated water is an undesirable contaminant for these reactions. Dry triflic acid was the chosen ligand source.

1.1 Synthesis and Structure

A series of monomers, \((\text{DME})_2\text{Ln}(\text{OC}_6\text{F}_5)_3\) where \(\text{Ln} = \text{Nd}, \text{Er}, \text{Tm}, \text{Eu}, \text{and Yb}\), were synthesized by two separate reaction mechanisms.\(^4,5\) The first successful attempt was performed with europium. Solid Eu was oxidized with PhSSPh in DME using catalytic mercury. After one week when the europium had fully dissolved to form a yellow solution with yellow-green precipitate, three equivalents of pentafluorophenol were added. The metathesis reaction began immediately. Within minutes the color slightly darkened and the precipitate redissolved noticeably. Reactions using the other metals followed the same pattern of immediate color change and dissolution of the powders upon adding the alcohol. The following day, the solution was filtered and layered with hexanes. After several attempts to crystallize the product using progressively less polar solvent mixtures, yellow lathes, \((\text{DME})_2\text{Eu}(\text{OC}_6\text{F}_5)_3\), (42% yield) were isolated and characterized. The structure is shown in Figure 2 with selected bond lengths in Table 1.

Scheme 3.

\[
\text{Ln} + 1.5(\text{EPh})_2 \xrightarrow{\text{cat. Hg}} \text{"Ln(EPh)"} \\
\text{“Ln(EPh)”} + 3\text{C}_6\text{F}_5\text{OH} \rightarrow \text{(DME)}_2\text{Ln}(\text{OC}_6\text{F}_5)_3
\]
Isomorphous crystals were obtained for the Er (60.\% yield), Tm (65\%) and Yb reactions following the same procedure. The metal center of (DME)$_2$Ln(OC$_6$F$_5$)$_3$ is seven coordinate with three X type aryloxide ligands and two bidentate DME L-type ligands. The Er–O bond distances for the phenoxide ligands ranged from 2.150(2) to 2.183(2) Å within normal Er–O distances. The Ln–O distances for the L-type DME ligands appropriately ranged from 2.390(2) to 2.426(2) Å. The closest Ln–F contacts, 3.520(2)-3.937(2) Å, are too long to have significant bonding nature. The Er–O bond lengths in the previously reported thiolate, (DME)$_2$Er(SC$_6$F$_5$)$_3$, ranged from 2.384 to 2.467 Å. This shows no effect of the lanthanide–alkoxide bonds on the bonding of the DME ligands around them in accordance with an ionic bonding model.

**Table 1.** Selected bond lengths (Å) and angles (deg) of (DME)$_2$Eu(OC$_6$F$_5$)$_3$

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(1)–O(1) = 2.205(1)</td>
<td>Eu(1)–O(2) = 2.245(1)</td>
</tr>
<tr>
<td>Eu(1)–O(3) = 2.232(1)</td>
<td>Eu(1)–O(5) = 2.456(1)</td>
</tr>
<tr>
<td>Eu(1)–O(6) = 2.482(1)</td>
<td>Eu(1)–O(7) = 2.488(1)</td>
</tr>
<tr>
<td>Eu(1)–O(4) = 2.492(1)</td>
<td>Eu(1)–O(1)–C(1) = 164.22(12)</td>
</tr>
<tr>
<td>Eu(1)–O(2)–C(7) = 132.23(10)</td>
<td>Eu(1)–O(3)–C(13) = 149.21(11)</td>
</tr>
</tbody>
</table>

Identical reactions with neodymium produced a lower yield and lesser quality crystals. The other three metals reliably produced crystals up to a centimeter long with little to no co-precipitates. The neodymium reaction produced crystals on the millimeter scale along with a dark viscous oil or powder. Although the complex is isostructural with the other phenoxides, the Nd monomer crystallizes in a different phase. The unit cell...
Figure 2. Ortep view of \((\text{DME})_2\text{Eu}(\text{OC}_6\text{F}_5)_3\)

Table 2. Crystallographic data for \((\text{DME})_2\text{Eu}(\text{OC}_6\text{F}_5)_3\) and \((\text{DME})_2\text{Nd}(\text{OC}_6\text{F}_5)_3\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>((\text{DME})_2\text{Eu}(\text{OC}_6\text{F}_5)_3)</th>
<th>((\text{DME})_2\text{Nd}(\text{OC}_6\text{F}_5)_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>(\text{C}<em>{26}\text{H}</em>{20}\text{EuF}<em>{15}\text{O}</em>{7})</td>
<td>(\text{C}<em>{26}\text{H}</em>{20}\text{F}<em>{15}\text{NdO}</em>{7})</td>
</tr>
<tr>
<td>formula weight</td>
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<td>873.66</td>
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<td>10.4086(5)</td>
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<td>(b) (Å)</td>
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<tr>
<td>(c) (Å)</td>
<td>23.480(1)</td>
<td>44.970(1)</td>
</tr>
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<td>(\beta) (deg)</td>
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<td>90.00</td>
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<td>(V) (Å³)</td>
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<td>6146.0(2)</td>
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<td>(\lambda) (Å)</td>
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<td>0.71073</td>
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<td>abs coeff (mm⁻¹)</td>
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<td>R(F)</td>
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<tr>
<td>(R_w(F^2))</td>
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<td>0.0765</td>
</tr>
</tbody>
</table>
contains two geometrically identical monomers which are not crystallographically related. Crystallographic details of the Nd and Eu structures are found in Table 2.

The observed speed of the substitution reactions monitored by color change and precipitate dissolution combined with the high oxidation potential of lanthanide metals suggested that the metals would be susceptible to direct oxidation by the alcohol. Combination of neodymium metal with three equivalents of pentafluorophenol stirred in DME showed no sign of reaction after one day, so a catalytic amount of mercury was added. The reaction then proceeded indicated by the metal dissolving and coloring the solution pale blue. This is consistent with the mercury-catalyzed oxidative addition of lanthanide metals proceeding through an amalgam in which mercury activates the lanthanide. The low oxidation potential of mercury and weak Hg–O bond enthalpy makes insertion into the O–H bond followed by transmetalation improbable. The single step synthesis reaction mixtures contained greater quantities of the side product which was never purified or identified, but the reaction also produced the same crystalline (DME)₂Nd(OC₆F₅)₃ as the two step reaction in lower (45%) yield compared to the two step reaction (62%).

Scheme 4.

$$\text{Ln} + 3 \text{C}_6\text{F}_5\text{OH} \rightarrow (\text{DME})_2\text{Ln(OC}_6\text{F}_5)_3$$

Solubilities of these compounds were greater than expected. Crystallization of related (DME)₂Ln(SC₆F₅)₃ is accomplished by layering a roughly 0.05 M solution of the monomer in DME with an equal volume of hexanes. Such quantities of the alkoxide monomer are fully soluble in an identical solvent system at this concentration. To recover a moderate yield in this reaction, the [Ln] in DME was raised to approximately
0.2 M, and it was layered with 2-5 equivalents by volume of hexanes. The isolated crystals are soluble in DME and toluene and slightly soluble in diethyl ether.

Related structures were synthesized with pyridine and THF replacing DME. The pyridine adduct produced seven coordinate trivalent monomers, \((\text{py})_4\text{Ln}(\text{OC}_6\text{F}_5)_3\) \((\text{Ln} = \text{Eu, Tb, Er, Tm, Yb})\).\(^5\) Erbium crystals were isolated in 30\% yield. The reactions from other metals appeared similar in quantity. Comparing the pyridine adduct for the erbium aryloxide, the Er–O bonds, 2.177(12) Å average, were statistically the same as the corresponding lanthanide–aryloxide bonds in \((\text{DME})_2\text{Er}(\text{OC}_6\text{F}_5)_3\) \((2.171(21)\ \text{Å average})\). The relative Lewis basicity of the L type ligands had no effect on the bonding of the X type ligands as predicted by an ionic model.

Comparing the bonding of the pyridine ligands in the alkoxide complex to the related thiolate complex shows a decrease in the bonding strength of the L type ligands. The four Yb – N bonds in \((\text{py})_4\text{Yb}(\text{OC}_6\text{F}_5)_3\) averaged 2.51(2) Å. These are noticeably longer than in the related perfluorothiolate compound \((\text{py})_4\text{Yb}(\text{SC}_6\text{F}_5)_3\), 2.44(2) Å. The greater relative strength and shorter length of the Ln – O bonds compared to the Ln – S bonds puts more electron density around the lanthanide, and this results in lengthening of the Ln – N bonds.

An ytterbium monomer, \((\text{THF})_3\text{Yb}(\text{OC}_6\text{F}_5)_3\), was synthesized in THF using similar procedures as the DME and pyridine adducts.\(^5\) Unlike the seven coordinate pyridine adduct of the ytterbium monomer, the THF derivative adopts an octahedral geometry with three alkoxide and three THF ligands in the meridional configuration. The bond distances in this structure add to the body of evidence supporting the theory that there is a small but significant contribution of covalent nature to lanthanide bonds. A
Table 3. Crystallographic data for (py)$_4$Er(OC$_6$F$_5$)$_3$ and (THF)$_3$Yb(OC$_6$F$_5$)$_3$

<table>
<thead>
<tr>
<th>Compound</th>
<th>(py)$_4$Er(OC$_6$F$_5$)$_3$</th>
<th>(THF)$_3$Yb(OC$_6$F$_5$)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>C$<em>{38}$H$</em>{20}$ErF$_{15}$N$_4$O$_3$</td>
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<td>β (deg)</td>
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<td>R$_{w}$(F$^2$)</td>
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**Table 4.** Selected bond lengths (Å) and angles (deg) of \((\text{THF})_3\text{Yb(OC}_6\text{F}_5)_3\)

<table>
<thead>
<tr>
<th>Bond Lengths/Angles</th>
<th>Value</th>
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<td>Yb(1)–O(1)</td>
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<tr>
<td>Yb(1)–O(2)</td>
<td>2.111(2)</td>
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<tr>
<td>Yb(1)–O(3)</td>
<td>2.332(2)</td>
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<tr>
<td>Yb(1)–O(4)</td>
<td>2.296(2)</td>
</tr>
<tr>
<td>O(1)–Yb(1)–O(2)′</td>
<td>95.76(4)</td>
</tr>
<tr>
<td>O(1)–Yb(1)–O(3)</td>
<td>97.35(4)</td>
</tr>
<tr>
<td>O(1)–Yb(1)–O(4)</td>
<td>97.35(4)</td>
</tr>
<tr>
<td>O(2)–Yb(1)–O(2)′</td>
<td>168.48(9)</td>
</tr>
<tr>
<td>O(3)–Yb(1)–O(4)</td>
<td>82.65(4)</td>
</tr>
<tr>
<td>O(2)–Yb(1)–O(4)′</td>
<td>88.07(7)</td>
</tr>
<tr>
<td>O(4)–Yb(1)–O(4)′</td>
<td>165.30(9)</td>
</tr>
<tr>
<td>O(2)–Yb(1)–O(4)′</td>
<td>90.46(7)</td>
</tr>
<tr>
<td>O(4)–Yb(1)–O(4)′</td>
<td>84.24(4)</td>
</tr>
<tr>
<td>O(3)–Yb(1)–O(4)†</td>
<td>82.65(4)</td>
</tr>
<tr>
<td>O(2)–Yb(1)–O(4)†</td>
<td>90.46(7)</td>
</tr>
<tr>
<td>O(4)–Yb(1)–O(4)†</td>
<td>88.07(7)</td>
</tr>
</tbody>
</table>
purely ionic bonding model would predict all bonds between a metal and a specific ligand type to be identical regardless of geometry assuming equivalent steric forces from the crystal packing. A covalent model predicts variation in bond lengths that depend on the ligand on the opposite side of the metal center affecting the electron density in the metal’s orbitals.

Theoretically, the delocalized $\pi$ electrons on aryloxide ligands should create increased electron density around the oxygen compared to an ether and provide a lengthening trans influence. Fluorides have an electron withdrawing effect on the aromatic ring which should decrease the electron density around the oxygen relative to hydrogenated phenol. Using a fluorinated aryloxide should produce a less substantial trans influence than aryloxides with other substituents. The two $C_6F_5O^-$ ligands trans to one another in this centrosymmetric phase have Yb–O bond lengths of 2.111(2) Å compared to the single 2.084(2) Å bond for the alkoxide oxygen atom trans to a THF. The distance between the metal and the oxygen atoms in the trans oriented THF ligands are 2.296(2) Å with the third THF bonding opposite to an alkoxide ligand having a Yb–O length of 2.332(2) Å. These data agree with results from previous work demonstrating a minor yet noticeable directional aspect to lanthanide bonds.

In addition to forming a monomer containing europium in the trivalent state, two other structures were isolated and characterized when similar reactions were run with varied stoichiometry. A 2:5 reaction of europium and pentafluorophenol yields a dimer with mixed oxidation states, $(DME)_3Eu_2(OC_6F_5)_5$. The structure is asymmetrical with distinct 2+ and 3+ positions. Eu(2) is bonded to all five alkoxide ligands. Two are terminally bound, while the other three bridge to Eu(1) which has no terminally bound X.
Figure 5. Ortep view of (DME)$_3$Eu$_2$(OC$_6$F$_5$)$_5$
type ligands. The average Eu(1)–O bond length for the alkoxides is 2.57 Å while the 
Eu(2)–O distances are 2.37 Å. This clearly establishes Eu(1) as divalent and Eu(2) as 
trivalent. The trivalent europium ion is chelated by a single bidentate DME ligand 
making it seven coordinate. A pair of DME molecules coordinates to the divalent metal 
center making it seven coordinate as well. The closest fluorine atom on the bridging 
ligands appears to have significant dative bonding character. The three shortest Eu(1)–F 
lengths are 2.796, 2.835, and 3.109 Å. The first two are close to the expected distances 
for dative interactions.\(^{11}\) It is likely that in solution phase, the fluorine atoms exhibit 
significant interaction with the metal. The shortest distance between a fluorine atom and 
the trivalent metal center with its smaller ionic radius is 3.072 Å. The preference for the 
fluoride to approach the divalent metal can be explained by its coordination to more L 
type ligands than X type. The more strongly coordinated terminal aryloxide ligands are 
expected to provide comparatively more competition.

Table 5. Selected bond lengths (Å) of \((\text{DME})_3\text{Eu}_2(\text{OC}_6\text{F}_5)_5\)

<table>
<thead>
<tr>
<th>Eu(1)–O(1) = 2.591(4)</th>
<th>Eu(1)–O(2) = 2.551(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(1)–O(3) = 2.564(4)</td>
<td>Eu(2)–O(1) = 2.373(4)</td>
</tr>
<tr>
<td>Eu(2)–O(2) = 2.410(4)</td>
<td>Eu(2)–O(3) = 2.348(4)</td>
</tr>
<tr>
<td>Eu(2)–O(4) = 2.223(4)</td>
<td>Eu(2)–O(5) = 2.221(4)</td>
</tr>
<tr>
<td>Eu(1)–F(11) = 2.796(4)</td>
<td>Eu(1)–F(6) = 2.835(4)</td>
</tr>
<tr>
<td>Eu(2)–F(5) = 3.072(4)</td>
<td>Eu(1)–F(1) = 3.109(5)</td>
</tr>
</tbody>
</table>
As with the synthesis of the trivalent monomers, this structure was synthesized both by direct oxidation of europium by the alcohol and by substitution of metal thiolate in solution. The substitution reaction was more efficient (63% yield) than the direct oxidation (26%). Both procedures produce the trivalent monomer as a minor side product. The dimer begins to crystallize at lower concentrations than the monomer, so low yield crystallization conditions give pure product, and successive crystallizations give successively worse purity. Higher purity in a single collection can be produced by reducing the ratio of alkoxide to metal at the cost of total yield. In the direct oxidation method, this leads to the introduction of another europium alkoxide species which was identified and targeted for reproduction.

Table 6. Crystallographic data for (DME)$_3$Eu$_2$(OC$_6$F$_5$)$_5$ and (DME)$_4$Eu$_3$(OC$_6$F$_5$)$_6$

<table>
<thead>
<tr>
<th>Compound</th>
<th>(DME)$_3$Eu$_2$(OC$_6$F$_5$)$_5$</th>
<th>(DME)$_4$Eu$_3$(OC$_6$F$_5$)$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>C$<em>{42}$H$</em>{27}$Eu$<em>2$F$</em>{25}$O$_{11}$</td>
<td>C$<em>{52}$H$</em>{40}$Eu$<em>3$F$</em>{30}$O$_{14}$</td>
</tr>
<tr>
<td>formula weight</td>
<td>1486.56</td>
<td>1914.72</td>
</tr>
<tr>
<td>Space group</td>
<td>Cc</td>
<td>C2/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>11.9347(6)</td>
<td>20.6837(12)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>20.997(1)</td>
<td>13.6139(8)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>20.660(1)</td>
<td>22.0265(13)</td>
</tr>
<tr>
<td>β (deg)</td>
<td>104.768(1)</td>
<td>92.989(1)</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>5006.4</td>
<td>6193.9(6)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>D$_{calc}$ (g cm$^{-3}$)</td>
<td>1.972</td>
<td>2.053</td>
</tr>
<tr>
<td>Temp (K)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>abs coeff (mm$^{-1}$)</td>
<td>2.632</td>
<td>3.153</td>
</tr>
<tr>
<td>R(F)</td>
<td>0.0424</td>
<td>0.0320</td>
</tr>
<tr>
<td>R$_{w}$(F$^2$)</td>
<td>0.0760</td>
<td>0.0979</td>
</tr>
</tbody>
</table>

Scheme 5.

a) 2 Eu + 5 C$_6$F$_5$OH $\rightarrow$ (DME)$_3$Eu$_2$(OC$_6$F$_5$)$_5$

b) “Eu(SPh)$_2$” + 2.5 C$_6$F$_5$OH $\rightarrow$ (DME)$_3$Eu$_2$(OC$_6$F$_5$)$_5$
The second structure unique to europium is a linear trimer with all three metal ions in the 2+ state. Reacting pentafluorophenol with europium metal in a 2:1 ratio or less with catalytic mercury produces \((\text{DME})_2\text{Eu}(\mu-\text{OC}_6\text{F}_5)_3\text{Eu}(\mu-\text{OC}_6\text{F}_5)_3\text{Eu}(\text{DME})_2\) as pale yellow lathes. Just as 2.5:1 reactions produce the monomer as a side product, 2:1 reactions produce the dimer as a side product illustrating europium’s preference for the 3+ oxidation state when coordinated to alkoxides. Pure crystals were synthesized in 40.% yield by reducing the amount of alcohol added by 15%.

![Ortep view of \((\text{DME})_4\text{Eu}_3(\text{OC}_6\text{F}_5)_6\) (Figure 6)]
**Table 7.** Selected bond lengths (Å) of \((\text{DME})_4\text{Eu}_3(\text{OC}_6\text{F}_5)_6\)

<table>
<thead>
<tr>
<th>Bond Length</th>
<th>Value (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(1)–O(1)</td>
<td>2.550(2)</td>
</tr>
<tr>
<td>Eu(1)–O(2)</td>
<td>2.533(2)</td>
</tr>
<tr>
<td>Eu(1)–O(3)</td>
<td>2.551(2)</td>
</tr>
<tr>
<td>Eu(2)–O(1)</td>
<td>2.457(2)</td>
</tr>
<tr>
<td>Eu(2)–O(2)</td>
<td>2.488(3)</td>
</tr>
<tr>
<td>Eu(2)–O(3)</td>
<td>2.569(2)</td>
</tr>
<tr>
<td>Eu(1)–F(1)</td>
<td>2.928(2)</td>
</tr>
<tr>
<td>Eu(2)–F(15)</td>
<td>3.004(2)</td>
</tr>
<tr>
<td>Eu(2)–F(10)</td>
<td>3.013(2)</td>
</tr>
</tbody>
</table>

This product was never obtained through a metathesis reaction. When less than two equivalents of the phenol was added to a solution of \(\text{Eu(II)}\) thiolate, some \(\text{Eu(II)}\) was oxidized to the \(\text{Eu(III)}\) to produce pure heterovalent dimer in meager yield. It should also be noted that no products were ever isolated with a mixture of chalcogenolate and alkoxide ligands coordinated to a lanthanide through any reactions using deficient quantities of alkoxide.

**Scheme 6.**

\[
\text{Eu} + 2 \text{C}_6\text{F}_5\text{OH} \rightarrow (\text{DME})_4\text{Eu}_3(\text{OC}_6\text{F}_5)_6
\]

The divalent trimer is a symmetric linear arrangement of \(\text{Eu(II)}\) ions with three phenoxide ligands bridging each of the terminal ions to the center. Two DME molecules cap each of the terminal ions making them seven coordinate. The central ion is only bound to the six aryloxide ligands. The potential interactions between the metals and the fluorine atoms in the ortho positions on the aryloxides are interesting. The significant bulk of the six ligands prevents the coordination of solvent molecules between them, and dative interactions with the fluorines can stabilize the central europium with a relatively
low coordination number. A symmetry related pair of fluorine atoms are separated from
the central europium by 2.928(2) Å. This distance is similar to the dative bond lengths in
the related polymer ((THF)$_2$Eu(SC$_6$F$_5$)$_2$)$_n$, 3.006(6) Å. Without the space for solvent
coordination, these weak interactions are all that is available to stabilize the six
coordinate central metal. The terminal europium atoms each have two close approaching
ortho fluorines at 3.004(2) Å and 3.013(2) Å. The significant lengthening of these Eu–F
distances compared to the central metal is explained by the increase in steric. Two of
the aryl groups exhibit a π–π interaction intramolecularly with no intermolecular
stacking. It is possible that in solution phase where the π–π stacking can be disrupted
temporarily, the Eu–F interactions could be different than the crystal structure suggests.
These interactions along with the oxidative strength of the phenol and precedence of
fluorine abstraction from fluorinated ligands by Ln(II) species$^{12}$ could explain why this
structure was never isolated from a metathesis reaction.

While pentafluorophenol is a strong oxidant relative to other chalcogenolates and
chalcogenides used in this work, it bonds more weakly than hydrogenated versions. The
terminal aryloxide ligands in these structures have noticeably longer bond lengths to the
lanthanide ions than aryloxides with different substituents reported in literature. In
(diglyme)$_2$(DME)Ba$_2$Eu(OC$_6$H$_4$-4-Me)$_7$ the Eu–O bond distances for the aryloxide
ligands are 2.16(1) Å and 2.19(1) Å.$^{13}$ In a closely related structure using the
unsubstituted phenoxide ligand, (DME)$_2$TmI$_2$(OC$_6$H$_5$) had a Tm–O distance of 2.025(7)
Å.$^{14}$ Accounting for the lanthanide contraction, the perfluoro substituted phenol has a
bond longer than the unsubstituted and the p-methyl phenoxides by 0.13(1) and 0.05(2) Å
respectively. This difference is attributed to the inductive effect of the fluoro substituents
drawing electron density away from the oxygen thereby weakening the electrostatic attraction to the cation. The limited trans-effect in (THF)$_3$Yb(O$_6$F$_5$)$_3$ is in agreement with this assessment.

The thermal decomposition products of three europium alkoxide phases, (DME)$_2$Eu(O$_6$F$_5$)$_3$, (DME)$_3$Eu$_2$(O$_6$F$_5$)$_5$, (DME)$_4$Eu$_3$(O$_6$F$_5$)$_6$, were inspected. Decomposition of lanthanide compounds with fluorinated oxygen based ligands can form LnOF phases. Fluorinated thiolates preferentially form LnF$_3$ over sulfides due to the relatively low electronegativity of sulfur. Thermolysis of all three was performed under vacuum by heating from room temperature to 650 °C at a rate of 15 °C min$^{-1}$ in sealed quartz tubes with one end in a furnace and the other in liquid N$_2$. The furnace temperature was maintained for 5 h then allowed to cool back to room temperature at a rate of 10 °C min$^{-1}$. Surprisingly, multiple LnF$_3$ phases were identified in the resulting powder by PXRD, but no oxide materials were found. Oxide or oxyfluoride phases had been expected. Loss of coordinated solvent is expected, but the removal of the oxygen in the alkoxide is surprising. The mechanism of the reaction is unknown.

Triflate was the second ligand investigated. Similarly to the case for the aryloxide, reactions between lanthanides and triflic acid produced different phases for divalent and trivalent metals. Although triflic acid could reasonably be expected to react directly with rare earth metals, all reactions targeting chalcogenide clusters would contain chalcogenolate and mercury, so attempts to crystallize binary complexes were attempted through a metathesis route instead of direct redox reactions. This route was chosen to produce the phases most likely to occur as side products in cluster synthesis reactions.
Europium was combined with one equivalent of diphenyldiselenide and catalytic mercury in pyridine and stirred to produce a dark red solution. Addition of two equivalents of triflic acid by syringe produced white vapor and caused the solution to become lighter in color. Yellow crystals were produced after the solution was filtered, concentrated and layered with hexanes.

X-ray diffraction revealed a one dimensional polymer, ((py)$_3$Eu(CF$_3$SO$_3$)$_2$)$_n$.

There is only one unique formula unit in the structure. The europium is eight coordinate with each metal coordinated to three pyridine molecules and five oxygen atoms on four triflates. Both triflate positions bridge metal centers in the polymer. One triflate position coordinates one oxygen to each metal with the third oxygen uncoordinated. The second position coordinates a single oxygen to one metal and two oxygen atoms to another.

Ignoring the bridging aspects, the three monodentate interactions are similar, 2.5345(1) – 2.5424(2) Å. The two bidentate bonds are much longer at 2.7425(2) and 2.7665(2) Å. Two of the three coordinated pyridine molecules exhibit $\pi$–$\pi$ interactions between adjacent polymer chains.

**Table 8.** Crystallographic data for ((py)$_3$Eu(CF$_3$SO$_3$)$_2$)$_n$ and [C$_3$H$_5$NH][((py)$_4$Tb(CF$_3$SO$_3$)$_4$)py]

<table>
<thead>
<tr>
<th>Compound</th>
<th>((py)$_3$Eu(CF$_3$SO$_3$)$_2$)$_n$</th>
<th>[C$_3$H$_5$NH][((py)$_4$Tb(CF$_3$SO$_3$)$_4$)py]</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>C$<em>{17}$H$</em>{15}$EuF$_9$N$_3$O$_6$</td>
<td>C$<em>{34}$H$</em>{31}$F$_{12}$N$<em>6$O$</em>{12}$S$_4$Tb</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/c$</td>
<td>$P$ -1</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>9.7594(9)</td>
<td>14(2)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>12.2326(11)</td>
<td>23.360(3)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>20.0936(19)</td>
<td>23.254(17)</td>
</tr>
<tr>
<td>$\alpha$ (deg)</td>
<td>90</td>
<td>116.522(3)</td>
</tr>
<tr>
<td>$\beta$ (deg)</td>
<td>101.697(2)</td>
<td>100.779(4)</td>
</tr>
<tr>
<td>$\gamma$ (deg)</td>
<td>90</td>
<td>96.659(3)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
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<td>6738.42</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>12</td>
</tr>
</tbody>
</table>
Figure 7. POV view of ((py)$_3$Eu(CF$_3$SO$_3$)$_2$)$_n$ with C and H atoms removed from pyridine for clarity
<table>
<thead>
<tr>
<th>Bond Length/Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(1)–O(1)</td>
<td>2.5424(2)</td>
</tr>
<tr>
<td>Eu(1)–O(4)</td>
<td>2.5345(1)</td>
</tr>
<tr>
<td>Eu(1)–O(5)</td>
<td>2.5345(2)</td>
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<td>Eu(1)–O(2)</td>
<td>2.7425(2)</td>
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<tr>
<td>Eu(1)–O(3)</td>
<td>2.7425(2)</td>
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<tr>
<td>Eu(1)–N(1)</td>
<td>2.603(2)</td>
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<tr>
<td>Eu(1)–N(2)</td>
<td>2.7302(2)</td>
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<tr>
<td>Eu(1)–N(3)</td>
<td>2.6824(2)</td>
</tr>
<tr>
<td>Eu(1)–O(1)–S(1)</td>
<td>164.74</td>
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<tr>
<td>Eu(1)–O(4)–S(2)</td>
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<td>174.27</td>
</tr>
<tr>
<td>Eu(1)–O(2)–S(1)</td>
<td>97.67</td>
</tr>
<tr>
<td>Eu(1)–O(3)–S(1)</td>
<td>96.58</td>
</tr>
</tbody>
</table>

A salt crystallized from various reactions in pyridine. Reaction of 3 equivalents of CF₃SO₃H with a solution of “Tb(SePh)₃” in pyridine produced an abundance of colorless crystals comprised of a novel form of lanthanide triflate, a [(py)₄Tb(CF₃SO₃)₄]⁻ anionic complex which is charge balanced with pyridinium cations. The structure contains three crystallographically distinct anions with the same geometry. Each triflate coordinates to the terbium through a single oxygen, and four pyridine molecules coordinate to fill the coordination sphere. There are no significant Tb–F interactions. The Tb–O bond lengths ranging 2.320(2)–2.369(7) Å are significantly longer than Ln–O lengths in the pentafluorophenoxide structures. One possibility for this disparity is the lower basicity of the triflate anion compared to the phenoxide. The weaker Ln–O bonding for triflate could also explain why a purely Eu(II) phase was synthesized through metathesis with triflate and not with the phenol. An alternative explanation of the length differences comes from steric. Conventional wisdom says the major factor in the difference comes from greater repulsion between the ligands in this eight coordinate
structure due to increase in steric repulsion and electrostatic repulsion of an additional anionic ligand.

**Table 10.** Selected bond lengths (Å) and angles (deg) of [(py)$_4$Tb(CF$_3$SO$_3$)$_4$]$_n$

<table>
<thead>
<tr>
<th>Bond Length (Å) or Angle (deg)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb(1)–O(1)</td>
<td>2.3542(2)</td>
</tr>
<tr>
<td>Tb(1)–O(4)</td>
<td>2.33(6)</td>
</tr>
<tr>
<td>Tb(1)–O(7)</td>
<td>2.33(6)</td>
</tr>
<tr>
<td>Tb(1)–O(10)</td>
<td>2.320(2)</td>
</tr>
<tr>
<td>Tb(1)–N(1)</td>
<td>2.6(3)</td>
</tr>
<tr>
<td>Tb(1)–N(2)</td>
<td>2.6(2)</td>
</tr>
<tr>
<td>Tb(1)–N(3)</td>
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</tr>
<tr>
<td>Tb(1)–N(4)</td>
<td>2.6(2)</td>
</tr>
<tr>
<td>Tb(1)–O(1)–S(1)</td>
<td>156.81</td>
</tr>
<tr>
<td>Tb(1)–O(4)–S(2)</td>
<td>155.35</td>
</tr>
<tr>
<td>Tb(1)–O(7)–S(3)</td>
<td>154.51</td>
</tr>
<tr>
<td>Tb(1)–O(10)–S(4)</td>
<td>150.89</td>
</tr>
</tbody>
</table>

The unit cell contains three [C$_5$H$_5$NH][(py)$_4$Tb(CF$_3$SO$_3$)$_4$] formula units and one extra pyridine molecule for each. The pyridines are hydrogen bonded to the pyridinium co-equatorially with N–N distances ranging 2.652(8) - 2.682(2) Å. This short distance indicates strong hydrogen bonds, but the hydrogen atoms were not resolved. The rings are indistinguishable as pyridine and pyridinium. The degeneracy of the two states implies at least a crystallographic average and possibly equal sharing of the hydrogen between the nitrogens.

**Scheme 7.**

\[
\text{Ln} + 4 \text{CF}_3\text{SO}_3\text{H} + \text{py} \rightarrow [\text{HNC}_5\text{H}_5][\text{Ln(CF}_3\text{SO}_3)_4]\cdot\text{py}
\]
One of the impetuses for pursuing fluorinated ligands in lanthanide materials is their potential use for photoemission applications. Solid-state lanthanide doped materials are used extensively in photoemission technologies. The reduced effect of a ligand field on f-orbitals of lanthanide ions causes their emission peaks from f-f transitions to be
narrow compared to transition metal and main group compounds, and the wavelengths of these signals spanning from UV to near IR do not shift drastically when ligands are changed. As a result, emission spectra are expected to be similar from one compound of a given lanthanide ion to another system with the same metal. While the peak shapes and positions are expected to be close, efficiency is variable due to the dependence of other relaxation processes on the other atoms around the metal. As a result, the challenge of designing highly emissive materials is more complicated.

Though the wavelengths of photons emitted by a given lanthanide are consistent for different systems, the efficiencies for emission processes of various lanthanide containing compounds can vary drastically. The quantum efficiencies of lanthanide doped solid state compounds such as YF\textsubscript{3}:Nd range from 50\% to 100\%.\textsuperscript{16} Excited states in bulk lanthanide oxide solids can relax through non-radiative processes reducing their efficiencies. Energy from an excited Ln ion can be transferred to nearby ions. This can repeat until the energy reaches a defect in the crystal that allows for non-radiative relaxation. Cross relaxation is also likely in cases with identical adjacent lanthanide ions with intermediate excited states. The accessibility of these energy transfer pathways are diminished in samples of host materials doped with low concentrations of emissive ions. They are also limited in small clusters, because phononic energy transfer is limited to intramolecular processes. Excited metal atoms in adjacent clusters do not undergo intermolecular cross relaxation.

While the range of wavelengths in which lanthanides emit is broad, here we are concerned with the NIR emissions, specifically from Nd, Er, and Tm, which emit in the fiber optic communication windows. Molecular species typically exhibit quantum
Solid state compounds have superior emission intensities over molecular compounds for multiple reasons. One is the quenching of IR radiation by ligands, most notably O–H, N–H, and C–H stretches which have second and third harmonics in line with the desired 1060 nm and 1550 nm emission maxima. By replacing hydrogen atoms with fluorine, those absorbance peaks are moved from around 3000 cm\(^{-1}\) for C–H bonds to around 1380 cm\(^{-1}\) reducing the total non-radiative losses compared to the parent hydrocarbons. Recently synthesized \((\text{DME})_2\text{Ln(SC}_6\text{F}_5)_3\) exhibited high efficiencies, 78% at 1544 nm from the Er compound, 9% at 1047 nm from Nd, and 2.2% at 1400 nm from Tm.\(^{18}\) The alkoxides described earlier in the chapter, \((\text{DME})_2\text{Ln(OC}_6\text{F}_5)_3\), provide direct comparison to investigate the effects of substituting sulfur for oxygen on emission properties.

In collaboration with Dr. Ajith Kumar, the emission properties of \((\text{DME})_2\text{Ln(OC}_6\text{F}_5)_3\) (\(\text{Ln} = \text{Nd, Er, and Tm}\)) were probed. The Nd compound was excited with 800 nm light from a Ti-sapphire laser. The emission spectrum (figure 9) is as expected with peaks at 928, 1059, and 1327 nm corresponding to relaxations from \(^4\text{F}_{3/2}\) to the \(^4\text{I}_{9/2}, \, ^4\text{I}_{11/2},\) and \(^4\text{I}_{13/2}\) states respectively. The emission maximum around 1800 nm which is typically weak for alkoxides did not extend beyond the background noise. The Tm compound, also excited with light at 800 nm, shows standard emission bands at 1458 and 1759 nm (figure 10) from the \(^3\text{H}_4 \rightarrow ^3\text{H}_5\) and \(^3\text{F}_4 \rightarrow ^3\text{H}_6\) transitions respectively. The Er compound was excited with a 980 nm diode laser producing an emission maximum at 1553 nm from the \(^4\text{I}_{13/2}\) to \(^4\text{I}_{15/2}\) transition (figure 11).
Figure 9. Absorption and emission spectrum for (DME)$_2$Nd(OC$_6$F$_5$)$_3$. 
Figure 10. Absorption and emission spectrum for (DME)$_2$Tm(OC$_6$F$_5$)$_3$
Figure 11. Absorption and emission spectrum for (DME)$_2$Er(OC$_6$F$_5$)$_3$
The quantum efficiency was calculated by dividing the measured decay times of emission peaks to Judd-Ofelt theoretical times.\textsuperscript{19} A spectrum of emission intensity over time was fit with an exponential decay curve, and the radiative decay time (\(\tau_{\text{eff}}\)) was extracted from the formula of the curve. The effective fluorescence decay for the Nd 1059 nm peak is given in figure 12 (a). The curve was fitted to give an effective decay time of 170 \(\mu\)s. Using 8.6 ms for the theoretical radiative decay time from Judd-Ofelt theory, the efficiency is nearly 2\%. The decay curves for Er in Figure 12 (b) and Tm in Figure 12 (c) and 12 (d) gave \(\tau_{\text{eff}}\) of 1 ms for the 1552 peak of Er and gave 145 and 127 \(\mu\)s for the 1458 and 1759 nm bands from Tm respectively. Efficiencies were calculated to be 16\% for the Er, 1.9\% for the Tm 1458 nm band and 4.5\% for the 1759 nm Tm band. These efficiencies are better than most molecular species due to eliminating O–H bonds and replacing C–H bonds with C–F bonds.

The efficiencies are noticeably lower than similar chalcogenolate compounds as expected. The aforementioned thiolate compounds (DME)\(_2\)Ln(SC\(_6\)F\(_5\))\(_3\) benefitted from the same advantages of fluorination and replaced oxygen with sulfur to further decrease losses. Creating complexes with great similarity and one key difference replacing sulfur with oxygen provided an unprecedented opportunity to analyze the effects of this variable on emission properties. The quantum efficiency of (DME)\(_2\)Nd(SC\(_6\)F\(_5\))\(_3\) was 7\% compared to 2\% for (DME)\(_2\)Nd(OC\(_6\)F\(_5\)). The reported efficiency of (DME)\(_2\)Er(SC\(_6\)F\(_5\))\(_3\) is 75\%. Quantum efficiencies of the (DME)\(_2\)Tm(SC\(_6\)F\(_5\))\(_3\) 1470 nm and 1772 nm emission peaks were 2.2 and 0.12\% respectively. Lower efficiencies of the alkoxide analogues were caused by the higher frequency of the Ln–O bond creating non-radiative vibronic coupling losses with the ligand.
Figure 12. Measured decay curves for (DME)$_2$Ln(OC$_6$F$_5$)$_3$: (a) Nd $^4F_{3/2} \rightarrow ^{4}I_{11/2}$ (b) Er $^4I_{13/2} \rightarrow ^{4}I_{15/2}$ (c) Tm $^3H_{4} \rightarrow ^3H_{5}$ (d) Tm $^3F_{4} \rightarrow ^3H_{6}$

1.3 Conclusion

A number of fluorinated lanthanide alkoxide species were synthesized:

(DME)$_2$Ln(OC$_6$F$_5$)$_3$ (Ln = Nd, Er, Tm, Eu, Yb), (py)$_4$Ln(OC$_6$F$_5$)$_3$ (Ln = Eu, Tb, Er, Tm, Yb), (THF)$_3$Yb(OC$_6$F$_5$)$_3$, ((py)$_3$Eu(CF$_3$SO$_3$)$_2$)$_n$, (DME)$_2$Eu($\mu$-OC$_6$F$_5$)$_3$Eu($\mu$-OC$_6$F$_5$)$_3$Eu(DME)$_2$, and (DME)(OC$_6$F$_5$)$_2$Eu($\mu$-OC$_6$F$_5$)$_3$Eu(DME)$_2$. Most of these were produced from metathesis reactions of C$_6$F$_5$OH or CF$_3$SO$_3$H with lanthanide chalcogenolate solutions prepared in situ. All attempts at reproducing them via direct
oxidation were successful but some at a lower yield. The divalent europium complex 
(DME)$_4$Eu$_3$(OC$_6$F$_5$)$_6$ was only produced through direct oxidation.

Due to the stabilizing effect of these alkoxides on the Eu(III) oxidation state, 
reactions of “Eu(SPh)$_2$” with limited C$_6$F$_5$OH produced the heterovalent dimer. This 
contrasted with the synthesis of ((py)$_3$Eu(CF$_3$SO$_3$)$_2$)$_n$ through a metathesis route. As a 
better base, the phenoxide coordinates more effectively. While the trivalent complexes 
were not compared for relative stability, it is believed that alkoxides with stronger Lewis 
basic character would produce more stable species than less basic ligands.

The bond lengths are all in expected ranges with variations explained by normal 
phenomena. The THF adduct is octahedral showing a small but significant trans 
influence with the Ln–O bonds trans to the alkoxides lengthened with respect to the ones 
trans to the THF. The heterovalent dimer, (DME)$_3$Eu(OC$_6$F$_5$)$_5$, is asymmetrical with 
distinct 2+ and 3+ positions. The geometry of bridging ligands lends itself to dative 
interactions between the metal and the fluorine on α-C atoms. Both (DME)$_3$Eu$_2$(OC$_6$F$_5$)$_5$ 
and (DME)$_4$Eu$_3$(OC$_6$F$_5$)$_6$ exhibited such C–F interactions, but none of the monomers did. 
The polymer, ((py)$_2$Eu(OC$_6$F$_5$)$_2$)$_n$, has longer Eu–O bonds for the bidentate ligands than 
the monodentate ones. The anionic complex, [(py)$_4$Tb(CF$_3$SO$_3$)$_4$], has longer Ln–O 
bonds than expected based on the other alkoxides described here, because it is the only 
eight coordinate metal center with four anionic ligands.

The three phases of europium alkoxides synthesized in DME were tested for 
thermal decomposition. Solid EuF$_3$ phases were produced, and no oxides or oxyfluorides 
were identified.
Samples of (DME)$_2$Ln(OC$_6$F$_5$)$_3$ (Ln = Nd, Er, Tm) were tested for NIR emission properties. By eliminating quenching by C–H bonds, these monomers exhibited relatively efficient emission compared to hydrogenated alkoxides. However, due to Ln–O vibrations, they did not perform as well as previously reported analogous fluorinated thiolate complexes.
References:


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Chapter 2. Lanthanide Chalcogenido Alkoxide Dimers

Clusters with lanthanide chalcogenide cores and capping alkoxide ligands are a goal primarily for potentially combining high efficiency photon emission with solubility in organic media and resistance against chemical reaction. The fluorinated aryloxide species discussed in Chapter 1 exhibited strong emission for monomers. Due to an increase in ion concentration, clusters are expected to possess improved emission intensity over monomers. These alkoxides also exhibited high solubility in organic media and a marked qualitative improvement in stability over lanthanide chalcogenolates. Lanthanide chalcogenido alkoxide clusters were targeted for the possible combination of these properties.

In order to make clusters with lanthanide chalcogenide cores and capping fluorinated alkoxide ligands, lanthanide chalcogenolates were combined with a chalcogenido source while limiting the number of alkoxide equivalents available to the metal ions. The redox substitution of elemental chalcogens for chalcogenolate anions to form chalcogenides or dichalcogenides is well established,¹ and the previously described syntheses demonstrate the ease of substitution with either the alcohol or acid employed here. This general reaction form followed previously published syntheses of lanthanide chalcogenido halide clusters similar to the desired alkoxide clusters.²

Scheme 8.

\[
\begin{align*}
\text{“Ln(EP)} & \text{h}_3 + x \text{C}_6\text{F}_5\text{OH} \rightarrow \text{“Ln(EP)\text{h}_3-x(OC}_6\text{F}_5)\text{x}”} \\
\text{“Ln(EP)h}_3-x(\text{OC}_6\text{F}_5)\text{x}” + n E \rightarrow \text{LnE}_n(\text{OC}_6\text{F}_5)\text{x}
\end{align*}
\]
Clusters capped with fluorinated alkoxides proved more elusive than chalcogenolate or iodide capped lanthanide chalcogenides. Reactions with lanthanide chalcogenolate, elemental chalcogen, and either pentafluorophenol or triflic acid predominately yield mixtures of products that do not crystallize well. A common occurrence was the precipitation of amorphous powder as solubility is reduced either through evaporation, cooling, or diffusion of a miscible non-polar solvent into a polar solution. In the case of solvent diffusion, the precipitate displayed a color gradient suggesting a change in composition through the precipitation process. Given the high concentrations needed to crystallize the lanthanide alkoxides described in Chapter 1, presumably, the powder was comprised of mixtures of chalcogenide clusters followed by alkoxide monomers. Despite the difficulty of isolating any large chalcogenido clusters, lanthanide dimers bridged by chalcogenidos having terminal alkoxides were successfully isolated and characterized.

2.1 (py)₆Ln₂S₄(OC₆F₅)₂

The most interesting example of these chalcogenido dimers is [(py)₃Lnη²-µ-(SS)(OC₆F₅)]₂·py (Ln = Sm, Eu, Gd). This dimer first synthesized with europium by layering a solution of “Eu(OC₆F₅)₂” with a solution of elemental sulfur is the first known example of a molecular Eu(III) compound containing sulfido ligands. It crystallizes in a P-1 triclinic cell with parameters a = 10.3816(6) Å, b = 10.4395(6) Å, c = 14.7562(8) Å, α = 89.923(1)°, β = 80.241(1)°, and γ = 63.602(1)°. The cell volume is 1406.8 Å³ and contains one formula unit. The existence of an inversion center leaves only one unique Eu–O bond, 2.218(2) Å, which is slightly shorter than the average bond lengths, 2.23(2)
Å, in the previously described monomer. The three Eu–N bonds range from 2.594(4) – 2.620(3) Å. As with the Eu–O bonds, the average Eu–N bond is slightly shorter than in the pyridine adduct of the monomer. The differences are smaller than expected for comparison between a seven coordinate europium with a six coordinate species. There are formally six ligands around each metal center, but the η-2 bonding of the disulfido ligands gives the metals eight points of coordination. If the center of each S–S bond is viewed as coordinating instead of each sulfur atom individually, the six coordinate europium atoms are distorted octahedra with pyridines bent away from the disulfidos. The ionic nature of lanthanides predicts a weak interaction with the S–S bond, so the relationships between the europium atoms and the individual sulfur atoms require more scrutiny.

Figure 13. Ortep view of (py)_6Eu_2(S_2)_2(OC_6F_5)_2
Table 11. Selected bond lengths (Å) of (py)$_6$Eu$_2$(S$_2$)$_2$(OC$_6$F$_5$)$_2$

<table>
<thead>
<tr>
<th>Bond Length</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(1)–O(1)</td>
<td>2.218(2) Å</td>
</tr>
<tr>
<td>Eu(1)–S(2)</td>
<td>2.8272(7) Å</td>
</tr>
<tr>
<td>Eu(1)–S(2A)</td>
<td>2.8207(6) Å</td>
</tr>
<tr>
<td>Eu(1)–S(2A)</td>
<td>3.7197(9) Å</td>
</tr>
<tr>
<td>S(1)–Eu(1A)</td>
<td>82.48(2) Å</td>
</tr>
</tbody>
</table>

The $S$–$S$ bond lengths are 2.092(1) Å, which is within the range of average organic disulfide bond lengths.$^4$ It is not significantly lengthened to allow the sulfur atoms to bond as separate sulfido ligands. The Eu–$S$ bonds are nearly orthogonal to the $S$–$S$ bonds. The Eu–$S$ distances range from 2.8154(6) – 2.8564(8) Å. These lengths are between what is expected for a six coordinate and eight coordinate Eu(III) complex. Based on the length of the $S$–$S$ bond and fact that the europium atoms are already fully oxidized to the the 3+ state, the long distances for six coordinate europium atoms are ascribed to steric and maximizing bonding interactions with both metal atoms. In the solid phase, the disulfido ligands are effectively equally shared by the two metals with minimal differences in bond lengths. In Figure 13, S(1) and S(2) are closer to Eu(1A) with bond lengths of 2.8154(6) and 2.8207(6) Å respectively, while their distances to Eu(1) are 2.8564(8) and 2.8272(7) Å respectively. Crystal packing of this structure is aided by intermolecular $\pi$–$\pi$ stacking of the aryloxide rings shown in Figure 14.

This compound was surprisingly difficult to isolate due to its unexpected insolubility in pyridine. The fluorinated phenol and its simple metal complexes were very soluble in py, DME and THF, and as a result, crystallization of the monomers,dimer,
Figure 14. POV view of (py)$_6$Eu$_2$(S$_2$)$_2$(OC$_6$F$_5$)$_2$ packing along b* and a axes
and trimer described previously required a high concentration in a low polarity solvent mixture. While those reactions were run at a concentration on the order of 0.05 M in DME, py, or THF, solvent was removed by vacuum to increase the concentration to approximately 0.2-0.5 M before adding enough hexanes to give roughly 1:4 ratio of polar to non-polar solvents, in which the products are only slightly soluble. Numerous variations of Scheme 8 and related reactions starting with divalent chalcogenolates of redox-active lanthanides were attempted under the assumption that desired clusters would be soluble in pyridine at 0.05M. They resulted in large quantities of precipitates during the reactions which were filtered and discarded without purification or characterization after they proved insoluble in pyridine, DME, THF, hexanes, and toluene. After filtration of the remaining solution, crystallization was attempted through cooling, solvent diffusion, and slow evaporation techniques separately. Powder mixtures and oils came out sometimes followed by the previously described monomers. The powders and oils were not characterized.

Previous work on the formation of lanthanide fluorides from reactions with fluorinated organic molecules⁵ led to the consideration that the precipitates might contain a wide variety of lanthanide chalcogenido and fluoride clusters with fragmented ligands. Reducing the number of reactants was a logical way to reduce the complexity of reaction mixtures and increase the chance of crystallizing a product. The aforementioned Eu(II) trimer was selected as a starting material. After synthesizing, collecting, and redissolving it to form a yellow solution in DME or a red solution in pyridine, elemental sulfur was added to produce a dark solution and precipitate. The dark color was indicative of a low energy Eu(III) – S ligand to metal charge transfer. While theoretically, the color could
have come from metal to ligand charge transfer with Eu(II), it would be highly unlikely for sulfur to displace the alkoxide in a substitution reaction. Synthesis attempts at the Eu(II) trimer from a thiolate intermediate (Scheme 5b) had already shown that two equivalents of pentafluorophenol in the presence of chalcogen species would oxidize Eu(II) to Eu(III). An oxidative addition to produce a mixed valence state or solely Eu(III) was much more likely. Initial attempts yielded brown and black precipitates similar to other attempts at chalcogenido clusters.

The continual insolubility of the products limited crystallization to the first attempt in a given reaction. Attempts to cut the reaction time down by layering the solution with hexanes within minutes of adding elemental sulfur and by moving reactions immediately into the freezer (-5°C) produced the same results. The final tactic was to slowly combine the reactants and hope they crystallize as they react. Europium metal (1.0 mmol) was reacted with two equivalents of pentafluorophenol in pyridine (15 mL). The resultant solution was filtered into a 10 mm diameter Schlenk flask and layered with a solution of sulfur (19 mg, 0.6 eq) in pyridine (10 mL). Extremely dark, essentially black, crystals were produced. Depending on the light, they have alternately appeared possibly red or blue. They are insoluble in pyridine and so dark in the solid form that no local maximum was found in a UV-vis absorbance or reflection spectrum of the dimer, so they are referred to here as black.

Attempts to produce a sulfido cluster instead of disulfido were fruitless. The product in the original reaction crystallized in reasonable yield despite the sulfur deficiency in the flask. Exclusive production of a disulfide at a maximum yield of 30% with respect to the metal makes it unlikely to produce a related sulfido cluster in place of
the disulfido shown here. Decreasing the concentration or quantity of the sulfur solution did not create such a sulfide species. If an $S^2$-containing transient species existed, it was undoubtedly soluble enough in pyridine to react further producing the disulfido dimer. Attempts to repeat the reaction with a stoichiometric quantity of sulfur produced a brown sludge in addition to the black crystals. If the reaction flask was covered with aluminum foil, the crystals were produced cleanly, and the solution remained more strongly colored than when left in the light. The most effective procedure was as follows: Eu, (SPh)$_2$, and Hg were combined in 20 mL pyridine and stirred 9 days to give a red solution. C$_6$F$_5$OH was added and stirred for 5 days with no visible change. It was filtered, concentrated in half by vacuum, layered with a solution of 2 equivalents of S in pyridine covered and put in a refrigerator for 10 days giving a 76% yield of the black crystals.

The synthesis of the light activated side products, which have not be identified, appears to come from the solution and not a degradation of the disulfido dimer. The crystals appear to be indefinitely stable in light when kept in the mother liquor sequestered from air, though they did degrade when removed from the pyridine solution. Crystals desolvated when removed from the liquid for an extended period of time and left under dry nitrogen as observed by the crystals crumbling. The material retained the dark color suggesting they maintain disulfide coordination, but results from elemental analysis via combustion run the day samples were removed from the solvent corresponded to only one lattice pyridine per unit cell instead of two. When dry crystals were open to air, they lightened to an off-white color suggesting sulfides were replaced with oxides or hydroxides as expected. Elemental sulfur was the likely side product, since the
degradation was not accompanied by the strong scent of H$_2$S, but the white powder was neither tested for S$_8$ by PXRD nor IR to confirm.

The crystals are insoluble in pyridine, THF, hexanes, ether, and toluene. The first attempt to ascertain the absorbance maximum was to measure the reflectance of the solid sample, but the spectrum lacked a local reflectance minimum. The inconclusive results were either due to an inherent lack of an absorbance maximum or because the samples were too dark for the sensitivity of the equipment, and the spectrum merely showed background signals. In order to get a reliable absorbance spectrum, the molecule had to be dissolved in something. It did not immediately dissolve in 4-ethylpyridine but did eventually dissolve when left overnight to produce a dark solution of nondescript color. A lighter version of the parent crystals, the solution looked grey or brown without an obvious spectral region. Since ethylypyridine is a better Lewis base than pyridine, it is believed that it replaced the coordinated pyridine, and since the ethyl groups will change the packing, the solubility can be drastically greater. Unfortunately any color arising from pyridine LMCT could have been shifted when changing the ligand. The weak inductive effect of the added ethyl group could shift the frequency of an absorbance maximum derived from the energy levels of the coordinated pyridine. This does not appear to matter for the characterization. The UV-vis spectrum in the 250-800 nm window had no local maximum. Furthermore, (py)$_4$Eu(OC$_6$F$_5$)$_3$ did not display such strong or broad charge transfer absorbance. S–Eu LMCT was the more likely cause of the absorbance, and that would not be significantly affected by substitution of the L type ligands.
The original synthesis procedure relied upon a stable 2+ oxidation state of the metal to allow oxidative addition. Following the same general procedure, scale, and stoichiometry, the samarium analog was produced as bright yellow crystals in good yield. With a total volume of 35 mL instead of the 30 mL used with the Eu synthesis 70.0% of pure product was produced. Through several attempts to produce an ytterbium analog, no crystalline phase was synthesized. Appropriate color changes proceeded with the reaction, but the product appeared to be soluble in pyridine. Layering with hexanes produced brown powder. It is likely that the Yb(III) ion was too small to accommodate the structure and that the complex was susceptible to further reaction in solution.

**Scheme 9.**

\[
\text{Ln} + (\text{SPh})_2 + C_6F_5\text{OH} \xrightarrow{\text{cat. Hg}} \text{Ln}(\text{SPh})_2OC_6F_5
\]

\[
\text{Ln}(\text{SPh})_2OC_6F_5 + 2S \rightarrow \text{Ln}_2(S_2)_2(OC_6F_5)_2
\]

**Scheme 10.**

\[
\text{Gd} + 1.5(\text{SPh})_2 \xrightarrow{\text{cat. Hg}} \text{Gd}(\text{SPh})_3
\]

\[
\text{Gd}(\text{SPh})_3 + \text{HOC}_6\text{F}_5 \rightarrow \text{Gd}(\text{SPh})_2OC_6F_5
\]

\[
\text{Gd}(\text{SPh})_2OC_6F_5 + 2S \rightarrow \text{Ln}_2(S_2)_2(OC_6F_5)_2
\]

Modified versions of this reaction were tested with metals lacking a stable 2+ state, neodymium, gadolinium and erbium specifically. In the first attempts, Scheme 9, a metal reacted with one equivalent each of diphenyldisulfide and pentafluorophenol followed by filtration and slow reaction with elemental sulfur. None of the trivalent metals produced a crystalline product. To reduce any side reactions, later attempts
employed a three-step synthesis, Scheme 10. Lanthanide metal was combined with 1.5 equivalents of diphenylidisulfide in pyridine with catalytic amounts of mercury. One equivalent of pentafluorophenol was added to each of the resultant solutions. Within a day, these solutions were filtered and layered with solutions of sulfur in pyridine similarly to the europium and samarium procedure. Reactions using neodymium, dysprosium, and erbium only produced powders, but the gadolinium reaction produced yellow crystals along with a brown-green powder. The crystals were composed of the same dimer as the Sm and Eu reaction proving that the reaction can proceed without access to a stable 2+ oxidation state.

The three step procedure was successful for Gd (86% yield) as well as Eu and Sm. Despite the necessity of a divalent state in the original synthesis procedure and the difficulty of producing crystals with other procedures, the inability to synthesize the structure with other lanthanides appears to have simply been size dependent.

Lanthanides had previously been oxidized by (SPh)_2 and C_6F_5OH separately when catalyzed with mercury. The failure of the two step reaction and success of the three step reaction indicates that simultaneous reaction of (SPh)_2 and C_6F_5OH suffered from an unintended side reaction. Like the europium dimer, the samarium and gadolinium crystals were all insoluble in pyridine and required a synthesis procedure that allowed crystallization during slow reaction.

The europium version of the dimer was interesting because of the novelty of the high oxidation state of europium coordinated to sulfide and because the LMCT suggested potential for unusual optical properties. Europium is used for green or blue emission when in the 2+ oxidation state and red emission in the 3+ state.\(^6\) With a natural 3+
oxidation state, red emission was expected from this species. The sulfur potentially offered additional access to the 2+ state through ligand to metal charge transfer. Depending on the specific wavelengths emitted and relative strengths, it would be theoretically possible to get white light from a single molecular source. Unfortunately, the crystals themselves were very dark with broad visible absorbance quenching nearly all emissions rendering it useless for optical applications.

The thermal decomposition still held potential. Like the fluorinated alkoxides tested previously, these dimers could potentially decompose to produce fluorides, oxides, or oxyfluorides. There was also the less likely possibility of sulfides or oxysulfides. Thermolysis of all three dimers was performed under vacuum by heating from room temperature to 650 °C at a rate of 15 °C min⁻¹ in quartz tubes with one end in a furnace and the other in liquid N₂. The furnace temperature was maintained for 5 h then allowed to cool back to room temperature at a rate of 10 °C min⁻¹. The solid state products from the Sm and Gd dimers were identified by PXRD to be LnF₃. The europium dimer produced a mixture of phases. EuS, EuF₂, and EuF₃ phases were positively identified. EuOF also seems to be present in small quantities, but most peaks from this phase overlap with the other known phases. Certainty is also reduced because the particles produced by this reaction appear to be less than 20 nm, and these structures have similar or identical space groups.

Attempts were made to synthesize similar structures using selenium in place of the sulfur, but a proper selenido analogue has not been discovered. If such a theoretical diselenido dimer is also insoluble in pyridine, synthesis would require different experimental methods. Elemental selenium is insoluble in pyridine, so the technique
used in the previous cases for slow reaction and immediate crystallization is not viable. Lanthanide selenido alkoxide crystals were only procured using triflic acid in place of pentafluorophenol. These products were soluble in pyridine and followed more traditional procedures of reaction followed by a separate crystallization process.

2.2 (py)$_6$Ln$_2$Se$_3$(CF$_3$SO$_3$)$_2$

Reacting samarium (III) phenylselenolate with elemental selenium and trifluoromethylsulfonic (triflic) acid in pyridine and layering with hexanes yielded a mixture of crystals. When using half an equivalent of selenium and two equivalents of triflic acid with respect to the metal, red crystals of (py)$_6$Sm$_2$(CF$_3$SO$_3$)$_2$(SeSe)$_2$ formed along with pale yellow samarium triflate monomers. The experiment was repeated successfully with a 1:1:2 stoichiometry of “Sm(SePh)$_3$,” triflic acid, and selenium powder, but powder precipitated along with the dimer crystals. Using diphenyldisulfide instead of the selenide to get the metal into solution followed by reaction with elemental selenium then triflic acid yielded better results. Using the same stoichiometry, crystal quality and yield were comparable (50%), but the side products formed an oil phase which was significantly easier to separate. The oil was not characterized.

Table 12. Selected bond lengths (Å) and angles (deg) of (py)$_6$Sm$_2$(Se$_2$)$_2$(CF$_3$SO$_3$)$_2$

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm(1)–O(1)</td>
<td>2.3704(1)</td>
</tr>
<tr>
<td>Sm(1)–Se(1)</td>
<td>2.9689(1)</td>
</tr>
<tr>
<td>Sm(1)–Se(2)</td>
<td>2.9627(1)</td>
</tr>
<tr>
<td>Sm(1)–Se(1A)</td>
<td>2.9722(2)</td>
</tr>
<tr>
<td>Sm(1)–Se(2A)</td>
<td>2.9660(1)</td>
</tr>
<tr>
<td>Se(1)–Se(2)</td>
<td>3.8871(1)</td>
</tr>
<tr>
<td>Se(1)–Sm(1)–Se(2)</td>
<td>81.89</td>
</tr>
<tr>
<td>Se(1)–Sm(1A)–Se(2)</td>
<td>81.78</td>
</tr>
</tbody>
</table>
Figure 15. POV view of (py)$_6$Sm$_2$(Se$_2$)$_2$(CF$_3$SO$_3$)$_2$

The metal centers of this samarium dimer are eight coordinate if all four selenium atoms are counted as coordinated, but when the Sm–Se$_2$ bond is viewed as a single bond bisecting the Se–Se bond, the Sm geometry is roughly octahedral. The Sm–Se distances ranged from 2.9627(1) to 2.9722(2) Å, and the Se–Se bonds are 2.3618(1) Å which all agree with literature bond lengths. Each metal ion is coordinated to a terminal triflate through a single oxygen atom. The coordination spheres are saturated with three pyridine molecules per metal, and two more free pyridine molecules fill the lattice voids. The distance between adjacent non-bonded selenium atoms is 3.8871(1) Å, and the Se–Sm–
Se angle between them is 82°. This is very close to the spacing in the sulfido dimer, 82° and 3.720 Å apart, showing that the Se₂ and S₂ have similar steric requirements.

Using diphenyldisulfide as the starting material, the procedure was repeated with thulium, ytterbium, and lutetium. The crystal data of the resulting products showed a gradation of selenium occupancy correlating to the Ln³⁺ ionic radii due to the change in steric forces. A given ligand has constant width orthogonal to the M–X bond. Geometry mandates that the cone angle is therefore inversely proportional to the bond length. As a result of lanthanide contraction, steric forces increase in a given structure for later lanthanides compared to earlier ones. The increased sterics are relieved in this case by replacing a diatomic anion, SeSe₂⁻, in the samarium structure with a monatomic anion, Se⁻², in the ytterbium and lutetium structure. Just as in the samarium case, each metal coordinates three pyridine and one monodentate triflate ligand in the structures of the later lanthanides. As shown above, the samarium dimer is bridged by a pair of diselenido ligands where each of the four selenium atoms has a formal charge of 1⁻. The crystals produced in the reactions of ytterbium or lutetium (Scheme 11) (36% and 30% yield respectively) are made of dimers similar to the samarium crystals but with one diselenido and one selenido bridging the metal ions, (py)₆Ln₂(SeSe)Se(CF₃SO₃)₂. The selenido, 2⁻ like the equivalent diselenido in the samarium structure, takes up less space without changing the charge balance of the molecule.

**Scheme 11.**

```
“Ln(SPh)₃” + CF₃SO₃H → “Ln(SPh)₂CF₃SO₃”
“Ln(SPh)₂CF₃SO₃” + Se → (py)₆Ln₂(SeSe)Se(CF₃SO₃)₂
```
**Figure 16.** Ortep view of (py)$_6$Yb$_2$Se$_2$(Se$_2$)(CF$_3$SO$_3$)$_2$

**Table 13.** Selected bond lengths (Å) and angles (deg) of (py)$_6$Yb$_2$(Se$_2$)Se(CF$_3$SO$_3$)$_2$

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb(1)–O(1)</td>
<td>2.260(6)</td>
<td>Yb (2)–O(4)</td>
<td>2.256(6)</td>
</tr>
<tr>
<td>Yb(1)–Se(1A)</td>
<td>2.900(1)</td>
<td>Yb(1)–Se(2A)</td>
<td>2.917(1)</td>
</tr>
<tr>
<td>Yb(1)–Se(3A)</td>
<td>2.6569(9)</td>
<td>Yb(2)–Se(1A)</td>
<td>2.8980(9)</td>
</tr>
<tr>
<td>Yb(2)–Se(2A)</td>
<td>2.8767(9)</td>
<td>Yb(2)–Se(3A)</td>
<td>2.629(1)</td>
</tr>
<tr>
<td>Se(1A)–Se(2A)</td>
<td>2.358(1)</td>
<td>Se(1A)–Se(3A)</td>
<td>4.001(1)</td>
</tr>
<tr>
<td>Se(2A)–Se(3A)</td>
<td>4.045(1)</td>
<td>Se(1A)–Yb(1)–Se(3A)</td>
<td>92.01(3)</td>
</tr>
<tr>
<td>Se(2A)–Yb(1)–Se(3A)</td>
<td>92.92(3)</td>
<td>Se(1A)–Yb(2)–Se(3A)</td>
<td>92.62(3)</td>
</tr>
<tr>
<td>Se(2A)–Yb(2)–Se(3A)</td>
<td>94.43(3)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


The Yb–Se bond distances for the diselenido ligands are shorter than the corresponding bonds in the samarium structure by 0.07 Å, roughly corresponding to the change in Ln$^{3+}$ ionic radius from the lanthanide contraction. The average Yb–Se distance for the selenido is 2.64(3) Å, appropriate for a Se$^{2-}$. The average Se–Se distance for non-bonded atoms in the ytterbium case (Se1A–Se3A and Se2A–Se3A) is 4.023 Å, and the Se–Yb–Se angles for non-bonded selenium atoms average 93°, representing a significant increase in spacing.

Table 14. Crystallographic data for (py)$_6$Sm$_2$(Se$_2$)$_2$(CF$_3$SO$_3$)$_2$·2py, (py)$_6$Tm$_2$Se$_{3.5}$(CF$_3$SO$_3$)$_2$·2py, and (py)$_6$Yb$_2$(Se$_2$)Se(CF$_3$SO$_3$)$_2$·2py

<table>
<thead>
<tr>
<th>Compound</th>
<th>(py)$_6$Sm$_2$(Se$_2$)$_2$(CF$_3$SO$_3$)$_2$</th>
<th>(py)$_6$Tm$<em>2$Se$</em>{3.5}$(CF$_3$SO$_3$)$_2$</th>
<th>(py)$_6$Yb$_2$Se$_3$(CF$_3$SO$_3$)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>C$<em>{42}$H$</em>{40}$F$_6$N$_8$O$_6$Se$_4$Sm$_2$</td>
<td>C$<em>{42}$H$</em>{40}$F$_6$N$_8$O$<em>6$Se$</em>{3.5}$Tm$_2$</td>
<td>C$<em>{42}$H$</em>{40}$F$_6$N$_8$O$_6$Se$_3$Yb$_2$</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
<td>C2/c</td>
<td>P2$_1$/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>22.9317(11)</td>
<td>22.492(3)</td>
<td>14.6183(7)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>13.6766(9)</td>
<td>16.7838(18)</td>
<td>16.7795(8)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>17.3649(9)</td>
<td>14.6081(16)</td>
<td>21.5212(10)</td>
</tr>
<tr>
<td>β (deg)</td>
<td>126.939(1)</td>
<td>112.466(2)</td>
<td>106.285(1)</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>5626.05</td>
<td>5096.1</td>
<td>5067.09</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Thulium, being between samarium and ytterbium in ionic radius, formed both structures. In the x-ray data of the thulium crystals, electronic densities in the possible selenium sites showed partial occupancy of Se$^{2-}$ and Se$_2^{2-}$. The data indicated roughly half the molecules in the crystal structure matched the samarium dimer, while half matched the ytterbium structure. Assuming equivalent population of the two forms, yield is calculated to be 79%. Both the thulium and ytterbium reactions were run with excess selenium, two equivalents to the lanthanide. This shows that the energy levels for the two molecules are roughly equivalent in the case of thulium. The diselenido is a lower
energy structure for larger lanthanides and is a higher energy structure for the smaller lanthanides due to the increase in steric strain resulting from decreasing ionic radius.

The reasonably high yield of these dimers suggested that the problem with isolating larger clusters does not come from an overwhelming thermodynamic drive to disproportionate into solid state Ln₂E₃ and Ln(OR)₃ or Ln(OR)₄ salts. However, the stability of Ln(OR)₃ monomers would explain why more species with E²⁻ ligands were not produced when the amount of chalcogen was reduced. Instead, dimers containing EE²⁻ were formed in low yield along with alkoxide monomers when the reaction mixture was deficient of elemental chalcogen necessary to form dichalcogenido dimers in high yield.

This shows a departure from other chalcogenido chemistry where different structures were synthesized by reacting different quantities of chalcogen. This resistance to form E²⁻ containing species indicates any larger clusters that might be produced through similar reactions are expected to be chalcogen rich. Cubane and double cubane type structures, which were originally expected based on previous similar experiments with chalcogenolates and halides, now seem to be unlikely products.

Scheme 12.

\[
\begin{align*}
2 \text{Ln}(\text{EPh})₃ + 2 \text{E'} + 2 \text{ROH} & \rightarrow \text{Ln}_2(\text{E'})(\text{OR})_2 \\
2 \text{Ln}(\text{EPh})₃ + 2 \text{E'} + 2 \text{ROH} & \rightarrow \frac{1}{2} \text{Ln}(\text{OR})₃ + \frac{1}{4} \text{Ln}_2(\text{E'})(\text{OR})_2 + \text{Ln}(\text{EPh})₃
\end{align*}
\]

Variations on the successful synthesis procedures were attempted using europium. The same procedure, combination of equal amounts of europium, diphenyldiselenide, and mercury in pyridine followed by addition of two equivalents of selenium and one
equivalent of triflic acid, resulted in a dark red solution with no visible solid besides a slight residue of unreacted selenium on the wall of the flask which never dissolved. Addition of selenium made the red solution darker, and the acid turned it brown. The solution was filtered and layered with hexanes (15 mL) producing dark red needles (0.050 g) which were surprisingly unrelated to the lanthanide dimers. The crystals were identified by single crystal x-ray diffraction as \([\text{C}_5\text{H}_5\text{NH}]_2[(\text{Se}_4\text{Hg}(\text{Se}_4))]\cdot2\text{py}\). This represents 20% yield with respect to the mercury. The reaction was reproduced twice, once covered in foil in attempt to reduce side reactions and once with reduced mercury (0.011 g) and excess selenium. Both reactions produced the same pure crystalline product as the original and yellow mother liquor likely to contain diphenyldiselenide. This mercury dianion is well known, and has been crystallized with other counterions.

This specific crystal structure is somewhat interesting compared to other \(\text{HgSe}_8\) structures. Each \(\text{Se}_4^{2-}\) ligand is bound at the 1 and 4 positions of the chain forming 5-membered rings. The complex is puckered creating chirality. The unit cell contains two different isomers, but they are not enantiomers. The resolution by crystallization is formally interesting, but the energetic barrier to transition between conformations of a five membered ring is expected to be low. Cyclopentane readily switches confirmations in solutions at room temperature with an activation energy around 10kJ/mol.\(^8\) It is unlikely that the separation of enantiomers in the solid phase would have any practical use. Neutral pyridine molecules are hydrogen bonded to the charge balancing pyridinium cations as is expected for pyridinium salts crystallized from pyridine.
The previously produced europium disulfide dimer was a novel and somewhat unexpected Eu(III) molecule for its high coordination of sulfur stabilized by the alkoxides. The closely related selenide was targeted to probe the extent of the ability of alkoxides to stabilize higher oxidation states in europium bound to chalcogens. It was
also a desirable target for potential optical properties. Substituting selenium for the sulfur would have changed the charge transfer band and potentially opened up the possibility of measurable emission in the optical region. The diselenido dimer was successfully produced with the larger cation Sm(III) and the smaller lanthanide Tm(III) using the same procedures, but the corresponding europium dimer was not formed using the same procedure or modified attempts. The hole in the series was probably due to the instability of the Eu(III) state bound to chalcogens relative to the Eu(II) state. Ln–Se bonds are significantly weaker than Ln–S bonds mostly due to the difference in ionic radii. Whereas the alkoxides were able to stabilize the higher oxidation state of the lanthanide sulfido dimer, the strongly oxidative triflic acid was insufficient to stabilize the selenido dimer.

2.3 Conclusion

Two series of lanthanide chalcogenido alkoxide dimers were synthesized. 

\[(\text{py})_3\text{Ln}\eta^2-\mu-(\text{SS})(\text{OC}_6\text{F}_5)\]. \(\text{Ln} = \text{Sm, Eu, Gd}\) was synthesized by a slow diffusion of a solution of sulfur in pyridine into a solution of “\(\text{Ln}(\text{OC}_6\text{F}_5)_2\)” or “\(\text{Ln}(\text{OC}_6\text{F}_5)_2(\text{SPh})\)” also in pyridine. The resultant crystals were insoluble in pyridine. They did dissolve slowly in 4 ethylpyridine, but that presumably occurred as the coordinated pyridine was replaced by the ethylpyridine interrupting the packing. The europium dimer is the first known example of a molecular Eu(III) sulfide. The strong, broad LMCT prevents any detectable optical photoemission from europium. Thermal decomposition of all three produced LnF₃, and the europium version also produced EuF₂, EuS, and possibly EuOF.
Two versions of lanthanide selenido alkoxide dimers were synthesized. Small lanthanides, Yb and Lu, formed \((\text{py})_6\text{Ln}_2(\text{Se}_2)\text{Se(CF}_3\text{SO}_3)_2\). The larger metal, Sm, formed \((\text{py})_6\text{Ln}_2(\text{Se}_2)_2(\text{CF}_3\text{SO}_3)_2\). The crystals formed from Tm reactions contained a mixture of the two molecules. The stoichiometry used in these reactions was the same. The identities of the products are dependent on the minor differences in Ln(III) radius. The structures are very similar to one another with the largest difference being the greater Se–Ln–Se angle in \((\text{py})_6\text{Ln}_2(\text{Se}_2)\text{Se(CF}_3\text{SO}_3)_2\) alleviating the steric strain for later lanthanides occurring in the bisdiselenido structure. Identical reactions with europium produced \([\text{C}_5\text{H}_5\text{NH}]_2[\text{Se}_4\text{Hg(Se}_4)]\) and no \((\text{py})_6\text{Eu}_2(\text{Se}_2)\text{Se(CF}_3\text{SO}_3)_2\). Given the successful synthesis of Sm and Tm diselenidos, the inability to produce the europium analog is most likely due to the relative instability of Eu(III) selenidos.

Dichalcogenido complexes are preferred over chalcogenidos. The only structures isolated with E\(^{2-}\) ligands were due to steric hindrance preventing the inclusion of E\(^{2-}\) in their place. Lanthanide chalcogenido alkoxides discovered in the future are expected to be chalcogen-rich.
References:


Chapter 3. Lanthanide Fluorido Alkoxides

Lanthanide trifluorides and oxyfluorides are useful for various technological uses including host lattices for phosphors\(^1\) and thin film coatings for optics.\(^2\) There is scientific interest in molecular lanthanide fluorides for this reason, but fluorides were not an initial target in this research into fluorinated alkoxides. In addition to producing chalcogenido dimers with fluorinated alkoxide ligands, investigation into these molecules also resulted in the formation of lanthanide fluoride clusters. After a serendipitous synthesis of a fluoride cluster, lanthanide fluorides became a divergent research path.

Use of fluorinated alkoxides along with chalcogenide ligands was intended for improved IR emission properties and solubility, but lanthanide fluorido clusters were not initially intended. Fluorido complexes were produced somewhat unexpectedly without traditional fluoride sources. Lanthanide induced C–F bond activation has been reported before,\(^3\) and similarly unintended fluoride structures have been produced using similar fluorinated organic ligands. With Hg(SC\(_6\)F\(_5\))\(_2\) as the only source of fluorine, a fluoride cluster, (DME)\(_3\)Yb\(_4\)F\(_2\)(OCH\(_2\)CH\(_2\)OCH\(_3\))\(_2\)(SeSe)(SC\(_6\)F\(_5\))\(_4\)•DME, had been repeatedly synthesized. It was produced when intending to coordinate the chalcogenolate intact along with elemental selenium, and the C–F and C–O cleavages were unexpected. Similarly during the course of this research, multiple lanthanide fluoride clusters resulted from attempts at fluorinated alkoxide capped lanthanide chalcogenido clusters. This occurred both from reactions with pentafluorophenol and sulfur as well as triflic acid and sulfur or selenium. No other sources of fluorine were present in these reactions.
3.1 (DME)$_6$(py)$_6$Nd$_{18}$(C$_6$F$_5$O)$_{18}$ F$_{24}$O$_3$S$_3$

The first fluoride cluster produced from this course of research was isolated from reacting 1.0 mmol neodymium with 1.5 equivalents diphenyldiselenide and 5 mol percent mercury in pyridine followed by addition of one equivalent each of sulfur and pentafluorophenol. The solvent was removed by vacuum, and the green-brown solid left was dissolved in DME and crystallized with hexanes. This produced about 10 mg of colorless crystals that were shown by XRD to be the largest and most complex cluster produced in this research project, (DME)$_6$(py)$_6$Nd$_{18}$(C$_6$F$_5$O)$_{18}$ F$_{24}$O$_3$S$_3$. It crystallizes in the $P2_1/n$ space group with parameters $a = 21.580(3)$ Å, $b = 29.537(4)$ Å, $c = 37.422(4)$ Å, $\beta = 91.779(2)$°, and $V = 23,842$ Å$^3$. The core of the structure is roughly D$_{3h}$ toroidal, a rather elegant design with an unusual void in the center. Figure 18 shows the core of the structure with carbon, hydrogen and fluorine atoms in C$_6$F$_5$O$, \text{py}$, and DME ligands removed for clarity.

There are three distinct neodymium positions, and all are eight coordinate. The six inner neodymium atoms are arranged in a trigonal prism with no atoms occupying the inner space. The next six metal atoms are also arranged in a larger trigonal prism. The triangle faces of the two polyhedra are coplanar. The vertices of the smaller triangles are located approximately at the midpoint of the edges on the larger triangles. In this way, the two planes of six neodymium atoms resemble fragments of distorted hexagonal lattices vertically aligned. The remaining six metal atoms are found in the central XY plane near the exterior of the cluster arranged in pairs. There are two off of each rectangular face of the larger prism.
The three sulfido ligands are located in the XY pseudo mirror plane just off the center of the rectangular faces of the central prism. Each is bonded to four of the inner metal atoms and two in the larger prism. The Nd–S bonds are significantly longer than

![Figure 18. POV view of (DME)$_6$(py)$_6$Nd$_{18}$(C$_6$F$_5$O)$_{18}$ F$_{24}$O$_3$S$_3$ along b with C, H, and aromatic F atoms removed for clarity](image)
normally expected for Ln – S\(^2\) distances. The Ln–S lengths in clusters such as (THF)\(_8\)Sm\(_8\)S\(_6\)(SePh)\(_{12}\) and (THF)\(_6\)Yb\(_4\)S\(_4\)(SS)\(_4\)(SC\(_6\)F\(_5\))\(_2\)–THF predict a Nd–S distance in the range of 2.7-2.9 Å after adjusting to account for lanthanide contraction. Here, the sulfur atoms are coordinated to six metal atoms each with expectedly lengthened bonds. There are two short bonds for each sulfur atom, 2.9219(2) - 2.9446(2) Å, and four longer bonds 2.9736(2) – 3.0042(2) Å. The presentation of a high coordination number with long bonds possibly suggests an average of multiple positions in which the sulfido is bonded closely to some metals with dative interactions to the others. The three oxo ligands are also in the central XY plane. They are located off of the edges of the smaller prism each bonding tetragonally between two inner neodymium atoms from the small prism and two outer neodymium atoms in the central plane.

There are three different fluoride positions, and all are three coordinate. Six fluoride atoms occupy the first position. They are above and below each sulfido with the top three just above the top metal hexagonal lattice and the bottom three just below the bottom metal lattice. Each of these fluorido is bound to two neodymium atoms from the central triangle and one towards the exterior. The bonds to the central atoms, 2.4250(2) - 2.4581(2) Å, are significantly shorter than the third bond, 2.5242(3) – 2.6119(2) Å. There are 12 fluorides that each bond to one inner, one intermediate, and one outer neodymium. The third and final fluoride environment is near the exterior of the cluster in the XY pseudo mirror plane bridging one metal atom in that plane with one metal above and one below. The bonds from these fluorides to metals in the mirror plane are significantly shorter (2.3845(2) – 2.4051(2) Å) than the ones to the metals in the hexagonal lattice (2.4572(2) – 2.5094(2) Å).
There are three phenoxide positions. Each of the six inner neodymium ions has one phenoxide coordinated in a roughly axial position. Each neodymium ion in the larger trigonal prism is coordinated to one phenoxide in a roughly equatorial direction and a pyridine molecule in an axial direction. The pyridines and the adjacent axial phenoxides on the top of the cluster are well aligned and supported by $\pi-\pi$ interactions. The distances between the faces of the rings are all approximately 3.6 Å. On the bottom of the cluster, one pair is well aligned, but the other two display deviation from parallel ring orientation. Figure 19 shows fragments of the top and bottom of the cluster with the majority of the structure removed to clearly show ring orientation. Each outer metal atom is bridged to the adjacent metal atom by a pair of phenoxides, one below the central XY plane and one above. Each of those outer metals is also coordinated to a single DME molecule through both oxygen atoms to fill its primary coordination sphere. The Nd–O distances for the six bridging alkoxides coordinated to the outer metals are significantly longer (2.4765(3) – 2.5596(2) Å) than the distances for the 12 terminal alkoxides, 2.2537(3) – 2.3954(3) Å. This difference can be explained by steric effects. The bridging nature adds additional constraints to the bond geometry compared to the terminal positions. Plus there is more steric bulk around the exterior metal positions. The metals arranged in the two hexagonal lattices have space for a more closely bound alkoxide due to a higher number of coordinated monatomic ligands (6-7), while the outer metal positions coordinate bulkier DME molecules and only four monatomic ligands each. The total coordination number is also in question.

The six metals in this outer position are unambiguously eight coordinate with all bonds to oxygen and fluorine atoms within normal distances. The other metal atoms are
Figure 19. POV view of \((\text{DME})_6(\text{py})_6\text{Nd}_{18}(\text{C}_6\text{F}_5\text{O})_{18}\text{F}_{24}\text{O}_3\text{S}_3\) fragments. (a) Top along b axis. (b) Bottom along b axis. (c) Top perpendicular to b. (d) Bottom perpendicular to b.
bonded to the six coordinate sulfur atoms making them also eight coordinate formally, but they might be more accurately described as a mixture of eight coordinate and seven coordinate metals with four coordinate sulfidos. Cleaving the Nd–S bonds with any pair of metal atoms aligned along the b axis would allow the sulfur to move into a square pyramidal or square planar geometry with the distances of the remaining four bonds moving into the expected range. The crystallographic data may represent a mixture of these small shifts in sulfur positions in which any given cluster would be comprised of 12 eight coordinate metals and six seven coordinate metals.

This structure posed two problems. First, it contains significant empty space. The void in the center is approximately 25 Å³ after subtracting the volume of the Nd(III) ions at the vertices of the central trigonal prism. A space of this size with an electron deficient exterior could host a small molecule such as H₂, H₂O or O₂. The eight coordinate neodymium ions which would theoretically coordinate to such a molecule are bonded to formally six coordinate sulfidos. The distortion of the structure necessary to include such a guest molecule through breaking Nd–S bonds would be small. H₂O and O₂ should not be present based on the reaction conditions, but the alkoxide was introduced in the form of an alcohol affording the possible formation of H₂ in the reaction mixture. There was not significant enough electron density in the crystallographic data to assign occupancy of such a molecule, but that is insufficient proof against disordered occupancy of one.

The second problem is reproduction. It was only made once in low yield. In addition to the structure containing six different types of ligands including two solvents, there was no intentional fluoride or oxo source. The fluorides were abstracted from the
fluorinated phenol, and the oxo ligands could have come from the phenol, the DME, or adventitious O₂ or H₂O. Such unintended oxides have been reported throughout the history of lanthanide oxide research.⁴ Adventitious oxygen sources give more credence to a possible molecule filling the central space. The procedure was repeated identically in all recorded variables. Reproductions were also attempted with modified procedures including many with intentional oxo and fluoride source materials. Potential fluoride sources used included HgF₂, NH₄F, and N(CH₃)₄F. Controlled addition of H₂O was accomplished by adding water by syringe to dry, degassed pyridine to make a stock solution. That solution was quantitatively added to solutions of Ln(EPh)₃ in dry solvent along with the other reactants. Alternatively, oxygen was added by charging the N₂ atmosphere in a reaction flask with a small balloon of O₂. No attempts were successful in reproducing the (DME)₆(py)₆Nd₁₈(C₆F₅O)₁₈F₂₄O₃S₃ cluster.

3.2 (py)₈Yb₄F₈(CF₃SO₃)₄ and (DME)₄Tb₄(CF₃SO₃)₆F₂S₂

Though that structure was only produced once, it was not the only structure synthesized by fluoride abstraction in this research. The second fluoride structure was produced from an early attempt to synthesize a lanthanide chalcogenido alkoxide by reaction conditions very similar to those yielding a dimer discussed in Chapter 2, (py)₆Yb₂Se₃(CF₃SO₃)₂. Reaction of Yb with one equivalent of diphenyldisulfide and catalytic mercury in pyridine followed by addition of two equivalents of elemental selenium and one equivalent of triflic acid produced a fluoride instead of a selenide. Filtering and layering the solution with hexanes produced colorless crystals. Any ytterbium selenido species produced from pyridine was expected to be strongly colored
due to either Yb(II) MLCT or Yb(III) LMCT. The lack of color in crystals produced by these reaction conditions elicited the assumption it was a simple lanthanide triflate monomer, salt, or polymer. The phase was characterized by single crystal XRD. The formula was \((\text{py})_8\text{Yb}_4\text{F}_8(\text{CF}_3\text{SO}_3)_4\). Despite the precedence of Ln activated C–F bond cleavage, this was a surprising structure given such likely alternatives.

In \((\text{py})_8\text{Yb}_4\text{F}_8(\text{CF}_3\text{SO}_3)_4\), the metal atoms are arranged in a mildly distorted tetrahedron around a central four coordinate fluoride. The Yb–F–Yb angles for this central fluoride are \(108.1(2) ^\circ - 110.7(2) ^\circ\), and the Yb–F distances range \(2.160(5) - 2.188(5) \text{ Å}\). Each metal ion is coordinated to two pyridine molecules and one terminal triflate ligand through a single oxygen atom. The Yb–O bonds are \(2.342(7) - 2.357(7) \text{ Å}\), and the Yb–O–S angles are \(137.8 - 149.8 ^\circ\). There is a two coordinate fluoride at each of the six edges of the tetrahedron with bond distances ranging \(2.191(7) - 2.235(7) \text{ Å}\). The four faces of the tetrahedron could each accommodate the final fluoride in a trigonal pyramidal configuration. The Yb–F bond distances for this unique fluorine are the longest and most varied of the three environments at \(2.37(2) - 2.82(2) \text{ Å}\).

Crystallographically, the occupancy of these positions is shared. The metals coordinated to that unique fluoride are eight coordinate, while the one metal atom located at the vertex on the opposite side of the tetrahedron with respect to the fluoride occupied face is seven coordinate. The core of the structure is shown in Figure 20 with the partially occupied positions colored yellow to clearly distinguish them from the fully occupied green fluoride positions. Only the coordinated oxygen and nitrogen atoms from the triflate and pyridine ligands are shown for clarity.
Figure 20. Ortep view of (py)$_8$Yb$_4$F$_8$(CF$_3$SO$_3$)$_4$

Table 15. Crystallographic data for (py)$_8$Yb$_4$F$_8$(CF$_3$SO$_3$)$_4$ and (DME)$_4$Tb$_4$(CF$_3$SO$_3$)$_6$F$_2$S$_2$

<table>
<thead>
<tr>
<th>Compound</th>
<th>(py)$_8$Yb$_4$F$_8$(CF$_3$SO$_3$)$_4$-4py</th>
<th>(DME)$_4$Tb$_4$(CF$_3$SO$_3$)$_6$F$_2$S$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>C$<em>{64}$H$</em>{60}$F$<em>{20}$N$</em>{12}$O$_{12}$S$_4$Yb$_4$</td>
<td>C$<em>{140}$H$</em>{40}$F$<em>{20}$O$</em>{26}$S$_8$Tb$_4$</td>
</tr>
<tr>
<td>Space group</td>
<td>P$_{2_1}$/n</td>
<td>P -1</td>
</tr>
<tr>
<td>a (Å)</td>
<td>24.1496(16)</td>
<td>11.2519(7)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>14.0166(9)</td>
<td>12.7457(8)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>24.5132(16)</td>
<td>21.3373(14)</td>
</tr>
<tr>
<td>α (deg)</td>
<td>90</td>
<td>86.394(1)</td>
</tr>
<tr>
<td>β (deg)</td>
<td>100.089</td>
<td>88.311(1)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>90</td>
<td>66.508(1)</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>8169.3</td>
<td>2800.83</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>
A third lanthanide fluoride complex was synthesized in this work. A terbium cluster was produced from a reaction of 1 mmol terbium, 1.5 equivalents diphenyldisulfide and catalytic Hg in DME followed by addition of 1 equivalent each of sulfur and triflic acid. After the acid was added, the reaction was stirred at room temperature for three days before black precipitate was filtered from grey solution, and the solution was concentrated and layered with hexanes. The colorless crystals made of \( (\text{DME})_4\text{Tb}_4(\text{CF}_3\text{SO}_3)_6\text{F}_2\text{S}_2 \) were poorly formed in low yield, but it was good enough to identify the structure by x-ray diffraction.

Table 16. Selected bond lengths (Å) and angles (deg) of \( (\text{DME})_4\text{Tb}_4(\text{CF}_3\text{SO}_3)_6\text{F}_2\text{S}_2 \)

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Bond Lengths</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb(1)–S(25) = 2.6363(1)</td>
<td>Tb(3)–S(25) = 2.7182(1)</td>
</tr>
<tr>
<td>Tb(4)–S(25) = 2.7199(1)</td>
<td>Tb(1)–S(26) = 2.6950(1)</td>
</tr>
<tr>
<td>Tb(2)–S(26) = 2.7203(1)</td>
<td>Tb(3)–S(26) = 2.7239(1)</td>
</tr>
<tr>
<td>Tb(2)–F(25) = 2.3842(1)</td>
<td>Tb(3)–F(25) = 2.3731(1)</td>
</tr>
<tr>
<td>Tb(4)–F(25) = 2.4000(1)</td>
<td>Tb(2)–F(26) = 2.2703(1)</td>
</tr>
<tr>
<td>Tb(4)–F(26) = 2.2557(1)</td>
<td>Tb(1)–O(11) = 2.3516(1)</td>
</tr>
<tr>
<td>Tb(3)–O(10) = 2.5120(1)</td>
<td>Tb(3)–O(5)–S(3) = 131</td>
</tr>
<tr>
<td>Tb(3)–O(1)–S(2) = 144</td>
<td></td>
</tr>
</tbody>
</table>

The cluster has four terbium atoms arranged in a distorted tetrahedron. The edges are occupied by \( \mu–\text{CF}_3\text{SO}_3^- \) ligands coordinated through one oxygen atom to either metal. The arrangement of the terbium atoms is distorted from a tetrahedral geometry due to the difference in the ionic radii of \( S^{2-} \) and \( F^- \) which bridge the faces. Two of the faces are
occupied by three coordinate sulfidos. One face contains a three coordinate fluoride.
The other fluoride is bonded to Tb2 and Tb4 with an average distance of 2.26(2) Å and
has a dative interaction with Tb1 at a distance of 3.910 Å. Each metal is coordinated to a
DME molecule through both oxygen atoms. The asymmetry caused by the two
coordinate fluoride ligand, F26, leaves Tb1 seven coordinate, while the other three are
eight coordinate. Like the previously described fluoride clusters, this was not reliably
reproduced from identical reaction conditions.

Figure 21. POV of (DME)$_4$Tb$_4$(CF$_3$SO$_3$)$_6$F$_2$S$_2$ with C, H, and F removed from
DME and CF$_3$SO$_3$ ligands for clarity
During the original synthesis of the ytterbium fluoride species, dark red crystals that decomposed before they could be characterized were also produced. When the reaction was repeated using similar conditions, only dark red crystals were produced. This phase was identified as the selenido dimer, \((\text{py})_6\text{Yb}_2\text{Se}_3(\text{CF}_3\text{SO}_3)_2\). The most notable difference between the syntheses is the longer time left in the crystallization flask in the synthesis of the fluoride. It is possible that the reaction mixture leading to the diselenido dimers would be sufficient to produce fluoride tetramers if the reaction were allowed to proceed longer. Fluctuations in temperature and intensity of light can also vary on a daily basis adding subtle differences to the reaction conditions. Following the synthesis of the dimer, a series of experiments varying chalcogenolate, time, temperature, and light were run to identify the variable(s) responsible for forming one product or the other. Attempts to isolate the variable(s) leading to different products from similar reaction conditions were inconclusive, but time appears to be the most important variable. Based upon visual inspection, the selenide appears to begin breaking down approximately one month after filtering and layering the reaction solution with hexanes. The fluoride crystals were characterized three months after layering. This fluoride cluster is not reliably reproduced from seemingly identical reaction conditions but was synthesized one other time in low yield in a reaction left to crystallize for three months. In agreement with this theory, the only time the neodymium fluoride cluster was synthesized, it was left to crystallize for 10 weeks before the crystals were observed.

Contrasting with the neodymium and ytterbium fluorides, the terbium crystals were observed only nine days after setting up crystallization conditions. This is significantly shorter than reaction times for the other fluoride containing clusters. It is
unclear if the yield was limited by the time because the fluoride abstraction reaction occurred at a low rate or if the C–F bonds were cleaved quickly, and the poor yield was due to relative instability of the structure. Theoretically, a slow reaction producing a stable cluster would form product in higher yield if the reaction time for a similar reaction mixture were increased. This structure was not reproduced by such reactions implying that this sulfidofluoro structure could be a metastable intermediate to a more stable fluoride cluster similar to the ytterbium tetramer. Despite the isolation of the sulfidofluoro in a relatively short timescale, time still appears to be an important variable in forming lanthanide fluorides in this family of reactions.

The forms of the chalcogen reactants also appeared to be an important variable. The neodymium and ytterbium clusters were synthesized from reaction mixtures containing both sulfur and selenium. The majority of reactions attempting to synthesize chalcogenide clusters contained SPh/S or SePh/Se, but the reactions yielding the neodymium and ytterbium fluorides were in the minority containing SePh/S or SPh/Se combinations. The neodymium cluster was produced from selenolate and elemental sulfur, and the ytterbium cluster was made from thiolate and elemental selenium. There is a history of substitution between chalcogens and C–E bond cleavage in similarly mixed reactions. It seemed possible that intermediate states in such substitution reactions were critical or at least helpful in Ln–F bond formation, but the literature shows C–F bond activation without chalcogen involvement. The terbium fluoride tetramer was not isolated until after exploring conditions responsible for producing the other fluorides. It was synthesized from a reaction utilizing thiolate and sulfur but no selenium. This disproves the necessity of a mixed chalcogen system for producing these fluorides. The
association between mixed chalcogen reactions and fluoride products in the original results was probably a statistical anomaly from running a limited number of reactions.

In an attempt to further understand the reaction mechanism for fluoride synthesis, the ytterbium tetramer procedure was repeated without adding elemental chalcogen. It was the one fluoride cluster of the three that did not include any chalcogenido ligands and therefore could be theoretically produced without any chalcogen. If fluoride replaced the chalcogenolate in a simple substitution, the reaction should proceed without either elemental sulfur or selenium. There was no direct evidence of participation of the elemental chalcogen in a more complex reaction pathway, but no products were isolated from any attempts with various reaction conditions that lacked elemental chalcogen including all reactions forming the lanthanide alkoxides described in Chapter 1.

However, such reactions have been reported in the literature. Burns and Anderson produced \( \text{Cp}^*\text{Yb}_2(\mu-\text{F}) \) by reacting \( \text{YbCp}^*_2 \) with \( \text{C}_6\text{F}_6 \) in hexanes and recrystallizing in hexanes without an additional reactant or catalyst. The same compound was also synthesized using \( \text{C}_6\text{H}_5\text{CF}_3 \) for a fluorine source. This proves that neither elemental sulfur nor selenium is inherently necessary for methyl or aryl fluoride abstraction by lanthanide ions. However, such reactions have not been observed during simple reactions of lanthanide chalcogenolates with fluorinated alkoxides. There is a major difference in the reactivities of the lanthanide complexes in these cases. \( \text{YbCp}^*_2 \) is highly susceptible to oxidative addition in a non-coordinating solvent. C–F bond cleavage was the only route to creating a trivalent complex with a full primary coordination sphere in the reaction of the metallocene, and they reported immediate reaction upon addition of \( \text{C}_6\text{F}_6 \). This is vastly different from starting with trivalent
lanthanide chalcogenolates dissolved in coordinating solvents. Reactions on this time scale would prevent isolation of chalcogenides described in Chapter 2 as well as the Eu(II) containing dimer and trimer described in Chapter 1.

The only reactions that vaguely resemble the Cp*₄Yb₂(µ-F) synthesis was the synthesis of (DME)₂Eu(C₆F₅O)₃Eu(C₆F₅O)₃Eu(DME)₂ and reactions using this trimer as an intermediate. It was produced in a single step starting with elemental europium which ended in a divalent state in high yield. The Eu(III) state is preferred when coordinated to C₆F₅O⁻ ligands as shown by the production of a heterovalent dimer instead of a solely divalent species when “Eu(SPh)₂” was reacted with two equivalents of C₆F₅OH. Based on the literature, it appeared that fluorine should have oxidatively added to the Eu(II) trimer in the presence of aryl fluorines in C₆F₅O⁻. This reaction was not observed. One difference in these systems was the solvent. The literature example of oxidation was performed in benzene. Conversely, the DME used here is able to coordinate to the Eu(II) complex stabilizing divalent structures. There is also a difference in the identity of the lanthanide. The preference for Yb to take the 3+ state over the 2+ state is greater than in the Eu case. The standard reduction potential from 3+ to 2+ for Eu is -0.35 V. For Yb it is -1.15 V. Ignoring any possible steric discrepancies, the difference in reduction potentials makes it more energetically favorable for ytterbium to be oxidized in a given situation. This stronger drive would allow a reaction pathway to include higher energy organic intermediates or products compared to reaction conditions that would proceed with europium.

In the reaction of YbCp*₂, one ytterbium ion was oxidized by a single electron with perfluorobenzene as the only available reactant to promote the ytterbium to the 3+
state. Charge balance presumably required homolytic cleavage of a C–F bond producing an aryl radical intermediate. YbCp*2(C6F5) was identified in the mixture of side products, and when the mixture was hydrolyzed, C6F5H was also identified in agreement with a homolytic mechanism. The favorability of the higher oxidation state drove the reaction through relatively high energy organic intermediates. This does not seem to hold for europium. Eu(II) having the greatest relative stability within the lanthanide group might explain why the divalent trimer was only isolated from europium and was never synthesized from ytterbium or samarium. Any Ln(II)–OC6F5 species produced in solution from Sm or Yb would have possessed greater potential to react further to form a fluoride complex which might not have crystallized under the same conditions used to isolate the europium complexes. The only products isolated from reactions targeting Sm(II) and Yb(II) alkoxides were (DME)2Ln(OC6F5)3.

All observed fluoride synthesis reactions in this project began with Ln(III). Reactions between “Ln(EPh)2” and two equivalents of C6F5OH were run with Eu, Sm, and Yb both with and without additional elemental chalcogen, but none of these reactions produced fluoride clusters. The driving force of Yb(II) or Sm(II) oxidation was not present in any fruitful reactions, and fluoride formation did not proceed in mixtures containing nothing but Ln, (EPh)2, and a fluorinated alkoxide. Because additional reactants in the form of sulfur or selenium were present in every mixture that produced fluorides, it is concluded that such a reactant is necessary to allow a lower energy reaction pathway. By starting the fluorination with a fully oxidized metal, it must have proceeded by substitution instead of oxidative addition. The presence of elemental chalcogen in all successful reaction mixtures implies chalcogenido involvement in the
mechanism where chalcogenolate alone appears unsuitable. Scheme 13 gives an example of a thermodynamically favorable reaction creating lanthanide fluoride bonds requiring a chalcogenido source instead of chalcogenolate.

**Scheme 13.**

While such reactions are thermodynamically favorable, it would require the cleavage of C–F bonds resulting in high activation energies. In agreement with this theory, these reactions proceeded slowly at room temperature typically taking months to yield crystals. In one attempt to synthesize \((\text{py})_8 \text{Yb}_4 \text{F}_8 (\text{CF}_3 \text{SO}_3)_4\), the reaction was run at near boiling point, and crystals grew in days. In later attempts to synthesize the originally intended chalcogenido structures, reactions were given less time and run at lower temperatures in order to avoid side reactions creating fluorides. No undesired fluorides were observed after this change in procedures.
3.3. Conclusion

Three lanthanide fluorido alkoxide clusters were synthesized. All of these clusters were formed through the cleavage of C–F bonds in alkoxides in reaction mixtures containing chalcogenides. These fluoride extraction reactions appear to be relatively slow compared to metathesis reactions of alkoxides or chalcogenides, and most reactions producing these structures ran for months.

(DME)$_6$(py)$_6$Nd$_{18}$(C$_6$F$_5$O)$_{18}$ F$_{24}$O$_3$S$_3$ was synthesized from the reaction of “Nd(SePh)$_3$” with C$_6$F$_5$OH and sulfur in pyridine followed by crystallization of the solid product in DME. The original reaction contained C$_6$F$_5$OH as the only fluoride source, and the alkoxide and DME were the only known potential oxide sources making the product an unexpected structure. Attempts at reproduction included other sources of fluorine and oxygen, but the structure was not reproduced. The cluster has formally six coordinate sulfidos with long bond lengths which could represent an average of four coordinate sulfidos in three slightly different positions. There is no direct evidence, but the void in the center of the cluster could be occupied by a small molecule such as H$_2$.

The tetramer (py)$_8$Yb$_4$F$_8$(CF$_3$SO$_3$)$_4$ was synthesized from a procedure almost identical to the reproducible synthesis of (py)$_6$Yb$_2$Se$_3$(CF$_3$SO$_3$)$_2$ described in Chapter 2. The main difference was the reaction time. At room temperature the selenido appeared to break down after a month, and the fluoride was collected three months after crystallization conditions were set. The fluoride was later reproduced more quickly with the aid of heat.

Another tetramer, (DME)$_4$Tb$_4$(CF$_3$SO$_3$)$_6$F$_2$S$_2$, was synthesized once in low yield. It is possibly a trapped intermediate on the route towards a fluoride cluster without
sulfide similar to the ytterbium structure. The long term stability in solution is brought into question due to the low one-time yield and the core geometry being a grossly distorted tetrahedron.

C–F bond cleavage has shown to be a significant source of unintended side reactions in attempts to synthesize lanthanide chalcogenido fluorinated alkoxides. Specifically, it was theorized that (DME)$_4$Ln$_3$(OC$_6$F$_5$)$_6$ (Ln = Sm, Yb) phases were not isolated in the same way as the europium trimer because of their greater susceptibility to oxidative addition of fluoride. Based on the conditions and results of the lanthanide fluorido producing experiments, future reactions targeting chalcogenidos were limited to room temperature and were no longer left for long periods of time to crystallize. These side reactions were not observed when these precautions were taken. With the aid of heat, C-F cleavage in coordinating solvents has potential as a route to molecular lanthanide fluorides from lanthanide chalcogenido clusters.
References:


Chapter 4. Lanthanide Oxychalcogenides

Lanthanide oxychalcogenido clusters are an interesting class of compounds. There is potential for technological applications, but there are synthetic challenges. Solid state oxides and oxysulfides are employed in various technologies including oxidative catalysis of CeO$_2$\textsuperscript{1} and lanthanide doped Y$_2$O$_2$S phosphors.\textsuperscript{2} The possibility to recreate properties of lanthanide oxides and oxychalcogenides in species soluble in organic media and possible single source precursors to solid state phases are attractive research goals.

The stability of solid state Ln$_2$O$_3$ creates a thermodynamic minimum opposing the synthesis of discrete molecules in solution making synthesis of oxide and oxychalcogenide clusters a challenging endeavor pursued for over a decade.\textsuperscript{3} Early reported examples of molecular lanthanide oxide clusters resulted from adventitious oxygen from impurities in the reaction mixture.\textsuperscript{4} Oxides are commonly produced from aqueous reactions, but these conditions are conducive for coordination of hydroxo and aqua ligands at the expense of softer ligands making it a poor route to synthesize chalcogenides. Reacting “Ln(SePh)$_3$” with SeO$_2$ had formed lanthanide oxyselenido clusters, (THF)$_8$Ln$_8$O$_2$Se$_2$(SePh)$_{16}$ (Ln = Ce, Pr, Nd, Sm), in good yield, and the resultant clusters exhibited notable NIR emission properties.\textsuperscript{5} Reactions with tellurium oxide or sulfur trioxide have posed more difficulty. Several former group members have had some success with lanthanide oxychalcogenide syntheses. This chapter will start by discussing work reproducing some of their reactions and continue with original, related work.
4.1 Oxysulfides (THF)_8Ln_8O_2S_2(SePh)_16

Following synthesis procedures originated by Louise Huebner and modified by Sayantani Das, synthesis of a lanthanide oxysulfidoselenolate cluster with early lanthanides was repeated. The neutral cluster (THF)_8Ln_8O_2S_2(SePh)_16 (Ln = Ce, Nd) was synthesized by reduction of pySO_3 by “Ln(SePh)_3” prepared in situ by the redox reaction of lanthanide metal with (SePh)_2 catalyzed by mercury. The single crystal data originally obtained showed partial occupancy of S and Se at the sulfur sites. Though sulfur will typically substitute for selenium, there is precedence of selenido substitution for sulfido and selenido formation from selenolate sources. In order to crystallize molecules with full sulfur occupancy in the expected sites, the reaction temperature was reduced from 20°C to -5°C. There is no evidence to suggest that cleaving selenolate C–Se bonds is a necessary step in the synthesis mechanism of (THF)_8Ln_8O_2S_2(SePh)_16. Like the synthesis of fluorides through C–F cleavage, it was believed that this side reaction is slower than the substitution of chalcogenide, and reaction speed was expected to be dependent on temperature. Decreasing the reaction temperature was intended to allow the formation and isolation of the oxysulfide before large amounts of selenide were formed. The reaction was run at reduced temperature but allowed to return to room temperature for filtration and crystallization providing opportunity for further reaction. This procedure improved the population of appropriate atoms in their ascribed locations but was imperfect including 5% selenido in place of the sulfido. Accounting for this imperfection in calculating the theoretical crystal mass, yields were 20% for cerium and 15% for neodymium.
Figure 22. ORTEP diagram of (THF)$_8$Ce$_8$O$_2$S$_2$(SePh)$_{16}$ at with C and H atoms removed for clarity

Table 17. Crystallographic data for (THF)$_8$Ce$_8$O$_2$S$_2$(SePh)$_{16}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>(THF)$_8$Ce$_8$O$_2$S$<em>2$(SePh)$</em>{16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>C$<em>{152}$H$</em>{192}$Ce$<em>8$O$</em>{16}$S$<em>2$Se$</em>{16}$</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td>a (Å)</td>
<td>16.8632(8)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>16.7202(8)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>28.7817(12)</td>
</tr>
<tr>
<td>β (deg)</td>
<td>91.369(2)</td>
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<tr>
<td>V (Å$^3$)</td>
<td>8112.9(6)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>$D_{calc}$ (g cm$^{-3}$)</td>
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<tr>
<td>Temp (K)</td>
<td>100(2)</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>0.71073</td>
</tr>
<tr>
<td>abs coeff (mm$^{-1}$)</td>
<td>5.868</td>
</tr>
<tr>
<td>R(F)</td>
<td>0.0396</td>
</tr>
<tr>
<td>$R_w$(F$^2$)</td>
<td>0.0977</td>
</tr>
</tbody>
</table>
There are four distinct cerium positions in the oxysulfido cluster related to the other four by an improper rotation axis. Ce1 and Ce2 are nearly equivalent, coordinated to identical ligand sets but have significantly different bond distances. The core of the cluster can be viewed as two Ce₄S units linked together. Those four Ce–S bonds in these units are very similar ranging from 2.9652(10)–2.9965(9) Å. There is an additional long bond between the sulfur from one Ce₄S to the nearest cerium in the other, Ce3–S1, at 3.1461(9) Å. This bond makes Ce3 and Ce3′ eight coordinate, while the other cerium atoms are seven coordinate. A pair of three coordinate oxo ligands is central to bringing the Ce₄S units into a cohesive cluster. The geometry of the oxo bonds are nearly planar with Ce–O–Ce angles adding up to 359.3°. The bond lengths are 2.232(3)–2.301(3) Å. The two metals not coordinated to the oxos each bond to a terminal selenolate. The different selenolates on the exterior of the structure range from terminal to tri-bridging as space permits and coordination is needed. Each metal also coordinates a single THF molecule. Figure 22 shows the core of the structure with C and H atoms removed.

The identity of solid state thermal decomposition products for these types of compounds are of interest from an academic perspective and for possible low temperature synthesis routes to useful oxysulfide phases. The mixture of oxygen, sulfur, and selenium around the lanthanide ions pointed towards lanthanide oxides and sulfides or oxysulfide as primary low temperature decomposition products. Thermolysis of the neodymium compound, (THF)₈Nd₈O₂S₂(SePh)₁₆, was performed under vacuum by heating from room temperature to 650 °C at a rate of 15 °C min⁻¹. The temperature was maintained for 5 h then allowed to cool back to room temperature at a rate of 10 °C min⁻¹. While the solid sample was heated, the far end of the tube was kept in liquid N₂. Despite
the comparatively stronger bonds between the neodymium and either oxygen or sulfur and despite the very high lattice energy of lanthanide oxides, when the crystals were decomposed in this process, Nd$_2$Se$_3$ was the only crystalline phase identified by PXRD. A small amount of yellow liquid collected in the cold end of the tube. It was tested by mass spectrometry. A mixture of organic molecules was present. The only one identified was diphenylselenide. Components of the liquid were not separated for further analysis.

The thermodynamics suggest preferential formation of lanthanide oxides and sulfides from thermolysis. A similar thermolysis experiment of the aforementioned selenido cluster (THF)$_8$Ln$_8$O$_2$Se$_2$(SePh)$_{16}$ had yielded Ln$_2$O$_3$ and Ln$_x$Se$_y$. The inclusion of sulfur in (THF)$_8$Nd$_8$O$_2$S$_2$(SePh)$_{16}$ of course increases the number of potential species that could be produced from decomposition. Oxides and oxysulfides were expected from this new cluster. Selenides were only expected to form from the excess of metal created if THF was cleaved intact. No such oxide phase was detected by PXRD. A possible explanation of this result is the selective separation of oxygen during decomposition. The low pressure in the reaction tube and low temperature at the far end in the thermolysis experiment promotes the loss of THF during the temperature ramp up and sequestration of organics for the remainder of the experiment. This would drastically reduce the amount of oxygen in the hot flux forming the most thermodynamically favorable solid products. The X-type selenolate ligands would be bound more strongly leading to eventual degradation leaving selenium and neodymium as the most populous elements in the flux. Oxygen and sulfur atoms that remain through the decomposition would bond strongly to surrounding lanthanide ions but would be too sparse to dictate long range order. They could act as impurities in the observed Nd$_2$Se$_3$ structures.
4.2 Oxytellurides

Oxytellurides were also targeted. The first foray into lanthanide oxytelluride chemistry discussed here was a reinvestigation into preliminary results of Dr. Santanu Banerjee. As with sulfur and selenium, oxytellurides can be formed with adventitious oxygen, but that is a crude technique with control and reproduction challenges. The work described here uses TeO$_2$ as an oxygen source to reproduce known structures and to synthesize novel lanthanide oxytelluride clusters.

Oxytelluride structures are difficult targets for multiple reasons. First, the weak Ln–Te bonds are sensitive to heat and light requiring extra precautions and patience in their synthesis. Contrasting with analogous oxyselenidos produced with selenium oxide, the oxytellurides appear more susceptible to disproportionation. The inequity of Ln–O and Ln–Te bonds will preferentially lead to oxos instead of oxytellurides if possible. Early attempts at oxytelluride cluster synthesis using TeO$_2$ produced oxides. Oxytellurides were not produced until elemental tellurium was also added to reaction mixtures. The second difficulty stems from the more metallic nature of tellurium than the lighter chalcogens. While sulfur and selenium form polyatomic rings in their elemental phases, in cluster chemistry they typically form monatomic chalcogenides, S$^{2-}$ and Se$^{2-}$, dianions, SS$^{2-}$ and SeSe$^{2-}$, and singly charged ER$. Tellurium readily forms longer chains.$^9$ The increased number of possible structures makes it less likely to produce a single phase in high yield especially considering the reaction mixtures contain tellurium in excess of the target cluster stoichiometry. It also increases the difficulty of reproduction after a phase is synthesized and identified.
A reproducible oxytelluride cluster came from the addition of Te and TeO₂ to a solution of “Ln(TePh)₃” in pyridine. This produced dark red-orange crystals of 

\[
[(py)_5Ln_3(\mu₃-O)(\mu₂-Te₂)(TePh)][(py)_7Ln_4(\mu₄-Te)(\mu₂-Te₂)₂(\mu-η²-η²-Te₂Te(Ph)Te₂)(TePh)], \quad (Ln = Ho, Er) \text{ identified by XRD.}
\]

The reaction from holmium produced 6.7% yield, and the neodymium reaction yielded 8% crystals. The tetrametallic telluride cluster had been previously synthesized from reactions of elemental tellurium with “Ln(TePh)₃” and reported. The four lanthanide ions in this cluster are arranged in a square bridged by a central Te²⁻. On two adjacent edges of the square are μ₂-Te₂⁻ ligands oriented with the Te–Te bonds roughly orthogonal to the plane of the metal atoms. There are Te₂ units at the other two edges as well, but they are distinguished by a TePh linking them into a single TeTe(PH)TeTe⁻⁵⁻ ligand. The bond distances between that TePh (Te17) and the two adjacent tellurium atoms are 3.0765(10) Å and 3.2410(13) Å, slightly long for Te–Te bonds. The distance from Te17 to the nearest tellurium atoms of the two Te₂⁻ ligands are 3.6201(12) Å and 3.6535(12) Å. These distances are too long to be considered bonds, but the ditellurido ligands tilt towards the tellurolate, because there is an intramolecular interaction. The other four Te–Te bonds range from 2.7592(12) Å – 2.9371(11) Å as expected for covalent Te–Te bonds. One lanthanide ion is also coordinated to a single terminal TePh⁻ making the cluster neutral. That metal coordinates a single pyridine molecule, and the remaining metal ions each coordinate a pair of pyridine molecules.
Figure 23. ORTEP diagram of (py)₇Ln₄(µ₄-Te)(µ₂-Te₂)(µ₂-η²-η²-Te₂Te(Ph)Te₂)(TePh) with C and H atoms removed for clarity

Table 18. Selected bond lengths (Å) of [(py)₇Ho₄Te(2µ₂-Te₂)(2µ₂-PhTe₂)(TePh)]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
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<tbody>
<tr>
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<td>Ho(9)–Te(8)</td>
<td>3.0962(11)</td>
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<tr>
<td>Te(13)–Te(17)</td>
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<tr>
<td>Te(15)–Te(17)</td>
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<tr>
<td>Te(11)–Te(17)</td>
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<td>Te(9)–Te(10)</td>
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<tr>
<td>Te(15)–Te(16)</td>
<td>2.8763(13)</td>
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</table>
**Table 19.** Crystallographic data for [(py)$_3$Ho$_3$(µ$_3$-O)(µ$_2$-Te$_2$)$_3$(TePh)][(py)$_7$Ho$_4$(µ$_4$-Te)(µ$_3$-Te$_2$)$_2$(µ-η$^2$-η$^2$-Te$_2$Te(Ph)Te$_2$)(TePh)]

<table>
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<tr>
<td>b (Å)</td>
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<td>c (Å)</td>
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<td>R$_{w}$(F$^2$)</td>
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The trimetallic cluster is a rare example of a reliably reproducible lanthanide oxytelluride. The three metals are arranged in a triangle with the lone three coordinate oxo ligand bridging them. The oxo has a pyramidal geometry with the three angles summing 340.8°. The Te–Te bond of the ditellurido bridging the lanthanides at the edges of the triangle are nearly perpendicular to the plane of the three metal atoms but slant in accommodation with the oxo. The three tellurium atoms on the same side of the cluster as the oxo are further away from one another than the three tellurium atoms on the other side. Two of the metals are each coordinated to two terminal pyridines making them seven coordinate. The third lanthanide has one pyridine and one phenyltellurolate thereby balancing the cluster’s charge and making it seven coordinate as well.
Figure 24. ORTEP diagram of (py)$_3$Ho$_5$(µ$_3$-O)(µ-Te$_2$)$_3$(TePh) with C and H atoms removed for clarity
Table 20. Selected bond lengths (Å) and angles (deg) of [(py)$_5$Ho$_3$(O)(Te$_2$)$_3$(TePh)]

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<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
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<td>3.0591(9)</td>
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<td>Ho(1)–Te(7)</td>
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<td>Te(1)–Te(5)’</td>
<td>3.5819(12)</td>
<td>Te(3)–Te(5)’</td>
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<tr>
<td>Te(5)–Te(5)’</td>
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</table>

While the structure itself is straightforward, the intermolecular interactions are interesting. First, the triangular arrangement of the lanthanide ions with Te–Te bonds nearly perpendicular to the plane allows dimerization through Te–Te ... Te–Te interactions. The five closest intermolecular Te–Te distances range from 3.50-3.58 Å. The other point of note is the co-crystallization of two dissimilar neutral clusters. It is typical for solvent molecules to crystallize with clusters to fill the voids created by inefficiently packed clusters. It is common for ionic clusters to crystallize with small
inorganic counterions for charge balancing. While relatively rare, there is precedent for different but similar sized clusters to co-crystallize wherein the pairing is driven by the need to balance charges.\textsuperscript{11} This appears to be the first example of co-crystallization of two similarly sized neutral lanthanide clusters. The crystal packing lacks uniformity. There is disorder in the solvent molecules filling the voids and some disorder in the orientation of the coordinated pyridine and phenyltellurolate ligands. There is a 7\% occupancy of PhTeTePh in the interstitial space where a pair of pyridine molecules resides the other 93\% of the time. The inefficient packing requiring inclusion of small molecules in the lattice combined with the significant disorder made it surprising that two clusters co-crystallized. Without a strong driving force like charge balancing or hydrogen bonding between the dissimilar clusters keeping them together it is unclear why they co-crystallize. It was even more surprising that such an unusual crystal structure was reproduced reliably.

As with lanthanide oxysulfido selenolate clusters, the products of thermal decomposition could hold potential. The thermolysis results were just as surprising as those garnered from the oxysulfido clusters. The same procedure was used for this thermolysis experiment as in the previously discussed decomposition. Crystalline samples were placed in one end of a quartz tube, evacuated, and placed in a furnace with the opposite end in liquid N\textsubscript{2}. The sample was raised from room temperature to 650 °C at 15 °C min\textsuperscript{-1}, held for five hours and brought back down at 10 °C min\textsuperscript{-1}. This produced a gray powder giving a PXRD spectrum with a high noise to signal ratio indicative of an amorphous substance. The only identifiable phase in the mixture was elemental tellurium. It is inconceivable that the lanthanide would have volatilized from the solid
sample, so the nearly featureless spectrum resulted from the lanthanide phases lacking order. Since the two molecules co-crystallize with pyridine primarily filling the voids, the decomposition comes from the total formula \( C_{93.15}H_{90}Ho_{7}N_{14.85}OTe_{18.15} \) accounting for the disorder in the lattice solvent position. Based on the excess of tellurium in the formula, the solid tellurium phase was expected. Recognizing the small amount of oxygen compared to heavy atoms, it is reasonable that an insufficient quantity of oxide or oxytelluride particles would grow with enough order to produce diffraction peaks above the background. The lack of a \( \text{Ln}_2\text{Te}_3 \) pattern in the spectrum is a mystery. The abundance of tellurium crossed with the poor bonding between it and lanthanides could explain the overall poor crystallinity of the sample and our inability to identify a distinct lanthanide telluride phase, which most likely is present according to precedent.

Other oxytellurides had been produced through inclusion of adventitious oxygen. Dr. Deborah Freedman first identified the cluster \([(4\text{etpy})_{12}\text{Ho}_6\text{O}_4\text{Te}_4]^2^+\) from a reaction of metallic holmium, diphenylditelluride, and mercury in 4-ethylpyridine. Te–C bonds were broken to produce Te\(^{2-}\), and either contaminant oxygen or the wall of the glass reaction vessel reacted to produce a very low yield of yellow crystals comprised of this cluster and two phenyltellurolate anions balancing the charge. Unsurprisingly, the initial attempt to reproduce this by the same synthetic method failed to produce an isolable product. In fact, no attempts recreated this exact compound, but the same cluster was produced once with ytterbium, \([(4\text{etpy})_{12}\text{Yb}_6\text{O}_4\text{Te}_4]^2^+\) (figure 25) with a modified procedure.

Following the previous success in lanthanide oxytelluride clusters, a combination of elemental tellurium and tellurium dioxide were used in synthetic attempts. To a
solution of “Yb(TePh)₃” (1.00 mmol) in 4-ethylpyridine covered in foil, Te (0.42 mmol) and TeO₂ (0.22 mmol) were added and stirred for five days before being filtered, concentrated by vacuum without heating and layered with hexanes. Concentration of ethylpyridine solutions is slow due to the low vapor pressure (BP = 168 °C), but Ln–Te bonds are sensitive to heat. No crystals were produced from reactions where concentration by vacuum was aided by hot oil bath. This successful synthesis produced a small amount of dark red crystals along with dark powder.

The six ytterbium atoms are octahedrally arranged. The geometries of the four tellurido ligands are trigonal pyramidal extending off alternating faces of the octahedron with Yb–Te–Yb angles ranging from 70.82-71.78°, and the sum of the three angles for a given tellurium averages 214.0°. The geometries about the oxo ligands are also three coordinate pyramidal at the remaining octahedral faces but are much closer to the plane of the metal atoms. The Yb–O–Yb angles range from 114.38 – 115.98°, and the sum of the angles for a given oxygen averages 347.1°. Because of the difference in how far the tellurium and oxygen extend from the faces of the octahedron, the overall shape of the cluster core appears tetrahedral with tellurium on at the vertices, oxygen on the faces, and holmium on the edges. Each of the ytterbium atoms coordinate two oxo ligands, two tellurido ligands, and two ethylpyridine molecules making them all six coordinate with distorted octahedral geometries. The original holmium cluster was charge balanced by a pair of TePh⁻ anions. This ytterbium version crystallized as a new phase with the cluster balanced by a [(TePh)₃]⁻ and a [Hg(TePh)₃]⁺.
Figure 25. ORTEP diagram of [(4etpy)$_{12}$Yb$_6$O$_4$Te$_4$]$^{2+}$ core with C and H atoms removed for clarity.

Table 21. Crystallographic data for [(4etpy)$_{12}$Yb$_6$O$_4$Te$_4$][(TePh)$_3$][Hg(TePh)$_3$]
and [(4etpy)$_{12}$Ho$_6$O$_4$Te$_4$TePh][Hg(TePh)$_3$]

<table>
<thead>
<tr>
<th>Compound</th>
<th>[(4etpy)$_{12}$Yb$_6$O$_4$Te$_4$]</th>
<th>[(4etpy)$_{11}$Ho$_6$O$_4$Te$_4$TePh]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[(TePh)$_3$][Hg(TePh)$_3$]</td>
<td>[Hg(TePh)$_3$]</td>
</tr>
<tr>
<td>empirical formula</td>
<td>C$<em>{120}$H$</em>{138}$HgN$_{12}$O$<em>4$Te$</em>{10}$Yb$_6$</td>
<td>C$<em>{101}$H$</em>{119}$HgHo$<em>6$N$</em>{11}$O$_4$Te$_8$</td>
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<tr>
<td>β (deg)</td>
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<td>γ (deg)</td>
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<td>Z</td>
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<td>2</td>
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</table>
Interestingly, attempts to reproduce this cluster with holmium produced a similar
ccluster but with one significant difference. A reaction of holmium (1.0 mmol) and
PhTeTePh (1.5 mmol) catalyzed by mercury (0.06 mmol) in ethylpyridine was stirred for
5 days before adding tellurium (0.31 mmol) and TeO₂ (0.36 mmol) and stirred an
additional 10 days at room temperature exposed to ambient light. The dark red-orange
solution was filtered from grey precipitate, concentrated to 15 mL, layered with hexanes
(10 mL) and covered in foil producing dark red crystals along with a second very dark
unidentified solid phase.

The product identified by XRD was a six metal oxytelluride cluster,

\[(4\text{etpy})_{11}\text{Ho}_6\text{O}_4\text{Te}_4\text{TePh}\]^+, and is very similar to \[(4\text{etpy})_{12}\text{Ln}_6\text{O}_4\text{Te}_4\]^{2+}. The core
structure is largely unchanged, and one of the coordinated ethylpyridine molecules in the
original structure is replaced here with a phenyltellurolate reducing the total charge to +1.
The charge is balanced with [Hg(TePh)_3]^− like in the ytterbium dianion. As with other
clusters containing Ln–Te bonds, this cluster was light, heat, and air sensitive, and the
synthesis reaction was slow. The reaction produced a mixture of products, of which the
crystalline phase, \[(\text{etpy})_{11}\text{Ho}_6\text{O}_4\text{Te}_4\text{TePh}] [\text{Hg(TePh)}_3]\], was minor.

After the original synthesis of this structure, the amount of mercury in successive
reactions was limited to 6 mol percent to holmium in attempt to synthesize the original
2+ cluster which crystallized with uncoordinated TePh^− anions to balance the charge.
Despite the effort to eliminate the mercury counterion and the fact that Dr. Freedman’s
reaction contained more Hg (12.5 mol% to Ho) but produced the Ho₆ cluster Hg-free,
\[(4\text{etpy})_{11}\text{Ho}_6\text{O}_4\text{Te}_4\text{TePh}] [\text{Hg(TePh)}_3]\] was reproduced in low yield from these reactions.
Figure 26. POV view of [(etpy)$_2$Ho$_6$O$_4$Te$_4$TePh]$^+$ core with C and H atoms removed for clarity
The structure of the [(4etpy)$_{11}$Ho$_6$O$_4$Te$_4$TePh]$^+$ cluster is very similar to [(4etpy)$_{12}$Ho$_6$O$_4$Te$_4$]$^{2+}$. The holmium atoms are octahedrally arranged. The geometries of the four tellurido ligands are still trigonal pyramidal extending off alternating faces of the octahedron with Ho–Te–Ho angles slightly wider ranging from 71.14–72.94°, and the sum of the three angles for a given tellurium averages 215.6°. The geometries of the oxo ligands are the same as in the dianionic cluster. The Ho–O–Ho angles range from 114.22–115.89°, and the sum of the angles for a given oxygen averages 345.3°. The one key difference is the coordination of one holmium per cluster. As with [(4etpy)$_{12}$Ln$_6$O$_4$Te$_4$]$^{2+}$, five of the six are bound to a pair of oxos, a pair of telluridos and a pair of coordinated ethylpyridine molecules. The sixth holmium here has a phenyltellurolate ligand in place of one of the ethylpyridine molecules.

### Table 22. Selected bond lengths (Å) of [(4etpy)$_{11}$Ho$_6$O$_4$Te$_4$TePh]$^+$

<table>
<thead>
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</tbody>
</table>
The cluster has potential as a precursor to low temperature synthesis of solid state lanthanide oxytellurides, because the Ln:Te:O ratio is much more favorable than the previously discussed cluster. Removal of the pyridine molecules and heterolytic cleavage of the Te–C bond in the lone tellurolate would leave a charge balanced cluster Ho₆O₄Te₅. Simple aggregation of these clusters has a high likelihood to form lanthanide oxytelluride solid state structures. The problem with such degradation is the counterion. Thermolysis products are expected to be contaminated with mercury. Experiments were performed with the intention to grow crystals with TePh⁻ instead of [Hg(TePh)₃]⁻ or synthesize a similar neutral cluster such as (etpy)₁₀Ho₆O₄Te₄(TePh)₂ by reducing the amount of catalytic mercury used, but the same phase crystallized. Most reactions were run at room temperature. When they were heated (80-130 °C) no products were isolated. If such a mercury-free phase could be isolated through modified reaction conditions or recrystallization with ion exchange, a thermolysis experiment would be of interest. The high r⁺/r⁻ ratio of lanthanide oxides, approximately 0.82, makes a cubic structure most stable. Lanthanide tellurides have a ratio around 0.5, appropriate for the lanthanides to occupy octahedral holes in a close packed telluride cell. A network of alternating oxygen and tellurium would have holes appropriately sized for octahedral coordination similar to its geometry in the cluster. Low temperature degradation of this cluster could theoretically form a corundum-like Ln₆O₄Te₅ structure. Mixtures of lanthanide oxide, telluride, and/or oxytelluride phases are of course also possible.
4.3 Conclusion

Lanthanide oxychalcogenide clusters were synthesized from TeO₂ and Te for Te²⁻ and O²⁻ sources or pySO₃ for the source of both S²⁻ and O²⁻. (THF)₈Ln₈O₂S₂(SePh)₁₆ (Ln = Ce, Nd) was synthesized at low temperature (-5 °C) in order to reduce the substitution of selenium into the sulfido positions. Thermal decomposition of the neodymium cluster produced Nd₂Se₃ as the only identifiable solid phase by PXRD. PhSePh was identified from the volatile phase.

\[
[(\text{py})₃Ln₃(\mu₃-\text{O})(\mu-\text{Te₂})₃(\text{TePh})][(\text{py})₇Ln₄(\mu₄-\text{Te})(\mu-\text{Te₂})₂(\mu-\eta²-\eta²-\text{Te₂Te(Ph)Te₂})(\text{TePh})] \quad (\text{Ln} = \text{Ho, Er})
\]

is comprised of two similarly sized neutral clusters that co-crystallize. This is especially surprising without an obvious cause such as strong intermolecular forces holding the disparate clusters together. The four-metal tellurido cluster was previously known. The oxytelluride, which forms a weak dimer through Te-Te interactions, was unique to this phase. The only identified solid phase from thermal decomposition was elemental tellurium.

Two other oxytelluride clusters, closely related to one another, were synthesized. Both are cationic. \([(\text{etpy})₁₁\text{Ho}_6\text{O}_4\text{Te}_₄\text{TePh}] [\text{Hg(TePh)}₃] \] and \([(\text{4etpy})₁₂\text{Yb}_6\text{O}_4\text{Te}_₄][\text{Hg(TePh)}₃] [(\text{TePh})₃] \] have the same octahedral core structure. The charge difference comes from the difference in one position of either a coordinated ethylpyridine or phenyltellurolate. Attempts to produce a similar neutral cluster by limiting mercury content in the reaction mixture were unsuccessful. Due to the problems of counterions in synthesizing these compounds in uniform isolable phases in high yield, stoichiometric reaction of mercury may be advisable in future work. Ion exchange can be attempted after isolation.
References:


Experimental

General Methods: All reactions were performed using standard drybox and Schlenk line techniques under an atmosphere of ultrapure nitrogen (WELCO CGI, Pine Brook, NJ). Dimethoxyethane, pyridine, tetrahydrofuran, hexanes, and ether were purified with a dual-column Solv-Tek solvent purification system (Solv-Tek Inc., Berryville, VA). 4-ethylpyridine was purified by distillation over potassium. Lanthanide metals, Hg and Se were purchased from Strem Chemicals (Newburyport, MA). C₆F₅OH, CF₃SO₃H, pySO₃, TeO₂, Te, C₆F₅S, NH₄F, N(CH₃)₂F, (CH₃)₂NCS₂, Zn((CH₂C₆H₅)₂NCS₂), diethylenetriamine, and acetylacetone were purchased from Aldrich and used as received. PhSSPh and S were purchased from Acros. PhSeSePh was purchased from Strem or Aldrich and recrystallized from hexanes. PhTeTePh was prepared according to literature procedure.¹ Melting points were performed with samples in sealed capillaries under nitrogen and are uncorrected. Elemental analyses were performed by QTI Intertek Pharmaceutical Services (Whitehouse, NJ). Because some compounds lose lattice solvent shortly after removal from mother liquor, theoretical values are for these samples were calculated assuming this loss. IR spectra were taken on a Thermo Nicolet Avatar 360 FT-IR spectrometer. As air stability permitted, samples were either deposited as thin films or suspended in Nujol mulls on NaCl plates scanned from 4000 to 600 cm⁻¹ or on CsI plates scanned from 4000 to 400 cm⁻¹. Electronic spectra were recorded on a Varian DMS 100S spectrometer with 1.0 mm special optical glass cells. Powder diffraction spectra were taken on either a Bruker AXS D8 Advance diffractometer or a Bruker HiStar area detector and an Enraf-Nonius FR571 rotating anode X-ray generator Cu Kα
radiation. Spectra were matched to PDF patterns of known phases using the program JADE7 (MDI, 2004). ESI-MS data were recorded on a Thermo Finnigan LCQ DUO system in negative ion detection mode scanning from the mass/charge ratio range m/z = 150 – 1000 with the sample dissolved in 10:1 MeOH:CH₃COOH mixture. For single crystal XRD structure determination, crystals were immersed in Paratone oil which had been degassed and kept dry with potassium. Data were collected at low temperatures. Samples were examined with a Bruker Smart APEX CCD diffractometer with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å) at 100 K. The data were corrected for Lorenz effects and polarization and absorption, the latter by a multi-scan (SADABS) method.² The structures were solved by direct methods (SHELXS86).³ All non-hydrogen atoms were refined (SHELXL97) based upon Fₙₒₙₛ²⁴. All hydrogen atoms coordinates were calculated with idealized geometries (SHELXL97). Scattering factors (f₀, f', f'') are as described in SHELXL97. Absorption spectra were measured from crystalline powders on a Perkin-Elmer Lambda 9 spectrophotometer. For emission spectra, powder samples were excited with the 800 nm band of a Ti-Sapphire laser (for Nd and Tm) or with a 980 nm diode laser (for Er). The emission was focused onto a 0.55 m Jobin Yvon Triax 550 monochromator and detected by a InGaAs detector. The signal was intensified with a SR 850 DSP lock-in amplifier (Stanford Research System, Sunnyvale, CA) and processed with a computer controlled by SynerJY commercial software. For decay time measurements, the laser beam was modulated by a beam chopper and the signal was collected on a TDS 220 oscilloscope (Tektronix, Beaverton, OR). Crystallography measurements and analysis were performed by Dr. Thomas J. Emge from the Department of Chemistry and Chemical Biology, Rutgers University.
Emission measurements and analysis were performed by Dr. Ajith Kumar and Dr. Richard Riman from the Materials Science and Engineering Department, Rutgers University.

**Synthesis of (DME)$_2$Eu(OC$_6$F$_5$)$_3$: Method A.** Eu metal (0.13 g, 0.84 mmol), PhSSPh (0.29 g, 1.3 mmol), and Hg (0.025 g, 0.12 mmol) were added to DME (20 mL), and the mixture was stirred magnetically for 7 days to give a yellow solution with a yellow-green precipitate. C$_6$F$_5$OH (0.46 g, 2.56 mmol) was added, and the mixture was stirred for two weeks and then filtered to separate trace gray precipitate from a bright yellow solution. The solution was concentrated to about 4 mL and layered with hexane (~25 mL) to give yellow rod-shaped crystals (0.24 g, 32%) that turn orange at 95 °C and then turn red and melt at 123-125 °C. Anal. Calcd. for C$_{26}$H$_{20}$EuF$_{15}$O$_7$: C, 35.4; H, 2.27. Found: C, 34.9; H, 2.20. The UV-Vis (DME) spectrum contained peaks at 575 (ε = 9 x 10$^{-2}$ L mol$^{-1}$ cm$^{-1}$) and 529 nm (ε = 1.5 x 10$^{-1}$ L mol$^{-1}$ cm$^{-1}$). In pyridine, no well-defined absorption maxima attributable to a MLCT excitation could be found. IR: 2923 (s), 2853 (s), 2727 (w), 2669 (w), 1763 (w), 1651 (w), 1622 (w), 1502 (m), 1460 (m), 1382 (s), 1307 (w), 1261 (m), 1175 (m), 1096 (m), 1049 (m), 1017 (m), 988 (w), 857 (m), 800 (m), 720 (w), 633 (w), 615 (s) cm$^{-1}$.

**Method B.** Eu metal (0.15 g, 1.0 mmol), C$_6$F$_5$OH (0.55 g, 3.0 mmol), and Hg (0.010 g, 0.05 mmol) were added to DME (20 mL), and the reaction mixture was stirred for 5 days to give a yellow solution with brown precipitate. The solution was filtered, concentrated to about 8 mL, and layered with hexane (15 mL) to give 0.36 g (42%).
Synthesis of \((\text{DME})_2\text{Nd(OC}_6\text{F}_5)_3\):

Nd (0.145 g, 1.01 mmol), diphenyldisulfide (0.330 g, 1.51 mmol), and Hg (0.020 g, 0.10 mmol) were combined in DME (20 mL) and stirred for 48 h to give a light blue solution with blue precipitate. Pentafluorophenol (0.540 g, 2.93 mmol) was added, and the solution was stirred for 5 days, resulting in a pale blue solution with a dark brown precipitate. The solution was filtered, concentrated to 5 mL, and layered with hexanes (10 mL) to give blue crystals (0.524 g, 62%) that melted and turned purple at 104-107 °C. Anal. Calcd. for \(\text{C}_{26}\text{H}_{20}\text{F}_{15}\text{O}_7\text{Nd}\): C, 35.7; H, 2.29. Found: C, 35.7; H, 2.42. IR: 2960 (m), 2849 (w), 2668 (w), 2478 (w), 1650 (m), 1621 (w), 1509 (s), 1370 (w), 1309 (m), 1260 (m), 1172 (m), 1094 (s), 1018 (s), 858 (m), 799 (m), 721 (w), 635 (m) cm\(^{-1}\).

Synthesis of \((\text{DME})_2\text{Er(OC}_6\text{F}_5)_3\):

Er (0.165 g, 0.988 mmol), diphenyldisulfide (0.326 g, 1.50 mmol), and Hg (0.010 g, 0.050 mmol) were combined in DME (20 mL) and stirred for 4 days to give a pink solution. Pentafluorophenol (0.550 g, 2.99 mmol) was added, and the solution was stirred for 2 days to give a pink solution with a black precipitate. The solution was filtered, concentrated to 5 mL, and layered with hexanes (20 mL) to give pink crystals (0.529 g, 60%) that melted at 122-129 °C. Anal. Calcd. for \(\text{C}_{26}\text{H}_{20}\text{F}_{15}\text{O}_7\text{Er}\): C, 34.8; H, 2.23. Found: C, 34.7; H, 2.42. IR: 2959 (m), 1652 (w), 1505 (s), 1475 (m), 1309 (w), 1246 (m), 1179 (m), 1098 (m), 1050 (s), 1022 (s), 988 (s), 873 (m), 862 (s), 800 (w), 636 (m) cm\(^{-1}\).
Synthesis of (DME)$_2$Tm(OC$_6$F$_5$)$_3$: Tm (0.167 g, 0.998 mmol), diphenyldisulfide (0.328 g, 1.50 mmol), and Hg (0.010 g, 0.050 mmol) were combined in DME (20 mL) and stirred for 4 days to give a tan solution. Pentafluorophenol (0.550 g, 2.99 mmol) was added, and the solution was stirred for 2 days resulting in a pale tan solution with a black precipitate. The solution was filtered, concentrated to 5 mL, and layered with hexanes (20 mL) to give colorless crystals (0.589 g, 65%) that melted at 114-121 °C. Anal. Calcd. for C$_{26}$H$_{20}$F$_{15}$O$_7$Tm: C, 34.7; H, 2.23. Found: C, 34.3; H, 2.15. IR: 2961 (m), 1650 (m), 1620 (w), 1503 (s), 1370 (w), 1309 (m), 1260 (m), 1177 (m), 1092 (s), 1048 (m), 1018 (s), 988 (s), 862 (m), 800 (m) cm$^{-1}$. Unit cell at 100 K from single crystal X-ray diffraction data: $P2_1/n$, $a = 10.3977(7)$ Å, $b = 12.7197(8)$ Å, $c = 23.4256(15)$ Å, $\beta = 96.483(1)$, $V = 3078.4(3)$ Å$^3$.

Synthesis of (DME)$_2$Yb(OC$_6$F$_5$)$_3$: Yb (0.173 g, 1.00 mmol), PhSSPh (0.327 g, 1.50 mmol), and Hg (0.025 g, 0.12 mmol) were combined in DME (25 mL) and stirred at room temperature. After 6 days when almost all metal was dissolved, C$_6$F$_5$OH (0.549 g, 2.98 mmol) was added to the orange-red solution. The remaining metal dissolved overnight, and the solution turned very pale yellow. After 2 more weeks of stirring, there was no change. It was filtered, concentrated to around 5 mL, and layered with hexanes (20 mL) to produce large pale yellow crystals.

Synthesis of (py)$_4$Er(OC$_6$F$_5$)$_3$: Er (0.165 g, 0.988 mmol), diphenyldisulfide (0.325 g, 1.49 mmol), and Hg (0.013 g, 0.05 mmol) were combined in pyridine (30 mL), and the mixture was stirred for 5 days to give a pink solution. Pentafluorophenol (0.562 g, 3.05
mmol) was added, and the solution was stirred for 7 days resulting in a pink solution with a black precipitate. The solution was filtered, concentrated to 5 mL, and layered with hexanes (5 mL) to give pink crystals (0.31 g, 30%) that melted at 127-130 °C. Anal. Calcd. for C_{38}H_{20}F_{15}N_{4}O_{3}Er: C, 44.2; H, 1.95; N, 5.42. Found: C, 43.7; H, 2.00; N, 5.46.
IR: 2962 (w), 1650 (m), 1602 (m), 1504 (s), 1444 (m), 1306 (m), 1260 (m), 1220 (w), 1172 (m), 1093 (w), 1068 (m), 1040 (w), 1016 (s), 988 (s), 799 (m), 752 (m), 701 (m), 625 (m) cm⁻¹.

**Synthesis of (py)₄Eu(OC₆F₅)₃:** Eu (0.145 g, 1.00 mmol), C₆F₅OH (0.358 g, 1.94 mmol), and Hg (0.010 g, 0.050 mmol) were combined in DME (25 mL) and stirred at room temperature overnight producing a brown solution. Sulfur (0.017 g, 0.53 mmol) was added and stirred 6 days. Yellow solution was filtered from brown powder, concentrated to 5 mL and layered with hexanes (12 mL). The solution produced more brown precipitate which was collected, dissolved in hot pyridine (3 mL), and layered with hexanes (10 mL) producing brown powder along with yellow crystals.

**Synthesis of (py)₄Yb(OC₆F₅)₃:** Yb (0.173 g, 1.00 mmol), PhSSPh (0.327 g, 1.50 mmol), and Hg (0.020 g, 0.10 mmol) were combined in pyridine (25 mL) and stirred at room temperature for a week yielding a dark red solution. C₆F₅OH (0.556 g, 3.00 mmol) was added, and the reaction turned green upon stirring. After several days yellow solution was filtered from darker precipitate. The solution was concentrated to 10 mL and layered with 20 mL hexanes producing yellow crystals.
Synthesis of (THF)$_3$Yb(OC$_6$F$_5$)$_3$: Yb (0.193 g, 1.12 mmol), PhSSPh (0.370 g, 1.70 mmol), and Hg (0.016 g, 0.080 mmol) were added to THF (20 mL), and the mixture was stirred for 6 days at room temperature to give an opaque dark red solution. C$_6$F$_5$OH (0.635 g, 3.45 mmol) was added, and the reaction was stirred for 8 days and then filtered to separate trace gray precipitate. The colorless solution was concentrated to about 5 mL and layered with hexanes (~10 mL) to give translucent colorless crystals that turn white at 179 °C and melt/turn yellow at 195-199 °C. Anal. Calcd. for C$_{30}$H$_{24}$YbF$_{15}$O$_6$: C, 38.4; H, 2.58. Found: C, 37.9; H, 2.38. The UV-vis (THF) spectrum contained one peak at 313 nm (ε = 1 × 10$^{-2}$ L mol$^{-1}$ cm$^{-1}$). IR: 2963 (w), 2283 (w), 1655 (w), 1509 (s), 1384 (s), 1260 (m), 1173 (w), 1019 (m), 992 (m), 800 (m) cm$^{-1}$.

Synthesis of (DME)(OC$_6$F$_5$)$_2$Eu($\mu$-OC$_6$F$_5$)$_3$Eu(DME)$_2$: Method A. Eu metal (0.14 g, 0.92 mmol), PhSSPh (0.205 g, 0.94 mmol), and Hg (0.03 g, 0.15 mmol) were added to DME (20 mL), and the mixture was stirred at room temperature for 2 days to give a yellow solution and green precipitate. C$_6$F$_5$OH (0.33 g, 1.79 mmol) was added to this mixture, and it was stirred for an additional 6 days. The mixture was filtered to separate a yellow-orange solution from the red-orange precipitate. The filtrate was concentrated to ~8 mL and layered with 15 mL of hexanes to give yellow-orange crystals (0.34 g, 63%) that darken at 132 °C and melt at 142-146 °C. Anal. Calcd. for C$_{42}$H$_{30}$Eu$_2$F$_{25}$O$_{11}$: C, 33.9; H, 2.03. Found: C, 33.6; H, 2.25. The UV-vis (DME) spectrum contained peaks at 575 (ε = 5 × 10$^{-2}$ L mol$^{-1}$ cm$^{-1}$) and 529 nm (ε = 1 × 10$^{-1}$ L mol$^{-1}$ cm$^{-1}$). In pyridine, no well-defined absorption maxima attributable to a MLCT excitation could be defined. IR: 2923 (s), 2853 (s), 2670 (w), 2457 (w), 1651 (m), 1504 (s), 1455 (s), 1382 (s), 1311 (m), 1246
(m), 1177 (m), 1164 (m), 1113 (m), 1068 (m), 1016 (m), 860 (m), 834 (w), 721 (m), 634 (m), 618 (m) cm⁻¹.

**Method B.** Eu metal (0.076 g, 0.50 mmol), C₆F₅OH (0.230 g, 1.25 mmol), and Hg (0.015 g, 0.075 mmol) were added to DME (20 mL), and the reaction mixture was stirred for 3 days to give a yellow solution with brown precipitate. The solution was filtered. The filtrate was concentrated to ~8 mL and layered with hexanes (15 mL) to give 0.096 g (26%).

**Synthesis of (DME)₂Eu(µ-OC₆F₅)₃Eu(µ-OC₆F₅)₃Eu(DME)₂:** Eu metal (0.15 g, 1.0 mmol), C₆F₅OH (0.307 g, 1.67 mmol), and Hg (0.025 g, 0.12 mmol) were added to DME (20 mL), and the mixture was stirred for two weeks at room temperature to give a green-gray solution with a black precipitate. The solution was filtered; the filtrate was concentrated to around 8 mL and layered with hexane (20 mL) to give pale yellow lathes (0.21 g, 40%) that become darker yellow at 160-170 °C and melt at 220 °C. Anal. Calcd. for C₅₂H₄₀Eu₃F₃₀O₁₄: C, 32.6; H, 2.10. Found: C, 32.4; H, 2.15. IR: 2923 (s), 2853 (s), 2729 (w), 2670 (w), 1653 (w), 1618 (w), 1501 (s), 1463 (s), 1377 (s), 1300 (w), 1247 (w), 1193 (w), 1173 (m), 1122 (w), 1067 (s), 1009 (s), 979 (s), 861 (m), 721 (m), 618 (m) cm⁻¹. No UV-vis absorption maxima were observed between 300 and 750 nm in either DME or pyridine.

**Synthesis of ((py)₃Eu(SO₃CF₃)₂)n:** Eu (0.152 g, 1.00 mmol), PhSeSePh (0.320 g, 1.02 mmol), and Hg (0.035 g, 0.18 mmol) were stirred in pyridine (18 mL) for 8 days. Selenium (0.080 g, 1.0 mmol) was added to the red solution and stirred for 3 hours.
CF₃SO₃H (0.18 mL, 2.0 mmol) was added to the dark red solution, and it was stirred for 9 days. The red solution was filtered from dark powder, concentrated to 10 mL and layered with hexanes (10 mL) producing yellow crystals.

**Synthesis of [(py)H(py)][(py)₄Tb(CF₃SO₃)₄]:** Tb (0.158 g, 0.994 mmol), PhSeSePh (0.468 g, 1.50 mmol), and Hg (0.012 g, 0.060 mmol) were stirred in pyridine for 3 days. CF₃SO₃H (0.26 mL, 2.9 mmol) was added to the green-yellow solution and stirred for 3 weeks. The orange solution was filtered from black precipitate, concentrated to 10 mL, and layered with hexanes (8 mL) producing colorless crystals.

**Synthesis of (py)₃(C₆F₅O)Eu(µ-η²-S₂)₂Eu(C₆F₅O)(py)₃·2(py):** Eu (0.153 g, 1.01 mmol), PhSSPh (0.219 g, 1.00 mmol) and Hg (0.017 g, 0.085 mmol) were combined in pyridine (20 mL), and the mixture was stirred until all the metal dissolved (24 hours). C₆F₅OH (0.186 g, 1.01 mmol) was added to the red solution and stirring resumed. In a separate flask, elemental sulfur (0.064 g, 2.00 mmol) was added to pyridine (10 mL) and stirred overnight to dissolve. The red Eu containing solution was filtered from minor brown precipitate, reduced in volume to approximately 10 mL and layered with the sulfur containing solution. The flask was covered in foil and placed in a refrigerator (5°C). Within a week, black crystals appeared (0.498 g, 69.6%) which do not melt, but slowly decompose up to 300°C. Anal. Caled. for C₅₂H₄₀Eu₂F₁₀N₈O₂S₄: C, 43.64; H, 2.82; N, 7.83 (for C₄₇H₃₅Eu₂F₁₀N₇O₂S₄: C, 41.75; H, 2.61; N, 7.25). Found: C, 41.63; H, 2.64; N, 7.19. UV-Vis: The compound is not soluble in pyridine and does not show any defined absorption maximum in the 350-750 nm wavelength range when dissolved in 4-
ethylpyridine. IR: 2360 (m), 2342 (m), 1594 (w), 1501 (s), 1438 (m), 1169 (w), 1016 (m), 985 (m), 744 (w), 700 (s) cm\(^{-1}\).

**Synthesis of (py)\(_3\)(C\(_6\)F\(_5\)O)Sm(μ-η\(^2\)-S\(_2\))\(_2\)Sm(C\(_6\)F\(_5\)O)(py)\(_3\)·2(py):** Sm (0.150 g, 1.00 mmol), PhSSPh (0.220 g, 1.01 mmol) and Hg (0.021 g, 0.10 mmol) were combined in pyridine (20 mL), and the mixture was stirred until all the metal dissolved (2 days). C\(_6\)F\(_5\)OH (0.184 g, 1.00 mmol) was added to the black solution and stirring resumed for 3 days. In a separate flask, elemental sulfur (0.064 g, 2.0 mmol) was added to pyridine (15 mL) and stirred overnight to dissolve. The amber Sm containing solution was filtered, reduced in volume to 15 mL, and layered with the S containing solution. The flask was covered in foil and left at room temperature. Within a week, yellow rod shaped crystals appeared (0.454 g, 63.8%). They do not melt but turn orange and lose crystallinity at 115-135 °C, gradually turn brown and lose pyridine up through 200 °C, and decomposes at 255 °C. Anal. Calcd. for C\(_{52}\)H\(_{40}\)Sm\(_2\)F\(_{10}\)N\(_8\)O\(_2\)S\(_4\): C, 43.74; H, 2.82; N, 7.85 (for C\(_{47}\)H\(_{35}\)Sm\(_2\)F\(_{10}\)N\(_7\)O\(_2\)S\(_4\): C, 41.85; H, 2.62; N, 7.27). Found: C, 41.93; H, 2.61; N, 7.21. UV-Vis: The compound does not show any defined absorption maximum in the 350-750 nm wavelength range in pyridine. IR: 2960 (w), 2922 (w), 2360 (w), 1596 (m), 1499 (s), 1485 (s), 1440 (m), 1260 (w), 1216 (w), 1175 (w), 1068 (w), 1018 (s), 983 (s), 799 (m), 751 (w), 700 (s), 620 (m) cm\(^{-1}\).

**Synthesis of (py)\(_3\)(C\(_6\)F\(_5\)O)Gd(μ-η\(^2\)-S\(_2\))\(_2\)Gd(C\(_6\)F\(_5\)O)(py)\(_3\)·2(py):** Gd (0.158 g, 1.01 mmol), PhSSPh (0.219 g, 1.00 mmol), C\(_6\)F\(_5\)OH (0.185 g, 1.00 mmol), and Hg (0.011 g, 0.055 mmol) were combined in pyridine (20 mL) and the mixture was stirred for 10 days.
Some metal remained under green solution. More PhSSPh (0.109 g, 0.500 mmol) was added, and the reaction stirred for another 10 days, after which time the metal had all reacted. The green solution was filtered from minor gray precipitate, reduced in volume to around 10 mL and layered with a prepared solution of sulfur (0.064 g, 2.0 mmol) dissolved in py (10 mL). The flask was covered in foil and placed in a refrigerator (5°C). Within two weeks, very pale green-yellow crystals appeared (0.621 g, 85.6%). They did not melt but lost crystallinity at 150-165 °C and gradually darkened to brown through 280 °C. Anal. Calcd. for C_{52}H_{40}Gd_{2}F_{10}N_{8}O_{2}S_{4}: C, 43.32; H, 2.80; N, 7.77. Found: C, 43.57; H, 2.86; N, 7.79. UV-Vis: The compound does not show any defined absorption maximum in the 350-750 nm wavelength range in pyridine. IR: 2962 (w), 2361 (w), 1594 (w), 1500 (s), 1481 (m), 1438 (m), 1260 (w), 1216 (w), 1197 (m), 1068 (w), 1018 (s), 985 (s), 802 (m), 753 (w), 699 (s), 619 (m) cm⁻¹.

**Synthesis of (py)₃(CF₃SO₃)Sm(µ-η²-Se₂)₂Sm(CF₃SO₃)(py)₃·2(py):** Sm (0.150 g, 1.00 mmol), PhSeSePh (0.468 g, 1.50 mmol), and Hg (0.030 g, 0.15 mmol) were stirred in pyridine for one week. Selenium (0.159 g, 2.01 mmol) was added to the yellow solution and stirred for 2 hours. CF₃SO₃H (0.08 mL, 0.9 mmol) was added to the red solution, stirred for 30 min, and allowed to settle for 1 hr. The red solution (10 mL) was filtered from orange precipitate and layered with hexanes (10 mL). After 5 days, a small amount of orange crystals were present along with a black film on the flask wall and red oil. The flask was refrigerated (5 °C) for 18 days producing dark red crystals (0.392 g, 50.6%) which darken and melt 91-94 °C. Anal. Calcd. for C_{42}H_{40}F_{6}N_{8}O_{5}S_{2}Se_{4}Sm_{2}: C, 32.60; H, 2.60; N, 7.24 (for C_{37}H_{35}F_{6}N_{7}O_{6}S_{2}Se_{4}Sm_{2}: C, 30.26; H, 2.40; N, 6.68). Found: C, 30.71;
H, 2.30; N, 6.57. The UV-vis (py) spectrum contained local maxima at 678 ($\varepsilon = 3 \times 10^{-1}$ L mol$^{-1}$ cm$^{-1}$) and 529 nm ($\varepsilon = 1 \times 10^{-1}$ L mol$^{-1}$ cm$^{-1}$). IR: 2923 (s), 2853 (s), 1596 (w), 1463 (s), 1377 (s), 1334 (w), 1299 (w), 1157 (w), 1066 (w), 1029 (w), 722 (w), 701 (w), 634 (w), 512 (w) cm$^{-1}$.

Synthesis of (py)$_3$(CF$_3$SO$_3$)Tm(µ-Se)$_{0.5}$($\mu$-$\eta^2$-SeSe)$_{1.5}$Tm(CF$_3$SO$_3$)(py)$_3$·2(py): Tm (0.169 g, 1.00 mmol), PhSSPh (0.327 g, 1.50 mmol), and Hg (0.013 g, 0.065 mmol) were stirred in pyridine (10 mL) until all metal was dissolved forming a gray solution. Selenium (0.158 g, 2.00 mmol) was added and stirred for 6 days. The red solution was filtered from brown precipitate. CF$_3$SO$_3$H (0.08 mL, 0.9 mmol) was added and the flask was shaken producing white vapor over the red solution and leaving a red coating on the wall of the flask. It was layered with hexanes (10 mL) producing yellow crystals (0.550 g, 79.1%) which melted from 103-108 °C. Anal. Calcd. for C$_{42}$H$_{40}$F$_6$N$_8$O$_6$S$_2$Se$_{3.5}$Tm$_2$: C, 32.65; H, 2.61; N, 7.25 (for C$_{37}$H$_{35}$F$_6$N$_7$O$_6$S$_2$Se$_{3.5}$Tm$_2$: C, 30.31, H, 2.41; N, 6.69). Found: C, 30.31; H, 2.34; N, 6.36. The UV-vis (py) spectrum contained an absorption maximum at 512 ($\varepsilon = 2 \times 10^{-1}$ L mol$^{-1}$ cm$^{-1}$). IR: 2924 (s), 2854 (s), 1599 (w), 1469 (m), 1388 (w), 1241 (w), 1201 (w), 1167 (w), 1067 (w), 1028 (w), 722 (w), 701 (w), 634 (w), 512 (w), 420 (w) cm$^{-1}$.

Synthesis of (py)$_3$(CF$_3$SO$_3$)Yb(µ-Se)(µ-$\eta^2$-SeSe)Yb(CF$_3$SO$_3$)(py)$_3$·2(py): Yb (0.174 g, 1.00 mmol), PhSSPh (0.325 g, 1.49 mmol), and Hg (0.010 g, 0.050 mmol) were stirred in pyridine (15 mL) for 5 days. Selenium (0.120 g, 1.52 mmol) was added to the red solution and stirred for 2 days. CF$_3$SO$_3$H (0.08 mL, 0.9 mmol) was added to the dark
purple solution and stirred for 1 hour and let settle for 2 hours. The solution was then filtered from dark residue and layered with hexanes (15 mL) producing dark red crystals (0.249 g, 35.6%) which melt between 88-97 °C. Anal. Calcd. for C_{42}H_{40}F_6O_6S_2Se_3Yb_2: C, 33.32; H, 2.66; N, 7.40. Found C, 33.03; H, 2.68; N, 7.21. No UV-vis absorption maxima were observed between 300 and 750 nm in pyridine. IR: 2923 (s), 2853 (s), 1599 (m), 1579 (w), 1462 (s), 1377 (s), 1338 (m), 1242 (m), 1201 (m), 1167 (m), 1067 (w), 1024 (m), 1005 (m), 755 (w), 745 (w), 722 (m), 701 (m), 634 (m), 626 (m), 583 (w), 515 (w), 422 (w) cm⁻¹.

**Synthesis of (py)₃(CF₃SO3)Lu(μ- Se)(μ-η²-SeSe)Lu(CF₃SO3)(py)₃·2(py):** Lu (0.175 g, 1.00 mmol), PhSSPh (0.327 g, 1.00 mmol), and Hg, (0.015 g, 0.075 mmol) were combined in pyridine (20 mL) and stirred for 3 days. Se (0.158 g, 2.00 mmol) was added to the black solution and stirred for 5 days. CF₃SO₃H (0.1 mL, 1 mmol) was added to the black solution and it was shaken vigorously and left to settle for 2 hours. The red orange solution was filtered from black powder, concentrated to 15 mL and layered with hexanes (10 mL) to produce yellow crystals (0.231 g, 30.4%) that turn red and melt at 104-109 °C. Anal. Calcd. for C_{42}H_{40}F_6O_6S_2Se_3Lu_2: C, 33.24; H, 2.66; N, 7.38 (for C_{37}H_{35}F_6N_7O_6S_2Se_3Lu_2: C, 30.89; H, 2.45; N, 6.82). Found: C, 31.22; H, 2.53; N, 6.95. No UV-vis absorption maxima were observed between 300 and 750 nm in pyridine. IR: 2923 (s), 2853 (s), 1600 (w), 1580 (w), 1463 (s), 1377 (m), 1328 (w), 1240 (w), 1201 (w), 1067 (w), 1026 (w), 743 (w), 722 (w), 701 (w), 633 (w), 509 (w), 422 (w) cm⁻¹.
Synthesis of [pyHpy][Se₄HgSe₄]: Eu (0.153 g, 1.01 mmol), PhSeSePh (0.314 g, 1.01 mmol), and Hg (0.021 g, 0.10 mmol) were stirred in pyridine (15 mL) for 2 days forming a red solution. Selenium (0.168 g, 2.13 mmol) was added and stirred 1 hr before adding CF₃SO₃H (0.1 mL, 0.1 mmol) to the now dark red solution. This was stirred for an additional hour, allowed to rest for 30 minutes, filtered, and layered with hexanes (15 mL) producing black needles.

Synthesis of (DME)₆(py)₆Nd₁₈F₂₄O₃S₃(OC₆F₅)₁₈: Nd (0.142 g, 0.986 mmol), PhSeSePh (0.462 g, 1.48 mmol), and Hg (0.010 g, 0.05 mmol) were combined in pyridine and stirred for 6 days. Sulfur (0.032 g, 1.00 mmol) was added to the green solution and stirred overnight. C₆F₅OH (0.186 g, 1.01 mmol) was added to the green solution which was stirred for another 6 days. A vacuum was drawn until all solvent evaporated and then for an additional 2 hours leaving green-brown solid. This solid was dissolved in DME (10 mL) to give a brown solution and layered with hexanes (12 mL). This resulted in a small amount of dark amorphous precipitate. Two months later, the solution was concentrated to 8 mL and layered with hexanes (15 mL) and put in a refrigerator. Two months later, a small amount of colorless plates were found on the wall above the original solvent interface.

Synthesis of (py)₈Yb₄F₈(CF₃SO₃)₄·4py: Yb (0.173 g, 1.00 mmol), PhSSPh (0.332 g, 1.02 mmol), and Hg (0.019 g, 0.095 mmol) were stirred in pyridine (20 mL) for 3 days. Selenium (0.163 g, 2.06 mmol) was added to red solution and stirred 7 days. CF₃SO₃H (0.1 mL, 1 mmol) was added to the violet solution and covered in foil as it was stirred for
a month. The dark red solution was filtered from red-brown precipitate, layered with hexanes (20 mL), and covered in foil. After two months, colorless crystals, which were not apparent one month into the diffusion, were found. They turn opaque at 90 °C and melt at 106 °C.

**Synthesis of Tb$_4$F$_2$S$_2$(CF$_3$SO$_3$)$_6$:** Tb (0.161 g, 1.01 mmol), PhSSPh (0.331 g, 1.52 mmol), and Hg (0.028 g, 0.14 mmol) were combined in DME (15 mL) and stirred 7 days producing a blue-grey solution. Sulfur (0.035 g, 1.1 mmol), was added and stirred 11 days turning the solution powder blue. CF$_3$SO$_3$H (0.1 mL, 1 mmol) was added and stirred 3 days. The resulting tan solution was filtered from black precipitate, concentrated to 10 mL, and layered with hexanes (15 mL). Alongside a grey powder, colorless crystals were produced.

**Synthesis of (THF)$_8$Ce$_8$O$_2$S$_2$(SePh)$_{16}$:** Ce (0.140 g, 1.00 mmol), PhSeSePh (0.468 g, 1.50 mmol), Hg (0.020 g, 0.10 mmol) were combined in THF (20 mL), and the mixture was stirred until all the metal was dissolved (2 days) to give a yellow solution with a greenish yellow solid at the bottom of the flask. To this mixture pySO$_3$ (0.040 g, 0.25 mmol) was added and the flask was kept in a freezer (-5 °C) for 3 days, which gave a golden yellow solution and trace black solid at the bottom of the flask. After warming to room temperature the solution was filtered, reduced in volume under vacuum (20 mL), and layered with 12 mL of hexanes to give yellow block shaped crystals (0.117 g, 20%) that turn yellow-brown between 120 °C to 200 °C, darken between 202 °C to 228 °C, turn dark brown between 230 °C to 280 °C, melt at 280 °C and remain black from 300 °C to
360 °C. IR: 2924 (s), 2853 (s), 1463 (m), 1377 (m), 1261 (w), 1069 (w) 1020 (w), 801 (w), 723 (m), 689 (w), 669 (w), 465 (w) cm⁻¹. UV-Vis: no absorption maximum appeared in the range 300 to 800 nm when the compound was dissolved in pyridine. Anal. Calcd. for C₁₂₈H₁₄₄Ce₈O₁₀S₂Se₁₆: C, 35.8; H, 3.39. Found: C, 34.4; H, 3.02.

Synthesis of (THF)₈Nd₈O₂S₂(SePh)₁₆: Nd (0.144 g, 1.00 mmol), PhSeSePh (0.468 g, 1.50 mmol), and Hg (0.024 g, 0.11 mmol) were combined in THF (30 mL), and the mixture was stirred until all the metal was dissolved (2 days) to give a grayish green solution with a grayish blue solid at the bottom of the flask. To this mixture pySO₃ (0.040 g, 0.25 mmol) was added and kept in a freezer (-5 °C) for 3 days, which gave a green solution with a little black solid at the bottom of the flask. It was taken out of the freezer and when room temperature was achieved, it was filtered, reduced in volume under vacuum (15 mL) and layered with 15 mL of hexane to give aquamarine needle shaped crystals (0.091 g, 15%) that do not melt but turn green from 110 °C to 120 °C, decompose and turn yellow from 165 °C to 170 °C and progressively darken to black up to 310 °C. IR: 2938 (s), 2852 (s), 2360 (m), 2341 (m), 1572 (w), 1463 (s), 1377 (s), 1154 (w), 1069 (w), 1020 (w), 966 (w), 803 (w), 722 (m), 690 (w), 668 (w), 467 (w), 431 (w) cm⁻¹. UV-Vis: no absorption maximum appeared in the range 300 to 800 nm when the compound was dissolved in pyridine or THF. Anal. Calcd. for C₁₂₈H₁₄₄Nd₈O₁₀S₂Se₁₆: C, 35.6; H, 3.36. Found: C, 34.3; H, 3.41. X-Ray diffraction (Mo-Kα, 100 K): the compound crystallizes with a small percentage of Se at the sulfido position that can be minimized if the initial preparations are kept below room temperature. Empirical formula: C₁₄₄H₁₇₆Nd₈O₁₄S₁.₇Se₁₆.₃, formula weight: 4626.08, crystal system: monoclinic,
\[a = 17.5991(12) \, \text{Å}, \quad b = 20.7335(14) \, \text{Å}, \quad c = 21.9371(15) \, \text{Å}, \quad \beta = 102.345(1) \, ^\circ, \quad V = 7819.6(9) \, \text{Å}^3, \]
\text{temperature: 100(2) K, space group: } P2_1/n \, (#14), \text{formula units in unit cell (Z): 2, number of reflections measured: 76 757, number of independent reflections: 23 709, } R_{\text{int}} = 0.0353, \text{final } R(F) \text{ values for data with } I > 2 \sigma(I): R_1 = 0.0366, \text{w}R_2 = 0.0882.\

**Synthesis of [(py)$_3$Ho$_3$(μ$_3$-O)(μ-Te$_2$)$_3$(TePh)][(py)$_7$Ho$_4$(μ$_4$-Te)(μ-Te$_2$)$_2$(μ-η$_2$-η$_2$-Te$_2$Te(Ph)Te$_2$)(TePh)]:** Ho (0.165 g, 1.00 mmol), PhTeTePh (0.616 g, 1.50 mmol) and Hg (0.043 g, 0.22 mmol) were combined in pyridine (40 mL) and the mixture was stirred until all the metal dissolved (24 h). Elemental Te (0.255 g, 2.00 mmol) and TeO$_2$ (0.320 g, 2.00 mmol) were added to the resulting dark red-brown colored solution and the mixture was stirred for 2 days. The final solution color was dark red with some grey-black precipitate at the bottom of the flask. The solution was filtered, reduced in volume to 30 mL and layered with 20 mL of hexane. Within 1–2 days, dark red-orange colored block-like crystals appeared (0.046 g, 6.7%) which do not melt, but decompose between 140–145 °C and turn charcoal black up to 300 °C. IR: 2852 (m), 2724 (s), 2659 (s), 1601 (s), 1581 (s), 1460 (w), 1376 (s), 1298 (s), 1213 (m), 1135 (m), 1029 (m), 737 (w), 722 (w), 701 (w), 621 (w) cm$^{-1}$. UV-Vis: The compound does not show any absorption maximum from 350–750 nm when dissolved in pyridine. Anal. Calcd. for C$_{88}$H$_{85}$OTe$_{18}$N$_{14}$Ho$_7$: C, 22.0; H, 1.77; N, 4.08. Found: C, 22.5; H, 2.09; N, 3.78.

**Synthesis of [(py)$_3$Er$_3$(μ$_3$-O)(μ-Te$_2$)$_3$(TePh)][(py)$_7$Er$_4$(μ$_4$-Te)(μ-Te$_2$)$_2$(μ-η$_2$-η$_2$-Te$_2$Te(Ph)Te$_2$)(TePh)]:** Er (0.167 g, 1.00 mmol), PhTeTePh (0.616 g, 1.50 mmol) and Hg (0.043 g, 0.22 mmol) were combined in pyridine (40 mL) and the mixture was stirred
until all the metal dissolved (24 h). Elemental Te (0.255 g, 2.00 mmol) and TeO\textsubscript{2} (0.320 g, 2.00 mmol) were added to the resulting dark red-brown colored solution and stirred for 2 days. The final solution color was dark red with a grey-black precipitate. The solution was filtered, reduced in volume to 30 mL and layered with 20 mL of hexane. Within 1–2 days there appeared dark red-orange colored crystals (0.055 g, 8.0%) that do not melt, but decompose between 140–145 °C and turn charcoal black up to 300 °C. IR: 2853 (m), 2727 (s), 1600 (s), 1579 (s), 1463 (w), 1376 (s), 1299 (s), 1210 (m), 1136 (m), 1030 (m), 738 (w), 722 (w), 699 (w), 625 (w), 499 (w) cm\textsuperscript{-1}. UV-Vis: the compound does not show any absorption maximum from 350–750 nm when dissolved in pyridine. Anal. Calcd. for C\textsubscript{88}H\textsubscript{85}OTe\textsubscript{18}N\textsubscript{14}Er\textsubscript{7}: C, 21.9; H, 1.76; N, 4.07. Found C, 22.3; H, 2.16; N, 4.52. X-Ray diffraction (Mo-K\textsubscript{α}, 100 K): empirical formula: C\textsubscript{93.15}H\textsubscript{90}Er\textsubscript{7}N\textsubscript{14.85}OTe\textsubscript{18.15}, formula weight: 4920.25, crystal system: triclinic, \(a = 13.5619(10) \ \text{Å} , b = 21.2791(15) \ \text{Å} , c = 24.3965(18) \ \text{Å} , \alpha = 112.039(1)^\circ, \beta = 102.531(1)^\circ, \gamma = 97.814(1)^\circ, V = 6184.0(13) \ \text{Å}^3, \) temperature: 100(2) K, space group: \(P\bar{1} (#2), \) formula units in unit cell (Z): 2.

**Synthesis of [(etpy)\textsubscript{11}Yb\textsubscript{6}O\textsubscript{4}Te\textsubscript{4}TePh][Hg(TePh)\textsubscript{3}][(TePh)\textsubscript{3}]:** Yb (0.172 g, 0.994 mmol), PhTeTePh (0.614 g, 1.99 mmol) and Hg (0.029 g, 0.14 mmol) were stirred in 4-ethylpyridine (12 mL) covered in foil for two days. To the dark red solution, Te (0.42 mmol) and TeO\textsubscript{2} (0.22 mmol) were added and stirred for five days before being filtered, concentrated to 10 mL by vacuum and layered with hexanes (10 mL) and covered in foil. A small amount of dark red crystals were produced along with very dark unidentified solid.
Synthesis of [(etpy)$_{11}$Ho$_6$O$_4$Te$_4$TePh][Hg(TePh)$_3$]: Ho (0.165 g, 1.01 mmol), PhTeTePh (0.613 g, 0.995 mmol), and Hg (0.012 g, 0.060 mmol) were stirred in 4-ethylpyridine (22 mL) for 5 days. Tellurium (0.040 g, 0.31 mmol) and TeO$_2$ (0.057 g, 0.36 mmol) were added to the red solution, covered in foil, and stirred 10 days. The dark red-orange solution was filtered from grey precipitate, concentrated to 15 mL, layered with hexanes (10 mL), and covered in foil producing dark red crystals that blacken at 96-125 °C and melt at 145-148 °C.

Synthesis of (DME)$_4$Eu$_3$(SPh)$_5$(SC$_6$F$_5$)$_2$: Eu (0.152 g, 1.00 mmol), PhSSPh (0.218 g, 1.50 mmol), and Hg (0.010 g, 0.005 mmol) were stirred in DME overnight to form a yellow solution and precipitate. C$_6$F$_5$OH (0.184 g, 1.00 mmol) was added which made the solution more pale. After 1 week more stirring, yellow solution (20 mL) was filtered from orange precipitate, concentrated to 10 mL and layered with hexanes (15 mL) yielding poor quality yellow crystals over 6 days. The solution was reduced in volume by vacuum to 10 mL, but the crystals did not redissolve. After layering with 20 mL hexanes a small number of red-orange crystals were produced along with a large amount of yellow polycrystalline material.

Synthesis of (py)$_{10}$Yb$_8$O$_2$(SO$_3$)$_9$(OC$_6$F$_5$)$_2$·6py: Yb (0.173 g, 1.00 mmol) PhSSPh (0.218 g, 1.00 mmol), and Hg (0.03 g, 0.015 mmol) were stirred in pyridine (20 mL) for three days. C$_6$F$_5$OH (0.182 g, 0.989 mmol) was added to the dark blue-green solution with much powder of the same color, and the solution turned more blue upon stirring. After
five days pySO₃ (0.160 g, 1.01 mmol) was added to the blue solution which quickly turned orange. After 15 minutes, it was pale green. After 3 hours the pale yellow-green solution was filtered from grey precipitate and layered with hexanes (10 mL) producing colorless lathes which turn grey at 198°C and darkened up through 300°C but did not melt.

**Synthesis of (DME)(py)₂Eu(OC₆F₅)₃:** Eu (0.151 g, 0.993 mmol), PhSSPh (0.327 g, 1.50 mmol), and Hg (0.019 g, 0.095 mmol) were stirred in pyridine for 2 weeks. Sulfur (0.006 g, 0.2 mmol) was added to the orange solution. The next day, TeO₂ was added to the red solution and stirred 4 days. C₆F₅OH (0.428 g, 2.33 mmol) was added to the green-brown reaction mixture and stirred 7 days. The pyridine was removed by vacuum leaving black solid to which DME (20 mL) was added. After 2 days of stirring, the yellow solution was filtered from black solid, concentrated to 5 mL, layered with hexanes (15 mL), and put in the freezer producing yellow and colorless rods, a mixture of (DME)₂Eu(OC₆F₅)₃ and this mixed solvent adduct. This mixed solvent adduct was not isolated for analysis beyond single crystal XRD and was not produced as a pure phase.

**Synthesis of [N(CH₃)₄][Eu(S₂CN(CH₂CH₃))₄]·2py:** Eu (0.154 g, 1.01 mmol), PhSeSePh (0.314 g, 1.01 mmol), diethyldithiocarbamic acid diethylammonium salt (0.442 g, 1.99 mmol), and Hg (0.015 g, 0.075 mmol) were stirred in THF (20 mL) for 3 weeks. NH₄F (0.055 g, 1.5 mmol) was added to the red solution and black solid and stirred for 7 days. The red solution was filtered from brown precipitate, concentrated to
10 mL, and layered with hexanes (10 mL) to produce red needles co-crystallized with colorless [N(CH₃)₄][SePh].

**Synthesis of (Na(μ-OH)₂₂(μ₃-OH)₂Na(μ-OH)₂₂(THF))ₙ:** Sm (0.150 g, 1.00 mmol), PhSeSePh (0.468 g, 1.5 mmol), and Hg (0.026 g, 0.13 mmol) were stirred in THF (20 mL) for 7 days. Na(CH₃)₂NCS₂·xH₂O (0.574 g) was added to red solution and minor grey powder. The solution turned green immediately then nearly colorless with white precipitate. The solution was stirred overnight. The pale yellow solution was filtered from the white powder and layered with hexanes (10 mL) producing colorless crystals that bent at 150 °C, become apparently dry and flaky and gradually darken from 200 to 265 °C.

**Synthesis of Na(py)₄Sm(S₂CN(CH₃)₂)₄·4py:** Sm (0.150 g, 1.00 mmol), PhSeSePh (0.468 g, 1.5 mmol), and Hg (0.026 g, 0.13 mmol) were stirred in THF (20 mL) for 7 days. Na(CH₃)₂NCS₂·xH₂O (0.574 g) to red solution and minor grey powder. The solution turned green immediately then nearly colorless with white precipitate. The solution was stirred overnight. The pale yellow solution was filtered from the white powder, and the powder was dissolved in pyridine (10 mL) and stirred for 7 days. The green-brown solution was filtered from brown powder and layered with hexanes (10 mL) forming green crystals.

**Synthesis of Zn₈(SePh)₁₂((CH₂C₆H₅)₂NCS₂)₄·THF:** Tb (0.158 g, 1.00 mmol), PhSeSePh (0.466 g, 1.49 mmol), and Hg (0.010 g, 0.050 mmol) were stirred for 2 weeks
in THF (18 mL). Zn(II)dibenzyldithiocarbamate (1.215 g, 1.991 mmol) was added to the opaque grey solution and stirred for 6 days. PhSeSePh (0.150 g, 0.481 mmol) was added to the dark green solution with minor undissolved metal and stirred for 2 days. The yellow solution was filtered from black powder, concentrated to 11 mL, and layered with hexanes (10 mL) producing yellow kite-shaped crystals.

**Synthesis of [(THF)$_3$Yb(S$_2$CN(CH$_2$C$_6$H$_5$)$_2$)$_2$][Yb$_4$HgZn$_4$Se(SePh)$_{18}$]:** Yb (0.173 g, 1.00 mmol), PhSeSePh (0.470 g, 1.51 mmol), and Hg (0.022 g, 0.011 mmol) were stirred in THF for 10 days. Zn(S$_2$CN(CH$_2$C$_6$H$_5$)$_2$)$_2$ (0.610 g, 1.00 mmol) was added to the dark red solution and stirred for 7 days turning the solution orange. HgF$_2$ (0.120 g, 0.504 mmol) was added and stirred overnight. The yellow solution (17 mL) was filtered, layered with hexanes (13 mL) and refrigerated (5 °C) for 12 days precipitating yellow oil. The flask was shaken and left at room temperature. A few pale yellow crystals were found in the oil months later.

**Reaction of Yb/SPh/Hg/C$_6$F$_5$OH/py:** Yb (0.173 g, 1.00 mmol), PhSSPh (0.327 g, 1.50 mmol), and Hg (0.020 g, 0.10 mmol) were combined in pyridine (25 mL) and stirred at room temperature for six days yielding a dark red solution. C$_6$F$_5$OH (0.276 g, 1.50 mmol) was added quickly turning the solution a yellow-orange color. After several days of stirring, the orange solution was filtered from a minor grey powder, concentrated to about 8 mL and layered with 25 mL hexanes and put in the freezer at -5 °C for several weeks forming red oil but no crystals. *Rxn. KN5.*
**Reaction of Yb/SPh/Hg/C₆F₅OH/DME:** Yb (0.173 g, 1.00 mmol), PhSSPh (0.327 g, 1.50 mmol), and Hg (0.020 g, 0.10 mmol) were combined in DME (25 mL) and stirred at room temperature. After 10 days, C₆F₅OH (0.275 g, 1.50 mmol) was added to a red solution with yellow precipitate and a small amount of metal. Overnight the solution turned orange and the remaining metal dissolved. After several more days of stirring, the solution turned red again. It was filtered from a small amount of orange precipitate, concentrated to about 5 mL, and layered with hexanes (20 mL) producing a red oil. *Rxn. KN7.*

**Reaction of Yb/SPh/Hg/C₆F₅OH/S/THF:** Yb (0.173 g, 1.00 mmol), PhSSPh (0.325 g, 0.994 mmol), and Hg (0.025 g, 0.12 mmol) were combined in THF (20 mL) and stirred at room temperature. After 5 days, C₆F₅OH (0.184 g, 1.00 mmol) was added to the dark red solution. After 2 days the solution was a slightly lighter orange-red color. Sulfur (0.032 g, 1.0 mmol) was added. After 2 weeks of stirring, the solution was orange with a green-brown precipitate. The solution was filtered and layered with 20 mL hexanes producing no state change after diffusion. Various attempts were made to crystallize the orange phase without producing XRD quality samples. *Rxn. KN9, KNA, KN11B.*

**Reaction of Eu/SPh/Hg/DME/C₆F₅OH/S:** Eu (0.152 g, 1.00 mmol), PhSSPh (0.218 g, 1.00 mmol), and Hg (0.030 g, 0.15 mmol) were stirred in DME (15 mL) overnight to produce a yellow solution with yellow-green precipitate to which C₆F₅OH (0.184 g, 1.00 mmol) was added. After 3 days, sulfur (0.032 g, 1.0 mmol) was added to the light yellow solution turning it dark yellow-brown. After a week of stirring, the dark solution was
filtered, concentrated to 12 mL and layered with hexanes (15 mL) to produce a heterogeneous mixture of dark powders upon diffusion. *Rxn. KNE.*

**Reaction of Tm/SPh/Hg/DME/C₆F₅OH:** Tm (0.165 g, 0.976 mmol) PhSSPh (0.323 g, 1.48 mmol) and Hg (0.02 g, 0.1 mmol) were stirred one week in 20 mL DME to produce a yellow-green solution. C₆F₅OH (0.55 g, 3.0 mmol) was added. Upon shaking, the solution became pale. It was immediately filtered, concentrated to 10 mL and layered with hexanes (15 mL) producing a powder. All solvent was removed by vacuum and dissolved in pyridine (15 mL). The solution was layered with hexanes (25 mL) producing oil and possibly a polycrystalline powder which was not analyzed. *Rxn. KN10.*

**Reaction of Nd/SPh/Hg/py/C₆F₅OH:** Nd (0.144 g, 1.00 mmol), PhSSPh (0.327 g, 1.50 mmol), and Hg (0.02 g, 0.1 mmol) were stirred 2 weeks in pyridine (15 mL) to form a green solution to which C₆F₅OH (0.550 g, 2.99 mmol) was added. After 3 days of stirring the green-brown solution was filtered from minor grey precipitate and layered with hexanes (10 mL). After two weeks, the solution was put in a freezer at – 5 °C. After two weeks, oil had come out of solution. *Rxn. KN11.*

**Reaction of Eu/SPh/Hg/DME/C₆F₅SH:** Eu (0.154 g, 1.01 mmol), PhSSPh (0.217 g, 0.995 mmol), and Hg (0.030 g, 0.15 mmol) were stirred in DME (10 mL) for 3 days. C₆F₅SH (130 µL, 0.98 mmol) was syringed into the yellow solution with green precipitate. The solution turned colorless then dark yellow-green upon swirling. The mixture was stirred 5 days becoming an orange solution with brown precipitate. The
solution was separated and layered with hexanes (20 mL) producing an orange oil under yellow solution. All solvent was vacuumed off leaving red oil and solid which was redissolved in DME (10 mL) and layered with ether (15 mL) again producing oil. \textit{Rxn. KN13.}

**Reaction of Er/SPh/Hg/pySO$_3$/C$_6$F$_5$OH/py:** Er (0.167 g, 1.00 mmol), PhSSPh (0.218 g, 1.00 mmol), and Hg (0.02 g, 0.1 mmol) were stirred in pyridine (15 mL) for two days producing a pink solution with undissolved metal. C$_6$F$_5$OH (0.184 g, 1.00 mmol) was added and stirred one week. pySO$_3$ (0.159 g, 1.00 mmol) was added to the pink solution and stirred two days. The resulting dark grey solution was filtered and layered with an equal volume of hexanes. After five days, a black powder was found on the bottom, and a colorless film coated the flask walls. \textit{Rxn. KN15.}

**Reaction of Eu/SPh/Hg/DME/C$_6$F$_5$OH/pySO$_3$:** Eu (0.11 g, 0.71 mmol), PhSSPh (0.18 g, 0.83 mmol), and Hg (0.022 g, 0.11 mmol) were stirred overnight in DME (12 mL) making an orange solution. C$_6$F$_5$OH (0.131 g, 0.712 mmol) was added and stirred one week. pySO$_3$ (0.11 g, 0.71 mmol) was added to the yellow solution and stirred five days producing a tan solution with brown precipitate. The solution was filtered and layered with hexanes (12 mL) to produce a brown powder. The hexane was removed by vacuum to redissolve, and the solution was layered with ether (15 mL) also yielding powder. \textit{Rxn. KN17.}
Reaction of Eu/C₆F₅OH/pySO₃/py: Eu (0.152 g, 1.00 mmol), C₆F₅OH (0.184 g, 1.00 mmol), and pySO₃ (0.318 g, 2.00 mmol) were stirred in pyridine for two weeks. Yellow solution was filtered from black powder and metallic flakes and layered with hexanes (15 mL). pySO₃ crystallized – identified by melting point. Rxn. KN1A.

Reaction of Er/SPh/C₆F₅OH/Hg/pySO₃/py: Er (0.167 g, 1.00 mmol), PhSSPh (0.218 g, 1.00 mmol), C₆F₅OH (0.276 g, 1.50 mmol), and Hg (0.020 g, 0.10 mmol) were stirred in pyridine (18 mL) for eight days. pySO₃ (0.24 g, 1.5 mmol) was added to the brown solution and stirred two days. The resulting dark green-brown solution was filtered from a small amount of black powder and layered with hexanes (15 mL) to produce an unidentified powder that is not soluble in pyridine. Rxn. KN1C.

Reaction of Yb/SPh/Hg/C₆F₅OH/pySO₃/H₂O/py: Yb (0.172 g, 0.994 mmol), PhSSPh (0.218 g, 1.00 mmol), and Hg (0.010 g, 0.05 mmol) were combined in pyridine (10 mL) and stirred 3 days. To the resulting green solution with green precipitate, C₆F₅OH (0.184 g, 1.00 mmol) was added. After stirring 5 days, pySO₃ complex (0.158 g, 0.995 mmol) was added. To the resulting orange mixture, a solution of H₂O (4.5 µL, 0.25 mmol) in pyridine (20 mL) was added, and the solution became pale. After two hours of stirring, the solution was filtered, concentrated to 20 mL, and layered with hexanes (10 mL) producing an oil after diffusion. Hexanes was removed via vacuum, and the solution was layered with ether (10 mL). White solid initially precipitated but redissolved. Tan and black powders were present after diffusion. Rxn. KN2D.
Reaction of Yb/C₆F₅OH/pySO₃/Hg/H₂O/py: Yb (0.174 g, 1.00 mmol), C₆F₅OH (0.06 g, 0.3 mmol), pySO₃ (0.190 g, 1.19 mmol), Hg (0.010 g, 0.05 mmol), and H₂O (4.5 µL, 0.25 mmol) were combined in pyridine (15 mL) and stirred 9 days. The clear solution was filtered and layered with hexanes (15 mL) producing pySO₃ complex. The solution was concentrated to 10 mL and layered with hexanes 10 mL producing a powder mixture. Rxn. KN2E.

Reaction of Tm/C₆F₅OH/pySO₃/H₂O/py: Tm (0.169 g, 1.00 mmol), C₆F₅OH (0.183 g, 0.995 mmol), and pySO₃ (0.162, 1.02 mmol) were stirred in pyridine 7 days. To the dark solution and solids, pyridine (20 mL) containing H₂O (4.5 mL, 0.25 mmol) was added and stirred 2 hours. The solution was filtered a second time the following day separating a black powder from pale tan solution. It was concentrated from 35 mL to 12 mL and layered with hexanes (12 mL) forming a mixture of powders. Rxn. KN31.

Reaction of Yb/SePh/Hg/C₆F₅OH/pySO₃/py: Yb (0.171 g, 0.988 mmol), PhSeSePh (0.315 g, 1.01 mmol), and Hg (0.020 g, 0.10 mmol) were stirred in pyridine (18 mL) 6 weeks. More PhSeSePh (0.160 g, 0.513 mmol) was added to the dark red solution. The following day pySO₃ (0.158 g, 0.994 mmol) and C₆F₅OH (0.184 g, 1.00 mmol) were added, and the solution was stirred 24h at 105 °C turning the solution orange with orange powder. The solution was filtered after cooling to room temperature and layered with 18 mL hexanes precipitating orange powder. Rxn. KN7C.
**Reaction of Nd/SPh/Hg/S/C₆F₅OH/DME:** Nd (0.144 g, 1.00 mmol), PhSSPh (0.327 g, 1.50 mmol) and Hg (0.015 g, 0.075 mmol) were stirred in DME (15 mL). In a separate flask Nd (0.096 g, 0.67 mmol), C₆F₅OH (0.37 g, 2.0 mmol), Hg (0.023 g, 0.12 mmol) and DME (15 mL) were combined and stirred. After 2 days, sulfur (0.032 g, 1.0 mmol) was added to the blue thiolate solution and stirred 4 more days. The alkoxide solution was filtered into the thiolate solution, and the mixture was stirred 3 days to produce a brown solution with black precipitate. The solution was filtered, concentrated to 15 mL and layered with hexanes (15 mL) forming a powder. *Rxn. KN2B.*

**Reaction of Er/SPh/Hg/C₆F₅OH/S/py:** Er (0.168 g, 1.00 mmol), PhSSPh (0.329 g, 1.51 mmol), and Hg (0.020 g, 0.10 mmol) were stirred in pyridine (15 mL) 5 days to dissolve. Sulfur (0.015 g, 0.47 mmol) was added to the grey solution and stirred overnight. C₆F₅OH (0.183 g, 0.995 mmol) was added and stirred 6 days turning the solution orange. It was filtered and layered with hexanes (20 mL) resulting in an oil. Hexanes was removed by vacuum, and the solution was layered with ether (15 mL) which became cloudy white before diffusion. After diffusion, a black powder precipitated. *Rxn. KN34.*

**Reaction of Er/SPh/Hg/C₆F₅OH/S/DME:** Er (0.168 g, 1.00 mmol), PhSSPh (0.327 g, 1.50 mmol), and Hg (0.030 g, 0.15 mmol) were stirred in DME for 5 days. C₆F₅OH (0.273 g, 1.48 mmol) was added to light blue opaque solution which turned darker grey clearer with some of the powder dissolving quickly. After 4 days stirring, sulfur (0.024 g, 0.75 mmol) was added. After stirring 1 month, the pink-orange solution was filtered, and more sulfur (0.023 g, 0.72 mmol) was added causing an off-white precipitate. The
solution was filtered again 5 days later and the 10 mL solution was layered with hexanes (10 mL) producing pink-orange powder. *Rxn. KN3C.*

**Reaction of (DME)$_2$Eu$_3$(C$_6$F$_5$O)$_6$/S/DME:** (DME)$_2$Eu($\mu$-OC$_6$F$_5$)$_3$Eu($\mu$-OC$_6$F$_5$)$_3$Eu(DME)$_2$ was prepared by the reported procedure. The trimer (0.480 g, 0.251 mmol) was combined with sulfur (0.013 g, 0.41 mmol) in DME (15 mL) and stirred for 10 days producing a dark yellow solution and dark brown precipitate. The solution was filtered, concentrated to 2 mL and layered with hexanes (10 mL) producing (DME)$_2$Eu(OC$_6$F$_5$)$_3$. *Rxn. KN140.*

**Reaction of Nd/SPh/Hg/S/C$_6$F$_5$OH/py:** Nd (0.142 g, 0.0986 mmol), PhSSPh (0.333 g, 0.153 mmol), and Hg (0.011 g, 0.055 mmol) were combined in pyridine and stirred 4 days. Sulfur (0.07 g, 2 mmol) and C$_6$F$_5$OH (0.191 g, 1.04 mmol) were added to dark blue solution producing a brown precipitate. The powder was dissolved in hot pyridine (90°C) and filtered hot leaving behind green powder. The resulting yellow filtrate was concentrated to 10 mL and layered with hexanes (20 mL) to give a small amount of black-brown powder. *Rxn. KN4D.*

**Reaction of Sm/SePh/Hg/C$_6$F$_5$OH/Se/THF:** Sm (0.149 g, 0.993 mmol), PhSeSePh (0.470 g, 1.51 mmol), and Hg (0.020 g, 0.1 mmol) were combined in THF (20 mL) and stirred 2 weeks to dissolve metal. C$_6$F$_5$OH (0.285 g, 1.55 mmol) was added to the red solution turning it yellow-orange. After 6 days, selenium (0.079 g, 1.0 mmol) was added. The solution turned green but after 10 days of stirring changed to orange with brown
precipitate. This was filtered and layered with hexanes (20 mL). An orange powder precipitated. *Rxn. KN52.*

**Reaction of (py)$_8$Yb$_4$Se$_4$(SePh)$_4$/C$_6$F$_5$OH/py:** (py)$_8$Yb$_4$Se$_4$(SePh)$_4$ was produced by literature procedures and isolated. The dry crystals (0.47 g, 0.21 mmol) and C$_6$F$_5$OH (0.15 g, 0.82 mmol) were stirred in pyridine (15 mL) overnight forming a red solution with brown precipitate. The solution was filtered, concentrated to 11 mL and layered with hexanes (15 mL) to produce red oil. The oil was put in a freezer (0 °C) for 3 months with no change. *Rxns. KN5C, KN5F, KN60.*

**Reaction of (py)$_{10}$Yb$_6$S$_6$(SPh)$_6$/C$_6$F$_5$OH/py:** (py)$_{10}$Yb$_6$S$_6$(SPh)$_6$ was produced by literature procedures and isolated. The dry crystals (0.56 g, 0.22 mmol) were combined with C$_6$F$_5$OH (0.144 g, 0.783 mmol) in pyridine (20 mL) and stirred overnight. The resultant orange-brown solution was filtered from brown precipitate, concentrated to 15 mL and layered with hexanes (15 mL). A mixture of powders precipitated. *Rxns. KN5D, KN5E.*

**Reaction of Pr/SePh/Hg/Se/C$_6$F$_5$OH/THF:** Pr (0.141 g, 1.00 mmol), PhSeSePh (0.465 g, 1.49 mmol), and Hg (0.01 g, 0.05 mmol) was stirred in THF (20 mL) for 2 weeks making a clear green solution. Se (0.061 g, 0.77 mmol) was added and stirred 3 days. C$_6$F$_5$OH (0.176 g, 0.956 mmol) was added to the green solution and stirred 9 days. The opaque green solution was filtered from brown precipitate, concentrated to 10 mL and layered with hexanes (10 mL) producing green-brown powder. *Rxn. KN63.*
**Reaction of Tm/SePh/Hg/C\textsubscript{6}F\textsubscript{5}OH/Se/THF:** Tm (0.169 g, 1.00 mmol), PhSeSePh (0.468 g, 1.50 mmol), and Hg (0.010 g, 0.05 mmol) was combined in THF (20 mL) and stirred 2 weeks. C\textsubscript{6}F\textsubscript{5}OH (0.136 g, 0.739 mmol) was added to the grey solution and solid and stirred 13 days. Se (0.079 g, 1.0 mmol) was added, immediately turning dark blue, and stirred 7 days. The solution turned orange with a green precipitate. The solution was filtered and layered with hexanes (18 mL) forming orange powder. *Rxn. KN65.*

**Reaction of (THF)\textsubscript{8}Sm\textsubscript{8}Se\textsubscript{6}(SePh)\textsubscript{12}/C\textsubscript{6}F\textsubscript{5}OH/THF:** (THF)\textsubscript{8}Sm\textsubscript{8}Se\textsubscript{6}(SePh)\textsubscript{12} was produced by literature procedures,\textsuperscript{6} and the dry crystalline powder (0.18 g, ) was combined with C\textsubscript{6}F\textsubscript{5}OH (0.092 g, 0.50 mmol) and stirred in THF (15 mL) for 9 days. The orange solution was filtered, concentrated to 10 mL and layered with hexanes (15 mL) producing a mixture of orange and black powders. *Rxns. KN6A KN6D.*

**Reaction of (THF)\textsubscript{8}Nd\textsubscript{8}S\textsubscript{6}(SPh)\textsubscript{12}/C\textsubscript{6}F\textsubscript{5}OH/THF:** (THF)\textsubscript{8}Nd\textsubscript{8}S\textsubscript{6}(SPh)\textsubscript{12} was produced by literature procedures,\textsuperscript{6} and the dry crystals (0.07 g, ) were combined with C\textsubscript{6}F\textsubscript{5}OH (0.05 g, 0.3 mmol) and stirred in THF (10 mL) for 5 days. The dark brown solution was filtered, concentrated to 5 mL and layered with hexanes (10 mL) producing a brown powder. *Rxn. KN6C.*

**Reaction of Nd/SePh/Hg/C\textsubscript{6}F\textsubscript{5}OH/NH\textsubscript{4}F/THF:** Nd (0.144 g, 1.00 mmol), PhSeSePh (0.464 g, 1.49 mmol), and Hg (0.005 g, 0.025 mmol) were stirred in THF (20 mL) for 2 weeks. C\textsubscript{6}F\textsubscript{5}OH (0.094 g, 0.51 mmol) was added to the green solution with blue powder
and continued to stir 8 days. NH₄F (0.039 g, 1.0 mmol) was added and stirred 3 weeks with no noticeable change in color or state. The solution was filtered, concentrated to 5 mL and layered with hexanes (5 mL) and put in a refrigerator precipitating an oil. *Rxn. KN78.*

**Reaction of Yb/SPh/Hg/C₆F₅OH/NH₄F/py:** Yb (0.173 g, 1.00 mmol), PhSSPh (0.218 g, 1.00 mmol), and Hg (0.020 g, 0.10 mmol) were stirred in pyridine (20 mL) for 2 days. C₆F₅OH (0.185 g, 1.00 mmol) was added to the dark red solution and continued to stir 4 days. NH₄F (0.069 g, 1.9 mmol) was added to the now dark green solution and stirred 6 weeks. The resulting yellow-red solution was filtered, concentrated to 2 mL and layered with hexanes (5 mL) and put in a refrigerator. After 8 days there was oil in the bottom of the flask along with solid that was possibly crystalline but not diffractometer quality. Repeated attempts to recrystallize with pyridine, DME, and hexanes resulted in red oil and red and yellow powders. *Rxns. KN79, KN80, KN81.*

**Reaction of Nd/SePh/Hg/S/C₆F₅OH/DME/py:** Failed attempts at repeating (DME)₆(py)₆Nd₁₈F₂₄O₃S₃(OC₆F₅)₁₈. Nd (0.144 g, 1.00 mmol), PhSeSePh (0.469 g, 1.50 mmol), and Hg (0.012 g, 0.060 mmol) were stirred in pyridine for 7 days. Sulfur (0.032 g, 1.0 mmol) was added to the dark green solution and stirred 7 more days when C₆F₅OH (0.183 g, 0.994 mmol) was added to the now yellow-green solution. This was stirred 7 days longer. The pyridine was removed by vacuum, and DME (20 mL) was added to redissolve the green-brown solid leaving some black solid. This brown solution was concentrated to 8 mL and layered with hexanes (15 mL) without filtering first and put in
a refrigerator. The solution turned yellow, and dark powder and PhSeSePh crystals precipitated. \textit{Rxns. KN96, KN98, KN10B, KN120, KN121, KN186, KN189, KN1CC.}

\textbf{Reaction of Nd/SePh/Hg/S/C}_6\textsubscript{F}_5\textsubscript{OH}/NH}_4F/pySO_3/DME/py: Failed attempts at repeating (DME)\textsubscript{6}(py)\textsubscript{6}Nd\textsubscript{18}F\textsubscript{24}O\textsubscript{3}S\textsubscript{3}(OC\textsubscript{6}F\textsubscript{5})\textsubscript{18}. Nd (0.144 g, 1.00 mmol), PhSeSePh (0.463 g, 1.48 mmol), and Hg (0.012 g, 0.060 mmol) were stirred in pyridine for 7 days. C\textsubscript{6}F\textsubscript{5}OH (0.234 g, 1.27 mmol), sulfur (0.010 g, 0.31 mmol), NH\textsubscript{4}F (0.049 g, 1.3 mmol), and pySO\textsubscript{3} (0.025 g, 0.032 mmol) were added. After the solution stirred for 4 weeks, vacuum was drawn to remove the solvent then was continued for 3 hours after the solvent was gone and the flask warmed to room temperature subliming off some PhSeSePh. DME (25 mL) was added and stirred 3 weeks. The resulting amber solution was filtered, concentrated to 10 mL, layered with hexanes (15 mL), and covered in foil. Yellow crystalline powder and oil was produced. In several recrystallization attempts, red and yellow oils and powders were produced. The only identified product was a minor mercury selenolate phase. \textit{Rxns. KN83, KN8A, KN9A, KN101, KN106, KN107, KN187, KN1A5, KN1AA.}

\textbf{Reaction of Nd/SePh/Hg/py/S/CF}_3SO_3H: Nd (0.143 g, 0.993 mmol), PhSeSePh (0.468 g, 1.00 mmol), and Hg (0.022 g, 0.11 mmol) were combined in pyridine (20 mL) and stirred for 4 days. Sulfur (0.048 g, 1.5 mmol) was added to the blue solution and stirred 1 month. CF\textsubscript{3}SO\textsubscript{3}H (0.10 mL, 1.1 mmol) was added to the green solution and precipitate and stirred 15 days. The suspension did not settle well, so it was partially filtered, and 12
mL was layered with hexanes (15 mL). A green powder precipitated leaving the solution yellow. Rxns. KN91 KN94, KN95.

**Reaction of Yb/SePh/Hg/Se/CF₃SO₃H/py:** Attempt at repeating (py)₈Yb₄F₈(CF₃SO₃)₄.
Yb (0.173 g, 1.00 mmol), PhSeSePh (0.470 g, 1.51 mmol), and Hg (0.015 g, 0.075 mmol) were stirred in pyridine (17 mL) for overnight. Selenium (0.159 g, 2.01 mmol) was added to the dark red solution and stirred for 4 weeks. CF₃SO₃H (0.12 mL, 1.4 mmol) was added. After 15 days of stirring, the brown solution was filtered from orange powder and layered with hexanes (15 mL) producing red oil which froze above -5 °C. Rxns. KN92, KN9E, KN11F, KN1CF, KN1D0, KN1D5, KN24F.

**Reaction of Sm/SePh/Hg/Se/CF₃SO₃H/py:** Sm (0.155 g, 1.03 mmol), PhSeSePh (0.468 g, 1.00 mmol), and Hg (0.011 g, 0.055 mmol) were stirred in pyridine (15 mL) for 7 days. Selenium (0.163 g, 2.06 mmol) was added to the green solution and stirred for 10 days. To the orange solution, CF₃SO₃H (0.1 mL, 1 mmol) was added, and it was stirred for 3 hours at 115 °C producing a brown precipitate. After 2 days at room temperature, the orange solution was filtered from brown powder and layered with hexanes (15 mL) causing brown precipitate. Rxns. KN11E, KN1D4.

**Reaction of Sm/SePh/Hg/Se/CF₃SO₃H/py:** Sm (0.151 g, 1.01 mmol), PhSeSePh (0.469 g, 1.50 mmol), and Hg (0.028 g, 0.14 mmol) were stirred in pyridine until the metal dissolved. CF₃SO₃H (0.3 mL, 3 mmol) was added and allowed to react for 2 weeks. The orange solution was filtered, concentrated to 11 mL and layered with hexanes (12 mL)
producing yellow crystals of the salt [pyH][(py)₄Sm(CF₃SO₃)₄]. These yellow plates (0.740 g, 0.602 mmol), were combined with metallic Sm (0.145 g, 0.967 mmol), PhSeSePh (0.455 g, 1.46 mmol), and Hg (0.025 g, 0.12 mmol) in pyridine (20 mL) and stirred for 4 weeks. Selenium (0.113 g, 1.43 mmol) was added to the orange solution, stirred 30 minutes, and allowed to settle for 30 minutes before filtering. The volume was reduced by half and layered with hexanes (10 mL). The flask was put in a refrigerator to diffuse. After 2 weeks red oil had precipitated out, leaving the solution yellow. *Rxn.* KN10E.

**Reaction of Eu/SePh/Hg/Se/CF₃SO₃H/py:** Eu (0.151 g, 0.993 mmol), PhSeSePh (0.314 g, 1.01 mmol), and Hg (0.011 g, 0.055 mmol) were stirred in pyridine (15 mL) for 6 days. Selenium (0.074 g, 0.94 mmol) was added to the red solution and stirred for 7 days. CF₃SO₃H (0.08 mL, 0.9 mmol) was added to the dark red solution and stirred overnight. The brown solution was filtered from powder, concentrated to 12 mL, and layered with hexanes (10 mL) producing brown powder. *Rxn.* KN1D2, KN1D8.

**Reaction of Yb/SePh/Hg/CF₃SO₃H/py:** Attempts at synthesizing (py)₈Yb₄F₈(CF₃SO₃)₄ without Se. Yb (0.173 g, 1.00 mmol), PhSeSePh (0.312 g, 1.00 mmol), and Hg (0.017 g, 0.085 mmol) were stirred in pyridine (15 mL) for 8 days. CF₃SO₃H (0.1 mL, 1 mmol) was added to the purple solution and stirred for 6 days. The purple solution was filtered, concentrated to 3 mL and layered with hexanes (15 mL) producing a dark red oil with red solution. *Rxn.* KN110, KN112.
**Reaction of Er/SePh/Hg/CF$_3$SO$_3$H/Se/py:** Er (0.169 g, 1.01 mmol), PhSeSePh (0.473 g, 1.52 mmol), and Hg (0.015 g, 0.075 mmol) were stirred in pyridine (12 mL) for 5 days. Selenium (0.161 g, 2.04 mmol) was added to the green solution and stirred for 10 days. CF$_3$SO$_3$H (0.1 mL, 1 mmol) was added to the yellow solution with yellow powder and stirred in an oil bath (90 °C) for 48 hours. The red solution was filtered from brown precipitate after it cooled to room temperature. Then, it was layered with hexanes (11 mL). Diffusion produced red oil and black solid under a yellow solution. The flask was placed in the freezer, and the pyridine and hexanes separated into a less dense yellow solution and a denser orange one. The flask was returned to room temperature, and the layers recombined to revert to the previous states. *Rxns. KN11C KN241.*

**Reaction of Tm/SePh/Hg/CF$_3$SO$_3$H/Se/py:** Tm (0.171 g, 1.01 mmol), PhSeSePh (0.473 g, 1.52 mmol), and Hg (0.009 g, 0.04 mmol) were combined in pyridine (15 mL) and stirred 5 days. Selenium (0.160 g, 2.02 mmol) was added to the yellow-green solution and stirred 10 days. CF$_3$SO$_3$H (0.1 mL, 1 mmol) was added to the orange solution and yellow powder and stirred in an oil bath (90 °C) for 48 hours. The red solution was filtered from brown powder at room temperature and layered with hexanes (25 mL). This produced red oil and black solid leaving the solution yellow. The reaction was put in a freezer (0 °C) for 6 months forming poor quality red crystals possibly (py)$_6$Tm$_2$Se$_4$(CF$_3$SO$_3$)$_2$. Attempts to recrystallize demonstrated insolubility in THF and ether. Red oil, and polycrystalline solid were produced from pyridine/hexane systems, but no single crystals were obtained for structure determination. *Rxn. KN11D.*
**Reaction of Er/SPh/Hg/CF₃SO₃H/S/DME:** Er (0.159 g, 0.952 mmol), PhSSPh (0.323 g, 1.48 mmol), and Hg (0.023 g, 0.12 mmol) were stirred in DME (12 mL) for 7 days. Sulfur (0.040 g, 1.2 mmol) was added to grey solution with minor undissolved metal flakes and stirred for 2 weeks. CF₃SO₃H (0.05 mL, 0.5 mmol) was added to the grey solution and powder and stirred for 2 weeks. The colorless solution was filtered from grey powder, layered with hexanes (12 mL) and covered in foil. White powder was produced. *Rxn. KN122.*

**Reaction of Eu/C₆F₅OH/Hg/Se/py:** Eu (0.142 g, 0.934 mmol), C₆F₅OH (0.357 g, 1.94 mmol), and Hg (0.025 g, 0.12 mmol) were stirred in pyridine (25 mL) for 6 days. The red solution was filtered and layered with a suspension of 200 mesh selenium powder (0.161 g, 2.04 mmol) in pyridine (10 mL). After 10 days, 10 mL of the red-orange solution was filtered from the black powder and layered with hexanes (12 mL). The dark powder that precipitated was not identified. *Rxn. KN166, KN1C4, KN1C6, KN1DA.*

**Reaction of Nd/SPh/Hg/C₆F₅OH/S/py:** Nd (0.146 g, 1.01 mmol), PhSSPh (0.337 g, 1.55 mmol), and Hg (0.008 g, 0.04 mmol) were stirred in pyridine (18 mL) for 9 days. C₆F₅OH (0.184 g, 1.00 mmol) was added to the dark blue solution and stirred for 3 weeks. The blue solution was filtered from minor grey precipitate and layered with sulfur (0.032 g, 1.0 mmol) in pyridine (10 mL). After full diffusion, there was no precipitate. The tan solution was concentrated to 5 mL and layered with hexanes (10 mL) producing (py)₄Nd(OC₆F₅)₃ crystals and unidentified powder. *Rxn. KN169, KN177.*
Reaction of Er/SPh/Hg/C₆F₅OH/S/py: Er (0.168 g, 1.00 mmol), PhSSPh (0.331 g, 1.52 mmol), and Hg (0.021 g, 0.10 mmol) were stirred in pyridine (17 mL) for 2 days. C₆F₅OH (0.201 g, 1.09 mmol) was added to the grey solution and stirred 3 weeks. The dark pink solution was filtered from minor grey precipitate and layered with sulfur (0.016 g, 0.50 mmol) dissolved in pyridine (10 mL). The tan solution was concentrated to 18 mL and layered with hexanes (10 mL) producing powder. *Rxn. KN16A, KN16B, KN178, KN19E, KN1A9, KN1AF, KN1C1, KN1C2.*

Reaction of Ln(III)/TePh/Hg/Te/TeO₂/4etpy: (0.168 g, 0.994 mmol), PhTeTePh (0.625 g, 1.53 mmol), and Hg (0.027 g, 0.14 mmol) were stirred in 4-ethylpyridine (20 mL) for 9 days. Tellurium (0.057 g, 0.45 mmol) and TeO₂ (0.039 g, 0.24 mmol) were added to the red solution, and it was covered in foil and stirred for 9 days. The dark red-orange solution was filtered from black precipitate, concentrated to 15 mL, layered with hexanes (15 mL) and covered in foil producing a small amount of dark oil. The solution was concentrated to 13 mL and layered with hexanes (15 mL) and put into a refrigerator (5 °C) for 3 weeks. Reactions of this type typically produced oils that did not crystallize. *Rxn. KN17C, KN17B, KN181, KN182, KN185, KN188, KN19C, KN19D, KN1A0, KN1B1, KN1B8, KN1BE, KN1BF, KN1C5, KN1CE, KN24D.*

Reaction of Yb/TePh/Hg/Te/TeO₂/4etpy: Yb (0.173 g, 1.00 mmol), PhTeTePh (0.617 g, 1.51 mmol), and Hg (0.048 g, 0.24 mmol) were combined in 4-ethylpyridine (15 mL) and stirred overnight. Tellurium (0.054 g, 0.42 mmol) and TeO₂ (0.044 g, 0.28 mmol) were added to the dark red solution, and the flask was covered in foil and stirred for 11
days. The dark red solution was filtered, concentrated to 10 mL, layered with hexanes (10 mL), and covered in foil producing red crystals which were not of sufficient quality to obtain a structure. *Rxn. KN18F.*

**Reaction of Ce/TePh/Hg/Te/4etpy:** Ce (0.140 g, 1.00 mmol), PhTeTePh (0.620 g, 1.52 mmol), and Hg (0.040 g, 0.20 mmol) were stirred in 4-ethylpyridine (20 mL) for 5 days. Tellurium (0.179 g, 1.00 mmol) was added to the dark red solution, and the flask was covered in foil and stirred for 7 days. The dark red solution was filtered from minor black precipitate, concentrated to 12 mL, layered with hexanes (10 mL) and covered in foil to produce very dark oil and amorphous solid. *Rxn. KN190, KN19B, KN19F, KN1B7, KN1BC.*

**Reaction of Nd/TePh/Hg/TeO₂/4etpy:** Nd (0.142 g, 0.986 mmol), PhTeTePh (0.609 g, 1.49 mmol), and Hg (0.034 g, 0.17 mmol) were stirred in 4-ethylpyridine (15 mL) for 10 days. TeO₂ (0.075 g, 0.47 mmol) was added to the dark red solution and black powder and stirred covered in foil for 11 days. The opaque, red-orange solution was filtered from black powder and layered with hexanes (12 mL) making brown powder. *Rxn. KN1B5, KN1CD.*

**Reaction of Ce/TePh/Hg/Te/TeO₂/py:** Ce (0.138 g, 0.986 mmol), PhTeTePh (0.618 g, 1.51 mmol), and Hg (0.025 g, 0.12 mmol) were stirred in pyridine (21 mL) for 8 days. Tellurium (0.256 g, 2.02 mmol) and TeO₂ (0.027 g, 0.17 mmol) were added to the red solution, and the flask was covered in foil and stirred for 5 days. The dark red solution
was filtered from minor black precipitate, concentrated to 18 mL, layered with hexanes (10 mL) and covered in foil. *Rxn. KN161, KN191.*

**Reaction of Ce/TePh/Hg/Te/py:** Ce (0.142 g, 1.01 mmol), PhTeTePh (0.620 g, 1.52 mmol), and Hg (0.045 g, 0.22 mmol) were stirred in pyridine (20 mL) for 2 weeks. Tellurium (0.124 g, 0.976 mmol) was added to the dark red solution and stirred covered in foil for 2 days. The dark red solution was filtered and layered with hexanes (25 mL). After 2 weeks a black film coated the inside of the flask. *Rxn. KN1A7.*

**Reaction of Eu/SePh/Hg/NH4F/py:** Eu (0.150 g, 0.987 mmol), PhSeSePh (0.467 g, 1.50 mmol), and Hg (0.013 g, 0.065 mmol) were stirred in pyridine (20 mL) for 2 weeks. NH$_4$F (0.072 g, 1.94 mmol) was added to the dark red solution and stirred for 1 hour. The orange-red solution was filtered from dark red powder, concentrated to 15 mL and layered with hexanes (15 mL) forming a red oil with diffusion. The flask was placed in a freezer (-5 °C) for 3 weeks separating the solvent layers and redissolving the oil. Successive diffusion and temperature induced separation produced oil and sometimes polycrystalline solid which was not identified. *Rxn. KN1A2, KN1A1, KN1A3, KN1A6, KN1AB, KN1AC, KN1B6, KN1C3.*

**Reaction of Eu/SePh/Hg/N(CH$_3$)$_4$F/py:** Eu (0.152 g, 1.00 mmol), PhSeSePh (0.312 g, 1.00 mmol), and Hg (0.012 g, 0.60 mmol) were stirred in pyridine (12 mL) overnight. N(CH$_3$)$_4$F (0.187 g, 2.15 mmol) was added to the dark red solution, stirred for 10 minutes
turning brown, let settle for 30 min and filtered. The dark orange solution was layered with hexanes (10 mL) producing brown powder.  *Rxn. KN1BD, KN1C0.*

**Reaction of Sm/SPh/Hg/NH4F/THF:** Sm (0.149 g, 0.993 mmol), PhSSPh (0.217 g, 0.995 mmol), and Hg (0.008 g, 0.040 mmol) were stirred in THF (18 mL) for 7 days. NH4F (0.055 g, 1.49 mmol) was added to the opaque green solution and stirred for 2 days turning pale yellow. The solution was filtered from brown powder, concentrated from 18 mL to 2 mL and layered with hexanes (6 mL) producing an amorphous powder. The residue from the filtration was partially dissolved in pyridine (20 mL) and filtered. The green-yellow solution was concentrated to 5 mL and layered with hexanes (10 mL) forming an oil.  *Rxn. KN1C7, KN1CB.*

**Reaction of Na(py)4Sm(S2CN(CH3)2)4py/HgF2/py:** Na(py)4Sm(S2CN(CH3)2)4py prepared by the above procedure and dried under N2 (0.63 g, 0.54 mmol) and HgF2 (0.125 g, 0.525 mmol) were stirred in pyridine (15 mL) for 3 days. The green solution was filtered from orange powder, concentrated to 10 mL and layered with hexanes (10 mL) producing dichromatic crystals Hg(S2CN(CH3)2)2 mostly looking green but some orange. The solution was filtered from the crystals, concentrated to < 1 mL, and put in a freezer (0 °C) producing yellow oil.  *Rxn. KN200.*

**Reaction of Eu/SPh/Hg/Se/CF3SO3H/py:** Eu (0.152 g, 1.00 mmol), PhSSPh (0.327 g, 1.50 mmol), and Hg (0.013 g, 0.065 mmol) were stirred in pyridine (15 mL) for 4 days. Selenium (0.082 g, 1.0 mmol) was added to the red solution and stirred for 4 days.
CF₃SO₃H (0.09 mL, 1 mmol) was added to the dark red solution and stirred overnight. The dark red solution was filtered, concentrated to 10 mL, layered with hexanes (10 mL), and covered in foil producing black amorphous precipitate and an orange solution. *Rxns. KN212, KN236.*

**Reaction of Sm/SPh/Hg/Se/CF₃SO₃H/py:** Sm (0.150 g, 1.00 mmol), PhSSPh (0.332 g, 1.52 mmol), and Hg (0.029 g, 0.14 mmol) were stirred in pyridine (12 mL) for 3 days. Selenium (0.162 g, 2.05 mmol) was added to the green solution and stirred for 4 days. CF₃SO₃H (0.09 mL, 1 mmol) was added to the yellow solution and large amount of green powder and stirred for 2 days. The red-orange solution was filtered from black precipitate and layered with hexanes (12 mL) forming orange powder. *Rxn. KN214, KN215, KN229, KN23A, KN23B.*

**Reaction of CH₃C(O)CH₂C(O)CH₃/Na/Nd/SePh/HgF₂/py:** Na (0.025 g, 1.1 mmol) and acetylacetone (0.1 mL, 1 mmol) were stirred in pyridine (15 mL) for 2 days. Nd (0.144 g, 1.00 mmol) and PhSeSePh (0.468 g, 1.50 mmol) were added to the colorless solution with off-white precipitate and stirred for 9 days. HgF₂ (0.350 g, 1.47 mmol) was added to the resulting dark green solution with black solid and stirred in an oil bath (120 °C) for several days. The very dark, possibly red, solution was filtered from brown precipitate and layered with hexanes (10 mL) producing black precipitate leaving a red solution. *Rxns. KN218, KN21C.*
Reaction of Ln(III)/SePh/Hg/(CH$_3$)$_2$NCS$_2$∙xH$_2$O/HgF$_2$: Er (0.167 g, 1.00 mmol), PhSeSePh (0.465 g, 1.00 mmol), and Hg (0.016 g, 0.08 mmol) were stirred in pyridine (15 mL) for 9 days before adding (CH$_3$)$_2$NCS$_2$ to the brown solution and stirred overnight. HgF$_2$ (0.186 g, 0.706 mmol) was added to the orange solution and stirred for one month. The yellow solution was filtered from minor brown precipitate and layered with hexanes (15 mL) producing yellow crystals, HgS$_2$CN(CH$_3$)$_2$. Cooling to -5 °C crystallized PhSeSePh. *Rxns. KN219, KN21A.*

Reaction of Dy/SePh/Hg/S/C$_6$F$_5$OH/py: Dy (0.163 g, 1.00 mmol), PhSeSePh (0.468 g, 1.50 mmol), and Hg (0.016 g, 0.08 mmol) was stirred in py (15 mL) for 8 days making a gray solution. C$_6$F$_5$OH (0.180 g, 0.978 mmol) was added and stirred 2 weeks. The green solution was filtered from minor black precipitate and concentrated to 8 mL. A solution of S (0.064 g, 2.0 mmol) in py (15 mL) was layered on top and refrigerated to -5 °C. Red and yellow solids, believed to be (py)$_4$Dy(C$_6$F$_5$OH)$_3$ and (py)$_6$Dy$_2$S$_4$(C$_6$F$_5$OH)$_2$ were produced but not isolated or tested. *Rxn. KN21B.*

Reaction of Eu/SePh/Hg/S/NH(CH$_2$CH$_2$NH$_2$)$_2$/py: Eu (0.152 g, 1.00 mmol), PhSeSePh (0.324 g, 1.04 mmol), and Hg (0.010 g, 0.05 mmol) were stirred in pyridine for 3 days. Sulfur (0.040 g, 1.2 mmol) was added to the red solution and stirred overnight. Diethylenetriamine (0.10 mL, 0.93 mmol) was added to the dark red solution and immediately filtered after liberal shaking formed brown precipitate. The red solution (18 mL) was layered with hexanes (10 mL) forming brown-black powder which wasn’t identified. *Rxns. KN232, KN233.*
Reaction of Ce/SePh/Hg/Se/CF$_3$SO$_3$H/py: Ce (0.145 g, 1.04 mmol), PhSeSePh (0.478 g, 1.53 mmol), and Hg (0.018 g, 0.090 mmol) were stirred in pyridine (20 mL) for 5 days. Selenium (0.159 g, 2.01 mmol) was added to the green solution and stirred for 9 days. CF$_3$SO$_3$H (0.1 mL, 1 mmol) was added to the dark brown solution and stirred for 30 min. Dark red solution was filtered from brown solid and layered with hexanes (20 mL) producing brown powder. *Rxn. KN249.*

ORTEP of (DME)$_4$Eu$_3$(SPh)$_5$(OC$_6$F$_5$)$_2$ with H atoms omitted
POV of (py)$_{10}$Y$_8$O$_2$(SO$_3$)$_9$(OC$_6$F$_5$)$_2$ with H atoms omitted
ORTEP of [Eu(S₂CN(CH₂CH₃))₄]⁻ with H atoms omitted
POV of ([Na(µ-OH₂)₂(µ-OH₂)Na(µ-OH₂)₂(THF)][SePh]₂)ₙ
ORTEP of Na\textsubscript{(py)}\textsubscript{4}Sm\textsubscript{2}CN(CH\textsubscript{3})\textsubscript{2}\textsubscript{4} with H atoms omitted
Ortep of Zn₈(SePh)₁₂((CH₂C₆H₅)₂NCS₂)₄*THF with H atoms omitted

POV of [(THF)₃Yb(S₂CN(CH₂C₆H₅)₂)₂]₂[Yb₄HgZn₄Se(SePh)₁₈] with C and H atoms Omitted
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