Lanthanide Compounds with Fluorinated OC₆F₅ Ligands: Homo- and Heterovalent Complexes of Eu(II) and Eu(III)

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The fluorinated phenoxide OC₆F₅ forms the stable Eu(II) and Eu(III) derivatives (DME)₂Eu(OC₆F₅)_3 and Eu(DME)(OC₆F₅)₂, as well as the heterovalent product (DME)₂Eu(OC₆F₅)_3Eu(DME)(OC₆F₅)₂, in redox reactions of Eu with HOC₆F₅ or in proton-transfer reactions of HOC₆F₅ with Eu(SPh)_2. The divalent complex crystallizes as a trimer with three bridging phenoxides bridging each pair of metals, with the terminal metals coordinating DME and the central metal ion encapsulated totally by O(C₆F₅) and dative fluoride interactions. The trivalent compound is monomeric with terminal phenoxide ligands and no Eu–F interactions. The heterovalent compound has clearly localized metal valence states and coordination features that mimic the homovalent species with the terminal OC₆F₅ bound to the Eu(III) ion, three bridging OR ligands spanning the Eu(II) and Eu(III) ions, and dative Eu(II)–F bonds. At elevated temperatures, these compounds decompose to give a mixture of solid-state fluoride phases.

Introduction

Fluorinated ligands impart unique chemical and physical properties to metal compounds, including superior solubility/volatility properties, unusual crystal packing motifs, and the stabilization of elements in high oxidation states. A number of fluorinated ligand systems have been used in lanthanide (Ln) chemistry. Most developed is the Ln chemistry of the nonchelating fluorinated ligand systems. The fluorinated thiolate structures invariably display dative interactions that are largely absent in related transition metal systems. The fluorinated thiolate structures invariably contained extensive π–π stacking interactions, a structural motif that has also been noted in related transition metal systems. These fluorinated Ln thiolates displayed remarkable NIR emission properties because the absence of CH bonds in the anionic ligand, coupled with the low Ln–S

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Ln Compounds with OC$_6$F$_5$ Ligands

phonon energies, minimizes competitive vibrational relaxation pathways.

The fluorinated phenoxy OC$_6$F$_5$ has been used frequently in main group$^5$ and transition metal$^6$ systems as a stabilizing, solubilizing, commercially available anion. This ligand has many properties that may be useful in lanthanide chemistry: OC$_6$F$_5$ has no C–H functional groups that might quench NIR emissions, and so it is potentially valuable for forming stable, emissive Ln complexes. The tendency of fluor substituents to enhance solubility properties is also important in composite emissive Ln complexes. The tendency of fluoro substituents in main group 9 and transition metal 10 systems as a stabilizing, reductively eliminates less electronegative EPh ligands (E = S, Se, Te) to form PhEPh and Eu(II) compounds.$^9$

Highly electronegative OC$_6$F$_5$ could be used as cluster capping reagents to produce soluble Eu sulfide complexes. Such materials are sought after for possible electronics applications, that is, as soluble analogs of Eu-doped Y$_2$O$_2$S,$^1$ the materials are sought after for possible electronics applications.

In this work, we outline our first experiments using OC$_6$F$_5$ to form stable Ln compounds. Our initial target is the chemistry of redox-active Eu, where we establish the stability and physical properties of both Eu(II) and Eu(III) compounds with OC$_6$F$_5$ ligands and the high yield synthesis of a heterovalent dimer.

Experimental Section

General Methods. All syntheses were carried out under ultrapure nitrogen (WELCO CGI, Pine Brook, NJ), using conventional dry box or Schlenk techniques. Dimethoxyethane (DME), hexane, and pyridine (Fisher Scientific, Agawam, MA) were purified with a dual-column Solv-Tek solvent purification system (Solv-Tek Inc., Berryville, VA). Eu and Hg were purchased from Strem Chemicals (Newburyport, MA). HOC$_6$F$_5$ was purchased from Aldrich. Melting points were taken in sealed capillaries and are uncorrected. IR spectra were taken on a Thermo Nicolet Avatar 360 FT-IR spectrometer and were recorded from 4000 to 600 cm$^{-1}$ as Nujol mulls on NaCl plates. Electronic spectra were recorded on a Varian DMS 100S spectrometer with the samples in a 1.0 mm quartz cell attached to a Teflon stopcock. Powder diffraction spectra were obtained from Bruker AXS D8 Advance diffractometer using Cu Kα radiation. Elemental analyses were performed by Quantitative Technologies, Inc. (Whitehouse Station, NJ).

Synthesis of (dme)Eu($\cdot$OC$_6$F$_5$)$_2$Eu($\cdot$OC$_6$F$_5$)$_2$Eu(dme)$_2$ (1). Eu metal (0.15 g, 1.0 mmol), C$_2$F$_5$OH (0.31 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%).

Table 1. Summary of Crystallographic Details for 1–3

<table>
<thead>
<tr>
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<th>1</th>
<th>2</th>
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<td>C$<em>{8}$H$</em>{10}$Eu$<em>{5}$F$</em>{10}$O$_{12}$</td>
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<td>tw</td>
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<td>881.38</td>
<td>1486.56</td>
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<td>C2/c</td>
<td>P2$_{1}$/n</td>
<td>Cc</td>
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<td>10.4086(5)</td>
<td>11.9347(6)</td>
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<td>c (Å)</td>
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<td>23.480(1)</td>
<td>20.660(1)</td>
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<td>90.585(1)</td>
<td>104.768(1)</td>
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<td>3116.6(3)</td>
<td>5006.4(4)</td>
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<td>Z</td>
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<td>4</td>
<td>4</td>
</tr>
<tr>
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<td>1.972</td>
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<td>0.71073</td>
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<tr>
<td>abs coeff (mm$^{-1}$)</td>
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<td>2.145</td>
<td>2.632</td>
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<tr>
<td>R(F$^2$) [I &gt; 2σ(I)]</td>
<td>0.0320</td>
<td>0.0212</td>
<td>0.0424</td>
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<td>R$_{w}$(F$^2$) [I &gt; 2σ(I)]</td>
<td>0.0797</td>
<td>0.0237</td>
<td>0.0760</td>
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</table>

Method B: Eu metal (0.15 g, 1.0 mmol), C$_{8}$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 2 (0.36 g, 42%).

Synthesis of (dme)$_{2}$Eu(OC$_{6}$F$_{5}$)$_{3}$ (3). Method A. Eu metal (0.14 g, 0.92 mmol), (SPh)$_{2}$ (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$_{8}$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. Anal. Calcd for C$_{42}$H$_{30}$Eu$_{2}$F$_{25}$O$_{11}$: C, 33.6; H, 2.25. The UV-visible absorption maxima attributable to a MLCT excitation could be defined. IR: 1068 (m), 1016 (m), 860 (m), 834 (w), 721 (m), 634 (m), 1382 (s), 1311 (m), 1246 (m), 1177 (m), 1164 (m), 1113 (m), 2923 (s), 2853 (s), 2670 (w), 2457 (w), 1651 (m), 1504 (s), 1455 (s).

Results

Divalent and trivalent Eu complexes with OC$_{6}$F$_{5}$ ligands are most easily prepared by direct oxidation of the metal.
bridging phenoxy groups (with Eu–O bond lengths that range from 2.457(2) to 2.569(2) Å) and two DME ligands (with Eu–O bond lengths that range from 2.638(2) to 2.757(3) Å) to give a seven-coordinate environment with three additional remote Eu–F interactions to the α-C–F atoms at 3.004(2), 3.013(2), and 3.32(1) Å.

Pyridine solutions of this yellow compound are deep orange, but an absorption maximum that would correspond to an Eu-to-pyridine charge-transfer excitation could not be obtained.

Trivalent 2 is monomeric with three terminal OC₆F₅ (three Eu–O in the range of 2.205(1)–2.415(1) Å) and two chelating DME ligands (four Eu–O in the range of 2.456(1)–2.492(1) Å). Figure 2 shows an ORTEP diagram of the complex with significant distances and angles given in the figure caption. Within the three phenoxy in 2, there is a wide range of Eu–O–C angles (C(1)–O(1)–Eu(1) = 164.22(12)°, C(7)–O(2)–Eu(1) = 132.23(10)°, C(13)–O(3)–Eu(1) = 149.21(11)°), with the larger angles found for the ligands with the shortest Eu–O bond lengths. There are no significant Eu–F interactions present because the six distances to α-C–F atoms range from 3.54(1) to 4.63(1) Å.

Bimetallic 3 is a localized heterovalent material. An ORTEP diagram of the molecule is given in Figure 3, and significant distances and angles are given in Table 3. The divalent Eu(1) ion bound to a pair of chelating DME ligands (four Eu–O in the range of 2.643(4)–2.696(5) Å), three bridging phenoxide oxygen atoms (three Eu–O in the range of 2.551(4)–2.591(4) Å), and three short Eu(1)–F interactions (2.796(4), 2.835(4), and 3.109(5) Å), of which the first two are closer to the “expected” distances for a formal Eu²⁺F dative interaction. The trivalent Eu(2) ion coordinates the three bridging phenoxy groups (three Eu–O in the range of 2.348(4)–2.410(4) Å), a pair of terminal phenoxide ligands (2.223(4) and 2.221(4) Å), and one chelating DME ligand (Eu–O bond lengths of 2.482(4) and 2.537(4) Å). The nearest Eu(2)³⁺–F contact interaction is at 3.072(4) Å, and the other three are in the range of 3.82–4.14 Å.

In 3, the metal oxygen bond lengths are clearly indicative of localized oxidation states. The three bridging Eu–O(C₆F₅) bond lengths average 2.57 Å for divalent Eu(1) and 2.37 Å for trivalent Eu(2). Similarly, for the neutral donors, the Eu–O(DME) average for Eu(1) is 2.66 Å, while that for Eu(2) is 2.51 Å. Given the smaller ionic radius of Eu³⁺, there does

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

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<tr>
<th>Distances/Angles</th>
<th>Eu(1)–O(1)</th>
<th>Eu(1)–O(2)</th>
<th>Eu(1)–O(3)</th>
<th>Eu(1)–O(4)</th>
<th>Eu(1)–O(5)</th>
<th>Eu(1)–O(6)</th>
<th>Eu(1)–O(7)</th>
<th>Eu(1)–O(8)</th>
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<tr>
<td>Eu(1)–O(2)</td>
<td>2.533(2)</td>
<td>2.590(2)</td>
<td>2.570(2)</td>
<td>2.796(4)</td>
<td>2.537(4)</td>
<td>2.696(5)</td>
<td>2.569(2)</td>
<td>2.591(4)</td>
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<tr>
<td>Eu(1)–O(3)</td>
<td>3.7528(2)</td>
<td>2.457(2)</td>
<td>2.569(2)</td>
<td>3.013(2)</td>
<td>2.676(2)</td>
<td>2.757(3)</td>
<td>2.492(1)</td>
<td>2.410(4)</td>
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<tr>
<td>Eu(2)–O(1)</td>
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<td>2.509(2)</td>
<td>2.643(4)</td>
<td>3.004(2)</td>
<td>3.013(2)</td>
<td>3.013(2)</td>
<td>2.410(4)</td>
<td>2.591(4)</td>
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<tr>
<td>Eu(2)–O(2)</td>
<td>2.638(2)</td>
<td>2.676(2)</td>
<td>2.757(3)</td>
<td>3.013(2)</td>
<td>3.013(2)</td>
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<td>2.410(4)</td>
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<td>C(1)–O(1)–Eu(2)</td>
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<td>123.5(2)</td>
<td>120.6(2)</td>
<td>120.4(5)</td>
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<td>C(7)–O(2)–Eu(1)</td>
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<td>133.5(2)</td>
<td>120.6(2)</td>
<td>120.4(5)</td>
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<td>120.4(5)</td>
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<tr>
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<td>120.6(2)</td>
<td>120.4(5)</td>
<td>120.4(5)</td>
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<td>Eu(2)–O(1)–Eu(1)</td>
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<td>96.74(8)</td>
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<td>96.74(8)</td>
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<tr>
<td>Eu(1)–O(3)–Eu(2)</td>
<td>94.27(7)</td>
<td>166.33(1)</td>
<td>166.33(1)</td>
<td>166.33(1)</td>
<td>166.33(1)</td>
<td>166.33(1)</td>
<td>166.33(1)</td>
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</table>

Figure 3. ORTEP diagram of heterovalent (DME)₂Eu(OC₆F₅)_₅: green, F; red, O; blue, Eu; gray, C. The H atoms were removed for clarity.
not appear to be a significant Eu(III)–F interaction, including the Eu(2)–F(5) separation at 3.072(4) Å. While both 1 and 2 are yellow crystalline solids, heterovalent 3 is deep orange.

When they are heated at 650 °C for 5 h, these compounds give a variety of solid-state EuF₃ phases, with the trivalent compound 2 giving a single LnF₃ phase and compounds 1 and 3 showing a pair of LnF₃ phases.¹⁹ CGMS analysis of the volatile products did not reveal the identity of the organic fluoride abstraction product.

Discussion

Direct reduction of HOR with elemental Ln is a particularly facile synthetic route to divalent and trivalent fluorinated phenoxides of Eu. Similar reactivity was noted in the preparation of Eu(OR)₂ₓ (R = C₆H₄Me₂, 2,6, 2,6-Me₂C₆H₃)(THF)₆, another linear trimer with an alkoxide and its 2-fold symmetry mate from reactions that were expected to yield Eu(O iPr)₂, ²¹c, ²² but these reactions required highly basic (NH₃, MeCN, N-methylimidazole) solvents. This chemistry is not necessarily extendable to the other R groups previously employed in Eu alkoxide syntheses, that is, the analogous isopropoxide of in situ-prepared Eu(O iPr)₂ with HOC₆H₃Me₂-2,6 led to the isolation of the phenoxide species.

The compounds that contain Eu(III) (2 and 3) can also be prepared in proton-transfer reactions of HOOCF₃ with in situ-prepared Eu(SPh)₂ (reaction 2). Attempts to isolate heteroleptic compounds (i.e., Eu(SPh)₂(OOCF₃)₂) from these reactions led only to the isolation of the phenoxide species.

Heterovalent lanthanide compounds are relatively uncommon, ²³ with all well-defined systems thus far behaving as localized valence materials, as is dimer 3. The absence of any crystallographic disorder in 3 is fortunate because the asymmetry of the complex allows for immediate assignment of oxidation states for divalent Eu(1) and trivalent Eu(2).

Within the structures, bond lengths can be predicted with ionic radius summation rules, ²⁴ where the difference between Eu(II) and Eu(III) Eu–O bond lengths is 0.20 Å, the ionic radii difference. ²⁵ Differences between the dative Eu–O(DME) bond lengths are slightly less than the predicted value, with a difference between Eu(II) and Eu(III) of 0.15 Å, and are probably more affected by steric considerations.

The constancy of the Eu–F contacts is even less ideal. In divalent 1, there are short Eu–F separations for both the internal (Eu(1)–F(1) = 2.928(2) Å) and external (Eu(2)–F(15) = 3.004(2) Å, Eu(2)–F(10) = 3.013(2) Å) metal ions, and the distances are similar to the 3.006(6) Å separation found in the related thiolate polymer [(THF)₂Eu(SC₆F₅)₃]ₙ.

There are no significant Eu(III)–F bonds in 2. Similarly, in 3, there are no significant Eu(III)–F interactions, whereas there are Eu–F bonds to the divalent ion that are within the range found in 1. One possible explanation for the different behavior between Ln(II) and Ln(III) is that electrostatic bonds to the former are weaker, and thus entropy considerations determine whether a phenoxide chelates or a neutral molecule coordinates to saturate a metal center. It should also be pointed out that such interactions with Ln(III) are not impossible, given similar distances in Sm(SC₆F₅)₃ coordination compounds (i.e., 2.582(7) and 2.641(6) Å in (THF)₂Sm₂(SC₆F₅)₆, ⁶⁰ but the electronegativity of O and the tendency for OR ligands to adopt more linear Ln–O–R geometries certainly disfavors the formation of Ln=F bonds.

Obvious π-stacking interactions are prevalent throughout the structures of 1–3, as found in both the analogous thiolates, as well as transition metal phenoxides. Monomeric 2 contains intra- and intermolecular π–π interactions along the crystallographic b+c direction. The intramolecular π–π interaction between the O(2) and O(3) C₆F₅ rings is quite close with a dihedral angle of 6.5° and a center-to-center distance of about 3.5 Å. This intramolecular π–π interaction links up with an adjacent coplanar pair (inversion related O(2’) and O(3’) with a dihedral angle of 0.0° and a 3.6 Å center-to-center distance) in one direction (b+c) and with a somewhat tilted O(1’) alkoxide C₆F₅ ring (with a dihedral angle of 18° and a 3.8 Å center-to-center distance) in the opposite direction (b–c) to yield true 1-D π-stacking overall.

The dimeric complex 3 has a remote π–π interaction (e.g., only 2 C atoms overlap, with a separation of > 4 Å) between arylxides at O(1) and O(3’) along the unit cell body diagonal. Within one dimer, no pair of C₆F₅ planes are even remotely coplanar, but the possibility of some π–π interaction does exist, namely, between rings O(1) and O(5) with a dihedral of 19°, because the center-to-center distance is short at 3.3 Å.

For the trimeric complex 1, the only π–π interaction is found within one trimer subunit, between the central bridging alkoxide and its 2-fold symmetry mate (e.g., O(3) and O(3’)). The two C₆F₅ rings for this π–π interaction are nearly coparallel; although they are not crystallographically constrained to be so, with a dihedral angle of only 4.4°.

Ln Compounds with OC$_6$F$_5$ Ligands

The effects of fluorination on the Eu–O bond length can be assessed, given the relative abundance of Eu–O–Ar bond lengths in the literature. Most straightforward would be comparisons with terminal phenoxide linkages, which seem to have a narrower range of separations relative to bridging interactions. Of the reported phenoxide compounds, three are reasonable for comparative purposes: in (diglyme)$_2$(DME)Ba$_2$Eu(OC$_6$H$_4$-4-Me)$_7$,\(^{26}\) the six coordinate Eu ion coordinates two terminal OAr with Eu–O bond lengths of 2.16(1) and 2.19(1) Å; in (pyrazolylborate)Sm(OC$_6$H$_4$-4-Pr)$_7$,\(^{27}\) the seven coordinate Sm ion bonds to a single phenoxide with a 2.16(1) Å Sm–O bond length; and in (DME)$_2$TmI$_2$(OC$_6$H$_5$)$_9$,\(^{28}\) the seven coordinate Tm(III) ion bonds to a single phenoxide with a 2.025(7) Å Tm–O bond length (the lanthanide contraction here is responsible for the Tm–O distances being shorter by ∼0.06 Å). When we compare the terminal Eu(III)–O distances in 2 (av 2.22(1) Å) and 3 (2.221(4) Å), it is clear that the bond lengths are significantly longer. This is attributed to the polarizing effect of the fluorine substituents, delocalizing the anionic charge and weakening the Ln–O bond.

In contrast, bridging Eu–O bond lengths for divalent 1 fall within the range of bridging distances found in the similar set of DME, THF, and N-methylimidazole coordination complexes of Eu(OC$_6$H$_3$Me$_2$-2,6)$_2$.\(^{26}\) These bridging bonds are both weaker electrostatically because of the lower charge on the Eu ion and more sensitive to steric influences with repulsions from two primary coordination spheres contributing to the observed distances.

The electronic properties of these compounds are readily understood. For Eu(II), there are allowed f–d transitions that fall in the UV spectrum when the ligands are relatively electronegative.\(^{29}\) Divalent Eu compounds also exhibit allowed MLCT transitions when the ligand has accessible $\pi^*$ orbitals. Divalent 1 is yellow, both in solution and as a DME adduct, because the only visible chromophore is the high-energy f–d process that tails into the visible portion of the spectrum. The addition of pyridine results in displacement of MLCT bands by the more basic nitrogen donor ligand, and upon coordination, there exists an allowed Eu-to-py CT process\(^{30}\) that generates a deep orange color, which unfortunately could not be defined quantitatively by a maximum in the absorption spectrum.

Trivalent Eu(III) compounds have characteristically weak ($\epsilon < 1$) f–f transitions, and absorptions from these transitions are noted in the visible spectra of both 2 and 3. When 2 and 3 are dissolved in DME, the visible spectra are essentially identical, but this is likely caused by the general insensitivity of f–f transitions to coordination environment and not by the solution state environments for the Eu(II) ions in 2 and 3 being identical. It should be noted that the absorption maxima are within 1–2 nm of the maxima found for a series of Eu(III) isopropoxo compounds.

Still, trivalent Eu compounds can be intensely colored, if the anions are sufficiently electropositive such that LMCT absorptions are in the visible, rather than UV portion of the spectrum. Examples of intensely colored Eu(III) compounds are those that contain sulfur-based anions such as S$_2$-NC$_x$H$_y$\(^{30c}\) or S$_2$CR\(^{32}\) or organometallic complexes such as (C$_5$H$_5$)$_2$Eu(THF).\(^{30}\) The fluorinated phenoxo anions are apparently electronegative enough to shift any phenoxide-related MLCT absorption into the UV spectrum, and so 2 is also light yellow.

Heterovalent 3 has two metal ions that are intrinsically light yellow derivatives of 1 and 2, and so the deeper color of 3 in the solid state may arise from an excitation process that transfers an electron from Eu(II) to Eu(III). Similar highly colored combinations of colorless ions has been observed previously in deep red heterovalent Ce$_2$O(OPr)$_3$, which is derived from yellow Ce(IV) and white Ce(III) alkoxides.\(^{33}\)

The presence of fluorine within the phenoxide ligand system complicates compound thermolysis because, in addition to the formation of pure oxide phases, fluorides can be abstracted to form either oxyfluorides or trifluoride solids. LnOF phases have been obtained frequently from oxygen based ligand systems, that is, in the decomposition of fluorinated diketonates\(^1,34\) and carboxylates.\(^2,35\) The trifluorides have only been noted in the thermolysis of fluorinated thioketones, in which the formation of relatively electropositive sulfide anions is clearly less favorable from an electrostatic perspective. In the present compounds, rapid thermolysis of 1–3 led to the formation of a mixture of solid-state EuF$_3$ phases with no indication of oxide materials. Apparently the ary transfer decomposition pathway that dominates the thermolysis of M(EPh)$_3$ systems ($E = S, Se, Te$)\(^{36}\) is inhibited by the strength of the C–O bond. This reactivity is still surprising, given the facility with which oxyfluoride solids have been prepared from fluorinated molecular precursors.

Oxidation of the divalent Ln ions by abstraction of fluoride

(34) Geloshov, N. I.; Suglobov, D. N.; Sidenenko, G. V. Radiokhimiya 1995, 37, 196.
has been noted previously for Sm and Yb organometallic complexes, but not for Eu(II), which has a more stable divalent oxidation state. The oxidation of Eu(II) to Eu(III) in the thermolysis of both 1 and 3 is presumably facilitated by the presence of highly electronegative anions that can stabilize the higher oxidation state. Unfortunately, there were no organic products that could be identified in these reactions.

**Conclusion**

The OC<sub>6</sub>F<sub>5</sub> ligand forms easily isolated compounds with both divalent and trivalent europium. Dative Ln–F interactions are noted with Eu(II) ions, while Eu(III) ions tend to adopt terminal phenoxide ligations. The OC<sub>6</sub>F<sub>5</sub> ligands bound to both Eu(II) and Eu(III) are involved in π stacking interactions. Because these phenoxides are soluble in apolar media, they are potentially useful as capping reagents in lanthanide cluster chemistry, and efforts along this direction are in progress.

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

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