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Lanthanide Compounds with Fluorinated OC_6F_5 Ligands: Homo- and Heterovalent Complexes of Eu(II) and Eu(III)

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The fluorinated phenoxide OC_6F_5 forms the stable Eu(II) and Eu(III) derivatives $(DME)_2Eu(\mu\text{-}OC_6F_5)_3Eu(\mu\text{-}OC_6F_5)_3\text{-}Eu(DME)_2$ and $(DME)_2Eu(OC_6F_5)_3$, as well as the heterovalent product $(DME)_2Eu(\mu\text{-}OC_6F_5)_3Eu(DME)(OC_6F_5)_2$, in redox reactions of Eu with HOC_6F_5 or in proton-transfer reactions of HOC_6F_5 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 $O(C_6F_5)$ 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 OC_6F_5 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 fluorinated acetylacetonate[1] and acetate ligands[2] because these volatile air-stable molecules can be used as volatile Ln sources for the synthesis of LnO_x thin films that have useful dielectric properties.[3]

Nonchelating fluorinated ligands have been investigated less extensively. Lanthanide compounds with fluorinated *t*-butoxides,[4] amido ligands such as $N(C_6F_5)_2$ or $N(SiMe_3)\text{-}(NC_6F_5)$,[5] and the arenethiolate SC_6F_5[6] have been described, and in the amido and thiolate compounds, there are Ln−F dative interactions that are largely absent in related transition metal systems. The fluorinated thiolate structures invariably contained extensitve $\pi-\pi$ stacking interactions, a structural motif that has also been noted in related transition metal compounds.[7] These fluorinated Ln thiolates displayed remarkable NIR emission properties[8] because the absence of CH bonds in the anionic ligand, coupled with the low Ln−S

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phonon energies, minimizes competitive vibrational relaxation pathways.

The fluorinated phenoxide OC_6F_5 has been used frequently in main group[9] and transition metal[10] systems as a stabilizing, solublizing, commercially available anion. This ligand has many properties that may be useful in lanthanide chemistry: OC_6F_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 fluoro substituents to enhance solubility properties is also important in composite materials synthesis.[11] Finally, such an electronegative pseudochalcogenolate is also potentially useful in the synthesis of chalcogenido clusters of Eu(III) because Eu(III) reductively eliminates less electronegative EPh ligands (E = S, Se, Te) to form PhEEPh and Eu(II) compounds.[12] Highly electronegative OC_6F_5 could be used as cluster capping reagents to produce soluble Eu sulfide clusters. Such materials are sought after for possible electronics applications, that is, as soluble analogs of Eu-doped Y_2O_2S,[13] the red phosphor in CRT screens.

In this work, we outline our first experiments using OC_6F_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_6F_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_6F_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 $(dme)_2Eu(\mu_2\text{-}OC_6F_5)_3Eu(\mu_2\text{-}OC_6F_5)_3Eu(dme)_2$ (1). Eu metal (0.15 g, 1.0 mmol), C_6F_5OH (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%) that become darker yellow at 160−170 °C and melt at 220 °C. Anal. Calcd for $C_{52}H_{40}Eu_3F_{30}O_{14}$: 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 $Eu(OC_6F_5)_3(dme)_2$ (2). 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_6F_5OH (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 ($\epsilon = 9 \times 10^{-2}$ L mol^{-1} cm^{-1}) and 529 nm ($\epsilon = 1.5 \times 10^{-1}$ 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}.

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

	1	**2**	**3**
empirical formula	$C_{52}H_{40}Eu_3F_{30}O_{14}$	$C_{26}H_{20}EuF_{15}O_7$	$C_{42}H_{27}Eu_2F_{25}O_{11}$
fw	1914.72	881.38	1486.56
space group	*C*2/*c*	*P*2$_1$/*n*	*Cc*
a (Å)	20.6837(12)	10.4086(5)	11.9347(6)
b (Å)	13.6138(8)	12.8244(6)	20.997(1)
c (Å)	22.0265(13)	23.480(1)	20.660(1)
β (deg)	92.989(1)	96.058(1)	104.768(1)
V (Å^3)	6193.9(6)	3116.6(3)	5006.4(4)
Z	4	4	4
D_{calcd} (g cm^{-3})	2.053	1.878	1.972
temp (K)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
abs coeff (mm^{-1})	3.153	2.145	2.632
$R(F)^a$ [$I > 2\sigma(I)$]	0.0320	0.0212	0.0424
$R_w(F^2)^b$ [$I > 2\sigma(I)$]	0.0797	0.0237	0.0760

^{a} $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Method B. Eu metal (0.15 g, 1.0 mmol), C_6F_5OH (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)(OC$_6$F$_5$)$_2$Eu(μ_2-OC$_6$F$_5$)$_3$Eu(dme)$_2$ (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_6F_5OH (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 $C_{42}H_{30}Eu_2F_{25}O_{11}$: C, 33.9; H, 2.03. Found: C, 33.6; H, 2.25. The UV−vis (DME) spectrum contained peaks at 575 ($\epsilon = 5 \times 10^{-2}$ L mol^{-1} cm^{-1}) and 529 nm ($\epsilon = 1 \times 10^{-1}$ 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), C_6F_5OH (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 **3** (0.096 g, 26%).

Thermolysis and X-ray Powder Diffraction Measurements. Samples of **1**−**3** were placed in quartz tubes that were then sealed under vacuum. The end of the tubes with the samples were placed side by side in an oven; the temperature was raised (20 °C min^{-1}) to 650 °C and held for 5 h. The other end of the thermolysis tubes were kept in liquid nitrogen during the experiment. Black powders formed and X-ray powder diffraction patterns were obtained by scanning from 20 to 80°.

X-ray Structure Determination. Data for **1**−**3** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 100 K. Crystals were immersed in Paratone oil and examined at low temperatures. The data were corrected for Lorenz effects, polarization, and absorption, the latter by a multiscan (SADABS)[14] method.

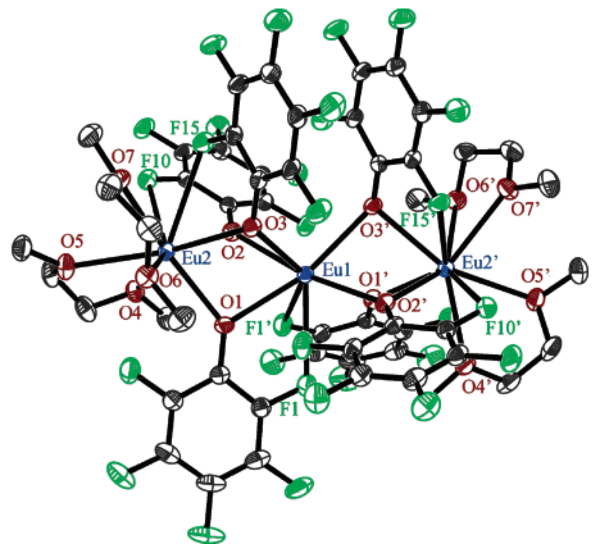

Figure 1. ORTEP diagram of trimetallic $(DME)_4Eu_3(OC_6F_5)_6$: green, F; red, O; blue, Eu; gray, C. The H atoms were removed for clarity.

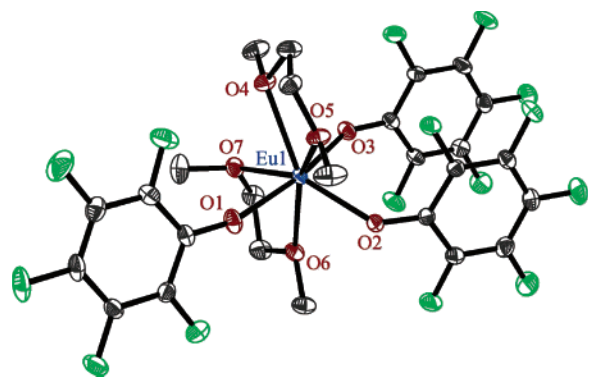

Figure 2. ORTEP diagram of molecular $(DME)_2Eu(OC_6F_5)_3$: green, F; red, O; blue, Eu; gray, C. The H atoms were removed for clarity. Significant distances (Å) and angles (deg): Eu(1)−O(1) = 2.205(1), Eu(1)−O(2) = 2.245(1), Eu(1)−O(3) = 2.232(1), Eu(1)−O(5) = 2.456(1), Eu(1)−O(6) = 2.482(1), Eu(1)−O(7) = 2.488(1), Eu(1)−O(4) = 2.492(1), 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).

The structures were solved by direct methods (SHELXS86).[15] All non-hydrogen atoms were refined (SHELXL97)[16] on the basis of F_{obs}^2. All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97). Scattering factors (fo, f′, f″) are as described in SHELXL97. Crystallographic data and final R indices for **1**−**3** are given in Table 1. ORTEP diagrams[17,18] for **1**−**3** are shown in Figures 1−3, respectively. Complete crystallographic details are given in the Supporting Information.

Results

Divalent and trivalent Eu complexes with OC_6F_5 ligands are most easily prepared by direct oxidation of the metal

(14) *SADABS, Bruker Nonius Area Detector Scaling and Absorption Correction*, version 2.05; Bruker-AXS Inc.: Madison, WI, 2003.
(15) Sheldrick, G. M. *SHELXS86, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1986.
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(17) Johnson, C. K. *ORTEP II*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, **1976**.
(18) Sheldrick, G. M. *SHELXTL (XP)*, version 6.14; Bruker-AXS, Inc.: Madison, WI, 2000.

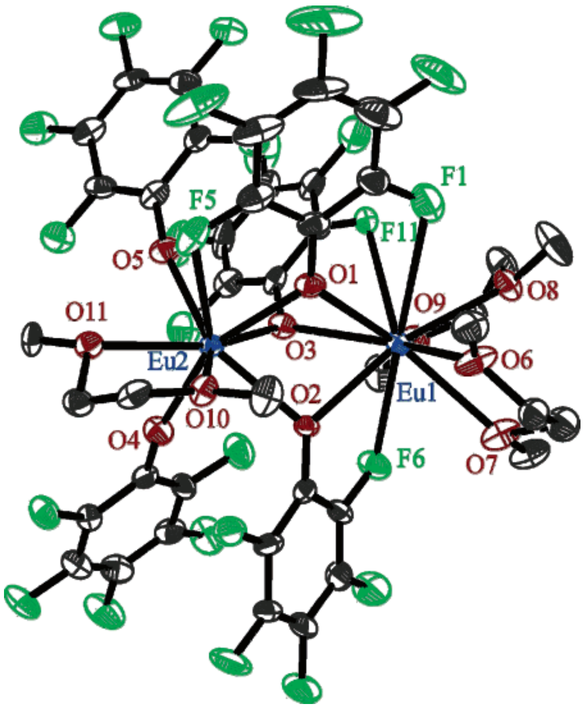

Figure 3. ORTEP diagram of heterovalent $(DME)_3Eu_2(OC_6F_5)_5$: green, F; red, O; blue, Eu; gray, C. The H atoms were removed for clarity.

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

Eu(1)−O(2)	2.533(2)	Eu(1)−O(1)	2.550(2)
Eu(1)−O(3)	2.551(2)	Eu(1)−F(1)	2.928(2)
Eu(1)−Eu(2)	3.7528(2)	Eu(2)−O(1)	2.457(2)
Eu(2)−O(2)	2.488(3)	Eu(2)−O(3)	2.569(2)
Eu(2)−O(4)	2.638(2)	Eu(2)−O(5)	2.667(2)
Eu(2)−O(7)	2.674(2)	Eu(2)−O(6)	2.757(3)
Eu(2)−F(15)	3.004(2)	Eu(2)−F(10)	3.013(2)
C(1)−O(1)−Eu(2)	136.0(2)	C(1)−O(1)−Eu(1)	127.0(2)
C(7)−O(2)−Eu(2)	129.4(2)	C(7)−O(2)−Eu(1)	133.5(2)
C(13)−O(3)−Eu(1)	129.9(2)	C(13)−O(3)−Eu(2)	120.6(2)
Eu(2)−O(1)−Eu(1)	97.07(8)	Eu(2)−O(2)−Eu(1)	96.74(8)
Eu(1)−O(3)−Eu(2)	94.27(7)	Eu(2)−Eu(1)−Eu(2′)	166.33(1)

with HOC_6F_5 (reaction 1), and the trivalent product can also be prepared in high yields from proton-transfer reactions of $Eu(SPh)_2$ with HOC_6F_5 (reaction 2).

$$\mathrm{Eu} + x\mathrm{HOC_6F_5} \rightarrow \mathrm{Eu(OC_6F_5\cdot)}_x + {}^{x}/_{2}\mathrm{H_2}\ (x = 2, 3) \quad (1)$$

$$\text{“Eu(SPh)}_2\text{”} + 3\mathrm{HOC_6F_5} \rightarrow \mathrm{Eu(OR)_3} + 2\mathrm{HSPh} + {}^{1}/_{2}\mathrm{H_2} \quad (2)$$

From DME, both divalent $(DME)_4Eu_3(OC_6F_5)_6$ (**1**) and trivalent $(DME)_2Eu(OC_6F_5)_3$ (**2**) were isolated and characterized completely. Trimer **1** contains a linear arrangement of Eu^{2+} ions. Figure 1 shows an ORTEP diagram of **1**, and Table 2 gives a listing of significant distances and angles for the complex. The central eight-coordinate Eu(1) is encapsulated by two sets of three μ_2-OC_6F_5 ligands and a symmetry-related pair of dative Eu(1)−F interactions to the F atom on the α-carbon, at 2.982(2) Å. The other Eu···F distances of this type are 3.21 and 4.26 Å and are outside the realm of dative interactions. The Eu(1)−O(C_6F_5) bond lengths range from 2.533(2) to 2.551(2) Å. The two end Eu^{2+} ions are symmetry related, and each coordinates three bridging phenoxides (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.

Table 3. Significant Distances (Å) and Angles (deg) for **3**

Eu(1)−O(1)	2.591(4)	Eu(2)−O(1)	2.373(4)
Eu(1)−O(2)	2.551(4)	Eu(2)−O(2)	2.410(4)
Eu(1)−O(3)	2.564(4)	Eu(2)−O(3)	2.348(4)
Eu(1)−O(6)	2.643(4)	Eu(2)−O(4)	2.223(4)
Eu(1)−O(8)	2.657(4)	Eu(2)−O(5)	2.221(4)
Eu(1)−O(9)	2.663(4)	Eu(1)−O(7)	2.696(5)
Eu(1)−F(11)	2.796(4)	Eu(1)−F(6)	2.835(4)
Eu(1)−F(1)	3.109(5)	Eu(2)−O(10)	2.482(4)
Eu(2)−O(11)	2.537(4)	Eu(2)−F(5)	3.072(4)
Eu(2)−O(1)−Eu(1)	96.60(14)	Eu(2)−O(2)−Eu(1)	96.77(13)
Eu(2)−O(3)−Eu(1)	97.99(14)	C(1)−O(1)−Eu(2)	129.1(4)
C(7)−O(2)−Eu(2)	126.4(4)	C(1)−O(1)−Eu(1)	130.5(4)
C(7)−O(2)−Eu(1)	122.8(4)	C(13)−O(3)−Eu(2)	126.8(4)
C(19)−O(4)−Eu(2)	161.0(4)	C(13)−O(3)−Eu(1)	120.4(4)
C(25)−O(5)−Eu(2)	164.3(4)		

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 OC_6F_5 (three Eu−O in the range of 2.205(1)−2.245(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 phenoxides 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 Eu^{2+}−F dative interaction. The trivalent Eu(2) ion coordinates the three bridging phenoxides (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(C_6F_5) 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 Eu^{3+}, there does 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 EuF_3 phases, with the trivalent compound **2** giving a single LnF_3 phase and compounds **1** and **3** showing a pair of LnF_3 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 $Eu(OR)_{2/3}$ (R = $C_6H_4Me_2$-2,6),[20] although these reactions required highly basic (NH_3, 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 system is considerably more complicated. Reactions of Eu with HO^iPr gave the heterovalent compound $[Eu_4(O^iPr)_{10}]$ from reactions that were expected to yield $Eu(O^iPr)_2$,[21c,22] and exposure to oxygen led to the isolation of $[Eu_5O(O^iPr)_{12}]$ and $[Eu_5O(O^iPr)_{13}]$.[21a,b] Additional reaction chemistry of in situ-prepared $Eu(O^iPr)_2$ with $HOC_6H_3Me_2$-2,6 led to both straightforward proton-transfer products (i.e., $Eu_3(O\text{-}2,6\text{-}Me_2C_6H_3)(THF)_6$, another linear trimer with an alkoxide encapsulated central Eu(II) ion), as well as a breathtaking array of polymetallic clusters, including $H_{10}[Eu_8O_8(OR)_{10}(O^iPr)_2(THF)_6]$ and $H_{18}\{[Eu_9O_8(OR)_{10}(THF)_7][Eu_9O_9(OR)_{10}(THF)_6]\}$.[22]

The compounds that contain Eu(III) (**2** and **3**) can also be prepared in proton-transfer reactions of HOC_6F_5 with in situ-prepared $Eu(SPh)_2$ (reaction 2). Attempts to isolate heteroleptic compounds (i.e., $Eu(SPh)_x(OC_6F_5)_{3-x}$) 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 $[(THF)_2Eu(SC_6F_5)_2]_n$. 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 $Sm(SC_6F_5)_3$ coordination compounds (i.e., 2.582(7) and 2.641(6) Å in $(THF)_4Sm_2(SC_6F_5)_6$),[6b] 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) C_6F_5 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 C_6F_5 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 aryloxides at O(1) and O(3)′ along the unit cell body diagonal. Within one dimer, no pair of C_6F_5 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 C_6F_5 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°.

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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 $(diglyme)_2(DME)Ba_2Eu(OC_6H_4\text{-}4\text{-}Me)_7$,[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-$(OC_6H_4\text{-}4\text{-}{}^tBu)$,[27] the seven coordinate Sm ion bonds to a single phenoxide with a 2.16(1) Å Sm−O bond length; and in $(DME)_2TmI_2(OC_6H_5)$,[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[20] coordination complexes of $Eu(OC_6H_3Me_2\text{-}2,6)_2$. 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 π^* 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 DME 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 characteristicly 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) isopropoxide 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_5H_4[30c,31] or S_2CR[32] or organometallic complexes such as $(C_5H_5)_3Eu(THF)$.[30] The fluorinated phenoxide anions are apparently electronegative enough to shift any phenoxide-related LMCT 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 $Ce_4O(O^iPr)_{13}$, 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 thiolates, 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 aryl transfer decomposition pathway that dominates the thermolysis of $M(EPh)_x$ 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

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has been noted previously for Sm and Yb organometallic complexes,[37] 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_6F_5 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_6F_5 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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