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The First Crystallographically Characterized (Perfluoroaryl)lanthanoid(II) Complex, $Eu(C_6F_5)_2(OC_4H_8)_5$

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*Summary: Reaction of europium metal with $Hg(C_6F_5)_2$ in thf (thf = tetrahydrofuran) followed by crystallization from thf/light petroleum affords the organoeuropium(II) complex $Eu(C_6F_5)_2(thf)_5$ (**1**). The X-ray crystal structure reveals axial C_6F_5 and equatorial thf ligands bound to a pentagonal-bipyramidal europium center.*

The organometallic chemistry of the 4f elements is characterized by much more ionic than covalent metal−carbon bonding, and π-bound carbocyclic anions such as cyclopentadienyl ligands (e.g., $C_5R_5^-$) are favored.[1] However, the exceptional reactivity of lanthanoid−σ-carbon fragments has stimulated extensive research in the isolation and characterization of $Ln^{III}R_3$ and $Ln^{II}R_2$ (R = alkyl, aryl) species.[1,2] Notably few in number are fluorocarbon ligands and, while (perfluoroaryl)lanthanoid compounds are known,[3] their stability is often limited due to facile fluoride migration driven by the formation of relatively strong Ln−F bonds.[4] Even so, we have successfully utilized $Ln-C_6F_5$ species as highly reactive synthetic intermediates for the preparation of lanthanoid cyclopentadienides, aryloxides, and diorganoamides (including pyrazolates) through "in situ" protolysis reactions with RH,[5a,b] ROH,[5c,d] and R_2NH.[5e,f] The unique (pentafluorophenyl)lanthanoid(II) species (e.g., $Yb(C_6F_5)_2$,[3a,b] $Yb(p\text{-}HC_6F_4)_2$,[3b] $Eu(C_6F_5)_2$,[3b] $Yb(C_6F_5)Br$[3c]) show moderate thermal stability (ca. 24 h at 20 °C; cf. $Li(C_6F_5)$ decomposes at −10 °C[6a]) and exhibit a high degree of reactivity (e.g., CO_2 insertion,[7a] $C_6F_5^-$ transfer,[7a,b] metalation[5a−c,e]) typical of an ionic organometallic, such as the commonly employed lithium reagents.[6] However, none of the above complexes have been unambiguously characterized by X-ray crystallography and only $Yb(C_6F_5)_2(thf)_4$ (thf = tetrahydrofuran) has been crystallized. We now report the isolation of $Eu(C_6F_5)_2$, which could not previously be crystallized,[3b]

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as $Eu(C_6F_5)_2(thf)_5$ (**1**) and its characterization by single-crystal X-ray diffraction. This is the first structure of a perfluoro-organolanthanoid complex, and it provides some insight into $Ln-C_6F_5$ bonding.

Reaction of $Hg(C_6F_5)_2$ with europium metal in thf under an inert atmosphere generates lemon yellow solutions of $Eu(C_6F_5)_2$ (eq 1).[8] Large yellow highly air-

$$Eu + Hg(C_6F_5)_2 \rightarrow Eu(C_6F_5)_2 + Hg \qquad (1)$$

and moisture-sensitive crystals of **1** were subsequently grown by addition of light petroleum to the filtered reaction mixture and cooling to −20 °C. These appeared moderately stable in suspension (~3 days) under these conditions, but, at room temperature under an argon atmosphere, significant deterioration of the *isolated* crystals occurred after only several hours with the formation of a black amorphous material. The infrared spectrum[8] of **1** was similar to that reported for $Yb(C_6F_5)_2(thf)_4$.[3b]

We were previously unable to obtain satisfactory low-temperature X-ray data for apparent single crystals of $Yb(C_6F_5)_2(thf)_4$. Utilizing the fast data collection capabilities of an area-detector diffractometer, excellent data were obtained for **1** at −150 °C.[9] The structure (Figure 1) comprises a monomeric and seven-coordinate europium(II) complex with two C_6F_5 and five thf ligands, situated on a crystallographic 2-fold axis through Eu(1) and O(4). The europium environment approximates a pentagonal bipyramid with axial C_6F_5 groups, and this appears to be a common structural motif for LnX_2L_5 species, e.g. $SmI_2(thf)_5$, $SmI_2(dme)(thf)_3$ (dme = 1,2-dimethoxyethane), $SmI_2(dme)_2(thf)$,[10a] $TmI_2(dme)_3$ (which contains one monodentate dme),[10b] and the lanthanoid(III) cations $[LnX_2(thf)_5]^+$ (X = Cl, I).[11] With the geometrical similarity of **1** and $SmI_2(thf)_5$ in mind, we predict that the structure of $Yb(C_6F_5)_2(thf)_4$ would therefore approximate that of $YbI_2(thf)_4$,[12] which has an octahedral geometry, with trans iodides.

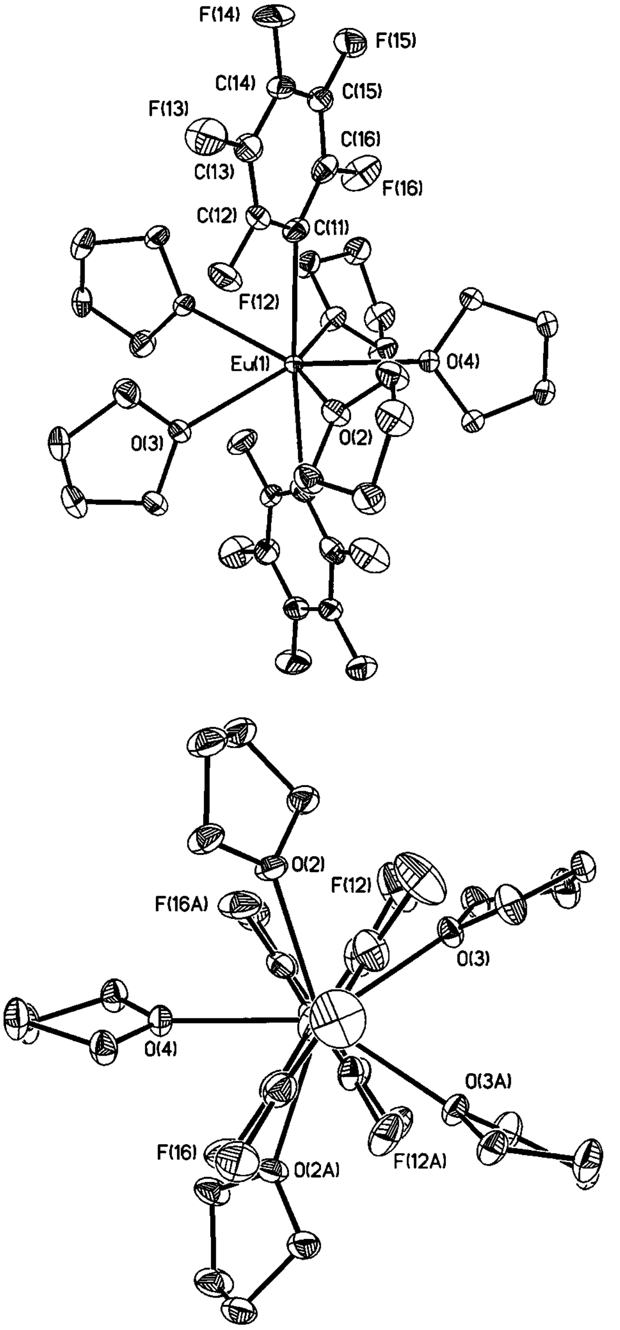

Figure 1. (a, top) Molecular structure of $Eu(C_6F_5)_2(thf)_5$ (**1**) (50% thermal ellipsoids). Only one orientation of the disordered thf O(3)−C(34) is shown, and the hydrogen atoms have been omitted. (b, bottom) **1** as viewed approximately down the C(11)−Eu(1) bond.

The C(11)−Eu(1)−C(11A) angle is near 180°, and the angle between the C_6 ring planes (65.7°) is slightly

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(8) A mixture of Eu metal (0.60 g, 4.0 mmol) and $Hg(C_6F_5)_2$[19] (0.53 g, 1.0 mmol) was stirred in thf (20 mL) at room temperature for 4 h. After filtration, the lemon yellow solution was treated with light petroleum (20 mL) and the volume reduced to 20 mL. Large yellow blocks deposited on cooling to −20 °C, which were collected and quickly dried under the ambient drybox conditions. IR (Nujol): 1622 m, 1600 m, 1412 vs, 1303 m, 1294 m, 1218 m, 1168 m, 1156 m, 1073 s, 1038 s, 1016 vs, 919 vs, 883 m, 722 s cm^{-1}.

(9) A prismatic yellow crystal, covered in a viscous oil, was mounted on a glass fiber. Data were collected on an Enraf-Nonius CCD diffractometer (λ = 0.710 73 Å) at 153 K. Crystal data for $C_{32}H_{40}EuF_{10}O_5$: monoclinic, space group *C*2/*c*, with cell dimensions a = 14.7425(2) Å, b = 12.4969(1) Å, c = 18.4452(2) Å, β = 101.543(1)°, and V = 3329(1) $Å^3$ with Z = 4 and D_{calcd} = 1.689 g/cm^3. The structure was solved by conventional heavy-atom methods and refined by full-matrix least squares on F^2 (4789 unique data (24 298 total data, R_{int} = 2.3%); anisotropic thermal parameter forms for the non-hydrogen atoms) to R = 2.15% and R_w = 7.77% (all data). Hydrogen atoms were included in calculated positions, with thermal parameters allowed to ride on the parent atom. One of the thf ligands was modeled as disordered, with C(32) refined in two positions at 0.5 occupancy.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1

Bond Lengths			
Eu(1)−C(11)	2.822(3)	Eu(1)−O(2)	2.595(2)
Eu(1)−O(3)	2.647(2)	Eu(1)−O(4)	2.580(2)
Bond Angles			
C(11)−Eu(1)-C(11A)	175.6(1)	O(2)−Eu(1)−O(3)	75.49(5)
O(2)−Eu(1)-O(4)	72.52(4)	O(3)−Eu(1)−O(3A)	72.60(7)
C(11)−Eu(1)−O(2)	83.46(7)	C(11)−Eu(1)−O(2A)	95.22(7)
C(11)−Eu(1)−O(3)	105.25(7)	C(11)−Eu(1)−O(3A)	78.39(7)
C(11)−Eu(1)−O(4)	87.80(5)		

larger than for the starting mercurial (58.0°).[13] This orientation presumably represents the most sterically comfortable position defined by competing *o*-F/*o*-F and/or *o*-F/thf repulsions (Figure 1b). Even so, the oxygen atoms of some of the equatorial thf ligands are displaced above (O(2), 0.34 Å; O(3A), 0.57 Å) and below (O(2A), 0.34 Å; O(3), 0.57 Å) the equatorial plane by the proximity of the *o*-fluorine atoms of the $C_6F_5^-$ groups. Conversely, O(4), which has no proximal *o*-fluorine atoms, lies within the equatorial plane. The europium−carbon bond length in **1** (Table 1) is significantly longer than the only other reported $Eu^{II}-(\sigma)C$ distances, 2.605(6) and 2.612(7) Å in $Eu\{C(SiMe_3)_3\}_2$,[2d] as expected for a higher coordination number. A more quantitative comparison is difficult, as $Eu\{C(SiMe_3)_3\}_2$ has several "agostic"[14] Eu−Me(Si) interactions, which imply that the coordination number in $Eu\{C(SiMe_3)_3\}_2$ is greater than 2. The current Eu−C distance is remarkably near that of π-bound C_5Me_5 ligands, e.g. in seven-coordinate $Eu(C_5Me_5)_2(OEt_2)$ (2.79(1) Å)[15a] and $[Eu(C_5Me_5)(\mu\text{-}CCPh)(thf)_2]_2$ (2.82(2) Å).[15b] This is in contrast with a lanthanoid(III)−phenyl moiety, where the $Ln^{III}-C$(phenyl) distance is shorter than $Ln^{III}-C(C_5Me_5)$; e.g., in $Sm(C_5Me_5)_2Ph(thf)$, Sm−C(phenyl) = 2.511(8) Å and $\langle Sm-C(C_5Me_5)\rangle = 2.73_8$ Å.[16] Further, an estimated terminal $Eu^{II}-C$(phenyl) distance of 2.74 Å for seven-coordination, derived from $\langle Ln^{III}-C\rangle$ of $LnPh_3(thf)_3$ (2.431 Å (Er), 2.421 Å (Tm))[2b] after accounting for differences in the metal ionic radii,[17] also suggests that the current terminal Eu−C distance is relatively long. The $\langle Eu-O(thf)\rangle$ (Table 1) distance of 2.61 Å for **1** is as expected for a seven-coordinate europium(II) center by comparison with the average value for seven-coordinate $[Eu(C_5Me_5)(\mu\text{-}CCPh)(thf)_2]_2$ (2.62 Å)[15b] and also with the value for the six-coordinate $Eu(cbz)_2(thf)_4$ ($\langle Eu-O\rangle$ = 2.58 Å),[5e] given an approximately 0.03−0.05 Å increase in the Eu^{2+} ionic radii with increasing coordination number.[17] These Eu−O data imply that **1** is not sterically overcrowded, presumably because of displacement of thf ligands from the equatorial plane, and hence the lengthening of the Eu−C bond is due, at least in part, to the fluorine substituents of the aryl group. Their inductive electron-withdrawing properties reduce the electron density on the ipso carbon, weakening the Eu−C bond.

Organolanthanoid(II) compounds devoid of stabilizing cyclopentadienyl ligands are rare, and structurally authenticated examples are limited to those utilizing heavily substituted alkyl groups which inhibit decomposition pathways.[2d,e,18] Thus, the existence of **1** is notable as a simple and relatively sterically unencumbered $Ln^{II}R_2$ derivative.

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Supporting Information Available: Details of the X-ray structure determination of **1**, including final coordinates, thermal parameters, and all bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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