4f Orbital Covalence in $(\eta^5\text{-}C_5H_5)_3Eu(THF)$ as Revealed by Europium-151 Mössbauer Spectroscopy

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One of the paradigms of lanthanide coordination and organometallic chemistry is that the 4f orbitals are strongly shielded from interaction with the ligands. The purpose of this communication is to report the first, to our knowledge, experimental evidence for a strong covalent bonding interaction of ligands with the 4f orbitals of europium in $(\eta^5\text{-}C_5H_5)_3Eu(THF)$. Europium-151 Mössbauer spectroscopy is an excellent probe for determining the electronic properties of organoeuropium compounds.[2] The europium-151 isomer shift is strongly dependent upon the valence state of europium, and europium(II) compounds typically have[3] isomer shifts of ca. −12.5 mm/s. In contrast, europium(III) compounds have isomer shifts[2,4] of ca. 0.3 mm/s. The extent of structural distortion from cubic symmetry at the europium-151 nucleus is probed by the quadrupole interaction. Most organoeuropium compounds[2-4] show small quadrupole interactions of less than ±15 mm/s, and the quadrupole interaction of +48 mm/s in $Eu_{1.03}Rh_3B_{2.1}$ is the largest ever reported.[5]

Herein, we report the crystal structure of $(\eta^5\text{-}C_5H_5)EuCl_2(THF)_3$ and the europium-151 Mössbauer spectra of several new organoeuropium(III) compounds with a variety of ligand environments. One compound, $(\eta^5\text{-}C_5H_5)_3Eu(THF)$, is unusual because it exhibits both a very negative isomer shift of −1.77 mm/s and a very large negative quadrupole interaction of −33.6 mm/s. These values are unique among those observed[2-4] for organoeuropium(III) compounds and are discussed in terms of the electronic structure of this compound.

All organometallic compounds were prepared and handled in a nitrogen atmosphere glovebox with rigorous exclusion of air and moisture. The solvents, THF and pentane, were dried according to standard methods[6] and distilled under nitrogen immediately prior to use. Anhydrous $EuCl_3$ and sodium cyclopentadienide were prepared according to standard methods.[7,8] $(\eta^5\text{-}C_5H_5)EuCl_2(THF)_3$ and $(\eta^5\text{-}C_5H_5)_3Eu(THF)$ were prepared as reported previously.[9-11a] $(\eta^5\text{-}C_5H_5)Eu(NCS)_2(THF)_3$ was
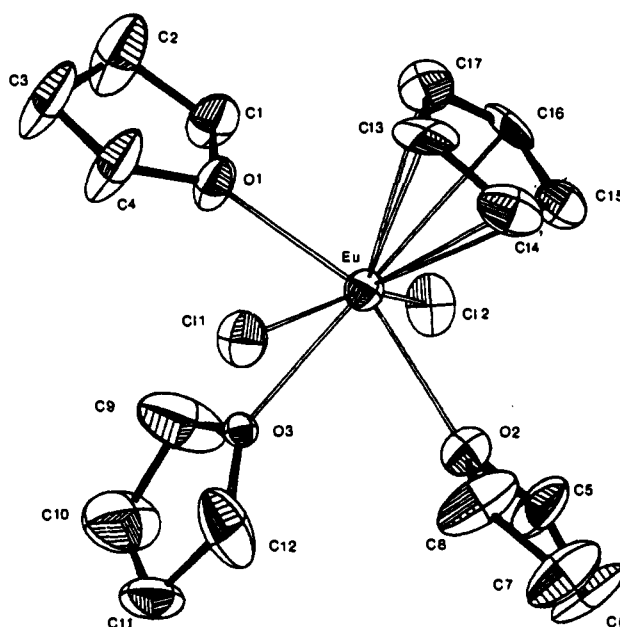

Figure 1. Crystallographic structure of $(\eta^5\text{-}C_5H_5)EuCl_2(THF)_3$.

prepared by the reaction in THF of $(\eta^5\text{-}C_5H_5)EuCl_2(THF)_3$ with KNCS in a 2:1 molar ratio. KCl was separated by centrifugation, and the resulting solution was dried under vacuum. The light violet product was recrystallized from a mixture of THF and pentane.[11b] Anal. Calcd for $EuC_{19}H_{29}O_3N_2S_2$: Eu, 27.68. Found: Eu, 27.65. $(\eta^5\text{-}C_5H_5)Eu(NCO)_2(THF)_x$, with x between 2 and 3, was prepared by the reaction of $(\eta^5\text{-}C_5H_5)EuCl_2(THF)_3$ with NaNCO in a fashion similar to that of the thiocyanate compound.[11c]

The single crystal X-ray structure of $(\eta^5\text{-}C_5H_5)EuCl_2(THF)_3$ has been determined,[12,14] see Figure 1. Positional parameters are given[15] in Table SI, and its selected bond distances and angles are given[15] in Table SII.

The Mössbauer spectra were measured[16] at 4.2 K in a liquid pool or vapor-cooled cryostat. The source was samarium-151 in SmF_3, the velocity scale was calibrated with room-temperature

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(11) (a) The purity of $(\eta^5\text{-}C_5H_5)_3Eu(THF)$ was confirmed by both infrared spectral analysis and elemental analysis on three independently prepared and recrystallized samples. (b) Several attempts to determine the X-ray structure of well-formed light violet crystals of this compound failed because under prolonged exposure to X-rays the crystals decomposed. (c) Analytical data indicate that the number of THF ligands is between 2 and 3.

(12) Single crystals of $(\eta^5\text{-}C_5H_5)EuCl_2(THF)_3$ crystallize in the monoclinic $P2_1/n$ space group with $a = 15.258(3)$ Å, $b = 17.216(3)$ Å, $c = 7.860(1)$ Å, $\beta = 95.5(3)°$, $V = 2055.3(6)$ Å³, $Z = 4$, and $D = 1.629$ g/cm³. The unit cell parameters were obtained by least-squares refinement of the angular setting of 25 medium to high angle ($8° < \theta < 13°$) reflections. Data were collected with 0.7107 Å Mo Kα radiation on a Philips PW1100 automatic four-circle diffractometer. A total of 3624 unique reflections were collected, of which 1583 were considered in the refinement for $I \geq 3\sigma$. The absorption coefficient was 33.2 cm⁻¹, and the usual atomic scattering factors and anomalous dispersion terms for europium were used.[13] The structure was solved by a three-dimensional Patterson synthesis which readily gave the position of the europium atom. The positions of the remaining non-hydrogen atoms were defined by a difference Fourier synthesis and refined with anisotropic temperature factors. The hydrogen atoms were introduced at calculated but unrefined positions (C–H, 0.94 Å) in the last stages of the analysis. The final agreement factor is $R = 0.057$. The calculations were performed with the SHELX-76 program.[14]

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Table 1. Europium-151 Mössbauer Spectral Hyperfine Parameters Measured at 4.2 K

compound	δ,[a] mm/s	Γ, mm/s	eQV_{zz}, mm/s	η	χ^2
$(\eta^5\text{-}C_5H_5)_3Eu(THF)$	-1.77	1.83(8)	-33.6(2)	0.00	1.34
$(\eta^5\text{-}C_5H_5)EuCl_2(THF)_3$	0.06	2.71(3)	11.0(1)	0.46	1.22
$(\eta^5\text{-}C_5H_5)Eu(NCO)_2(THF)_x$	0.04	2.94(7)	11.0(3)	0.38	1.24
$(\eta^5\text{-}C_5H_5)Eu(NCS)_2(THF)_3$	0.14	3.18(6)	13.1(2)	0.42	1.51

[a] Relative at room temperature EuF_3.
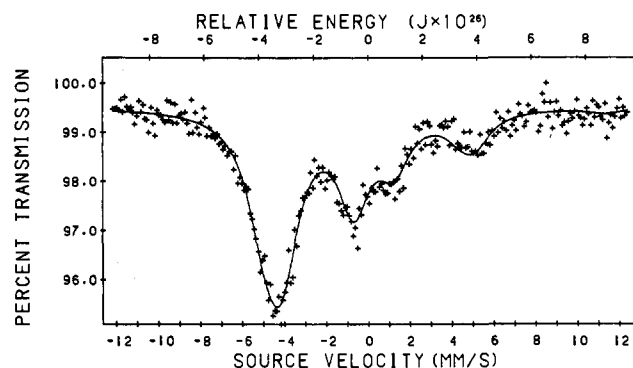
Figure 2. Mössbauer spectrum of $(\eta^5\text{-}C_5H_5)_3Eu(THF)$ measured at 4.2 K.

α-iron foil, and zero velocity was determined at room temperature with EuF_3, which is the reference for all isomer shifts reported herein. Absorbers contained 30–40 mg of natural abundance Eu/cm^2.

The 4.2 K Mössbauer spectra of $(\eta^5\text{-}C_5H_5)EuCl_2(THF)_3$, $(\eta^5\text{-}C_5H_5)Eu(NCO)_2(THF)_x$, and $(\eta^5\text{-}C_5H_5)Eu(NCS)_2(THF)_3$ consist of a broad unresolved asymmetric absorption centered at ca. 0.3 mm/s and are characteristic of organoeuropium(III) compounds.[2,4] The hyperfine spectral parameters are given in Table 1. As might be expected, all the compounds except $(\eta^5\text{-}C_5H_5)_3$-Eu(THF) have very similar quadrupole interactions, and the chloride and pseudohalide compounds have very similar isomer shifts. The X-ray structure of $(\eta^5\text{-}C_5H_5)EuCl_2(THF)_3$, see Figure 1, is isostructural with the analogous erbium[17] and ytterbium[18] compounds and shows a nonaxial symmetry about the europium-(III) ion in agreement with the observed asymmetry parameter of 0.46.[19]

The Mössbauer spectrum of $(\eta^5\text{-}C_5H_5)_3Eu(THF)$, measured at 4.2 K, is shown in Figure 2 and is unique among the Mössbauer spectra of organoeuropium compounds.[20] The presence of a large negative quadrupole interaction with a zero asymmetry parameter may be deduced[2] from the observed shape of the spectrum and is confirmed by the least-squares fit shown in the figure. The X-ray structure of $(\eta^5\text{-}C_5H_5)_3Eu(THF)$ is unknown, but it is reasonable to assume that $(\eta^5\text{-}C_5H_5)_3Eu(THF)$ is structurally similar to the isostructural complexes, $(\eta^5\text{-}C_5H_5)_3M(THF)$, where

M is yttrium,[21] lanthanum,[21] samarium,[22] gadolinium,[23] dysprosium,[22] and lutetium,[24] in $v^{\cdot\,\cdot}$ h the three metal bonds to the $\eta^5\text{-}C_5H_5$ rings are virtually trigonal[25] and THF occupies an axial position to produce trigonal-pyramidal structures. This structure is consistent with the observed zero asymmetry parameter. The magnitude of the quadrupole coupling is very large compared to other europium(III) organometallic compounds, and the positive quadrupole moments of the europium-151 nucleus imply that the electric field gradient is negative. In the europium(III) $4f^6$ configuration, the seventh 4f orbital is unoccupied, and the observed negative electric field gradient requires this orbital to be localized in the equatorial plane. This can only arise from a strong interaction of the 4f orbitals with the three $\eta^5\text{-}C_5H_5$ ligands. The existence of such a strong interaction is supported by the unusually negative isomer shift of -1.77 mm/s as compared to the other compounds in Table 1 and to other europium(III) compounds.[2] This negative isomer shift corresponds to the transfer of ca. 0.14 electrons[26] from the $\eta^5\text{-}C_5H_5$ ligands into the 4f orbitals of europium. An alternative explanation, in which the electric field gradient arises from donation to the 5d orbitals, may be excluded because this would lead to a concentration of charge in the equatorial plane and thus to a positive electric field gradient. Furthermore, calculations[26] suggest that this would require a much greater degree of electron donation to the metal.

In conclusion, the europium-151 Mössbauer spectrum of $(\eta^5\text{-}C_5H_5)_3Eu(THF)$ can only be interpreted in terms of a weak but definite covalent interaction between the 4f orbitals of europium(III) and the ligands, and this is, to our knowledge, the first report of such an interaction. Unresolved is why $(\eta^5\text{-}C_5H_5)_3$-Eu(THF) is so different from other europium compounds, and more especially from the monocyclopentadienyl complexes listed in Table 1. The most plausible explanation is that the presence of the three very soft $\eta^5\text{-}C_5H_5$ ligands produces an extensive nephelauxetic effect and results in an expansion of the 4f orbital radial functions and thereby a greater interaction of the 4f orbitals with the ligands. This effect will be less marked in the compounds containing the harder chloride and pseudohalide ligands.

Supplementary Material Available: Tables SI and SII, giving positional parameters and selected bond distances and angles, respectively, for $(\eta^5\text{-}C_5H_5)EuCl_2(THF)_3$ (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(20) The three independently prepared samples of $(\eta^5\text{-}C_5H_5)_3Eu(THF)$ all gave virtually identical Mössbauer spectra at 4.2 K.

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