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Notes

Synthesis and Characterization of the First Pentamethylcyclopentadienyl Complex of Trivalent Europium: $[(C_5Me_5)Eu(OCMe_3)(\mu\text{-}OCMe_3)]_2$

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Summary: $EuCl_3$ reacts with 2 equiv of $NaOCMe_3$ in THF to form a complex which analyzes as $Eu_3(OCMe_3)_7Cl_2(THF)_2$, 1. 1 reacts with KC_5Me_5 to form $[(C_5Me_5)Eu(OCMe_3)(\mu\text{-}OCMe_3)]_2$, 2, in 60% yield. 2 was characterized by elemental analysis and spectroscopic methods and by X-ray crystallography. 2 crystallizes from Et_2O at -34 °C in the space group $P2_1/c$ with $a = 12.847(3)$ Å, $b = 17.329(5)$ Å, $c = 18.670(4)$ Å, $\beta = 99.41(2)°$, $V = 4100(2)$ Å^3, and $D_{calcd} = 1.404$ Mg/m^3 for $Z = 4$. The two europium atoms and the two oxygen atoms of the bridging ligands form a plane which is perpendicular to the plane defined by the two C_5Me_5 ring centroids and the oxygen atoms of the terminal tert-butoxide ligands. The C_5Me_5 rings are arranged in a cis orientation around the $(Me_3CO)Eu(\mu\text{-}OCMe_3)_2Eu(OCMe_3)$ central core.

The pentamethylcyclopentadienyl ligand, C_5Me_5, has been used extensively in organometallic chemistry to provide isolable, characterizable complexes for a wide range of metals in various oxidation states.[1] This ligand has not stabilized Eu(III) complexes, however, because it has been shown[2] that the $C_5Me_5^-$ anion reduces Eu(III) to Eu(II), eq 1.

$$EuCl_3 + 3NaC_5Me_5 \xrightarrow[2.\ Et_2O]{1.\ THF\ reflux} (C_5Me_5)_2Eu(Et_2O)(THF) \quad (1)$$

This behavior is consistent with the low reduction potential reported for Eu(III) in aqueous solution, −0.35 ± 0.03 V vs SHE.[3] We now report that by using *tert*-butoxide coligands, a C_5Me_5 complex of Eu(III) can be isolated and crystallographically characterized.

This system was investigated to determine the generality of the tendency of *tert*-butoxide coligands to stabilize higher oxidation states of the lanthanides. In the past, it has been shown that alkoxide ligands stabilize Ce(IV) with respect to reduction by cyclopentadienyl ligands.[4–6] For example, the first crystallographically characterizable cerium complex containing the seemingly-incompatible cyclopentadienide/Ce(IV) combination, namely $(C_5H_5)_3Ce(OCMe_3)$,[6] contained a *tert*-butoxide ligand. To determine if *tert*-butoxide could also stabilize Eu(III), we attempted the synthesis of a mixed ligand $(C_5Me_5)/(OCMe_3)$ complex of europium. The ideal target appeared to be $[(C_5Me_5)Eu(OCMe_3)(\mu\text{-}OCMe_3)]_2$, since recent studies of yttrium *tert*-butoxide chemistry had shown that the yttrium analog, $[(C_5Me_5)Y(OCMe_3)(\mu\text{-}OCMe_3)]_2$, was particularly stable.[7] To accomplish this synthesis, it was first necessary to make the europium analog of $Y_3(\mu_3\text{-}OCMe_3)(\mu_3\text{-}Cl)(\mu\text{-}OCMe_3)_3(OCMe_3)_3Cl(THF)_2$,[8] which is a precursor to $[(C_5Me_5)Y(OCMe_3)(\mu\text{-}OCMe_3)]_2$[7] and this is also reported.

Experimental Section

All compounds described below were handled under nitrogen with rigorous exclusion of air and water using standard Schlenk, vacuum line, and glovebox techniques. All solvents were freshly distilled and dried as previously described.[9] $EuCl_3$ was dried as previously described.[10] NMR data were obtained using GE QE-300 and GE Ω500 instruments. UV/vis spectra were recorded on a Shimadzu UV160U. Infrared spectra were recorded with a Nicolet 50 FTIR. Luminescence spectra were recorded on a SPEX Fluorolog 1680 0.22 double spectrometer. Elemental analysis was performed at Analytische Laboratorien GMBH, Fritz-Pregl-Strasse 24, D-5270 Gummersbach, Germany.

"$Eu_3(OCMe_3)_7Cl_2(THF)_2$", 1. In a glovebox, $NaOCMe_3$ (558 mg, 5.81 mmol) was added to a suspension of $EuCl_3$ (750 mg, 2.90 mmol) in THF (12 mL) which had been previously stirred for 5 min. The reaction mixture was stirred 18 h and centrifuged to remove insolubles. Removal of the solvent from the supernatant followed by subsequent toluene extraction and washing with hexanes yielded a cream colored solid, 1 (672 mg, 59% yield). ^1H NMR (C_4D_8O): δ 93.9 (s, 9H), −9.7 (s, 18H), −14.4 (s, 18H), −16.0 (s, 9H,), −25.2 (s, 9H). IR (neat): 2981 (s br), 1625 (m), 1456 (m), 1368 (m), 1250 (w), 1181 (w), 1018 (s), 868 (m), 756 (w) cm^{-1}. Anal. Calcd for $Eu_3Cl_2C_{36}H_{79}O_9$: Eu, 38.54; Cl, 5.99; C 36.56; H, 6.73. Found: Eu, 38.95; Cl, 6.33; C, 36.13; H, 6.50.

$[(C_5Me_5)Eu(OCMe_3)_2]_2$, 2. In a glovebox, KC_5Me_5 (88 mg, 0.51 mmol) was added to 1 (200 mg, 0.17 mmol) in toluene (5 mL), and the mixture was stirred 18 h. The pale yellow solution became dark purple. The reaction mixture was centrifuged to

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remove an orange solid, and the solvent was removed by rotary evaporation. Subsequent extraction with hexanes left 2 as an oily, dark purple solid (130 mg, 0.15 mmol, 60% yield). ^{1}H NMR (C_6D_6, $\Delta\nu_{1/2}$ = 150 Hz): δ 98.8 (9H, $OCMe_3$), −19.7 (15H, C_5Me_5), −35.1 (9H, $OCMe_3$). ^{13}C NMR (C_6D_6): δ 195 (br, $\Delta\nu_{1/2}$ = 350 Hz), 69 (br, 150 Hz), 66 (br, 120 Hz), −15 (br, 245 Hz), −37 (br, 145 Hz), −65 (br, 265 Hz). IR (neat): 2965 (s), 2823 (s), 2880 (s), 1455 (m), 1378 (m), 1353 (s), 1219 (w), 1201 (s), 996 (s), 934 (m), 915 (m) cm^{-1}. UV/vis (2.6×10^{-3} M, hexanes; λ_{max} nm (ϵ)): 570 (440), 232 (2.2×10^4). Luminescence: λ_{max} = 429 (very broad, $\Delta\nu_{1/2}$ = 80 nm), at excitation of 232 nm; λ_{max} = 600 and 619 nm at excitation of 570 nm. Magnetic susceptibility (295 K, Evans' method[11]): $\chi_g = 1.726 \times 10^{-5}$ cgsu (μ_{eff} = 4.22 μ_B). Isopiestic molecular weight (C_6H_6): calcd, 866.8; found, 830. Anal. Calcd for $Eu_2C_{36}H_{66}O_4$: Eu, 35.06; C, 49.88; H, 7.67. Found: Eu, 34.70; C, 49.42; H, 7.46; Cl, 0.77. Complexometric analysis: Eu, 35.5.

X-ray Data Collection, Structure Determination, and Refinement for $[(C_5Me_5)Eu(OCMe_3)(\mu\text{-}OCMe_3)]_2$. Crystals of 2 were grown at −34 °C from a concentrated Et_2O solution. A dark purple crystal measuring approximately 0.24 × 0.30 × 0.36 mm was mounted under Paratone D oil onto a Siemens P3 diffractometer equipped with a modified LT-2 low temperature system. Since the crystals were of poor quality, a limited data set (2θ range 4–43°) was collected at 163 K and only the atomic connectivity of the compound could be unambiguously determined. A summary of the crystallographic data is given in the supplementary material. Compound 2 crystallizes from Et_2O in the space group $P2_1/c$ with a = 12.847(3) Å, b = 17.329(5) Å, c = 18.670(4) Å, β = 99.41 (2)°, V = 4100 (2) Å^3, and D_{calcd} = 1.404 Mg/m^3 for Z = 4.

Results and Discussion

Attempts to make a stable C_5Me_5 complex of trivalent europium focused on the synthesis of an analog of the crystallographically characterized $[(C_5Me_5)Y(OCMe_3)(\mu\text{-}OCMe_3)]_2$, which has previously been shown to be rather stable.[7] The two routes by which $[(C_5Me_5)Y(OCMe_3)_2]_2$ can be generated are shown in eqs 2 and 3.[7]

$$2YCl_3 + 4NaOCMe_3 + 2KC_5Me_5 \xrightarrow[\text{reflux}]{\text{THF}} [(C_5Me_5)Y(OCMe_3)_2]_2 \quad (2)$$

$$Y_3(OCMe_3)_7Cl_2(THF)_2 + 3KC_5Me_5 \xrightarrow[\text{reflux}]{\text{toluene}} [(C_5Me_5)Y(OCMe_3)_2]_2 \quad (3)$$

The europium analog of eq 2 was not favored as a route to a Eu(III) C_5Me_5 complex, since reduction of $EuCl_3$ by NaC_5Me_5 had previously been reported.[2] A synthetic route analogous to eq 3 was preferable since the potentially stabilizing *tert*-butoxide ligands are already in place before the cyclopentadienide reagent is added. This required the synthesis of the europium analog of $Y_3(\mu_3\text{-}OCMe_3)(\mu_3\text{-}Cl)(\mu\text{-}OCMe_3)_3(OCMe_3)_3Cl(THF)_2$,[8] i.e. $Eu_3(OCMe_3)_7Cl_2(THF)_2$.

Previous studies of $EuCl_3/NaOCMe_3$ reactions showed that the product obtained in these reactions depended crucially on the isolation procedure and that the nonametallic complex, $EuNa_8(OCMe_3)_{10}Cl$ readily formed in this system.[12] The reaction of $EuCl_3$ with 2 equiv of $NaOCMe_3$ gives a single primary europium alkoxide product, 1, when the reaction mixture is centrifuged and extracted with toluene. This product has ^{1}H NMR data and an elemental analysis consistent with the formula $Eu_3(OCMe_3)_7Cl_2(THF)_2$, a direct analog of the fully characterized $Y_3(OCMe_3)_7Cl_2(THF)_2$.[8] However, given the paramagnetism of this system (for Eu(III), μ = 3.7–4.2 μ_B),[13] the NMR data are not structurally definitive, and in the absence of crystallographic data, unequivocal identification of 1 is not possible. Nevertheless, the product of the $EuCl_3$/2$NaOCMe_3$ reaction does function as a reliable starting material for the desired Eu(III) C_5Me_5 product.

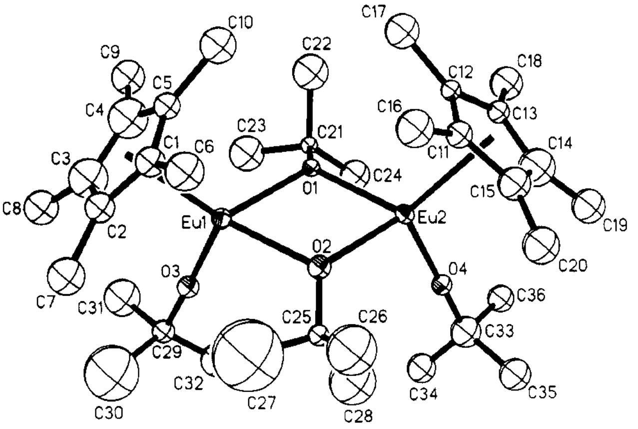

Figure 1. Thermal ellipsoid plot of $[(C_5Me_5)Eu(OCMe_3)(\mu\text{-}OCMe_3)]_2$, 2, with ellipsoids drawn at the 30% probability level.

Reaction of 1 with KC_5Me_5 generates a dark purple product which was fully characterized by analytical and spectroscopic means and by X-ray crystallography as $[(C_5Me_5)Eu(OCMe_3)(\mu\text{-}OCMe_3)]_2$, Figure 1. Equation 4 shows the entire reaction sequence starting with $EuCl_3$.

$$EuCl_3 + 2NaOCMe_3 \xrightarrow[\text{24 h, -NaCl}]{\text{THF}} \text{“}\underset{1}{Eu_3(OCMe_3)_7Cl_2(THF)_2}\text{”} \quad (4)$$

$$1 + 3KC_5Me_5 \xrightarrow[\text{18 h}]{\text{toluene}} \underset{2}{[(C_5Me_5)Eu(OCMe_3)(\mu\text{-}OCMe_3)]_2}$$

Complete elemental analysis established the composition of 2, and a molecular weight determination indicated that it was dimeric in solution. Although the crystals of 2 examined by X-ray diffraction were not of high quality, they did reveal the atomic connectivity of the complex, which is shown in Figure 1. 2 is the desired europium analog of $[(C_5Me_5)Y(OCMe_3)(\mu\text{-}OCMe_3)]_2$,[7] and in fact it is isostructural with this complex.

Magnetic susceptibility studies indicated a magnetic moment of 4.2 μ_B, which is consistent with Eu(III) (typical range 3.7–4.2 μ_B) rather than Eu(II) (typical range 7.6–8.0 μ_B). The ^{1}H NMR spectrum contained resonances over a 140 ppm range which had line widths (ca. 150 Hz) more similar to those observed in Eu(III) complexes than for Eu(II), which generally gives greatly broadened resonances.[14] The ^{13}C NMR resonances extended from +195 to −65 ppm and were reasonable but not structurally definitive for 2. The UV/vis spectrum of 2 contained a strong (for a lanthanide) absorption at 570 nm, which is reasonable

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for a complex involving an easily oxidized ligand attached to a trivalent lanthanide which has an accessible divalent state.[15] The emission spectrum of 2 contains signals at 600 and 619 nm, which are consistent with previously observed emission spectra of Eu^{3+} complexes.[15]

Conclusion

The successful isolation of $[(C_5Me_5)Eu(OCMe_3)(\mu\text{-}OCMe_3)]_2$ as the first example of a trivalent europium complex containing the pentamethylcyclopentadienyl ligand suggests that alkoxide ligands can be used broadly in lanthanide chemistry to stabilize higher oxidation states, i.e. this phenomena is not just limited to Ce(IV).[4-6] Hence, utilization of alkoxide coligands may lead to a wider variety of accessible organometallic Eu(III) compounds. Furthermore, since the alkoxide coligands stabilize higher lanthanide oxidation states, this suggests that alkoxide ligands may be used to manipulate redox reactions involving the lanthanides. Specifically, alkoxide complexes of Sm(II) and Yb(II) may have enhanced reduction capacity.

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Supplementary Material Available: Figures of emission spectra of 2 and a structure with atom labels, a textual description of crystallographic details, and tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (16 pages). Ordering information is given on any current masthead page.

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