



## Enthalpies of formation of europium alkoxides: What lessons can be drawn from them



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### ABSTRACT

The synthesis and characterization of two europium alkoxides, Eu(OCH<sub>3</sub>)<sub>2</sub> and Eu(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, were described. For the first time the enthalpies of formation of divalent lanthanide alkoxides were determined by using reaction-solution calorimetry. The values obtained are  $\Delta_f H^0$  [Eu(OCH<sub>3</sub>)<sub>2</sub>,cr] =  $-850.5 \pm 5.0$  kJ/mol and  $\Delta_f H^0$  [Eu(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>,cr] =  $-902.5 \pm 5.5$  kJ/mol, respectively. Since these compounds have a large use as catalysts or catalysts precursors, the first step of the reaction of them with CO<sub>2</sub> was addressed, which permits to have an idea of the kind of bond involved in those compounds. Moreover, insertion of CO<sub>2</sub> in the europium oxygen bond and formation of metal carboxylate complexes, is in both cases presumably bidentate.

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### 1. Introduction

The applications of lanthanide alkoxides and aryloxides are diverse, ranging from catalysis to the synthesis of high purity oxide materials. Alkoxides are known for almost all the elements, but due to the large ionic radii of the lanthanides, the formation of multinuclear species is usual for lanthanide alkoxides, leading to compounds with low solubility and reactivity. In order to obtain low nuclearity, several authors used sterically demanding and/or donor functionalized alkoxides [1].

In our laboratories, we have been studying the synthesis, using non-conventional synthetic routes such as direct reactions of alcohols with lanthanide metals, e.g. in liquid ammonia or using the metal vapor synthesis technique [2], and also the reactivity of lanthanide alkoxides and aryloxides [2,3]. Nevertheless, the structural chemistry of these compounds is dominated by the formation of polymeric structures and a complete characterization of most of

these compounds was not achieved due to the lack of crystals suitable for X-ray diffraction studies. We are also interested in the direct conversion of carbon dioxide to more valuable products [4], namely through its use as a functionalization agent, e.g. for the synthesis of dimethyl carbonate via the oxidative carboxylation of methanol.

In this work, we have synthesized and characterized two europium alkoxides, Eu[OR]<sub>2</sub> (R=Me, Et). As stated before, a full characterization of these compounds is difficult due to the lack of crystals suitable for X-ray diffraction studies. In order to elucidate the compound's structure, studies by Extended X-ray Absorption Fine Structure (EXAFS) were undertaken. To get a deeper understanding of what really happens, reaction-solution calorimetry was used in order to obtain the enthalpies of formation for Eu[OR]<sub>2</sub> (R=Me, Et). Moreover, since these compounds are used as catalysts or catalysts precursors, the product of the reaction of these compounds with carbon dioxide, as the first step for the carboxylation of methanol by CO<sub>2</sub> catalyzed by f-element alkoxides, was also characterized by EXAFS, infrared spectroscopy and elemental analysis. Unfortunately, it was not possible to arrange a fast and clean reaction to determine the enthalpies of formation of the products obtained, in order to have an energetic profile of CO<sub>2</sub> insertion reaction on these compounds.

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## 2. Experimental

### 2.1. General data

All manipulations were carried out on a standard high-vacuum line or in a nitrogen-filled glove box ( $O_2 < 5$  ppm).  $NH_3$  anhydrous (Air Liquide, N36) was dried over Na (Riedel-de Haën, 99%) prior to use. THF (Riedel-de Haën, 99.9%) was dried by refluxing under argon with Na/benzophenone (Riedel-de Haën, 99.5%) and distilled prior to use. Pentane (Lab-Scan, 99%) was dried by fractional distillation from  $P_2O_5$  (Riedel-de Haën, 98%). The solvents were degassed on a vacuum line before use. Methanol (Merck, 99.8%) and ethanol (Merck, 99.8%) were pre-dried over calcium sulfate, heated under reflux over activated magnesium and iodine, and finally distilled. Eu (Research Chemicals, 99.9%) was used as received. Carbon dioxide (Air Liquide) was used as supplied.

IR spectra were recorded on a Perkin-Elmer 577 spectrometer with samples mounted as Nujol mulls between CsI plates. CHN analyses were performed on a CE instrument EA1110 automatic analyzer (samples sealed in silver capsules in the glove box). Eu analyses were performed according to a standard gravimetric method.

### 2.2. Synthesis of $Eu(OR)_2$ ( $R=CH_3, C_2H_5$ )

The synthesis of the two europium alkoxides,  $Eu(OR)_2$  ( $R=Me, Et$ ), was performed as described earlier in reference [3]. Elemental analysis for  $Eu(OCH_3)_2$  gave (%): Eu, 69.33; C, 11.00; H, 3.12. Calculated for  $EuC_2H_6O_2$ : Eu, 71.00; C, 11.22; H, 2.83. IR (Nujol, relevant bands,  $cm^{-1}$ ): 1460 w, 1378 s. Elemental analysis for  $Eu(OC_2H_5)_2$  gave (%): Eu, 63.14; C, 19.47; H, 4.45. Calculated for  $EuC_4H_{10}O_2$ : Eu, 62.77; C, 19.84; H, 4.17. IR (Nujol, relevant bands,  $cm^{-1}$ ): 1430 w, 1350 s.

### 2.3. Reaction-solution calorimetry

The enthalpies of formation of some of the alkoxides were determined by measuring the enthalpies of reaction and solution in water or in 0.1 M HCl aqueous solution. The calorimeter used was specifically built for the study of oxygen- and water-sensitive compounds, and the experimental procedure was described in a previous paper [5]. The accuracy of the calorimeter was determined by frequent measurements of the hydrolysis of TRIS in a 0.1 M HCl aqueous solution. Briefly, the calorimeter reaction vessel consisted of a 220  $cm^3$  Dewar flask with two acrylic flanges closed by a lid, which supported a stirred, a quartz crystal thermometer probe, a resistance for electrical calibration, and an ampoule-breaking system. The reaction vessel was immersed in a thermostatic water bath  $T=(298 \pm 10^{-3})$  K controlled by a Tronac PTC-40 unit. In a typical experiment, 12 mm diameter glass ampoules were loaded with (20 to 30) mg of the compound inside a glove box, sealed under vacuum and weighed to  $\pm 10^{-5}$  g with a Mettler H54AR balance. A mass correction for vacuum was always done. The reaction was started by breaking the glass ampoule in 170  $cm^3$  of the appropriate reaction mixture. This was preceded by an electrical calibration in which a potential difference of ca. 2.0 V was applied to a 48  $\Omega$  resistance during ca. 180 s. The results were averaged using at least five runs. The errors presented are twice the standard deviation of the mean in each case.

### 2.4. EXAFS

EXAFS spectra were measured at beamline E4 at the Hamburger Synchrotronstrahlungslabor (HASYLAB) at Deutsches Elektronen Synchrotron (DESY), Hamburg, Germany. The samples were

prepared as a thin layer of powder on adhesive tape using Schlenk techniques, i.e. avoiding the access of air or moisture as far as possible. Experiments were performed at the Eu L3-edge (ca. 6976 eV) in transmission mode at liquid nitrogen temperature under high vacuum. The programs SPLINE and XFIT were used for quantitative data evaluation. Theoretical standards were computed with the program FEFX 6.01a [6,7]. EXAFS fit parameters were:  $k$ -range 15 to about 90  $nm^{-1}$ ,  $R$ -range (0.12 to 0.45) nm,  $S_o^2 = 1$  (fixed). Variation parameters were  $N$ ,  $\sigma^2$ ,  $R$  (for each shell) and  $E_o$ .

### 2.5. $CO_2$ activation studies

The experiments were carried out in a stainless steel autoclave with inner volume of 100  $cm^3$  provided with an external heater. In a typical procedure, lanthanide alkoxide (1 mmol) was charged into the autoclave (carried out under  $N_2$  in the glove box) and then pressurised with 50 bar of  $CO_2$ , at room temperature. After heated at 50  $^\circ C$  for 18 h, the autoclave is cooled to room temperature and the compound recovered for analysis. The late manipulation is carried out under  $N_2$  inside the glove box.

#### 2.5.1. Activation of $[Eu(OCH_3)_2]$

After 18 h of reaction a white solid formulated as  $EuC_4H_6O_6$  was obtained. Elemental analysis gave (%): C, 16.1; H, 1.8. Calculated for  $EuC_4H_6O_6$ : C, 15.9; H, 2.0. IR (Nujol,  $cm^{-1}$ ): 1570 vs 1370 vs 1200 m, 1100 m, 925 m, 830 m.

#### 2.5.2. Activation of $[Eu(OC_2H_5)_2]$

After 18 h of reaction a white solid formulated as  $EuC_6H_{10}O_6$  was obtained. Elemental analysis gave (%): C, 20.9; H, 2.7. Calculated for  $EuC_6H_{10}O_6$ : C, 21.8; H, 3.0. IR (Nujol,  $cm^{-1}$ ): 1575 vs 1330 vs 1105 m, 1100 m, 885 m, 840 m, 810 w, 400 w.

## 3. Results and discussion

### 3.1. EXAFS results

In this study, several europium compounds were studied by EXAFS. Beside the relevant compounds for this study, i.e.  $Eu(OCH_3)_2$ ,  $Eu(OCH_3)_2 \cdot CO_2$ ,  $Eu(OC_2H_5)_2$ , and  $Eu(OC_2H_5)_2 \cdot CO_2$ ,  $Eu_2O_3$  was also studied as a reference compound. EXAFS studies allowed the calculation of the Eu–O distance as well as an estimate of the number of neighboring atoms ( $N$ ) present around the europium center. The europium–oxygen distance obtained from the fitted results for the first shell corresponds to the first peak in the Fourier transform magnitude spectra. The results for the two closer shells (Eu–O and Eu–Eu) for the measured compounds are presented in table 1.

The first shell (oxygen) gives reasonable fits, as it also make sense to assume that europium is surrounded by oxygen in the first shell. The second shell (Eu–Eu) was derived assuming a structure similar to the one of europium(III) oxide. There is some indication

**TABLE 1**  
EXAFS data for several europium compounds.

| Compound            | Oxygen                            |          | Europium                          |            |
|---------------------|-----------------------------------|----------|-----------------------------------|------------|
|                     | $R$ ( $\text{\AA}$ ) <sup>a</sup> | $N^b$    | $R$ ( $\text{\AA}$ ) <sup>a</sup> | $N^b$      |
| $Eu_2O_3$           | 2.36(2)                           | 6(fixed) | 3.66(2)                           | 7.5(fixed) |
| $Eu(OCH_3)_2$       | 2.59(2)                           | 5.8(1)   | 3.64(2)                           | 2.3(2)     |
| $Eu(OCH_3)_2CO_2$   | 2.60(2)                           | 6.4(4)   | 3.65(2)                           | 2.8(2)     |
| $Eu(OC_2H_5)_2$     | 2.36(3)                           | 4.3(7)   | 3.70(4)                           | 3.8(2)     |
| $Eu(OC_2H_5)_2CO_2$ | 2.60(2)                           | 6.5(13)  | 3.64(3)                           | 1.7(14)    |

<sup>a</sup> Fourier transform plots give distances lower by (0.2 to 0.3)  $\text{\AA}$  due to electron backscattering. The presented values are already the corrected ones.

<sup>b</sup> The accuracy of coordination numbers is around 20%.

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