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The ‘dissolution’ of europium and ytterbium in alcohols

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Abstract

Direct ‘dissolution’ of metallic europium and ytterbium in alcohols, without the use of a catalyst, was studied. In this work we report the reactions with methanol, ethanol and isopropanol. The Mössbauer spectra of the europium compounds indicated that the element in the obtained products is in the oxidation state II, whereas for the ytterbium compounds the oxidation sate of the element is III. Some of the compounds were also prepared by the metal vapour synthesis technique for comparison. © 1998 Elsevier Science S.A.

Keywords: Europium; Ytterbium; Alkoxides

1. Introduction

The synthesis of metal alkoxides has been the object of recent interest as they are good precursors for the deposition of metal oxides with several applications [1–3]. The conventional route using the reaction between a lanthanide halide and an alkoxide of an alkaline metal introduces undesired impurities (alkaline metal and halogen) in the final product. The high electropositive character of the lanthanides allows direct reactions with some alcohols but usually a catalyst, for example mercury chloride or iodine, are required, which also introduces impurities in the obtained products.

In our laboratories we have been exploring the direct reactions of alcohols with lanthanide metals, either using the metal vapour synthesis (MVS) technique [4], by bubbling ammonia gas through a suspension of metal pieces of Yb or Eu in a solution of the alcohol in tetrahydrofuran, or condensing the ammonia in the alcohol at low temperature after addition of the metals. Evolution of H_2 on the surface of the metals is accompanied by its dissolution. During our experiments we observed that metallic europium reacted directly with the alcohols even without the use of ammonia. A first characterization of the compound obtained, using elemental analysis and Mössbauer spectroscopy, showed that it can be formulated as $Eu(OR)_2$. In this work we report reactions with methanol, ethanol and isopropanol, and the respective Mössbauer spectra. The direct reaction of ytterbium metal with alcohols was also studied.

2. Experimental

All manipulations were routinely performed under N_2 using the glovebox and Schlenk techniques. Solvents were purified by standard methods. MVS experiments were made in a Planer Products plant VPS 500. ^{1}H NMR spectra were recorded using a Bruker SY80FT multinuclear spectrometer. C, H, N analyses were performed with a Perkin-Elmer automatic analyser. Eu and Yb analyses were performed according to a standard gravimetric method.

The Mössbauer spectra were measured at 80 K using a liquid nitrogen flow cryostat. The spectrometer was operated in constant acceleration mode and in the velocity range ± 30 mm s^{-1}. The velocity gradient was calibrated using a metallic α-Fe foil and a ^{57}Co source in a Rh matrix. The isomer shifts are given relative to the $^{151}SmF_3$ source at room temperature. Inside an inert atmosphere glovebox the powdered sample, pressed between two perspex disks, was introduced in an o-ring sealed copper holder. The sample holder was transferred under dry nitrogen into the vacuum shroud of the Mössbauer flow cryostat and kept under a vacuum of more than 10^{-5} mbar throughout data accumulation.

The spectra were fitted by varying the isomer shift δ, the quadrupole interaction e^2qQ, the line width Γ and the total absorption area with a fixed asymmetry parameter η. The function fitted by using the non-linear least-squares method

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of Stone [5] was a pure quadrupole-split spectrum calculated for a 5/2–7/2 transition [6]. The optimum value for η was found by a series of fits with different η values. The small absorption always observed around 0 mm s^{-1} was fitted by a single Lorentzian line.

2.1. Eu(OMe)$_2$

Europium (1 g; 6.58 mmol) was added to 50 ml of methanol. After several hours of stirring all the metal was consumed and the insoluble fraction was separated by centrifugation. The resultant greenish yellow solid was washed with pentane and dried under vacuum (yield, 35.2%). Anal. Calc. for $EuC_2H_6O_2$: Eu, 71.00; C, 11.22; H, 2.83; Found: Eu, 69.33; C, 11.00; H, 3.12.

2.2. Yb(OMe)$_3$

Ytterbium (1 g; 5.78 mmol) was added to 80 ml of methanol. After several hours of stirring the mixture was filtered through a Celite bed. The solution obtained was evaporated until dryness and gave a brick red solid (yield, 23.8%). Anal. Calc. for $YbC_3H_9O_3$: Yb, 65.01; C, 13.54; H, 3.42; Found: Yb, 63.87; C, 13.13; H, 3.16.

2.3. Eu(OEt)$_2$

(a) Europium atoms (1.98 g; 13.03 mmol) were vaporized with a resistance heating furnace and were co-condensed with 30 ml of ethanol onto a liquid nitrogen-cooled surface over a period of 3 h. The resultant mixture was allowed to warm slowly to room temperature under a nitrogen atmosphere. The product was washed out with pentane and ethanol and filtered through a Celite bed. Volatile components were removed under vacuum to give a yellow solid (yield, ≅50%). Anal. Calc. for $EuC_4H_{10}O_2$: Eu, 62.77; C, 19.84; H, 4.17; Found: Eu, 61.53; C, 19.17; H, 4.43.

(b) Europium (1.5 g; 9.87 mmol) was added to 80 ml of ethanol. After several hours of stirring the mixture was filtered through a Celite bed and the solution was evaporated until dryness. A yellow solid was then obtained (yield, 39.7%). Found: Eu, 63.14; C, 19.47; H 4.45.

2.4. Eu(OPr^i)$_2$

(a) Europium atoms (2.03 g; 13.36 mmol) were co-condensed with 30 ml of isopropanol as above. The product was washed out with pentane and THF and filtered through a Celite bed. A brown solid was obtained after removal of the solvent and drying under vacuum (yield, ≅50%). Anal. Calc. for $EuC_6H_{14}O_2$: Eu, 56.25; C, 26.67; H, 5.23; Found: Eu, 56.00; C, 24.89; H, 5.38.

(b) Europium (2.1 g; 13.82 mmol) was added to 80 ml of isopropanol. After several hours of stirring the mixture was filtered through a Celite bed and the solution evaporated. The product was extracted with pentane and a yellow solid was obtained after drying under vacuum (yield 33.8%). Found: Eu, 54.48; C, 24.19; H, 5.32.

2.5. Yb$_5$O(OPr^i)$_{13}$

(a) Ytterbium atoms (2.18 g; 12.60 mmol) were co-condensed with 30 ml of isopropanol. The product was washed out with pentane and toluene and filtered through a Celite bed. A white solid was obtained after drying under vacuum. This compound was purified by sublimation (190–200°C/10^{-5} mbar) (yield, ≅50%). Anal. Calc. for $Yb_5C_{39}H_{91}O_{14}$: Yb, 52.45; C, 28.40; H, 5.57; Found: Yb, 52.56; C, 27.75; H, 6.00; ^{1}H NMR (C_7D_8; δ, ppm vs. TMS) 97.8 (24 H CH_3), 61.8 (24 H CH_3), 2.0 (6 H CH_3), −71.0 (24 H CH_3), 193.7 (4 H CH), 112.1 (4 H CH), −46.8 (1 H CH), −136.7 (4 H CH).

(b) Ytterbium (1.6 g; 9.25 mmol) was added to 80 ml of isopropanol in a 250-ml flask double manifold. The flask was connected to a vacuum line and liquid ammonia was condensed into the reaction vessel at −78°C. As soon as the blue color appeared, gas was observed to evolve and the solution became dark. After 3 h the reaction mixture was allowed to slowly warm to room temperature and was purged with N_2. This mixture was then filtered through a Celite bed and removal of the solvent gave a white solid. The characterization gave similar results as above (yield, 32.0%).

3. Results and discussion

The direct reaction of the lanthanide metals with the alcohols seemed to be an alternative process to the conventional routes for the preparation of the alkoxides as it avoids the contamination with chlorine or alkaline metals. The yields of the reactions by direct dissolution are about 30%, and comparable with previously reported data by Poncelet et al. for the yttrium compound $Y_5O(OPr^i)_{13}$ if a mercury catalyst is not used in the reaction between the metal and isopropanol [7]. Part of the metal remained in the reaction vessel as an insoluble slurry and was retained in the filter. The same authors reported that no reaction was observed between Y turnings and methanol or ter-butyl alcohol, even in the presence of a mercury catalyst. For europium metal we observed that it reacts directly with methanol, ethanol and isopropanol giving the bisalkoxide compounds. The europium ethoxide and isopropoxide were also synthesized by the metal vapour synthesis technique and the results are comparable; however, the estimated yields are around 50%. All the europium compounds have the metal in the oxidation state II as indicated by the Mössbauer spectra which are discussed below.

Ytterbium reacts directly with methanol giving Yb(OMe)$_3$. The reaction with ethanol gave a mixture of

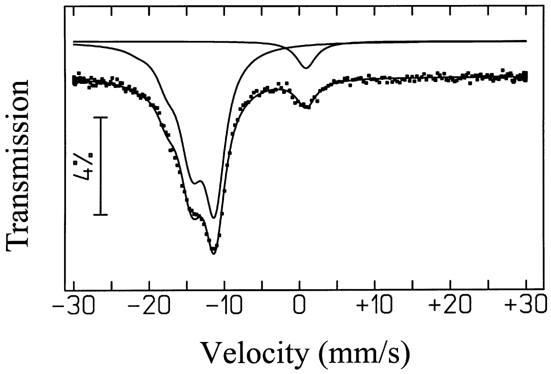

Fig. 1. ^{151}Eu Mössbauer spectrum of $Eu(OCH_3)_2$ taken at 80 K.

products which could not be identified. Ytterbium does not react directly with isopropanol. The reaction proceeded only if ammonia was condensed in the reaction vessel, after addition of the metal to isopropanol. Either using this procedure or the MVS technique the compound $Yb_5O(OPr^i)_{13}$ was obtained. This polynuclear compound was previously reported by Bradley et al. It was obtained by reaction of the metal with isopropanol using $HgCl_2$ as catalyst [8]. Both ytterbium compounds synthesized here have the element in the oxidation state III, whereas the europium compounds are in the oxidation state II. This observation is in agreement with their different reduction potentials ($E_{1/2}$ vs. NHE: Eu (−0.34 V) and Yb (−1.04) ($Ln^{3+} + e^- \rightarrow Ln^{2+}$)].

As referred above, the europium compounds were characterized by Mössbauer spectroscopy. A typical spectrum is shown in Fig. 1. Table 1 shows the hyperfine parameters for the synthesized europium alkoxides. The estimated δ of the main component of the spectra (>90% of the total area of the spectrum) is typical of Eu^{2+}, while that estimated for the peaks around 0 mm s^{-1} is typical of Eu^{3+} [6]. This suggests that the Eu present in the alkoxides is essentially in the form of Eu^{2+}.

4. Final remarks

The direct reaction of europium and ytterbium with alcohols seemed to be a convenient method to prepare alkoxides free of alkaline metals or halogens. The direct dissolution works well for europium, but for ytterbium only the methoxide could be prepared by this process. In the cases where the direct reaction does not work alternative routes include the addition of ammonia to a suspension of the metal in tetrahydrofuran or the metal vapour synthesis technique.

Acknowledgements

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Table 1
Hyperfine parameters estimated from the ^{151}Eu Mössbauer spectra taken at 80 K

Compound	δ (mm s^{-1})	e^2qQ (mm s^{-1})	η	Γ (mm s^{-1})	I (%)
$Eu(OMe)_2$	−13.1(1)	22.2(2)	0.37	3.3(4)	92(1)
	0.90(8)	—	—	3.2(2)	8(1)
$Eu(OEt)_2$	−13.0(1)	23.3(1)	0.83	3.28(6)	93(1)
	0.4(1)	—	—	2.7(3)	7(1)
$Eu(OPr^i)_2$	−12.3(3)	−19.8(2)	0.96	3.1(8)	91(1)
	0.93(5)	—	—	2.9(1)	9(1)