Journal of Alloys and Compounds 323–324 (2001) 169–172

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Synthesis and characterization of polynuclear lanthanide aryloxides

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Abstract

The reactions of europium and ytterbium in liquid ammonia with a solution of 1-naphthol in tetrahydrofuran provide a convenient route to lanthanide aryloxides. The polymetallic lanthanide complexes $[Eu_4(\mu\text{-}OC_{10}H_7)_6(OC_{10}H_7)_2(THF)_{10}].2THF$ **1** and $[Yb(\mu\text{-}OC_{10}H_7)(OC_{10}H_7)_2(THF)(MeCN)]_2.2MeCN$ **2** were synthesized and characterized by X-ray diffraction studies.

Keywords: Europium; Ytterbium; Aryloxides

1. Introduction

Lanthanide alkoxides and aryloxides can be used in catalysis of organic reactions [1] and as precursors to prepare materials containing high purity oxides [2,3]. In our Laboratories we have studied the reactions of europium and ytterbium metals with alcohols using the direct reaction [4], the metal vapour synthesis technique (MVS) [5] and the dissolution in liquid ammonia [4].

In this work we studied the reactions of europium and ytterbium with 1-naphthol in liquid ammonia. We report here the crystal structures of the compounds obtained.

2. Experimental

All manipulations were routinely performed under N_2 using glove-box and Schlenk techniques. Solvents were purified by standard methods. 1-Naphthol was sublimed before use. CHN analyses were performed on a CE instrument EA1110 automatic analyser. Eu and Yb analyses were performed according to a standard gravimetric method. IR spectra were registered in a 577 Perkin-Elmer spectrometer with samples prepared as Nujol mulls. ^1H NMR spectra were recorded using a Varian Unity Inova 300 Hz spectrometer.

2.1. $[Eu_4(\mu\text{-}OC_{10}H_7)_6(OC_{10}H_7)_2(THF)_{10}].2THF$ **1**

Europium (2.4 g, 15.79 mmol) was added to a solution of 3.8 g of 1-naphthol (26.36 mmol) in THF (100 ml), in a 250 ml Schlenk flask. The flask was connected to a vacuum line and liquid ammonia was condensed into the reaction vessel at −78°C. 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 the solution evaporated. The product was washed several times with pentane and an orange solid formulated as $Eu_4(OC_{10}H_7)_8(THF)_{10}$ was obtained after drying under vacuum (yield=57%). Analysis found (%): Eu, 25.89; C, 57.13; H, 5.61. Calculated for $Eu_4O_{18}C_{120}H_{136}$: Eu, 24.57; C, 58,24; H, 5.55. IR (cm^{-1}): 2700w, 2580w, 1560m, 1490w, 1450s, 1370s, 1360m, 1330w, 1310w, 1265m, 1230w, 1155w, 1140w, 1080w, 1065w, 1040m, 1025w, 1010w, 965w, 930w, 880w, 845w, 790w, 780w, 760m, 710m, 680w, 650w, 580w, 540w, 490w, 470w. X-ray quality crystals were grown from a solution of the orange solid in THF at room temperature and the compound **1** was characterized.

2.2. $[Yb(\mu\text{-}OC_{10}H_7)(OC_{10}H_7)_2(THF)(MeCN)]_2.2MeCN$ **2**

Ytterbium (2.2 g, 12.71 mmol) was added to a solution of 5.2 g of 1-naphthol (36.07 mmol) in THF (100 ml). The reaction procedure was similar as above. A yellow solid

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0925-8388/01/$ – see front matter
PII: S0925-8388(01)01122-7

Table 1
Crystallographic data for complexes **1** and **2**

	1	2
Formula	$C_{120}H_{136}O_{18}Eu_4.2C_4H_8O$	$C_{72}H_{64}N_2O_8Yb_2.2CH_3CN$
mol. wt.	2618.34	1513.44
Crystal system	Triclinic	Monoclinic
space group	P	$P2_1/n$
a, Å	12.218(3)	12.529(3)
b, Å	14.820(2)	11.574(2)
c, Å	18.790(3)	24.135(3)
α, deg	108.35(1)	
β, deg	94.04(1)	99.34(2)
γ, deg	108.76(1)	
V, Å^3	3001.4(10)	3453.4(11)
Z	1	2
d_{calc}, g cm^{-3}	1.449	1.455
R_1 [a]	0.0617	0.0562
wR_2 [a]	0.1137	0.1051

[a] The values were calculated for data with $I>2\sigma(I)$.

formulated as $Yb_2(OC_{10}H_7)_6(THF)_4$ was then obtained (yield=64%). Analysis found: Yb, 23.74; C, 59.47; H, 4.98. Calculated for $Yb_2O_{10}C_{76}H_{74}$: Yb, 23.17; C, 61.11; H, 5.00. IR (cm^{-1}): 2700w, 1900w, 1650w, 1600w, 1550s, 1490w, 1450s, 1360s, 1330m, 1310w, 1280m, 1255m, 1220m, 1155w, 1135w, 1080m, 1030m, 1000m, 970w, 940w, 920w, 920w, 900w, 880m, 870m, 850m, 780m, 770w, 760s, 720m, 705m, 650w, 630w, 595w, 580w, 540w, 500w, 480w, 470w, 410w. X-ray quality crystals were grown from a solution of the yellow solid in MeCN at −20°C and the compound **2** was characterized.

2.3. X-ray crystallographic analysis

Orange and yellow crystals of **1** and **2** were mounted in thin-walled glass capillaries in a nitrogen-filled glove-box. Data were collected at room temperature on an Enraf-Nonius CAD4-diffractometer with graphite-monochromatized MoKα radiation, using a $\omega-2\theta$ scan mode. A summary of the crystallographic data is given in Table 1. Data were corrected [6] for Lorentz and polarization effects, for linear decay and for absorption by empirical corrections based on Ψ scans. The structures were solved by Patterson methods [7] and refined by full matrix least-squares on F^2 using SHELXL-93 [8]. For **1** there is one molecule of THF of crystallization and for **2** one molecule of acetonitrile, per asymmetric unit. All the non-hydrogen atoms (except the solvent atoms for **1**) were refined with anisotropic thermal motion parameters and the contribution of the hydrogen atoms were included in calculated positions. Atomic scattering factors and anomalous disperson terms were taken as in Ref. [8]. The drawings were made with ORTEPII [9] and all the calculations were performed on a DEC α 3000 computer.

3. Results and discussion

Metallic europium and ytterbium react with a THF solution of 1-naphthol in liquid ammonia to produce respectively, an orange and a yellow solid, both unvolatile and soluble in tetrahydrofuran, toluene, dichloromethane and acetonitrile. These compounds were not readily identified by common spectroscopy methods and elemental analysis. The IR spectra were consistent with the presence of aryloxide ligands. The ^{1}H NMR spectrum of the ytterbium compound contained broad peaks in the aromatic region, but did not reveal useful information, except the existence of coordinated THF. Since these data were not structurally definitive we tried to characterize these products by X-ray crystallography.

Crystallization of the Eu/1-naphthol reaction product in the presence of THF at room temperature forms $[Eu_4(\mu\text{-}OC_{10}H_7)_6(OC_{10}H_7)_2(THF)_{10}].2THF$ **1**, whereas crystallization of the Yb/1-naphthol reaction product in the presence of acetonitrile at −20°C forms $[Yb(\mu\text{-}OC_{10}H_7)(OC_{10}H_7)_2(THF)(MeCN)]_2.2MeCN$ **2**, as shown in the Figs. 1 and 2, respectively. In the tetrameric (Eu) and the dimeric (Yb) structures all the metallic centers are hexacoordinated. As expected, the element with the largest ionic radius gave the most oligomeric complex. The oxidation states of the divalent europium and the trivalent ytterbium are in agreement with their different reduction potentials ($E_{1/2}$ vs. NHE; Eu: −0.34 V, Yb: −1.04; $Ln^{3+}+e^- \rightarrow Ln^{2+}$).

3.1. Crystal structures of *1* and *2*

The structure of **1** revealed a tetrametallic complex, $[(THF)_3(OC_{10}H_7)Eu(\mu\text{-}OC_{10}H_7)_2Eu(\mu\text{-}OC_{10}H_7)(THF)_2]_2.2THF$, composed of a nonlinear array of four

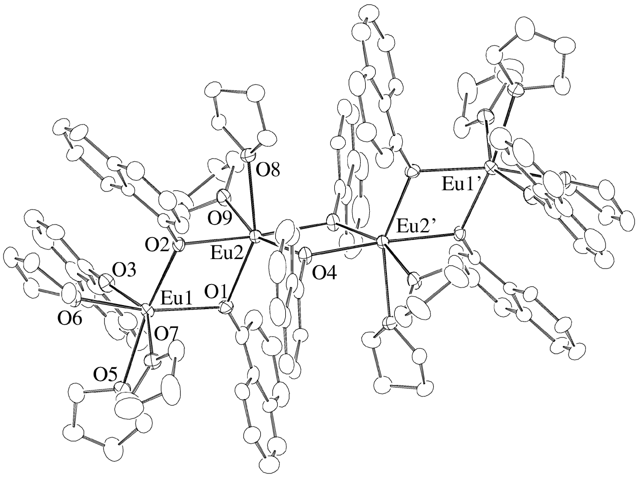

Fig. 1. ORTEP diagram of **1**.

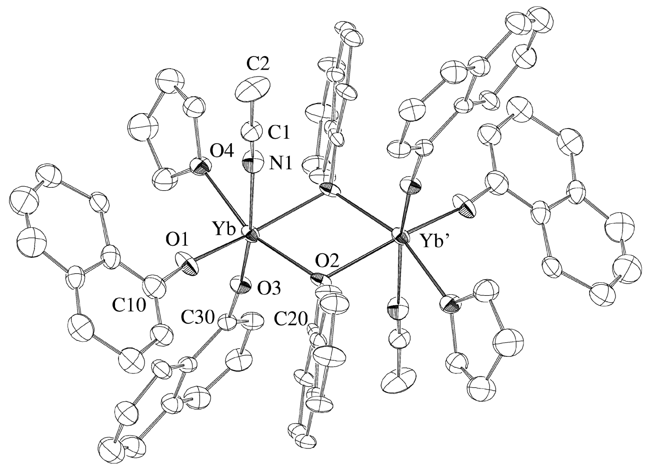

Fig. 2. ORTEP diagram of **2**.

Eu(II) ions, as can be seen in Fig. 3. The molecule has a centre of symmetry. Selected bond distances and angles are given in Table 2. The Eu(1) and Eu(2) atoms have different environments. The coordination sphere of the two inner Eu(II) ions is composed of four bridging aryloxide and two THF groups, while each exterior Eu ion is coordinated to three THF groups, two bridging and one terminal aryloxide ligands. The coordination geometry around the Eu ions is distorted from octahedral due to the presence of the bridging ligands, with the axial O(3)–Eu(1)–O(7) and O(4)–Eu(2)–O(9) angles of 149.9(3) and 161.0(2)°, respectively. The planar Eu(2)$_2$O(4)$_2$ ring and the almost planar Eu(1)–O(1)–Eu(2)–O(2) ring make an angle of 77.8(3)°.

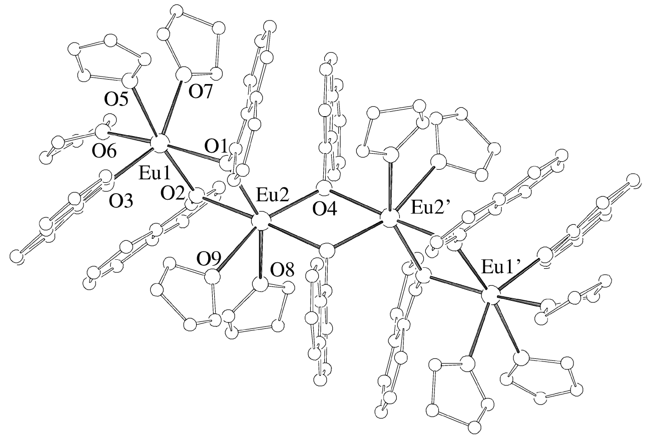

Fig. 3. Molecular structure of **1**.

Table 2
Selected bond lengths (Å) and angles (deg) for **1**

Eu(1)–O(1)	2.485(8)	Eu(2)–O(1)	2.465(8)
Eu(1)–O(2)	2.417(7)	Eu(2)–O(2)	2.497(6)
Eu(1)–O(3)	2.314(8)	Eu(2)–O(4)	2.466(7)
Eu(1)–O(5)	2.652(9)	Eu(2)–O(4)[a]	2.505(7)
Eu(1)–O(6)	2.605(8)	Eu(2)–O(8)	2.595(8)
Eu(1)–O(7)	2.604(8)	Eu(2)–O(9)	2.648(7)
O(1)–Eu(1)–O(6)	161.9(3)	O(2)–Eu(2)–O(4)[a]	175.7(2)
O(2)–Eu(1)–O(5)	172.1(3)	O(1)–Eu(2)–O(8)	153.5(2)
O(3)–Eu(1)–O(7)	149.9(3)	O(4)–Eu(2)–O(9)	161.0(2)
Eu(1)–O(3)–C(3)	176.6(9)		

[a] Atoms related by the symmetry operation: $-x,-y,-z$.

The terminal aryloxide Eu(1)–O(3) distance, 2.314(8) Å, is the shortest Eu–O distance in the molecule, while the bridging Eu–μO distances are in the range 2.417(7)–2.505(7) Å. The terminal Eu–O and the range of Eu–μO distances in **1** are similar to the Eu^{II} aryloxide bond distances observed in other structurally characterized complexes [10–13]. Tetrametallic Eu(II) aryloxides complexes have been observed in $\{[\mathrm{Eu}(\mu_3\text{-}\eta^2\text{-OCH}_2\text{CH}_2\text{OMe})(\eta^2\text{ - OCH}_2\text{CH}_2\text{OMe})\ (\mathrm{OC}_6\mathrm{H}_3\mathrm{R}_2\text{ - 2, 6})^-][\mathrm{H}^+]\}_4$ (R=Me, Pr^i) [14] and in $[\mathrm{Eu}_4(\mu\text{-OC}_6\mathrm{H}_3\mathrm{Pr}^i_2\text{-2,6})_4(\mathrm{OC}_6\mathrm{H}_3\text{-}\mathrm{Pr}^i_2\text{-2,6})_2(\mu_3\text{-OH})_2(\mathrm{MeCN})_6]$ [10].

The structure of **2,** $[\mathrm{Yb}(\mu\text{-OC}_{10}\mathrm{H}_7)(\mathrm{OC}_{10}\mathrm{H}_7)_2\text{-}(\mathrm{THF})(\mathrm{MeCN})]_2$.2MeCN, is a centrosymmetric dimer, with asymmetrically bridging aryloxide ligands (2.215(8) and 2.244(8) Å), which are almost perpendicular to the plane of the Yb$_2$O$_2$ ring (76.8(2)°), as shown in Fig. 2. Selected bond distances and angles are given in Table 3. The coordination geometry around Yb is quite distorted from octahedral, due to the presence of bridging ligands, with the acetonitrile and one terminal aryloxide ligand in axial positions (N(1)–Yb–O(3) 170.9(4)°).

The terminal aryloxide Yb–O bond lengths (2.047(8), 2.052(8) Å; av. 2.05(1) Å) are, as expected, shorter than those of the bridging ligands (2.215(8), 2.244(8) Å; av. 2.23(1) Å). Comparison can be made with the five-coordinate $[\mathrm{Y}(\mu\text{-OC}_6\mathrm{H}_3\mathrm{Me}_2\text{-2,6})(\mathrm{OC}_6\mathrm{H}_3\mathrm{Me}_2\text{-2,6})_2(\mathrm{THF})]_2$ [15], considering that Y(III) is 0.03 Å greater than Yb(III) for six-coordination. The terminal and bridging Y–O aryloxide distances are 2.06(1) and 2.276(1) Å, respectively (compared with the av. values of 2.05(1), 2.23(1) Å for **2**). The values of the terminal Yb–OAr bond lengths in **2** are similar to those in the related five-coordinate [Yb(Odpp)$_3$(DME)].0.5DME and [Yb(Odpp)$_3$(THF)$_2$].-

Table 3
Selected bond lengths (Å) and angles (deg) for **2**

Yb–O(1)	2.047(8)	Yb–O(2)[a]	2.244(8)
Yb–O(2)	2.215(8)	Yb–O(4)	2.297(10)
Yb–O(3)	2.052(8)	Yb–N(1)	2.472(13)
O(1)–Yb–O(2)[a]	159.4(3)	Yb–O(1)–C(10)	166.7(11)
O(2)–Yb–O(4)	161.5(3)	Yb–O(3)–C(30)	170.0(9)
O(3)–Yb–N(1)	170.9(4)	Yb–N(1)–C(1)	175(2)

[a] Atoms related by the symmetry operation: $-x+1,-y,-z$.

(THF) (Odpp=2,6-diphenylphenolate) [16]. The structure **2**, as compared to the structure of the [Yb($OC_6H_3Bu^t_2$-2,6)$_2$(MeCN)$_4$] [13], shows shorter terminal Yb–OR and Yb–N(MeCN) bond lengths (respectively, av. 2.05(1) and 2.472(13) Å compared with 2.23(1) and 2.61(2) Å) which is consistent with the difference of 0.15 Å between the ionic radii of Yb^{3+}/Yb^{2+}. There is a close intramolecular contact Yb···C(20) of 3.15(2) Å which could possibly indicate a $\eta^1-\pi$ interaction between the aryloxide ligand and the Yb atom.

4. Final remarks

To our knowledge the structures **1** and **2** are the first crystallographically characterized examples of lanthanide aryloxides with naphthol ligands. The reactions of the europium and ytterbium metals in liquid ammonia proved to be a convenient route to synthesize these aryloxides.

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