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Polyhedron 22 (2003) 1425–1429

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Europium(II) and ytterbium(II) aryloxide chemistry: synthesis and crystal structure of $[Eu(OC_6H_3Bu^t_2\text{-}2,6)_2(THF)_3]\cdot 0.75C_7H_8$ and $[Yb(OC_6H_3Bu^t_2\text{-}2,6)_2(NCMe)_4]$

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Received 19 December 2002; accepted 21 February 2003

Abstract

The reactions of europium and ytterbium with 2,6-di-*tert*-butylphenol were studied by the metal vapour synthesis technique and by dissolution in liquid ammonia. The lanthanide complexes $[Eu(OC_6H_3Bu^t_2\text{-}2,6)_2(THF)_3]\cdot 0.75C_7H_8$ **1** and $[Yb(OC_6H_3Bu^t_2\text{-}2,6)_2(NCMe)_4]$ **2** were synthesized and characterized by X-ray diffraction studies.

Keywords: Europium; Ytterbium; MVS; Dissolution in ammonia; Aryloxides

1. Introduction

Lanthanide alkoxides and aryloxides have been extensively studied due to the applicability of these complexes as precursors to high purity oxides [1,2] and catalysts for organic reactions [3]. The reactions with the elemental metal are the most convenient routes to lanthanide alkoxides and aryloxides, since the presence of undesirable ligands can be avoided, as they can contaminate the final product. In our laboratories we have studied the reactions of lanthanide metals with alcohols and phenols using the metal vapour synthesis technique (MVS) [4], the direct metal-alcohol reaction [5] and metal dissolution in liquid ammonia [5,6], having in mind the preparation of very pure aryloxides as precursors of catalysts supported on silica substrates.

In this work we studied the reactions of europium and ytterbium with 2,6-di-*tert*-butylphenol by the MVS technique and by dissolution in liquid ammonia. We report here the characterization of the compounds obtained, including the crystal and molecular structures.

2. Experimental

2.1. Materials and instrumentation

All manipulations were routinely performed under N_2 using glove-box and Schlenk techniques. MVS experiments were made in a Planer products plant VPS 500. Solvents were purified by standard methods [7]. Europium and ytterbium ingots were obtained commercially from the Baotou Research Institute of Rare Earth. 2,6-Di-*tert*-butylphenol was sublimed before use. C, H and N analyses were performed in a CE instruments EA1110 automatic analyser. Eu and Yb analyses were performed according to a standard gravimetric method [8]. 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 MHz spectrometer.

2.2. Preparation of complexes

$[Eu(OC_6H_3Bu^t_2\text{-}2,6)_2(THF)_3]\cdot 0.75C_7H_8$ **1** and $[Yb(OC_6H_3Bu^t_2\text{-}2,6)_2(NCMe)_4]$ **2**.

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0277-5387/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0277-5387(03)00193-1

2.2.1. Dissolution in liquid ammonia

Europium (2.50 g, 16.45 mmol) was added to a solution of 2,6-di-*tert*-butylphenol (6.7 g, 32.47 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 a yellow solid formulated as $[Eu(OC_6H_3Bu^t_2\text{-}2,6)_2(THF)_3]$ was obtained after drying under vacuum (yield = 76%). Analysis found (%): Eu, 19.10; C, 59.91; H, 9.00. Calculated for $EuO_5C_{40}H_{66}$: Eu, 19.51; C, 61.67; H, 8.56. IR (cm^{-1}): 3620w, 3040w, 2700w, 2660w, 2515w, 1570m, 1450s, 1400s, 1370s, 1360w, 1340w, 1330w, 1270s, 1250w, 1190m, 1170w, 1140w, 1130w, 1110w, 1100s, 1020s, 935w, 930w, 910w, 870s, 850s, 810m, 740m, 730m, 660w, 630m, 535m, 460w, 440m. X-ray quality crystals of **1** were grown from a solution of the yellow solid in toluene at room temperature.

The procedure for the reaction of ytterbium (2.89 g, 16.70 mmol) with 2,6-di-*tert*-butylphenol (6.9 g, 33.44 mmol) was identical to that for the europium reaction. A red solid formulated as $[Yb(OC_6H_3Bu^t_2\text{-}2,6)_2(THF)_3]$ was obtained (yield = 73%). Analysis found (%): Yb, 21.24; C, 58.55; H, 7.54. Calculated for $YbO_5C_{40}H_{66}$: Yb, 21.63; C, 60.04; H, 8.33. IR (cm^{-1}): 3610w, 3140w, 2700w, 1570m, 1450s, 1400s, 1370s, 1355w, 1345w, 1335w, 1330w, 1310w, 1270s, 1250w, 1220w, 1200w, 1190m, 1160w, 1140w, 1130w, 1090m, 1030w, 1010m, 950w, 930w, 910w, 900w, 870w, 860s, 840s, 830s, 810w, 800w, 790w, 735s, 725w, 715w, 660w, 640m, 540w, 440w. ^1H NMR (298 K; C_7D_8; δ; ppm/TMS): 7.42 (4 H *m*-H), 6.84 (2 H *p*-H), 3.80 {12 H CH_2 (THF)}, 1.75 (36 H Bu^t), 1.36 {12 H CH_2 (THF)}. X-ray quality crystals of **2** were grown from a solution of the red solid in acetonitrile at room temperature.

2.2.2. Metal vapour synthesis

Europium atoms (1.50 g, 9.87 mmol) were vaporized with a resistance heating furnace (432 W) and were co-condensed with 2,6-di-*tert*-butylphenol (32 g, 15.51 mmol) onto a liquid nitrogen-cooled surface over a period of 2 h. The resultant mixture was allowed to warm slowly to room temperature under a nitrogen atmosphere. The product was washed out with THF and filtered through a Celite bed. Volatile components were removed under vacuum to give a yellow solid formulated as $[Eu(OC_6H_3Bu^t_2\text{-}2,6)_2(THF)_3]$. The characterization of the europium compound gave similar results as in (yield = 42%).

The procedure for the reaction of ytterbium (1.74 g, 10.06 mmol) with 2,6-di-*tert*-butylphenol (35 g, 16.96 mmol) by MVS was identical to that for the europium reaction, and the characterization of the ytterbium compound gave similar results as in (yield = 40%).

2.3. X-ray structure determination

Very air sensitive yellow and red crystals of **1** and **2** were mounted under nujol in thin-walled glass capillaries, with atmosphere of solvent of crystallization, in a nitrogen-filled glove-box. Data were collected at room temperature on an Enraf-Nonius CAD4-diffractometer with graphite-monochromatized Mo Kα radiation, using a $\omega-2\theta$ scan mode. The value $\theta_{max} = 23°$ was imposed by the expected decay and the quality of the crystals. A summary of the crystallographic data is given in Table 1. Data were corrected [9] 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 [10] and refined by full matrix least-squares on F^2 using SHELXL-93 [11]. For **1** there are two crystallographically independent molecules and one and a half molecules of toluene of crystallization per asymmetric unity. All the non-hydrogen atoms were refined with anisotropic thermal motion parameters except those of the solvent, which were severely disordered, and were refined with positional restraints and so the corresponding hydrogen atoms were neglected. In compound **1**, the carbon atoms

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

	1	**2**
Formula	$C_{40}H_{66}O_5Eu \cdot 0.75C_7H_8$	$C_{36}H_{54}N_4O_2Yb$
Molecular weight	847.99	747.87
Crystal size (mm)	0.23 × 0.18 × 0.13	0.65 × 0.23 × 0.16
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	13.422(2)	11.833(2)
b (Å)	18.864(3)	17.691(1)
c (Å)	19.732(2)	18.073(1)
α (°)	111.76(1)	
β (°)	99.63(1)	91.123(13)
γ (°)	92.28(1)	
V (Å^3)	4546.3(11)	3782.6(7)
Z	4	4
D_{calc} (g cm^{-3})	1.239	1.313
R_1 [a]	0.0988	0.0889
wR_2 [b]	0.2083	0.1658
Reflections collected	13069	5454
Reflections independent (R_{int})	12615 (0.0623)	5259 (0.0662)
Reflections observed [$I > 2\sigma(I)$]	6169	2965
Parameters varied	873	388

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

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

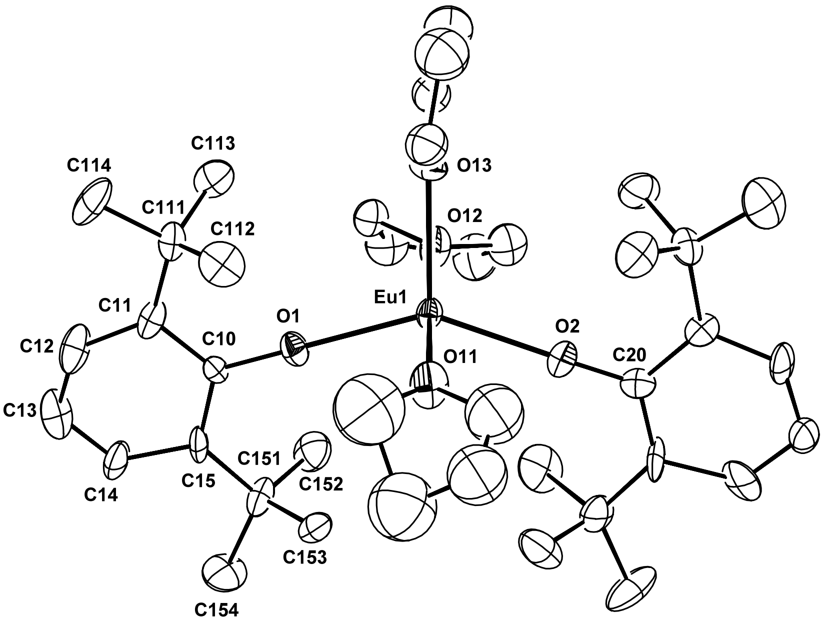

Fig. 1. ORTEP diagram of **1**, using 20% probability ellipsoids.

of one of the THF molecules (O_{11}) show exceptionally high displacement parameters. The contribution of the hydrogen atoms were included in calculated positions. Atomic scattering factors and anomalous dispersion terms were taken as in Ref. [11]. The drawings were made with ORTEP-3 [12] and all the calculations were performed on a DECα 3000 computer.

3. Results and discussion

Metallic europium and ytterbium react with a solution of 2,6-di-*tert*-butylphenol in liquid ammonia to produce, respectively, a yellow and a red solid, soluble in tetrahydrofuran, dichloromethane and acetonitrile. These compounds were formulated by elemental analysis as $Ln(OC_6H_3Bu^t_2\text{-}2,6)_2(THF)_3$ ($Ln = Eu$, Yb). The IR spectra were consistent with the presence of aryloxide and tetrahydrofuran ligands. The ^1H NMR spectrum of the ytterbium compound confirmed the formulation suggested. These reactions were also studied by the MVS and gave similar results as above. These MVS experiments involving europium and ytterbium confirmed the higher stability of the divalent state of these elements, comparing to the analogous reaction with samarium using the same synthetic method, where only a trivalent samarium aryloxide was obtained [4].

$$Ln + 2C_6H_3Bu^t_2\text{-}2,6\text{-}OH \xrightarrow{NH_3 \text{ or } MVS} [Ln(OC_6H_3Bu^t_2\text{-}2,6)_2(THF)_3] + H_2$$

The compounds $[Eu(OC_6H_3Bu^t_2\text{-}2,6)_2(THF)_3]$ [13] and $[Yb(OC_6H_3Bu^t_2\text{-}2,6)_2(THF)_3]$ [13–15] were previously synthesized by several authors using other methods, but no crystal structures were reported. Only the crystal structure of the complex $[Eu(OC_6H_3Bu^t_2\text{-}2,6)_2(NCMe)_4]$ has been determined [16].

Crystallization of $[Eu(OC_6H_3Bu^t_2\text{-}2,6)_2(THF)_3]$ in the presence of toluene at room temperature forms $[Eu(OC_6H_3Bu^t_2\text{-}2,6)_2(THF)_3]\cdot 0.75C_7H_8$ **1**, whereas crystallization of $[Yb(OC_6H_3Bu^t_2\text{-}2,6)_2(THF)_3]$ in the presence of acetonitrile at room temperature forms $[Yb(OC_6H_3Bu^t_2\text{-}2,6)_2(NCMe)_4]$ **2**.

The crystal structure of **1** consists of discrete molecular units, with two independent but chemically identical molecules per asymmetric unit. For both molecules the coordination geometry around the euro-

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

Bond lengths			
Eu(1)–O(1)	2.313(12)	Eu(2)–O(3)	2.302(12)
Eu(1)–O(2)	2.309(14)	Eu(2)–O(4)	2.352(12)
Eu(1)–O(11)	2.57(2)	Eu(2)–O(21)	2.579(13)
Eu(1)–O(12)	2.530(14)	Eu(2)–O(22)	2.553(13)
Eu(1)–O(13)	2.564(12)	Eu(2)–O(23)	2.53(2)
Bond angles			
O(1)–Eu(1)–O(2)	143.6(5)	O(3)–Eu(2)–O(4)	146.2(5)
O(1)–Eu(1)–O(11)	91.1(5)	O(3)–Eu(2)–O(21)	88.1(5)
O(1)–Eu(1)–O(12)	90.3(4)	O(3)–Eu(2)–O(22)	91.3(5)
O(1)–Eu(1)–O(13)	106.4(5)	O(3)–Eu(2)–O(23)	108.3(5)
O(2)–Eu(1)–O(11)	86.2(6)	O(4)–Eu(2)–O(21)	86.3(4)
O(2)–Eu(1)–O(12)	91.2(5)	O(4)–Eu(2)–O(22)	93.6(4)
O(2)–Eu(1)–O(13)	109.9(5)	O(4)–Eu(2)–O(23)	105.4(5)
O(11)–Eu(1)–O(12)	177.2(6)	O(21)–Eu(2)–O(22)	178.8(5)
O(11)–Eu(1)–O(13)	97.0(6)	O(21)–Eu(2)–O(23)	98.5(5)
O(12)–Eu(1)–O(13)	84.9(5)	O(22)–Eu(2)–O(23)	82.7(5)
Eu(1)–O(1)–C(10)	177.6(12)	Eu(2)–O(3)–C(30)	176.3(13)
Eu(1)–O(2)–C(20)	178.6(14)	Eu(2)–O(4)–C(40)	176.5(12)

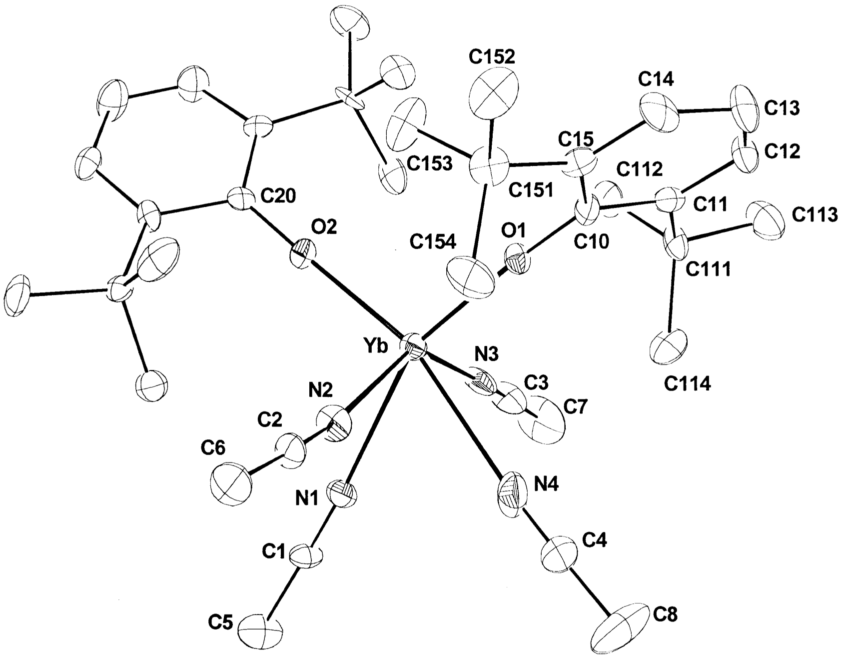

Fig. 2. ORTEP diagram of **2**, using 20% probability ellipsoids.

pium atom is best described as distorted trigonal-bipyramidal, with two aryloxide groups and one THF molecule in the equatorial plane and two THF molecules in the axial positions. The ORTEP diagram for one of the molecules can be seen in Fig. 1. Selected bond distances and angles for the molecule 1 and 2 are given in Table 2.

The distances Eu–O to the aryloxide groups are for molecule 1, 2.313(12) and 2.309(14) Å, and for molecule 2, 2.302(12) and 2.352(12) Å, which are comparable to analogue distances in the complex [Eu(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$(NCMe)$_4$] [16], 2.313(12) and 2.35(2) Å. Comparison can also be made with the Eu–O bond distances in the aryloxide groups of the complex [Eu(OC$_6$H$_2$Bu$^t_2$-2,6-Me-4)$_2$(THF)$_3$].THF: 2.321(5) and 2.337(5) Å [15]. The average value for the Eu–O distance to the THF groups, 2.55(2) Å for both molecules is also comparable with the analogue average value in the latter complex: 2.559(5) Å. The bond angles between the two aryloxide groups are for molecule 1, 143.6(5)° and for molecule 2, 146.2(5)°, which are comparable with the analogue bond angle in the complex [Eu(OC$_6$H$_2$Bu$^t_2$-2,6-Me-4)$_2$(THF)$_3$].THF: 150.3(2)° [15]. In this complex the bond angle between the two THF molecules in axial positions is 178.6(2)°, whereas for complex **1** the bond angles are 177.2(6)° and 178.8(5)°, respectively, for molecule 1 and 2.

The monomeric complex **2** has a distorted octahedral geometry with one acetonitrile molecule and one aryloxide ligand in axial positions {O(2)–Yb–N(4): 164.3(5)°}. The equatorial plane is defined by an aryloxide ligand and three acetonitrile molecules. The ORTEP diagram for the complex [Yb(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$(NCMe)$_4$] can be seen in Fig. 2. Selected bond distances and angles are given in Table 3. The Yb–O bond lengths for the aryloxide groups are 2.204(12) and 2.245(10) Å, which are comparable with analogue values in the complex [Yb(OC$_6$H$_2$Bu$^t_2$-2,6-Me-4)$_2$(THF)$_3$], 2.217(12) and 2.196(18) Å [17]. The average values of the Yb–O bonds in the aryloxide groups and the Yb–N bonds, respectively, 2.22(2) and 2.61(2) Å, can be compared with analogue values in the complex [Eu(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$(NCMe)$_4$]: Eu–O = 2.33(2) Å and Eu–N = 2.74(2) Å [16]. The observed differences can be explained considering the different ionic radius of Eu^{2+} (1.17 Å) and Yb^{2+} (1.02 Å) in complexes with a coordination number of 6. The bond angle between the two aryloxide groups is 108.2(4)°, which is compar-

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

Bond lengths			
Yb–O(1)	2.204(12)	Yb–N(2)	2.52(2)
Yb–O(2)	2.245(10)	Yb–N(3)	2.63(2)
Yb–N(1)	2.62(2)	Yb–N(4)	2.66(2)
Bond angles			
O(1)–Yb–O(2)	108.2(4)	N(1)–Yb–N(4)	74.1(6)
O(1)–Yb–N(1)	158.0(5)	N(2)–Yb–N(3)	143.9(6)
O(1)–Yb–N(2)	102.5(5)	N(2)–Yb–N(4)	72.5(5)
O(1)–Yb–N(3)	101.9(5)	N(3)–Yb–N(4)	83.8(6)
O(1)–Yb–N(4)	84.8(5)	Yb–O(1)–C(10)	175.7(11)
O(2)–Yb–N(1)	93.7(5)	Yb–O(2)–C(20)	175.5(10)
O(2)–Yb–N(2)	95.5(5)	Yb–N(1)–C(1)	172(2)
O(2)–Yb–N(3)	101.6(5)	Yb–N(2)–C(2)	173(2)
O(2)–Yb–N(4)	164.3(5)	Yb–N(3)–C(3)	177(2)
N(1)–Yb–N(2)	76.9(5)	Yb–N(4)–C(4)	174(2)
N(1)–Yb–N(3)	70.5(5)		

able with the analogue bond angle 105.2(4)° in the complex $[Eu(OC_6H_3Bu^t_2\text{-}2,6)_2(NCMe)_4]$ [16]. These two complexes can be considered as isostructural.

4. Conclusion

The reactions of the europium and ytterbium metals with 2,6-di-*tert*-butylphenol in liquid ammonia and by the MVS technique proved to be convenient routes to synthesize monomeric divalent aryloxides. The new crystallographic structures **1** and **2** were determined.

5. Supplementary material

Supplementary data are available from the Cambridge Crystallographic Data Center, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on request, quoting the deposition numbers 198682 for compound **1** and 198683 for compound **2**.

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