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Convenient Preparation of Lanthanide Aryloxides from Lanthanide Nitrate Polyether Complexes and the Crystal Structure of $[La(OC_6H_3Me_2\text{-}2,6)_3(MeO(CH_2CH_2O)_4Me)]$

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Introduction

The applications of lanthanide alkoxides and aryloxides are diverse, ranging from homogeneous catalysis of organic reactions[1−3] to synthesis of high purity oxide materials.[4] Preparative routes to alkoxides include reaction of the lanthanide metal with an appropriate alcohol, reaction of the anhydrous lanthanide chloride with an alkali metal alkoxide, and alcoholysis of lanthanide tris(dialkylamides),[5] all of which require the use of starting materials which must be prepared and handled under strictly anhydrous and/or anaerobic conditions. While this is feasible on a laboratory scale, it is much less attractive if preparation on an industrial scale is required. In this paper, we describe the preparation of lanthanum and praseodymium aryloxides from lanthanide nitrate polyether complexes, which are easily prepared anhydrous starting materials.

Results and Discussion

Complexes of lanthanide nitrates with glycol and polyether ligands were reported several years ago,[6] and are among a small number of anhydrous lanthanide complexes which may be prepared readily from hydrated lanthanide salts without the use of rigorously anhydrous conditions. When Ln = La, $[Ln(NO_3)_3(M_2EO_n)]$ is readily precipitated in high yields as an analytically pure compound by addition of one equivalent of M_2EO_4 to an ethylacetate solution of $La(NO_3)_3{\cdot}nH_2O$ (M_2EO_n is $MeO(CH_2CH_2O)_nMe$; $n = 3$ is triglyme; $n = 4$ is tetraglyme).

For the later lanthanides $[Ln(NO_3)_3(M_2EO_n)]$ compounds become increasingly hygroscopic and their precipitation from ethyl acetate solution is effected by drying with molecular sieve. Lanthanide trichlorides are the most widely used anhydrous starting materials for lanthanide chemistry; they are extremely hygroscopic and their preparation from the hydrated chlorides can be a tedious procedure. The ready availability of $[Ln(NO_3)_3(M_2EO_4)]$ for early lanthanides suggested that these complexes may be convenient starting materials for the synthesis of lanthanide alkoxides and aryloxides. We began our investigations with the preparation of 2,6-dimethylphenoxide complexes.

Reaction of a THF suspension of $[Ln(NO_3)_3(M_2EO_4)]$ with 3 equiv of $Na(OC_6H_3Me_2\text{-}2,6)$ in THF at room temperature led to rapid formation of $[Ln(OC_6H_3Me_2\text{-}2,6)_3(M_2EO_4)]$ and precipitation of $NaNO_3$. The product was obtained in high yield as colorless (Ln = La, **1**) or pale green (Ln = Pr, **2**) prisms from cold concentrated THF. An analogous reaction between $[La(NO_3)_3(M_2EO_3)]$ gave $[La(OC_6H_3Me_2\text{-}2,6)_3(M_2EO_3)]$, **3**, also in high yield. The mixed ligand complex $[La(OC_6H_3Me_2\text{-}2,6)_2(NO_3)(M_2EO_4)]$, **4**, was formed as the only product when $[La(NO_3)_3(M_2EO_4)]$ reacted with 2 equiv of $Na(OC_6H_3Me_2\text{-}2,6)$ under similar conditions, and was found to be stable with respect to ligand redistribution reactions. These preparations may be carried out reasonably successfully without taking any rigorous precautions to exclude moisture; however, the yields are higher and the products easier to isolate when anhydrous conditions are used.

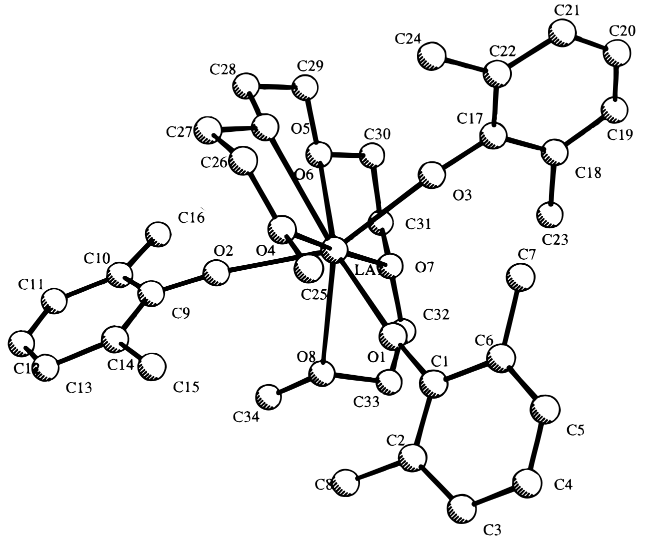

Figure 1. PLUTO plot of **1**.

All new complexes were characterized by elemental analysis and NMR spectroscopy (^1H and ^{13}C); NMR data are given in Table 1. We found it necessary to record NMR spectra in THF-d_8 as spectra recorded in less expensive noncoordinating solvents (*e.g.* $CDCl_3$) were very broad and poorly resolved, possibly due to some degree of association in such solvents. The chemical shifts of resonances due to the polyether ligands in the La complexes are insensitive to the number or nature of the other ligands, and are essentially indistinguishable from those found for $[La(M_2EO_n)X_3]$ ($X = NO_3$, CF_3SO_3) in $CDCl_3$. The ^1H NMR spectrum of **2** at 298 K was extremely broad and indecipherable due to the paramagnetism of the $4f^2$ Pr^{3+} ion. However, on cooling the sample to 253 K, three resonances in the ratio 1:2:6 were resolved due to the three dimethylphenoxide ligands which were equivalent on an NMR time scale at this temperature. When the temperature was lowered to 233 K, two sets of resonances were observed for the dimethylphenoxide ligands; these sets of resonances were in the ratio 2:1 and demonstrate the freezing out of a structure analogous to that found in the solid state for **1**. It is perhaps surprising that the resonances due to the M_2EO_4 ligand in **2** show only a very small paramagnetic shift. This must be due to geometrical factors rather than dissociation from the metal as, at room temperature, these resonances as well as those from the dimethylphenoxide ligands are very broad.

X-ray Crystal Structure of 1. Crystals suitable for X-ray diffraction were grown from a mixture of THF and diethyl ether. A PLUTO plot of the complex is shown in Figure 1; fractional atomic coordinates are given in Table 2, and selected bond lengths and angles are given in Table 3. The compound crystallizes with a non-stoichiometric quantity of sovent (probably diethyl ether) which occupies a disordered position in the crystal. This solvent is very readily lost from the crystal as it does not appear either in NMR spectra or in elemental analysis.

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Table 1. ^{1}H and ^{13}C NMR Data

	^{1}H NMR			^{13}C NMR		
compound	$C_6H_3\mathit{Me}_2$	$C_6\mathit{H}_3Me_2$	polyether	$C_6H_3\mathit{Me}_2$	$\mathit{C}_6\mathit{H}_3Me_2$	polyether
$La(OC_6H_3Me_2\text{-}2,6)_3(M_2EO_4)$	2.24 (s, 18H)	6.20 (t,3H, J=7.2Hz); 6.72 (d, 6H, J=7.2Hz)	3.28 (s, 6H); 3.48 (m); 3.60 (m)	19.78	115.20; 126.93; 129.72	59.09; 72.84; 73.10; 74.33
$Pr(OC_6H_3Me_2\text{-}2,6)_3(M_2EO_4)^a$	26.35(s, 18H)	15.75 (s, 3H); 19.85 (s, 6H)	2.90; 2.99; 3.47; 3.72; 4.21			
$Pr(OC_6H_3Me_2\text{-}2,6)_3(M_2EO_4)^b$	57.55 (br, s, 6H); 29.26 (br, s, 12H)	49.92 (s, 2H); 39.57 (s, 1H); 21.12 (s, 4H); 16.59 (s, 2H)	2.75, 2.86, 3.31, 3.55, 4.14			
$La(OC_6H_3Me_2\text{-}2,6)_2(NO_3)(M_2EO_4)$	2.26 (s, 12H)	6.46 (t, 2H); 6.84 (d, 4H)	3.37 (s, 6H); 3.56 (m); 3.72 (m)	18.77	126.42; 129.79	60.46; 72.57; 72.72; 74.10
$La(OC_6H_3Me_2\text{-}2,6)_3(M_2EO_3)$	2.23 (s, 18H)	6.25 (t, 3H); 6.74 (d, 6H)	3.37 (s, 6H); 3.59 (m); 3.63 (m)	18.30	120.16; 126.30; 130.19; 156.76	60.45; 72.76; 72.99; 74.39

^{a} Recorded at 253 K. ^{b} Recorded at 233 K.

Table 2. Positional Parameters for **1**

atom	*x*	*y*	*z*
La(1)	0.5365(2)	0.22600(7)	0.96189(9)
O(1)	0.434(1)	0.2998(7)	0.8841(9)
O(2)	0.681(1)	0.272(1)	1.0486(8)
O(3)	0.395(1)	0.1449(7)	0.9203(8)
O(4)	0.362(2)	0.285(1)	1.0517(8)
O(5)	0.479(2)	0.170(1)	1.0947(8)
O(6)	0.659(1)	0.1108(7)	1.001(1)
O(7)	0.693(2)	0.1660(9)	0.867(1)
O(8)	0.730(2)	0.295(1)	0.885(1)
C(1)	0.359(1)	0.3385(8)	0.8404(8)
C(2)	0.405(1)	0.4004(8)	0.8201(9)
C(3)	0.330(2)	0.4400(6)	0.7715(9)
C(4)	0.208(1)	0.4178(8)	0.7433(8)
C(5)	0.162(1)	0.3559(8)	0.7636(9)
C(6)	0.238(2)	0.3163(6)	0.8122(9)
C(7)	0.185(2)	0.252(1)	0.833(1)
C(8)	0.533(3)	0.426(1)	0.851(2)
C(9)	0.769(1)	0.3034(8)	1.0929(8)
C(10)	0.887(2)	0.2750(6)	1.1182(9)
C(11)	0.978(1)	0.3120(8)	1.1603(9)
C(12)	0.951(1)	0.3774(8)	1.1770(8)
C(13)	0.833(2)	0.4059(6)	1.1517(9)
C(14)	0.742(1)	0.3689(8)	1.1096(9)
C(15)	0.617(3)	0.403(1)	1.080(2)
C(16)	0.918(2)	0.207(1)	1.096(1)
C(17)	0.309(1)	0.1005(7)	0.890(1)
C(18)	0.323(1)	0.0759(8)	0.8176(9)
C(19)	0.234(2)	0.0293(8)	0.7889(7)
C(20)	0.131(1)	0.0074(7)	0.8331(9)
C(21)	0.117(1)	0.0320(8)	0.9060(8)
C(22)	0.206(2)	0.0785(8)	0.9346(7)
C(23)	0.428(2)	0.102(1)	0.770(1)
C(24)	0.180(3)	0.107(1)	1.011(2)
C(25)	0.260(3)	0.330(2)	1.028(2)
C(26)	0.333(2)	0.256(1)	1.122(1)
C(27)	0.450(2)	0.214(1)	1.153(1)
C(28)	0.562(2)	0.118(1)	1.123(2)
C(29)	0.590(2)	0.074(1)	1.057(1)
C(30)	0.689(3)	0.069(1)	0.938(2)
C(31)	0.763(3)	0.108(1)	0.884(2)
C(32)	0.755(4)	0.204(2)	0.809(2)
C(33)	0.719(4)	0.270(3)	0.810(2)
C(34)	0.846(3)	0.317(2)	0.911(1)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**

La(1)−O(1)	2.28(2)	La(1)−O(5)	2.69(2)
La(1)−O(2)	2.30(2)	La(1)−O(6)	2.74(2)
La(1)−O(3)	2.30(2)	La(1)−O(7)	2.64(2)
La(1)−O(4)	2.70(2)	La(1)−O(8)	2.80(2)
O(1)−La(1)−O(2)	114.4(6)	O(3)−La(1)−O(6)	74.9(5)
O(1)−La(1)−O(3)	90.4(5)	O(3)−La(1)−O(7)	81.2(6)
O(1)−La(1)−O(4)	76.3(5)	O(3)−La(1)−O(8)	130.3(6)
O(1)−La(1)−O(8)	71.9(6)	O(4)−La(1)−O(5)	60.9(5)
O(2)−La(1)−O(3)	152.9(6)	O(4)−La(1)−O(8)	122.9(5)
O(2)−La(1)−O(4)	81.1(5)	O(5)−La(1)−O(6)	61.4(5)
O(2)−La(1)−O(5)	74.8(6)	O(6)−La(1)−O(7)	59.2(5)
O(2)−La(1)−O(6)	84.3(6)	O(7)−La(1)−O(8)	58.7(6)
O(2)−La(1)−O(7)	103.0(6)	La(1)−O(1)−C(1)	172(1)
O(2)−La(1)−O(8)	71.2(6)	La(1)−O(2)−C(9)	173(2)
O(3)−La(1)−O(4)	95.4(5)	La(1)−O(3)−C(17)	175(1)
O(3)−La(1)−O(5)	80.0(5)		

1 is 8-coordinate; the five oxygen donors of the M_2EO_4 ligand are approximately coplanar with the La atom (La(1) lies 0.46 Å out of the least-squares plane defined by O(4)−O(8)), and the dimethylphenoxide ligands occupy meridional sites in a plane perpendicular to that defined by the M_2EO_4 oxygen atoms. The dihedral angle between the phenyl groups attached to O(1) and O(2) is 40.24°; the corresponding angle for O(1) and O(3) is 73.73°, and for O(2) and O(3) it is 104.50°. Inspection of space-filling diagrams of **1** indicate that there is sufficient room for coordination of an additional small ligand, and we are investigating the Lewis acid activity of **1**, **3**, **4**, and related compounds.

The other structurally characterized rare earth dimethylphenoxides are $[Y(OC_6H_3Me_2\text{-}2,6)_3(THF)_2]_2$, **5**,[7] and $[Ln(OC_6H_3Me_2\text{-}2,6)_2(THF)(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_2AlMe_2]$, **6** (Ln = Nd, Yb).[8] The La−O−C bond angles for the dimethylphenoxide ligands of **1** are all somewhat larger than those found for the terminal phenoxides of **5** (162.6(5)°) and **6** (165.5(12)° for Yb; 169(8)° for Nd). Allowing for differences between the ionic radii of Y^{3+}, Nd^{3+}, Yb^{3+}, and La^{3+}, the Ln−O distances for the dimethylphenoxide ligands of **1** are similar to those for the terminal dimethylphenoxide ligands of **5** (2.075(6) and 2.046(6) Å) and **6** (2.057(11) Å for Yb and 2.153(9) Å for Nd). Diglyme has been used to stabilize monomeric rate earth alkoxides and coordinates facially in the 6-coordinate complex $[Y\{OCMe(CF_3)_2\}_3(diglyme)]$,[9] but there are no reported examples of rare earth alkoxide complexes containing triglyme or tetraglyme ligands. Bridged complexes of the type $[GdL_3]_2(\mu\text{-}M_2EO_n)$ with M_2EO_n bonded through two O atoms to each Gd have been reported for $n = 3$ or 4 where L is the sterically demanding bidentate ligand 2,2,6,6-tetramethyl-3,5-heptanedionate.[10]

Conclusions

We have prepared rare earth dimethylphenoxides with polyether ligands M_2EO_n ($n = 3$ or 4) from $[Ln(NO_3)_3(M_2EO_3)]$ and $[Ln(NO_3)_3(M_2EO_4)]$, respectively, demonstrating that these polyether complexes of lanthanide nitrates are valuable anhydrous starting materials for synthetic lanthanide chemistry.

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Table 4. Crystallographic Data for **1**

Crystal Data	
formula	$C_{34}H_{49}O_8La$
fw	724.66
crystal syst	monoclinic
space group	$P2_1/c$ (No. 14)
lattice paras	
a, Å	10.16(3)
b, Å	20.38(2)
c Å	17.71(4)
β, deg	91.5(2)
V, Å^3	3667
Z	4
D_{calc}, g cm^{-3}	1.312
F_{000}	1496
μ(Mo Kα), cm^{-1}	12.10
Intensity Measurements	
diffractometer	Rigaku AFC6S
radiation	MoKα ($\lambda = 0.710\,69$ Å)
temp, °C	−120
take-off angle, deg	6.0
detector aperture, mm	
horizontal	6.0
vertical	6.0
cryst to detector dist, cm	40
scan type, deg min^{-1}	4.0 (in ω) (2 rescans)
scan width, deg	$(1.42 + 0.30 \tan \theta)$
$2\theta_{max}$, deg	50.0
no. of reflcns	
tot.	7028
unique	6615 ($R_{int} = 0.301$)
corrections	Lorentz−polarization
Structure Solution and Refinement	
structure solution	direct methods
hydrogen atom treatment	included in calculated positions ($d_{C-H} = 0.95$ Å)
phenyl rings	refined as rigid groups
refinement	full-matrix least-squares
function minimized	$\sum w(\lvert F_o \rvert - \lvert F_c \rvert)^2$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
p-factor	0.03
anomolous dispersion	all non-hydrogen atoms
no. of observns ($I > 3.00\sigma(I)$)	2181
no. of variables	237
reflection/param ratio	9.20
residuals: R; R_w	0.082; 0.078
goodness of fit indicator	1.37
max shift/error in final cycle	0.73
max peak in final difference map, e/Å^3	1.17
min peak in final difference map, e/Å^3	−1.68

Experimental Section

$Ln(NO_3)_3(M_2EO_4)$ and $Ln(NO_3)_3(M_2EO_3)$ were prepared using the published procedure.[11] Preparations of aryloxide complexes were carried out using standard Schlenk techniques. Solvents for preparative work were distilled from sodium benzophenone ketyl; THF-d_8 for NMR spectroscopy was distilled from CaH_2. All solvents were stored under N_2 and over 4 Å molecular sieves prior to use. Samples for NMR spectroscopy were sealed under vacuum, and spectra were recorded on Bruker WM250 and AC200 spectrometers. Elemental analyses were performed in duplicate by Mr. S. Apter of this Department.

Preparation of [Ln($OC_6H_3Me_2$-2,6)$_3$(M_2EO_4)], Ln = La, Pr. A solution of 2,6-dimethylphenol (1.015 g, 8.31 mmol) was dissolved in THF (20 cm^3), and NaH (80 % in mineral oil, 0.43 g, 17.8 mmol) was added, resulting in vigorous effervescence. The resulting colorless solution of Na($OC_6H_3Me_2$-2,6) was separated by decantation from the unreacted NaH and added, with stirring, to a suspension of Ln(NO_3)$_3$(M_2EO_4) (2.77 mmol) in THF (100 cm^3), which had been dried by refluxing for 2 h through a Soxhlet thimble containing 4 Å molecular sieves. Stirring at room temperature was continued for 1.5 h, and then the precipitated $NaNO_3$ was allowed to settle out. The clear, colorless solution of [Ln($OC_6H_3Me_2$-2,6)$_3$(M_2EO_4)] was separated by decantation. The solution was concentrated to *ca*. 20 cm^3 and diethyl ether (*ca*. 20 cm^3) was added; prisms were formed (colorless for La; very pale green for Pr) on cooling to −10 °C. Yield = 85% (La), 75% (Pr). Anal. Calcd for $C_{34}H_{49}LaO_8$: C, 56.38; H, 6.81. Found: C, 56.25; H, 7.12%. Calcd for $C_{34}H_{49}O_8Pr$: C, 56.20; H, 6.80%. Found: C, 53.09; H, 6.69.

Preparation of [La($OC_6H_3Me_2$)$_2$(NO_3)(M_2EO_4). The preparation was carried out in a manner analogous to that described above for [Ln($OC_6H_3Me_2$-2,6)$_3$(M_2EO_4)], using 2 equiv of Na($OC_6H_3Me_2$-2,6) instead of 3. The product was obtained as colorless needles by crystallization from CH_2Cl_2 and petroleum ether at −10 °C. Yield = 67%. Anal. Calcd for $C_{26}H_{40}NLaO_{10}$: C, 46.92; H, 6.06; N, 2.11. Found: C, 42.00; H, 5.74; N, 2.30.

Preparation of [La($OC_6H_3Me_2$-2,6)$_3$(M_2EO_3)]. [La($OC_6H_3Me_2$-2,6)$_3$(M_2EO_3)] was prepared by a method analogous to that for [La($OC_6H_3Me_2$-2,6)$_3$(M_2EO_4)], using La(NO_3)$_3$(M_2EO_3) as a starting material. The product was crystallised as colourless needles from THF/diethyl ether at −10 °C. Yield = 84%.

X-ray Data Collection, Structure Determination, and Refinement for [La($OC_6H_3Me_2$-2,6)$_3$(M_2EO_4)]. Crystals of [La($OC_6H_3Me_2$-2,6)$_3$(M_2EO_4)] suitable for X-ray diffraction were grown from THF/diethyl ether at −10 °C. An air sensitive colorless prism, approximate dimensions 0.5 × 0.1 × 0.5 mm, was mounted on a glass fiber in Nujol oil and cooled to −120 °C in a stream of N_2 gas. The cell constants were obtained from nine carefully centered reflections in the range $7.39 < 2\theta < 12.66°$. Crystal data and details of data collection and structure solution are summarized in Table 4.

Acknowledgment. We are grateful to SERC for a studentship (M.W.), to Glaxo Process Development for Additional financial support, to Mr. J. V. Barkley for assistance with the crystal structure determination and to Mr. S. Apter for elemental analyses.

Supporting Information Available: Tables of positional and thermal parameters, intramolecular bond distances and angles, and torsion angles (18 pages). Ordering information is given on any current masthead page.

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