Utility of 2-Methoxyethanol in the Synthesis of Polyeuropium Complexes: $\{[Eu(OCH_2CH_2OMe)_2(OC_6H_3R_2\text{-}2,6)^-][H^+]\}_4$ (R = Me, ^{i}Pr) and $[EuAl_2(OCH_2CH_2OMe)_3Me_5]_2$

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Europium reacts with 2-methoxyethanol at room temperature to form arene-soluble $[Eu(OCH_2CH_2OMe)_2]_n$, **1**. Reaction of **1** with 2,6-dimethylphenol or 2,6-diisopropylphenol forms the tetrametallic complexes $\{[Eu(\mu_3\text{-}\eta^2\text{-}OCH_2CH_2OMe)(\eta^2\text{-}OCH_2CH_2OMe)(OC_6H_3R_2\text{-}2,6)^-][H^+]\}_4$ (R = Me, **2**; R = ^{i}Pr, **3**). Magnetic measurements of **1**−**3** in solution are consistent with the presence of divalent europium. **2** and **3** are isostructural and contain a tetrahedral arrangement of europium atoms. Coordinated to each seven-coordinate metal are one terminal bidentate alkoxide, one bridging bidentate alkoxide, which bridges through its alkoxide oxygen to two other europium atoms, a terminal aryloxide, and two bridging oxygen atoms from other such units. The presence of protons in **2** was probed by reaction with Al_2Me_6, which forms hexametallic $[Me_3Al(\mu\text{-}\eta^2\text{-}OCH_2CH_2OMe)Eu(\mu\text{-}\eta^2\text{-}OCH_2CH_2OMe)_2AlMe_2]_2$, **4**. Each six-coordinate europium in **4** is surrounded by three bidentate 2-methoxyethoxide ligands, which bridge via their alkoxide oxygen atoms. One ligand bridges to one $AlMe_3$ unit, and the other two ligands bridge to $AlMe_2$ units.

Introduction

Europium-based phosphors are currently used in color televisions, computer displays, and energy efficient trichromatic fluorescent lighting.[1] These phosphors typically consist of a small amount of europium doped into an inert oxide matrix, such as Y_2O_3.[2] A potentially convenient preparative route to such oxide materials is the sol−gel process,[3] which offers the possibility of forming powders with molecular homogeneity at low temperature with control of particle size and shape by hydrolysis of appropriately chosen molecular precursors.[4] Starting materials for the sol−gel processes are typically soluble metal alkoxides, aryloxides, acetylacetonates, and related ligands.

Unfortunately, relatively little is known about europium alkoxides and aryloxides, and even less is known about heterometallic species which could be appropriate precursors to europium-doped oxide materials. We have recently begun an investigation of the principles of forming poly- and heteropolymetallic europium species which could provide compounds of this type.[5−7] Since the most convenient route to such complexes involves the direct reaction of an alcohol with the elemental metal, we have investigated such reactions in liquid ammonia.[6] It has also been reported that europium, in the presence of mercury salts, will react directly with alcohols.[8] However, it has been found[9,10] that europium can react with alcohols without the addition of mercury, and these direct reactions provide the simplest route to polyeuropium complexes.

We report here on the direct reaction of europium metal with the chelating alcohol, 2-methoxyethanol, and the subsequent reactions of this product with 2,6-disubstituted phenols to make fully characterizable products. Chelating alcohols are of interest in sol−gel chemistry since they can be added during processing to slow hydrolysis rates and help to avoid segregation of different components.[11] Disubstituted phenols were chosen because we have previously shown the utility of aryloxide ligands in isolating polymetallic europium complexes. Described here are the effects of varying the substituents in the $HOC_6H_4R_2$-2,6 phenol as well as efforts to chemically probe the presence of protonated ligands in these systems, which led to a heterometallic Eu/Al complex.

Experimental Section

All reactions were performed in a nitrogen glovebox or using standard Schlenk and vacuum line techniques under a nitrogen atmosphere. Europium ingots (Rhone Poulenc) were washed with hexanes, dried, and cut to appropriate size before use. 2-Methoxyethanol (Aldrich, 99.8%) was dried by addition of 0.02 equiv of Na per equivalent of $HOCH_2CH_2OMe$ at 0 °C followed by vacuum transfer

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of the alcohol from this mixture into the reaction flasks. 2,6-Dimethylphenol (Aldrich) was sublimed three times before use. 2,6-Diisopropylphenol (Aldrich) was dried and vacuum distilled from 3A molecular sieves. Al_2Me_6 (Aldrich) was used as received. Other solvents were dried, and physical measurements were made as previously described.[12] Magnetic moments were measured by the method of Evans[13] on a Bruker DRX400 or General Electric QE300 NMR spectrometer. Carbon and hydrogen analyses were performed on a Carlo Erba EA 1108 instrument and europium analysis was performed by complexometric titration with EDTA and a xylenol orange indicator,[14] or the elemental analyses were performed by Desert Analytics, Tuscon, AZ 85719.

$[Eu(OCH_2CH_2OMe)_2]_n$, 1. Pieces of Eu metal, typically 5−10 mm in diameter (644 mg, 4.24 mmol), were reacted with excess $HOCH_2CH_2OMe$ at room temperature under N_2 for 4 h to yield an orange solution containing no trace of europium ingot. Excess $HOCH_2CH_2OMe$ was removed under vacuum, and the resulting orange paste was transferred to a nitrogen glovebox. The orange paste was dissolved in toluene and centrifuged to remove a small amount of insoluble material (<10 mg). Toluene was removed in vacuo to yield an orange oil. Several cycles of dissolving the orange oil in hexanes and drying by rotary evaporation yielded an orange powder, $[Eu(OCH_2CH_2OMe)_2]_n$, **1** (1.27 mg, 99% based on Eu). Isopiestic molecular weight measurements in toluene indicate $n > 10$. Magnetic susceptibility: $\chi_g^{298K} = 7.9 \times 10^{-5}$, $\mu_{eff}^{298K} = 7.7\ \mu_B$. IR (KBr): 2805 w, 2653 w, 1446 m, 1373 w, 1353 m, 1275 w, 1231 m, 1187 m, 1119 s, 1072 s, 1011 s, 894 m, 822 s, 727 w cm^{-1}. Anal. Calcd for $EuO_4C_6H_{14}$: Eu, 49.9; C, 23.9; H, 4.7. Found: Eu, 48.8; C, 23.0; H, 4.8.

$\{[Eu(\mu_3\text{-}\eta^2\text{-}OCH_2CH_2OMe)(\eta^2\text{-}OCH_2CH_2OMe)(OC_6H_3Me_2\text{-}2,6)^-][H^+]\}_4$, 2. Addition of a solution of $HOC_6H_4Me_2$-2,6 (42 mg, 0.34 mmol) in 2 mL of toluene to an orange solution of **1** (103 mg, 0.34 mmol) in 2 mL of toluene resulted in a color change from orange to yellow. Yellow crystals of **2** suitable for X-ray diffraction formed overnight after reduction of the solution volume to 2 mL. The excess solution was removed from the crystals by pipet, and the crystals were washed with hexanes and dried to constant weight by rotary evaporation (101 mg, 70% based on Eu). Magnetic susceptibility: $\chi_g^{298K} = 6.1 \times 10^{-5}$, $\mu_{eff}^{298K} = 7.9\ \mu_B$. IR (KBr): 3005 m, 2913 s, 2841 w, 2697 w, 1739 w, 1697 w, 1646 w, 1585 w, 1513 w, 1462 s, 1421 s, 1364 w, 1277 s, 1236 m, 1190 w, 1108 s, 1067 s, 1015 m, 900 m, 828 m, 798 sh, 755 m, 686 w, 667 w cm^{-1}. Anal. Calcd for $Eu_4O_{20}C_{56}H_{96}$: Eu, 35.81; C, 39.63; H, 5.70. Found: Eu, 35.99; C, 39.82; H, 5.76.

$\{[Eu(\mu_3\text{-}\eta^2\text{-}OCH_2CH_2OMe)(\eta^2\text{-}OCH_2CH_2OMe)(OC_6H_3{}^iPr_2\text{-}2,6)^-][H^+]\}_4$, 3. Addition of a solution of $HOC_6H_4{}^iPr_2$-2,6 (96 mg, 0.505 mmol) in 2 mL of toluene to an orange solution of **1** (153 mg, 0.539 mmol) in 2 mL of toluene resulted in a color change from orange to yellow. Yellow crystals of **3** suitable for X-ray diffraction formed overnight after reduction of the solution volume to 2 mL. The crystals lost clarity after the excess solution was removed from the crystals by pipet. The material was dried by rotary evaporation for 1 h to a constant weight of 217 mg (88%). Magnetic susceptibility: $\chi_g^{298K} = 5.63 \times 10^{-5}$, $\mu_{eff}^{298K} = 7.99\ \mu_B$. IR (KBr): 3003 w, 2956 s, 2921 s, 2900 s, 2866 s, 2832 m, 2721 w, 1640 w, 1583 w, 1457 m, 1424 s, 1355 m, 1329 m, 1255 s, 1204 m, 1193 m, 1116 s, 1109 s, 1066 s, 1042 w, 1014 m, 920 w, 897 w, 885 w, 855 w, 834 m, 799 w, 749 m, 727 w, 691 w, 681 w cm^{-1}. Anal. Calcd for $Eu_4O_{20}C_{72}H_{128}$: Eu, 31.6. Found: Eu, 32.2.

$[Me_3Al(\mu\text{-}\eta^2\text{-}OCH_2CH_2OMe)Eu(\mu\text{-}\eta^2\text{-}OCH_2CH_2OMe)_2\text{-}AlMe_2]_2$, 4. A solution of **2** (103 mg, 0.06 mmol) in 5 mL of toluene was added dropwise to a vial containing Al_2Me_6 (34 mg, 0.27 mmol) in 2 mL of toluene at room temperature. A color change to light yellow and the formation of bubbles were noted during the addition of the solution of **2**. Reduction of the total solution volume to approximately 2 mL produced a small amount of diffraction quality single crystals overnight (<20 mg).

Alternative Preparation of 4. In the glovebox, Al_2Me_6 (72 mg, 0.48 mmol) was dissolved in 2 mL of toluene in a Schlenk flask. The flask was capped with a septum, transferred to a Schlenk line, and cooled to −78 °C in a dry ice/2-propanol bath. $HOCH_2CH_2OMe$ (75 mg, 0.989 mmol) in 2 mL of toluene was added to the Al_2Me_6 solution via syringe over a period of 2 min. After 20 min, the temperature was raised to 0 °C using an ice water bath. $Eu(OCH_2CH_2OMe)_2$, **1** (299 mg, 0.99 mmol), dissolved in 4 mL of toluene was then added to the reaction mixture via syringe. After 20 min the ice bath was removed and the reaction was allowed to warm to room temperature. The reaction flask was then placed under partial vacuum and transferred to the glovebox. An additional amount of Al_2Me_6 (72 mg, 0.50 mmol) dissolved in 2 mL of toluene was added to the reaction mixture, and the formation of insoluble materials and a color change from orange to yellow occurred. The insoluble materials were removed by centrifugation, and the supernatant was dried by rotary evaporation. The yellow/green solid was washed twice with hexanes and dried to yield microcrystalline **4** (305 mg, 61%). The microcrystalline solids were recrystallized from a saturated hot toluene solution overnight and found to have the same unit cell parameters as those obtained in the initial preparation of **4**. IR (KBr): 2885 br, 2718 m, 2630 w, 2125 w, 22031 w, 1894 w, 1471 s, 1457 s, 1395 m, 1367 s, 1281 m, 1245 s, 1197 s, 1181 s, 11113 m, 1080 s, 1064 s, 1018 s, 964 s, 838 s cm^{-1}. Anal. Calcd for $Eu_2Al_4O_{12}C_{28}H_{72}$: Eu, 30.02; Al, 10.66; C, 33.19; H, 7.17. Found: Eu, 30.11; Al, 11.11; C, 33.00; H, 6.94.

X-ray Data Collection and Solution and Refinement for 2, 3, and 4. All crystals were mounted on glass fibers and transferred to the Siemens P4 diffractometer. The determination of symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix was carried out according to standard procedures.[15] A $2\theta/\omega$ scan technique with Mo Kα radiation was used. The raw data were processed with a local version of CARESS[16] which employs a modified version of the Lehman−Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. All data were corrected for absorption and Lorentz and polarization effects and were placed on an approximately absolute scale. All calculations were carried out using the SHELXTL program.[17] The analytical scattering factors for neutral atoms were used throughout the analysis.[18] Structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Absolute structures of **2** and **3** were assigned by refinement of Flack parameters.[19]

A yellow crystal of **2** with approximate dimensions 0.5 × 0.33 × 0.33 mm was handled as described above. A total of 2388 intensity data were collected at 163 K. The diffraction symmetry was $4/m$, and systematic absences were consistent with the noncentrosymmetric tetragonal space group $\bar{P}42_1c$ [$D^4{}_{2d}$; No. 114]. Disorder in the carbon atoms of the 2-methoxyethoxide groups and in a methyl group of the aryloxide was modeled by assigning partial occupancy to the disordered fragments and refining the site occupancy factor during refinement. All atoms, except those in disordered fragments, were refined anisotropically. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0603 and GOF = 1.147 for 180 variables refined against all 1234 unique data (as a comparison for refinement on F, R1 = 0.0305 for those 1113 data with $F > 4.0\sigma(F)$).

A yellow crystal of **3** with approximate dimensions 0.5 × 0.33 × 0.33 mm was handled as described above. A total of 7643 intensity data were collected at 153 K. The diffraction symmetry was mmm, and systematic absences were consistent with the noncentrosymmetric orthorhombic space group $P2_12_12_1$ [$D^4{}_2$; No. 19]. Several atoms from four molecules of toluene per formula unit were found via difference Fourier maps. The toluene molecules were fitted to a rigid hexagon and were free to rotate on a well-defined pivot atom during refinements.

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The atoms in the toluene molecules were constrained to have isotropic displacement parameters (U_{ij}) similar to neighboring atoms with an effective standard deviation of 0.04 by the SIMU command in SHELXTL V.5. The methyl groups were not located on three of the toluene molecules. All europium atoms were refined anisotropically, while all oxygen and carbon atoms were refined isotropically. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.3038 and GOF = 1.083 for 446 variables refined against all 7643 unique data (as a comparison for refinement on F, R1 = 0.1043 for those 5054 data with $F > 4.0\sigma(F)$).

A yellow crystal of **4** with approximate dimensions 0.25 × 0.46 × 0.52 mm was handled as described above. A total of 5696 intensity data were collected at 168 K. The diffraction symmetry was *mmm*, and systematic absences were consistent with the centrosymmetric orthorhombic space group *Pbca* [D^{15}_{2h}; No. 61]. Disorder in carbon atoms of the 2-methoxyethoxide groups was modeled by assigning partial occupancy to the disordered fragments and refining the site occupancy factor during refinement. All atoms, except those in disordered fragments, were refined anisotropically. At convergence, wR2 = 0.1385 and GOF = 0.939 for 205 variables refined against all 5695 unique data (as a comparison for refinement on F, R1 = 0.0452 for those 3665 data with $F > 4.0\sigma(F)$).

Results

Synthesis. Europium ingots react rapidly with 2-methoxyethanol at room temperature to produce an arene-soluble homoleptic europium alkoxide, $[\mathrm{Eu(OCH_2CH_2OMe)_2}]_n$, **1**, in high yield, eq 1. **1** was characterized by infrared spectroscopy

$$n\mathrm{Eu} + 2n\mathrm{HOCH_2CH_2OMe} \rightarrow [\mathrm{Eu(OCH_2CH_2OMe)_2}]_n + n\mathrm{H_2} \quad (1)$$

and elemental analysis and was found to have an effective magnetic moment of 7.7 μ_B per europium, which is in the range of other divalent europium complexes.[5-7,20] Isopiestic molecular weight determination in toluene suggests that **1** is highly aggregated in solution, $n > 10$. **1** was very soluble in both arenes and ethers and did not readily form crystals suitable for X-ray diffraction studies from a variety of coordinating and noncoordinating solvents.

In efforts to obtain fully characterizable europium 2-methoxyethoxide products, **1** was reacted with 2,6-disubstituted phenols, which have been used successfully in previous studies to obtain crystalline europium complexes.[5-7,10] The addition of 1 equiv of the colorless phenol $\mathrm{HOC_6H_3Me_2}$-2,6 per europium to **1** in toluene results in a color change of the solution from orange to yellow. The IR spectra of crystals formed from the solutions were found to have absorptions in the C−C (aromatic) stretching region after drying, indicating the incorporation of aryloxides or aryl alcohols in the product. The effective magnetic moment of europium in the crystalline product, 7.9 μ_B, was consistent with divalent europium.[5-7,20] X-ray crystallographic studies, undertaken on the single crystals grown from toluene, identified the product as the tetrametallic species $\{[\mathrm{Eu}(\mu_3\text{-}\eta^2\text{-OCH_2CH_2OMe})(\eta^2\text{-OCH_2CH_2OMe})(\mathrm{OC_6H_3Me_2}\text{-}2,6)^-][\mathrm{H}^+]\}_4$, **2**, Figure 1.

Since earlier work with 2,6-disubstituted aryloxide complexes of europium showed that varying the size of the 2,6-substituents of the aryl alcohol could effect structural changes in the product,[5,6] the analogous reaction with $\mathrm{HOC_6H_3{}^iPr_2}$-2,6 was examined. This phenol reacts with complex **1** in toluene in much the same way as the dimethylphenol: a color change from orange to yellow occurred and crystals formed from toluene upon reduction of volume. The IR spectrum and the effective magnetic moment of europium in the crystalline product, 8.0 μ_B, were also similar to those of **2**. X-ray crystallography identified the product as $\{[\mathrm{Eu}(\mu_3\text{-}\eta^2\text{-OCH_2CH_2OMe})(\eta^2\text{-OCH_2CH_2OMe})(\mathrm{OC_6H_3{}^iPr_2}\text{-}2,6)^-][\mathrm{H}^+]\}_4$, **3**, a direct analogue of **2**. Although **3** and **2** are not isomorphous, they are structurally very similar. The main difference between **2** and **3** was that four molecules of toluene cocrystallized with **3**, whereas no solvent molecules cocrystallized with **2**. In addition, the crystals of **3** lost clarity when removed from solvent and poorer quality X-ray data were obtained for **3**. Accordingly, only the metrical parameters for **2** will be discussed.

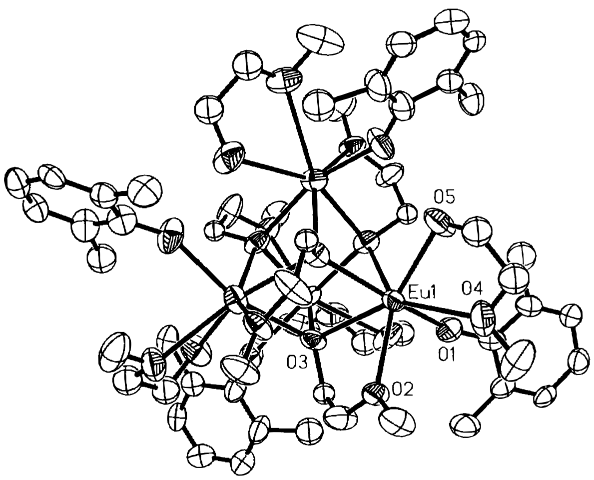

Figure 1. Thermal ellipsoid plot of $\{[\mathrm{Eu}(\mu_3\text{-}\eta^2\text{-OCH_2CH_2OMe})(\eta^2\text{-OCH_2CH_2OMe})(\mathrm{OC_6H_3Me_2}\text{-}2,6)^-][\mathrm{H}^+]\}_4$, **2**, drawn at the 50% probability level.

Structure of 2 and 3. The four europium atoms in both **2** and **3** describe a slightly distorted tetrahedron. In **2**, the Eu−Eu−Eu angles are 57.161(9)−65.68(2)° compared to the 60° of an ideal tetrahedron. **2** and **3** are the first structurally characterized polymetallic divalent europium complexes with a tetrahedral europium structure. The other tetrametallic europium complex that has been reported, $\mathrm{Eu_4}(\mu\text{-OC_6H_3{}^iPr_2}\text{-}2,6)_4(\mathrm{OC_6H_3{}^iPr_2}\text{-}2,6)_2(\mu_3\text{-OH})_2(\mathrm{NCMe})_6$, **5**, contains a butterfly arrangement of europium atoms.[6] The 3.8367(11)−4.1611(13) Å Eu···Eu distances in **2** are generally longer than the 3.7631(9)−3.9372(9) Å Eu···Eu distances in **5**.

Each europium center in **2** and **3** is associated with one terminal aryloxide and two chelating 2-methoxyethoxide ligands. One chelating 2-methoxyethoxide is coordinated as a terminal ligand to each europium atom, and the other one bridges through its alkoxide oxygen atom to two other europium atoms; that is, it bridges a face of the europium tetrahedron. Since the magnetic moment data indicate that this is a divalent europium complex, one proton must be present per europium. No hydrogens were located in the X-ray data, but the presence of these protons was confirmed by the subsequent reactivity of **2** and **3** as described below.

The bond distances and angles involving the aryloxide ligands in **2** indicate that the proton may be associated with this ligand. The 2.420(8) Å Eu−O(OAr) bond distance in **2** is generally longer than terminal Eu−O(OAr) bond distances in other structurally characterized europium(II) aryloxides: **5**, 2.284(6)−2.299(6) Å;[6] $\mathrm{Eu(OC_6H_3{}^tBu_2}\text{-}2,6)_2(\mathrm{NCMe})_4$, **6**, 2.313(12)−2.35(2) Å;[6] $(\mathrm{DME})_2\mathrm{Eu}(\mu\text{-OC_6H_3Me_2}\text{-}2,6)_3\mathrm{Eu(OC_6H_3Me_2}\text{-}2,6)(\mathrm{DME})$, **7**, 2.350(5) Å;[5] $\mathrm{Eu(OC_6H_2{}^tBu_2}\text{-}2,6\text{-Me-}4)_2(\mathrm{THF})_3$, **8**, 2.321(5)−2.337(5) Å.[21] The only case in the above

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list in which the Eu−O(OAr) bond distances in **2** are within experimental error of others involves **6**, which has bulkier 2,6-dialkyl substituents and rather large standard deviations for the bond lengths. The fact that the 153.6(8)° Eu−O−C(Ar) angle in **2** is the smallest Eu−O−C(Ar) angle in structurally characterized divalent europium terminal aryloxides (**5**, 170.0(6)−174.0(6)°;[6] **6**, 174.5(11)−173.6(12)°;[6] **7**, 166.5(5)°;[5] **8**, 174.1(4)−175.2(4)°[21]) is also consistent with the presence of a proton on this ligand.

The Eu−O(OCH_2CH_2OMe) alkoxide bond distances in **2** are more difficult to evaluate, since to our knowledge **2** is the first structurally characterized homometallic divalent europium alkoxide to be reported. The 2.458(7)−2.591(7) Å Eu−O(μ_3-OR) distances in **2** can be compared with a heterometallic complex, and on this basis they appear to be normal. For example, they are similar to the 2.541(5) and 2.600(5) Å Eu−(μ_3-O^{i}Pr) distances in the heterometallic complex, $\{[Zr_2(O^iPr)_9]EuI\}_2$, but in this case these triply bridging isopropoxide ligands bridge one europium(II) and two zirconium(IV) atoms rather than three Eu(II) centers.[7] The bridging Eu−O(μ_3-OR) distances in **2** are also reasonable compared to the 2.474(4)−2.495(4) Å Eu−O(μ-OCH_2CH_2OMe) distances in **4**, discussed below.

The 2.560(8) Å Eu−O(OR) distance involving the terminal alkoxide ligand is in the range of the triply bridging Eu−O(μ_3-OR) distances in **2**. This is unexpected since M−O bond distances in bridging alkoxides are generally longer than those in terminal alkoxides.[22] Since both the aryloxide and the terminal 2-methoxyethoxide Eu−O distances are longer than expected, we examined the O···O distance between these two ligands to see if the proton could be located between the oxygen atoms. Indeed the O1···O5A distance of 2.523 Å is well within the range of other O···O distances in which O··H··O hydrogen bonds are present.[23]

The 2.637(7) and 2.760(8) Å Eu−O(ether) distances are rather disparate, differing by 0.123 Å. However, this is not surprising when compared to the range of Ln−O(ether) distances in other lanthanide complexes with alkoxides possessing chelating ethers. These vary by as much as 0.22 Å within a molecule: $Gd_6O(OCH_2CH_2OMe)_{16}$, 2.477(9)−2.64(1) Å;[24] $Lu_2(OCMe_2CH_2OMe)_6$, 2.381(4)−2.468(3) Å;[25] $Lu_4(O)(OH)(OCMe_2CH_2OMe)_9$, 2.31(2)−2.53(2) Å.[25] These large ranges are likely the consequence of the several binding modes of the chelating ligands.

Reactivity. In an attempt to chemically show the existence of the protons in **2** and to replace them with a larger cation, in this case $AlMe_2^+$, complex **2** was reacted with Al_2Me_6. Evolution of gas was noted, as expected, but only a low yield of the single identifiable, crystalline product, $[Me_3Al(\mu\text{-}\eta^2\text{-}OCH_2CH_2OMe)Eu(\mu\text{-}\eta^2\text{-}OCH_2CH_2OMe)_2AlMe_2]_2$, **4**, Figure 2, was obtained. Due to the large magnetic moment of divalent europium, NMR spectra of the more soluble products in the reaction mixture were uninformative. The formation of the $AlMe_2$ components in **4** is consistent with the reaction of the acidic protons in **2** with Al_2Me_6 to form methane gas. This type of reactivity of coordinated alcohols has previously been observed.[26] In the reaction of **3** with Al_2Me_6, a product analogous to **4** was not isolated, and no other products proved suitable for X-ray diffraction study, although gas formation and a color change were noted.

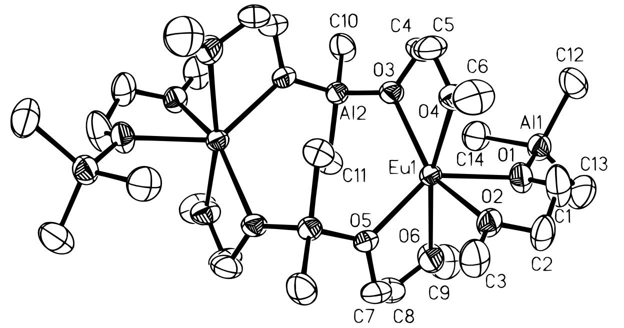

Figure 2. Thermal ellipsoid plot of $[Me_3Al(\mu\text{-}\eta^2\text{-}OCH_2CH_2OMe)Eu(\mu\text{-}\eta^2\text{-}OCH_2CH_2OMe)_2AlMe_2]_2$, **4**, drawn at the 50% probability level.

Since **4** was obtained in low yield and contained no aryloxide ligands, an alternative preparative method involving direct reaction with **1** was investigated. Since **4** is effectively composed of equal amounts of the components $Eu(OCH_2CH_2OMe)_2$ (i.e., **1**), $MeOCH_2CH_2OAlMe_2$, and $AlMe_3$, a stepwise synthesis involving the addition of **1** to $(MeOCH_2CH_2AlMe_2)_2$[27] (prepared in situ) followed by addition of Al_2Me_6 was attempted. This heterometallic synthesis provided **4** in 60%yield according to eq 2.

$$[AlMe_2(OCH_2CH_2OMe)]_2 + (2/n)[Eu(OCH_2CH_2OMe)_2]n + Al_2Me_6 \rightarrow [AlMe_3(\mu\text{-}OCH_2CH_2OMe)Eu(\mu\text{-}OCH_2CH_2OMe)_2AlMe_2]_2 \quad (2)$$

Structure of 4. Complex **4** comprises six-coordinate europium and four-coordinate aluminum centers bridged by 2-methoxyethoxide ligands. The geometry of the metals in **4** is best described in terms of a square planar Eu_2Al_2 unit containing europium atoms at diagonal positions, each of which is bridged to additional aluminum atoms, which lie 0.46 Å out of the Eu_2Al_2 plane. The alkoxide oxygen atoms of the 2-methoxyethoxide ligands bridge all of the metal atoms. Each europium atom is attached to three 2-methoxyethoxide ligands. Two of the three 2-methoxyethoxide ligands bridge to $AlMe_2$ units with 2.474(4) and 2.495(4) Å Eu−O distances and 1.771(4) and 1.780(4) Å Al−O distances. The third 2-methoxyethoxide ligand bridges to an $AlMe_3$ unit with 2.443(4) Å Eu−O and 1.811(5) Å Al−O distances. Each of the ether functionalities in the three 2-methoxyethoxide ligands coordinates only to Eu, and the Eu−O(ether) distances fall in the range 2.583(4)−2.636(5) Å. The smaller range of Eu−O(ether) distances in **4**, 0.047 Å, compared to **2**, is consistent with only one binding mode of the 2-methoxyethoxide ligand observed in **4**, namely, μ-η^2. In $[Y(OCH_2CH_2OMe)_3]_{10}$, the 2.52(2) Å Y−O(ether) distances are similarly longer than the 2.29(2) Y−O(bridging alkoxide) lengths (which are longer than the 2.09(2) Å terminal lengths).[28]

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Table 1. Experimental Data for the X-ray Diffraction Studies of $\{[\mathrm{Eu}(\mu_3\text{-}\eta^2\text{-}\mathrm{OCH_2CH_2OMe})(\eta^2\text{-}\mathrm{OCH_2CH_2OMe})(\mathrm{OC_6H_3Me_2\text{-}2,6})^-][\mathrm{H}^+]\}_4$, **2**, $\{[\mathrm{Eu}(\mu_3\text{-}\eta^2\text{-}\mathrm{OCH_2CH_2OMe})(\eta^2\text{-}\mathrm{OCH_2CH_2OMe})(\mathrm{OC_6H_3IPr_2\text{-}2,6})^-][\mathrm{H}^+]\}_4\cdot 4(\mathrm{C_6H_5Me})$, $3\cdot 4(\mathrm{C_6H_5Me})$, and $[\mathrm{Me_3Al}(\mu\text{-}\eta^2\text{-}\mathrm{OCH_2CH_2OMe})\mathrm{Eu}(\mu\text{-}\eta^2\text{-}\mathrm{OCH_2CH_2OMe})_2\mathrm{AlMe_2}]_2$, **4**

	2	**3**·4C$_6$H$_5$Me	**4**
formula	$C_{56}H_{96}O_{20}Eu_4$	$C_{100}H_{160}O_{20}Eu_4$	$C_{28}H_{72}O_{12}Eu_2Al_4$
fw	1697.2	2290.1	1012.7
temp (°C)	−110	−120	−105
cryst syst	tetragonal	orthorhombic	orthorhombic
space group	$P\bar{4}2_1c$	$P2_12_12_1$	*Pbca*
a (Å)	14.837(2)	16.623(2)	16.3747(11)
b (Å)	14.837(2)	16.808(2)	15.855(2)
c (Å)	15.117(3)	38.103(6)	18.1999(10)
V (Å^3)	3327.7(10)	10 646(2)	4725.1(7)
Z	2	4	4
D_{calcd} (g/cm^3)	1.694	1.429	1.424
scan speed, deg min^{-1} (in ω)	3.0 (in ω)	3.0 (in ω)	4.0 (in ω)
2θ range (deg)	4.0−45.0	4.0−45.0	4.0−56.0
μ (Mo Kα) (cm^{-1})	37.84	23.86	27.49
no. of reflns collected	2388	7643	5696
no. of reflns used in least squares refinement	1234	7643	5695
no. of variables	180	446	208
R1, wR2	0.0305, 0.0603	0.1043, 0.3038	0.0452, 0.1385
goodness of fit	1.147	1.083	0.939

[a] Radiation: Mo Kα (λ = 0.710 730 Å). Monochromator: highly oriented graphite. Absorption correction: semiempirical (φ-scan method).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2 and 4

2		**4**	
Eu(1)−O(1)	2.420(8)	Eu(1)−O(1)	2.443(4)
Eu(1)−O(2)	2.637(7)	Eu(l)−O(2)	2.583(4)
Eu(1)−O(3)	2.548(7)	Eu(1)−O(3)	2.474(4)
Eu(1)−O(3)#1	2.458(7)	Eu(l)−O(4)	2.636(5)
Eu(1)−O(3)#2	2.591(7)	Eu(l)−O(5)	2.495(4)
Eu(1)−O(5)	2.560(8)	Eu(l)−O(6)	2.600(5)
Eu(1)−O(4)	2.760(8)	Eu(l)···Al(1)	3.689(2)
Eu(1)···Eu(1)#1	3.8367(11)	Eu(l)···Al(2)	3.674(2)
Eu(1)···Eu(1)#2	4.1611(13)	Al(1)−O(1)	1.811(5)
Eu(1)···Eu(1)#3	3.8367(11)	Al(1)−C(12)	2.004(9)
		Al(1)−C(13)	1.988(10)
Eu(1)−O(1)−C(1)	153.6(8)	Al(1)−C(14)	1.992(8)
Eu(1)−O(5)−C(12)	118.0(14)	Al(2)−O(3)	1.771(4)
		Al(2)−O(5)	1.780(4)
		Al(2)−C(10)	1.964(7)
		Al(2)−C(11)	1.967(7)

The geometry around the aluminum atoms is distorted tetrahedral. The 102.7(3)−113.3(4)° donor atom−Al(1)−donor atom angles are quite normal and are in the range of those in $[(\mathrm{Me_3Al})_2(\mu\text{-}\mathrm{OC(CH_3)_3})][\mathrm{N(CH_3)_4}]$, 103.1(4)−115.8(5)°.[29] The 103.6(3)−118.4(3)° donor atom−Al(2)−donor atom angles have a much narrower range than other structurally characterized complexes of the form $\mathrm{R_2Al}(\mu\text{-}\mathrm{OR})_2\mathrm{ML}_n$: $[(\mathrm{Me_2Al}(\mu\text{-}\mathrm{OC_6H_4\text{-}Me\text{-}4})_2]_3\mathrm{Nd}$, 84.4(2)−121.2(4)°;[30] $(\mathrm{thf})_2(2,6\text{-}\mathrm{Me_2C_6H_3O})_2\mathrm{Yb}(\mu\text{-}\mathrm{OC_6H_3Me_2\text{-}2,6})_2\mathrm{AlMe_2}$,[31] 85.1(6)−114.3(9)°; $(\mathrm{thf})_2(2,6\text{-}\mathrm{Me_2C_6H_3O})_2\mathrm{Nd}(\mu\text{-}\mathrm{OC_6H_3Me_2\text{-}2,6})_2\mathrm{AlEt_2}$, 87.4(5)−114.4(8)°;[31] $[\mathrm{Me_2Al}(\mu\text{-}\mathrm{O}^t\mathrm{Bu})_2]_2\mathrm{Mg}$, 85.3(2)−113.8(4)°;[31] $[\mathrm{Me_2Al}(\mu\text{-}\mathrm{O}^t\mathrm{Bu})_2\mathrm{Mg}(\mu\text{-}\mathrm{O}^t\mathrm{Bu})]_2$, 89.2(3)−116.0(7)°.[32] The Al−C and Al −O bond distances are quite normal and are listed in Table 2.

Discussion

The reaction of europium metal with 2-methoxyethanol to form $[\mathrm{Eu(OCH_2CH_2OMe)_2}]_n$, **1,** constitutes a convenient direct route to a soluble homoleptic divalent europium alkoxide. This reaction is preferable to the more usual ionic metathesis syntheses of lanthanide alkoxides which involve the reaction between a lanthanide halide and an alkali metal alkoxide because the metal halide and the alkali alkoxide do not need to be prepared from the metal and the alcohol and there is no danger of incorporation or contamination of alkali metal and halide in the lanthanide product.[33] The formation of a divalent europium product in this reaction is consistent with the reactivity of europium with phenols observed in liquid ammonia.[5]

Although conveniently formed, **1** was not easy to crystallize for complete structural characterization. However, simple addition of 2,6-disubstituted phenols allowed structural characterization of adducts of **1**. Remarkably, both $\mathrm{HOC_6H_3Me_2}$-2,6 and $\mathrm{HOC_6H_3{}^iPr_2}$-2,6 provide crystalline 2-methoxyethoxide products **2** and **3**, respectively, which are structurally very similar. Previous studies of europium with 2,6-disubstituted aryloxides have shown that the nature of the 2,6-substitutent strongly affects the bridging ability of the aryloxide.[6] The reason that **2** and **3** are the same structurally despite the difference in the phenol is likely due to the fact that the basic structure is determined by the bridging 2-methoxyethoxide ligands; that is, the phenols merely function as terminal ligands. Although the protons were not located in the crystal structure, the O···O distances suggest that they are located between the oxygens of the terminal aryloxide group and a terminal 2-methoxyethoxide. The phenols are thus acting as terminal ligands that can hydrogen bond their proton to the 2-methoxyethoxide. The fact that **2** and **3** are structurally similar indicates that this coordination position is rather flexible, and one would expect a variety of HO-bearing ligands to form similar complexes. Ether adducts are common in alkoxide chemistry, but in the case of **1**, phenols appear to be superior to ethers for forming crystalline products.

The presence of acidic protons of coordinated alcohols has previously been shown to facilitate further reactivity in metal alkoxide complexes.[26] In this case, the presence of one acidic proton per metal center in **2** can be used to generate a heterometallic complex, $[\mathrm{Me_3Al}(\mu\text{-}\eta^2\text{-}\mathrm{OCH_2CH_2OMe})\mathrm{Eu}(\mu\text{-}\eta^2\text{-}\mathrm{OCH_2CH_2OMe})_2\mathrm{AlMe_2}]_2$**, 4**. The formation of a complex

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containing $AlMe_2$ units is not unusual from a reaction of a phenol with Al_2Me_6, but the isolation of $AlMe_3$ units that survived the phenolysis is interesting. This is reminiscent of the hydrolysis of Al_2Me_6, which makes the methylalumoxane polymerization cocatalyst, which is believed to contain both $AlMe_3$ and $AlMe_x(O)$ units.[34] The presence of readily hydrolyzable ligands in **4** is also advantageous for sol−gel applications. Since it was desirable to have a higher yield route to **4**, a direct route from **1** was developed, which further demonstrates the utility of **1** as a precursor to well-defined polymetallic complexes.

Conclusion

Europium readily reacts directly with 2-methyoxyethanol to form soluble divalent europium complexes, which serve as precursors to poly- and heteropolymetallic europium compounds. The similarity of the products obtained with $HOC_6H_3Me_2$-2,6 and $HOC_6H_3{}^iPr_2$-2,6 indicates that hydrogen bonding and the 2-methoxyethoxide ligand play the dominant role in determining the structure in these complexes.

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Supporting Information Available: X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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