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Reactivity of “$\mathrm{Eu(O^iPr)_2}$” with Phenols: Formation of Linear $\mathrm{Eu_3}$, Square Pyramidal $\mathrm{Eu_5}$, Cubic $\mathrm{Eu_8}$, and Capped Cubic $\mathrm{Eu_9}$ Polymetallic Europium Complexes

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The direct reaction of europium with 2-propanol and phenols has been investigated under a variety of conditions. The reaction of europium metal with 2,6-dimethylphenol and 2,6-diisopropylphenol in 2-propanol at reflux revealed that polymetallic europium complexes could be generated by this method. $\mathrm{H_x[Eu_8O_6(OC_6H_3Me_2\text{-}2,6)_{12}(O^iPr)_8]}$, **1**, and $\mathrm{H_5[Eu_5O_5(OC_6H_3{}^iPr_2\text{-}2,6)_6(NCCH_3)_8]}$, **2**, were isolated by recrystallization in the presence of hexanes and acetonitrile, respectively, and characterized by X-ray crystallography. Complex **1** has a cubic arrangement of europium ions with face-bridging μ_4-O donor atoms, edge-bridging μ-O(phenoxide/phenol) ligands, and terminal O(isopropoxide/2-propanol) ligands. Complex **2** is mixed valent and has a square pyramidal europium core with four Eu(II) ions at the basal positions and one Eu(III) ion at the apex. Since these reactions gave complicated mixtures of products from which **1** and **2** could only be obtained in low yields, direct reactions under less forcing reaction conditions were investigated. Europium reacts slowly at room temperature to form arene-soluble divalent $\mathrm{[Eu(O^iPr)_2(THF)_x]_n}$, **3**. Complex **3** reacts with 2,6-dimethylphenol to form the arene-insoluble complex $\mathrm{\{H[Eu(OC_6H_3Me_2)_2(O^iPr)]\}_n}$, **4**. Recrystallization of **4** in the presence of THF results in the crystallographically characterizable divalent trimetallic complex $\mathrm{[Eu(OC_6H_3Me_2\text{-}2,6)_2(THF)_2]_3}$, **5**, which has an unusual linear metal geometry. In the presence of $\mathrm{HO^iPr}$ at ambient conditions in the glovebox, crystals of **5** slowly convert to the mixed valent $\mathrm{H_{10}[Eu_8O_8(OC_6H_3Me_2\text{-}2,6)_{10}(O^iPr)_2(THF)_6]}$, **6**, which was found to have a cubic arrangement of europium atoms similar to **1** by X-ray crystallography. Complex **4**, upon heating under vacuum, followed by reaction with THF, forms the arene-soluble divalent complex $\mathrm{H_{18}\{[Eu_9O_8(OC_6H_3Me_2\text{-}2,6)_{10}(THF)_7][Eu_9O_9(OC_6H_3Me_2\text{-}2,6)_{10}(THF)_6]\}}$, **7**, which contains two types of capped cubic arrangements of europium ions in the solid state.

Introduction

The emission properties of Eu(II) in the blue and Eu(III) in the red make europium a desirable component in phosphor-based devices such as color televisions, flat panel displays, and energy efficient trichromatic fluorescent lamps.[1] Improvements in these devices could be derived from (a) a more homogeneous distribution of the europium in the optically inert matrix, (b) a better understanding of the factors that limit the amount of europium that can be put into the matrix, and (c) better control of particle size. Information on polymetallic and heteropolymetallic europium alkoxide, aryloxide, and oxide compounds could be helpful in this regard, since these compounds could be useful precursors via sol−gel techniques to europium-containing oxide materials.[2]

As part of a program to establish the principles of synthesis and structure of polymetallic europium complexes,[3−7] we have been investigating reactions of europium metal that lead directly to alkoxide and aryloxide complexes. Syntheses starting with the elemental metal are experimentally desirable, since problems of drying precursor salts and incorporation of extraneous ligands can be avoided.[8]

Several approaches to polymetallic europium complexes have been explored. Since europium dissolves in liquid ammonia, direct syntheses in this solvent were investigated, and it was found that phenols react directly with europium in liquid ammonia to provide europium aryloxide complexes in good yield.[3,4] Structurally characterizable mono-, bi-, and tetrametallic complexes $\mathrm{Eu(OC_6H_3Bu^t{}_2\text{-}2,6)_2(NCMe)_4}$, $\mathrm{Eu_2(OC_6H_3Me_2\text{-}2,6)_4(DME)_3}$, and $\mathrm{Eu_4(OC_6H_3Pr^i{}_2\text{-}2,6)_6(OH)_2(NCMe)_6}$ were obtained in this way depending on the substitution of the phenol.[3,4] Subsequently, it was found that acetonitrile and *N*-methylimidazole were also suitable solvents for reactions of europium with phenols, and the bimetallic species $\mathrm{Eu_2(OC_6H_3Me_2\text{-}2,6)_4}$(*N*-methylimidazole)$_5$ and $\mathrm{Eu_2(OC_6H_3Me_2\text{-}2,6)_4(NCCH_3)_5}$ were isolated by this route.[5] An additional approach to europium aryloxides, developed earlier by Deacon, involves the reaction

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of $Eu(C_6F_5)_2$, which can be generated directly from europium metal and $Hg(C_6F_5)_2$, with phenols to generate $Eu(OC_6H_2{}^tBu_2$-2,6-R-4$)_2(THF)_n$ (R = H, Me, and ^{t}Bu).[9] Divalent lanthanide aryloxides can also be made from amide precursors as shown in 1989.[10]

The formation of europium alkoxides directly from the metal has proven to be much more difficult than the aryloxide chemistry. In 1970, it was reported that europium in the presence of mercury chloride reacts with 2-propanol at reflux to form "$Eu(O^iPr)_2$"; however, little information was available about this composition.[11] Many years later, it was found that europium reacts directly with MeOH, EtOH, ^{i}PrOH, ^{t}BuOH, and $MeOCH_2CH_2OH$ without the addition of mercury salts.[6,12] Magnetic susceptibility[6] and Mossbauer[12] data indicated that europium is in the divalent oxidation state in all of these compounds, but structural information on these alkoxide complexes has been elusive. However, in the chelating 2-methoxyethanol system, it was found that the subsequent addition of phenols led to crystallographically characterizable tetrametallic complexes, $\{H[Eu(OCH_2CH_2OMe)_2(OC_6H_3R_2$-2,6$)]\}_4$ (R = Me, ^{i}Pr).[6] Hence, the combination of the aryloxide and alkoxide chemistry led to more tractable products.

We report here that by combining the reactivity of europium in 2-propanol with the coordinating ability of phenols, one can obtain a variety of fully characterizable polymetallic europium complexes whose composition depends on the reaction conditions. Synthetic details, structural characterization, and the implications of this chemistry in constructing polymetallic arrays of europium are discussed.

Experimental Section

All reactions were performed in a nitrogen-filled glovebox or by using standard Schlenk and vacuum line techniques under nitrogen. Europium ingots (Rhone Poulenc) were washed with hexanes, dried, and cut to appropriate size before use. 2-Propanol was dried by addition of 0.02 equiv of sodium per mole of 2-propanol at 20 °C followed by vacuum transfer of the alcohol from this mixture into the reaction flasks. 2,6-Dimethylphenol (Aldrich) was thrice sublimed before use. 2,6-Diisopropylphenol (Aldrich) was dried and vacuum-distilled from 3 Å molecular sieves. Other solvents were dried, and physical measurements were made as previously described.[13] Magnetic moments were measured by the method of Evans[14] on a Bruker DRX400 or General Electric QE300 NMR spectrometer. Complete elemental analyses were performed by Analytische Laboratorien, Lindlar, Germany. Europium analysis was done by complexometric titration with EDTA and a xylenol orange indicator.[15]

$H_x[Eu_8O_6(OC_6H_3Me_2$-2,6$)_{12}(O^iPr)_8]$, 1, and $H_5[Eu_5O_5(OC_6H_3{}^iPr_2$-2,6$)_6(NCCH_3)_8]$, 2. Pieces of Eu metal, typically 5−10 mm in diameter (**1**, 250 mg, 1.65 mmol; **2,** 561 mg, 3.69 mmol) were reacted with approximately 10 mL of HO^iPr and $HOC_6H_4R_2$-2,6 (R = Me, 400 mg, 3.3 mmol; R = ^{i}Pr, 1.302 g, 7.3 mmol) at reflux under N_2 for 1 day to yield orange solutions. Excess HO^iPr was removed under vacuum, and the resulting orange solids were transferred to a glovebox. In both cases, a single pure product was not obtainable and recrystallization from a variety of solvents was attempted. For the R = Me case, extraction of the product with hexanes followed by recrystallization from hexanes yielded <30 mg of dark-orange crystals of **1** after several days at room temperature. For the R = ^{i}Pr case, extraction of the product with CH_3CN followed by recrystallization yielded <30 mg of dark-orange crystals of **2** after several days. **1** and **2** were identified by X-ray crystallography. Attempts to obtain large amounts of these compounds for further study were unsuccessful, and syntheses of similar complexes under milder conditions were sought.

$[Eu(O^iPr)_2(THF)_x]_n$, 3. Pieces of Eu metal, typically 5−10 mm in diameter (10 g, 65.8 mmol), were reacted with approximately 50 mL of HO^iPr at room temperature under nitrogen for 6 days to yield an orange solution containing some insoluble material. Excess HO^iPr was removed under vacuum, and the resulting orange paste was transferred to a nitrogen glovebox. The orange paste was dissolved in THF and centrifuged to remove insoluble materials (1.7 g). THF was removed from the solution in vacuo to yield a solid, **3** (16.24 g, 80% based on Eu). Elemental analysis was consistent with the presence of 0.4 equiv of THF per europium. Anal. Calcd for $EuO_{2.4}C_{7.6}H_{17.2}$: Eu, 50.3; C, 30.7; H, 5.8. Found: Eu, 50.3; C, 30.1; H, 6.0. Digestion of **3** in acid followed by extraction with toluene yielded the organic products ^{i}PrOH and THF in a ratio of 2:0.3, which is consistent with the elemental analysis of the dry product. In a synthesis in a closed system, the gas evolved during the formation of **3** was found to be H_2 by mass spectrometry. The product does not sublime and decomposes between 225 and 275 °C under vacuum. Magnetic susceptibility: $\chi_G{}^{298K} = 7.6 \times 10^{-5}$, $\mu_{eff}{}^{298K} = 7.5\ \mu_B$. IR(KBr): 2943s, 2847m, 2603w, 1454m, 1366m, 1347m, 1153s, 1133s, 967s, 816m cm^{-1}. Similar yields of complex **3** were obtained by running the reaction at 45 °C for 4 days. Attempts to make **3** faster by conducting the reaction at reflux resulted in formation of varying mixtures of Eu(II) and Eu(III) products.

$\{H[Eu(OC_6H_3Me_2)_2(O^iPr)\}_n$, 4. Addition of a solution of $HOC_6H_4Me_2$-2,6 (1.83 g, 15 mmol) in 8 mL of hot toluene to a solution of **3** (2.261 g, 7.5 mmol) in 2 mL of toluene formed a yellow precipitate. Isolation of the yellow precipitate by centrifugation followed by several toluene washes (3 × 3 mL) and drying under vacuum resulted in a free-flowing yellow powder, $\{H[Eu(OC_6H_3Me_2)_2(O^iPr)\}_n$, **4** (2.99 g, 88%). Anal. Calcd for $EuO_3C_{19}H_{26}$: Eu, 33.4; C, 50.2; H, 5.8. Found: Eu, 33.8; C, 52.1; H, 5.1. Magnetic susceptibility: $\chi_G{}^{298K} = 1.77 \times 10^{-5}$, $\mu_{eff}{}^{298K} = 7.6\ \mu_B$. IR(KBr): 3430s, 2963s, 2916s, 1587m, 1460s, 1420s, 1263s, 1230s, 1157w, 1087m, 1076m, 1031m, 972w, 934w, 912w, 841s, 815w, 753s, 729w, 684m cm^{-1}.

$[Eu(OC_6H_3Me_2$-2,6$)_2(THF)_2]_3$, 5. A sample of **4** was generated in situ by addition of a solution of $HOC_6H_4Me_2$-2,6 (287 mg, 2.35 mmol) in 6 mL of hot toluene to a solution of **3** (710 mg, 1.17 mmol) in 1 mL of toluene. THF was added dropwise to a stirred suspension of the yellow precipitate until all of the precipitate was dissolved. Yellow crystals of $[Eu(OC_6H_3Me_2$-2,6$)_2(THF)_2]_3$, **5** (462 mg, 74%), formed from the solution over 2 days. Alternatively, **5** could be formed from isolated **4** following the same procedure. Anal. Calcd for $Eu_3O_{12}C_{72}H_{100}$: Eu, 28.2. Found: Eu, 28.1. Magnetic susceptibility: $\chi_G{}^{298K} = 4.4 \times 10^{-5}$, $\mu_{eff}{}^{298K} = 7.6\ \mu_B$. IR(KBr): 2978m, 2926m, 2866m, 1586m, 1460s, 1422s, 1367w, 1322w, 1274s, 1234m, 1090m, 1037m, 972w, 888w, 842s, 746s, 684w cm^{-1}.

$H_{10}[Eu_8O_8(OC_6H_3Me_2$-2,6$)_{10}(O^iPr)_2(THF)_6]$, 6. Yellow crystals of **5** left in their mother liquor started to change color from yellow to orange after approximately 3 weeks. After 2 months all of the yellow crystalline material was orange. Single crystals of orange **6** suitable for X-ray diffraction were obtained from this sample. Anal. Calcd for $Eu_3O_{12}C_{72}H_{100}$: Eu, 37.0. Found: Eu, 37.1. Magnetic susceptibility: $\chi_G{}^{298K} = 4.83 \times 10^{-5}$, $\mu_{eff}{}^{298K} = 6.7\ \mu_B$. IR(KBr): 3569m, 3433m, 2962s, 2721w, 1655w, 1592s, 1466s, 1425s, 1367m, 1315m, 1273s, 1231s, 1153w, 1090s, 1032m, 975w, 938w, 886w, 844s, 813w, 750s, 687m, 509m cm^{-1}.

$H_{18}\{[Eu_9O_8(OC_6H_3Me_2$-2,6$)_{10}(THF)_7][Eu_9O_9(OC_6H_3Me_2$-2,6$)_{10}(THF)_6]\}$, 7. **4** was heated to 140 °C under vacuum at 5×10^{-5} Torr for 1 day. The orange/yellow solids obtained were dissolved in THF, and after several days yellow crystals suitable for X-ray diffraction were obtained. Subsequent attempts to reproduce crystalline products resulted in the formation of gels rather than crystals. The following data are for the uncrystallized product before treatment with THF. Anal.

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Table 1. Experimental Data for the X-ray Diffraction Studies of $H_x[Eu_8O_6(OC_6H_3Me_2\text{-}2,6)_{12}(O^iPr)_8]$, **1**, $H_5[Eu_5O_5(OC_6H_3{}^iPr_2\text{-}2,6)_6(NCCH_3)_8]$, **2**, $[Eu(OC_6H_3Me_2\text{-}2,6)_2(THF)_2]_3$, **5**, $H_{10}[Eu_8O_8(OC_6H_3Me_2\text{-}2,6)_{10}(O^iPr)_2(THF)_6]$, **6**, and $H_{18}\{[Eu_9O_8(OC_6H_3Me_2\text{-}2,6)_{10}(THF)_7][Eu_9O_9(OC_6H_3Me_2\text{-}2,6)_{10}(THF)_6]\}$, **7**

compound	**1**	**2**·CH_3CN	**5**	**6**	**7**·$3.5C_7H_8$·OC_4H_8
formula	$C_{115}H_{150}Eu_8O_{26}$	$C_{90}H_{129}Eu_5N_9O_{11}$	$C_{72}H_{100}Eu_3O_{12}$	$C_{124}H_{168}Eu_8O_{26}$	$C_{239.5}H_{304}Eu_{18}O_{51}$
fw	3164.03	2272.82	1613.4	3290.26	3367.05
temp (K)	158	153	158	158	153
space group	$Pa\bar{3}$	$C2/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	29.9377(14)	19.268(3)	12.0468(6)	15.4628(7)	14.9535(7)
b (Å)	29.9377(14)	27.986(4)	11.9257(6)	16.0409(7)	28.3557(13)
c (Å)	29.9377(14)	18.794(3)	24.2959(13)	26.0241(12)	30.0169(14)
α (deg)	90	90	90	90	89.0460(10)
β (deg)	90	90.545(13)	100.1190(10)	99.8630(10)	86.6180(10)
γ (deg)	90	90	90	90	80.7500(10)
vol (Å^3)	26832(2)	10134(3)	3436.2(3)	6359.5(5)	12540.0(10)
Z	8	4	2	2	2
D_{calcd} (mg/m^3)	1.566	1.490	1.559	1.718	1.783
μ(Mo Kα) (mm^{-1})	3.741	3.104	2.764	3.949	4.494
R1, wR2	0.1086, 0.3037	0.0672, 0.2048	0.1419, 0.2966	0.0527, 0.1023	0.0942, 0.1557
radiation	Mo Kα ($\lambda = 0.710\ 730$ Å). Monochromator: highly oriented graphite.				

Calcd for **7**: Eu, 40.6. Found: Eu, 41.8. $\chi_G{}^{298K} = 6.5 \times 10^{-5}$, $\mu_{eff}{}^{298K} = 7.5\ \mu_B$. IR(KBr): 2907m, 2846w, 2242w, 1586m, 1459s, 1419s, 1367w, 1271s, 1227s, 1087s, 1030m, 973w, 912w, 842s, 741s, 680m cm^{-1}.

X-ray Data Collection and Solution and Refinement for 1 and 2. The crystals were mounted on glass fibers and transferred to a 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.[16] A $2\theta/\omega$ scan technique with Mo Kα radiation was used. The raw data were processed with a local version of CARESS,[17] 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.[18] The analytical scattering factors for neutral atoms were used throughout the analysis.[19] Structure were solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Details are given in Table 1.

A total of 3688 intensity data points were collected at 158 K for an orange crystal of **1** with approximate dimensions of 0.24 mm × 0.20 mm × 0.13 mm. The space group was the centrosymmetric cubic $Pa\bar{3}$. Several of the terminal ligands coordinated to the europium atoms were not identifiable. Heteroatoms were refined anisotropically. Hydrogen atoms were included on the aryloxide ligands using a riding model. At convergence, wR2 = 0.3037 and GOF = 1.038 for 212 variables refined against 3524 unique data points (as a comparison for refinement on F, R1 = 0.1086 for those 1655 data points with $I > 2.0\sigma(I)$).

A total of 10 258 intensity data points were collected at 153 K for an orange crystal of **2**·CH_3CN with approximate dimensions of 0.33 mm × 0.20 mm × 0.17 mm. The space group was the centrosymmetric monoclinic $C2/c$. One molecule of uncoordinated acetonitrile was located per pentametallic unit. All atoms, except those in the uncoordinated acetonitrile molecule, were refined anisotropically. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.2048 and GOF = 0.973 for 534 variables refined against 9953 unique data (as a comparison for refinement on F, R1 = 0.0672 for those 6568 data points with $I > 2.0\sigma(I)$).

X-ray Data Collection and Solution and Refinement for 5−7. These crystals were mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[20] program package was used to determine the unit cell parameters and for data collection. The raw frame data was processed using SAINT[21] and SADABS[22] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[18] program. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[19] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

Intensity data (30 s/frame scan time for a hemisphere of diffraction data) were collected at 158 K for a yellow crystal of **5** with approximate dimensions of 0.20 mm × 0.13 mm × 0.10 mm. The space group was the centrosymmetric monoclinic $P2_1/c$. The intensity data were generally weak because of the rather small size of the crystals of **5**, but larger single crystals were not obtainable in our hands. Metrical data of **5** were considered because they were internally consistent and reasonable relative to other divalent europium aryloxide complexes in the literature (see Discussion). At convergence, wR2 = 0.2966 and GOF = 1.338 for 394 variables refined against 7989 unique data points (as a comparison for refinement on F, R1 = 0.1419 for those 5806 data points with $I > 2.0\sigma(I)$).

Intensity data (30 s/frame scan time for a hemisphere of diffraction data) were collected at 158 K for a yellow crystal of **6** with approximate dimensions of 0.30 mm × 0.20 mm × 0.07 mm. The space group was the centrosymmetric monoclinic $P2_1/c$. At convergence, wR2 = 0.1023 and GOF = 1.151 for 655 variables refined against 14894 unique data points (as a comparison for refinement on F, R1 = 0.0527 for those 11 629 data points with $I > 2.0\sigma(I)$).

Intensity data (20 s/frame scan time for a sphere of diffraction data) were collected at 158 K on a yellow crystal of **7**·$3.5C_7H_8$·OC_4H_8 with approximate dimensions of 0.13 mm × 0.10 mm × 0.07 mm. The space group was the centrosymmetric $P\bar{1}$. There were two independent nonametallic molecules, one molecule of THF, and 3.5 molecules of toluene present in the asymmetric unit. Toluene molecules were constrained to a regular hexagon during refinement. At convergence, wR2 = 0.1557 and GOF = 1.196 for 2371 variables refined against 41 419 unique data (as a comparison for refinement on F, R1 = 0.0942 for those 26 524 data with $I > 2.0\sigma(I)$).

Results

Reactions in 2-Propanol at Reflux. Europium metal reacts directly with 2-propanol at reflux without the need to employ mercury salts as catalysts.[11] The product of this reaction can be dried under vacuum and is very soluble in ethers and somewhat soluble in arenes. Elemental analysis and the effective magnetic moment of europium in the product varied in a nonsystematic

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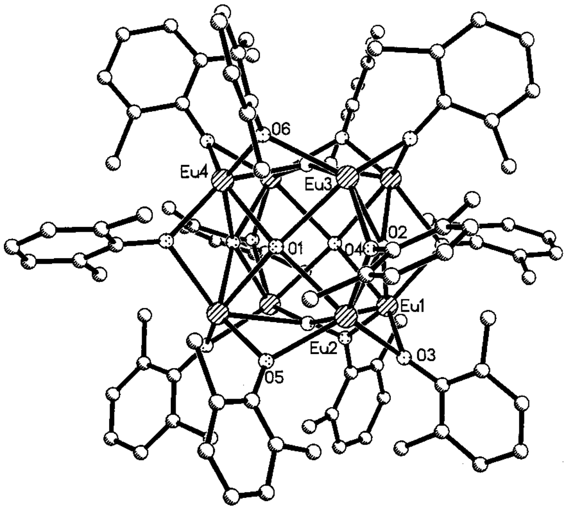

Figure 1. Ball and stick plot of $H_x[Eu_8O_6(OC_6H_3Me_2\text{-}2,6)_{12}(O^iPr)_8]$, **1**, with hydrogen atoms and disordered isopropyl carbons omitted for clarity.

Scheme 1. Formation of **1**−**7**

$$Eu + {}^iPrOH + HOAr \xrightarrow{\text{reflux}} \xrightarrow{\text{hexanes}} H_x[Eu_8O_6(OAr)_{12}(O^iPr)_8],\ \mathbf{1}$$

$$Eu + {}^iPrOH + HOAr' \xrightarrow{\text{reflux}} \xrightarrow{\text{MeCN}} H_5[Eu_5O_5(OAr')_6(NCMe)_8],\ \mathbf{2}$$

$$Eu + {}^iPrOH \xrightarrow{\text{RT, -}H_2} \xrightarrow{\text{THF}} [Eu(O^iPr)_2(THF)_x]_n,\ \mathbf{3}$$

$$\downarrow HOAr$$

$$\{H[Eu(OAr)_2(O^iPr)]\}_m,\ \mathbf{4}$$

$$\downarrow THF$$

$$Eu_3(OAr)_6(THF)_6,\ \mathbf{5}$$

$$\downarrow HO^iPr$$

$$H_{10}[Eu_8O_8(OAr)_{10}(O^iPr)_2(THF)_6],\ \mathbf{6}$$

$$\underset{\mathbf{4}}{\{H[Eu(OAr)_2(O^iPr)]\}_m} \xrightarrow[\text{vacuum}]{\text{heat}} \xrightarrow{\text{THF}}$$

$$H_{18}[Eu_9O_8(OAr)_{10}(THF)_7][Eu_9O_9(OAr)_{10}(THF)_6],\ \mathbf{7}$$

$(OAr = OC_6H_3Me_2\text{-}2,6;\ OAr' = OC_6H_3{}^iPr_2\text{-}2,6)$

way with reaction times and temperatures. Single crystals of this highly soluble material suitable for X-ray crystallography were not obtainable in our hands.

In efforts to generate crystallographically characterizable products from this reaction, phenols were added at the beginning of the reaction as shown in Scheme 1. This led to the isolation of two crystallographically characterizable polymetallic europium complexes $H_x[Eu_8O_6(OC_6H_3Me_2\text{-}2,6)_{12}(O^iPr)_8]$, **1** (Figure 1), and $H_5[Eu_5O_5(OC_6H_3{}^iPr_2\text{-}2,6)_6(NCCH_3)_8]$, **2** (Figure 2). Unfortunately, the yields of these products were low, and subsequent efforts to increase the yields have not been successful. To avoid these problems, syntheses under milder conditions were sought and are described in later sections.

The reflux reaction did show that this mixed alcohol/phenol approach could generate polymetallic species. Unfortunately, structural details can only be presented on **2**, since the X-ray data on **1** was of poor quality and gave only the gross structure of the complex. Reliable bond distances were not obtained, and not all of the eight terminal ligands assigned as isopropoxide or 2-propanol were well defined. In many cases, the gross structure is enough to define the product, since the ligands and metal valences are not ambiguous. However, in **1**, both Eu(II) and Eu(III) oxidation states are possible and the ligands could be aryloxides, phenols, alkoxides, or alcohols, or any combination thereof. The inclusion of an unknown number of protons in the formula of **1** reflects the ambiguity in oxidation states in this compound, while the inclusion of five protons in the formula of **2** is based on charge balance in this crystallographically well-defined mixed valence complex. The presence of protons in europium alkoxide complexes has been probed both structurally and chemically in the 2-methoxyethoxide system with the complexes $\{H[Eu(OCH_2CH_2OMe)_2(OC_6H_3R_2\text{-}2,6)]\}_4$ (R = Me, ^{i}Pr).[6] In these complexes, the bond distances and angles suggested that the protons are hydrogen-bonded between the alkoxide and aryloxide ligands. However, since the positions could not be definitely determined, the protons are written separately in these formulas and throughout the paper.

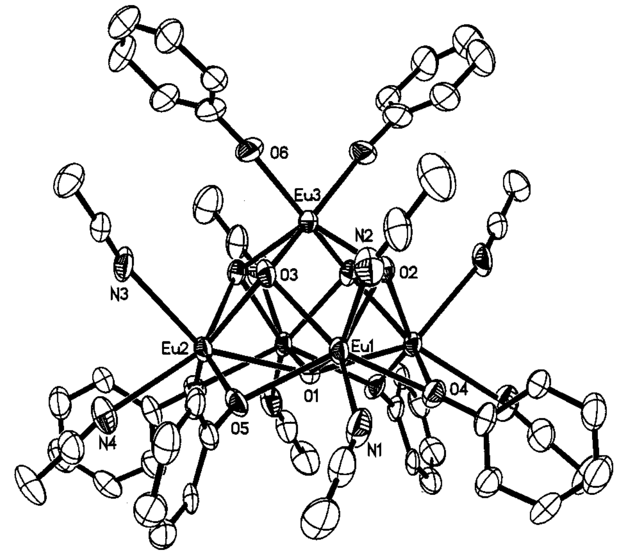

Figure 2. Thermal ellipsoid plot of $H_5[Eu_5O_5(OC_6H_3{}^iPr_2\text{-}2,6)_6\text{-}(NCCH_3)_8]$, **2**, drawn at the 50% probability level with hydrogens and isopropyl groups of the aryloxide ligands omitted for clarity.

$H_5[Eu_5O_5(OC_6H_3{}^iPr_2\text{-}2,6)_6(NCCH_3)_8]$, 2. Complex **2** has a square pyramidal arrangement of europium atoms (Figure 2) and contains a 2-fold crystallographic axis that runs through the apical europium atom and the center of the base of the square pyramid. The Eu(basal)···Eu(basal) distances are 3.6410(9) and 3.6634(9) Å, and the Eu(apical)···Eu(basal) distances are 3.8733(8) and 3.9171(8) Å. The basal europium atoms in **2**, Eu(1) and Eu(2), have Eu−ligand distances that are consistent with reported divalent europium complexes, while the apical europium atom Eu(3) has metal−ligand distances that are consistent with trivalent lanthanide compounds.

The triangular faces of the square pyramid in **2** are bridged by four oxygen atoms. The 2.483(7)−2.553(7) Å Eu(basal)−O(μ_3-O) distances are in the range of the 2.473(6)−2.521(5) Å Eu−O(μ_3-O) distances in divalent $H_2[Eu_4(OC_6H_3Pr^i{}_2\text{-}2,6)_6(O)_2\text{-}(NCMe)_6]$, **8**,[11] and are longer than the 2.337(7)−2.365(7) Å Eu(apical)-O(μ_3-O) distances in **2**. The basal face of the square pyramid in **2** is bridged by an oxygen atom, and the 2.629(2) and 2.675(2) Å Eu(basal)−O(μ_4-O) distances are in the range of the 2.637(5)−2.684(5) Å Eu−O(μ_4-O) distances involving the divalent Eu atoms in $H_{10}[Eu_8O_8(OC_6H_3Me_2\text{-}2,6)_{10}(O^iPr)_2\text{-}(THF)_6]$, **6**, described later, and longer than the 2.455(4)−2.474(4) Å Eu−O(μ_4-O) involving the trivalent europium atom in **6**. The 3.52 Å Eu(apical)−O(μ_4-O) distance in **2** is outside the usual bonding distance range.

The apical europium atom in **2** is coordinated by two symmetry-equivalent terminal aryloxide ligands with a 2.246(8) Å Eu(apical)−O(terminal aryloxide) distance. This is consistent with the 2.214(4) and 2.228(4) Å trivalent Eu−O(terminal OAr) distances in $Eu_3[\mu_3\text{-}(O(CH_2CH_2O)_2CH_2CH_3]_4(\mu\text{-}OC_6H_3{}^iPr_2\text{-}2,6)(OC_6H_3{}^iPr_2\text{-}2,6)_2$[7] and the 2.087(5)−2.179(5) Å Sm(III)−O(terminal OAr) distances in trivalent $Sm(OC_6H_3{}^iPr_2\text{-}2,6)_3(THF)_2$ [23] when the differences in ionic radii are considered.[24] The 2.505(7)−2.565(7) Å Eu(basal)−O(μ_2-OAr) distances and the 2.685(11)−2.715(11) Å Eu(basal)−N(NCCH$_3$ terminal) distances are in the range of those in the divalent europium complexes $[(CH_3CN)_2(2,6\text{-}{}^iPr_2C_6H_3O)Eu]_2(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}NCCH_3)$[6] and **8**.[5]

Reactions in 2-Propanol at Room Temperature. Since the high-temperature europium/2-propanol reactions were not easily controlled, room-temperature reactions were examined as shown in Scheme 1. Although the reaction was slow, it was found that europium would react with 2-propanol at room temperature. After 6 days at room temperature or 4 days at 45 °C, an orange solution was obtained. Removal of 2-propanol left a slightly arene- and ether-soluble orange paste. Mass spectroscopic analysis of the gaseous products in a sealed reaction vessel indicated that H$_2$ gas was formed during the reaction, as expected in

$$Eu + {}^iPrOH \rightarrow [Eu(O^iPr)_2]_n + H_2 \qquad (1)$$

Extraction of this material with THF, removal of insoluble materials by centrifugation, and subsequent removal of THF provided in good yield a solid that was analyzed to be $[Eu(O^iPr)_2(THF)_x]_n$, **3**. Attempts to obtain crystals of **3** for crystallographic analysis from a variety of coordinating and noncoordinating solvents were not successful.

Since phenols had previously been found to be useful in converting the europium/2-methoxyethoxide reaction product "$Eu(OCH_2CH_2OMe)_2$" into the toluene-soluble, structurally characterizable derivatives $\{H[Eu(OCH_2CH_2OMe)_2(OC_6H_3R_2\text{-}2,6)]\}_4$ (R = Me, **9** and ^{i}Pr **10**),[6] the reaction of **3** with phenols was examined. In contrast to the 2-methoxyethanol system, which formed arene-soluble products, addition of $HOC_6H_3Me_2$-2,6 to **3** in toluene caused immediate formation of a yellow precipitate. After thorough washing with toluene, the yellow precipitate had an elemental analysis consistent with the formula $\{H[Eu(OC_6H_3Me_2)_2(O^iPr)\}_n$, **4**, similar to the previously reported mixed alkoxide/aryloxide complexes **9** and **10**.[6] The presence of protons in **4** is supported by the IR spectrum, which contains a sharp peak at 3430 cm^{-1} in the O−H stretching frequency range. The presence of Eu(II) in **4** is supported by its magnetic moment, $\mu_{eff} = 7.6\ \mu_B$, and by its subsequent reaction chemistry with THF described below.

$[Eu(OC_6H_3Me_2\text{-}2,6)_2(THF)_2]_3$, 5. Addition of THF to **4** in hot toluene formed a new complex, which is sparingly soluble in arenes, and could be recrystallized from toluene/THF as $Eu_3(OC_6H_3Me_2\text{-}2,6)_6(THF)_6$, **5**. Both the magnetic moment of 7.6 μ_B and the structural data presented below indicate that **5** contains divalent europium.

Complex **5** does not adopt the triangular arrangement of metal atoms common for trimetallic systems but rather a linear Eu−Eu−Eu geometry: $(THF)_3Eu(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_3Eu(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_3Eu(THF)_3$ (Figure 3). The positions of the bridging aryloxide ligands in **5** are similar to those in the previously reported DME and *N*-methylimidazole adducts $(DME)_2Eu(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_3Eu(OC_6H_3Me_2\text{-}2,6)(DME)$ [3] (DME = 1,2-dimethoxyethane), **11**, and (*N*-methylimidazole)$_3$Eu(μ-OC$_6$H$_3$Me$_2$-2,6)$_3$Eu(*N*-methylimidazole)$_2$(OC$_6$H$_3$Me$_2$-2,6),[5] **12**. Hence, **5**, **11**, and **12** each have Eu(II) centers connected by three doubly bridging 2,6-dimethylphenoxide ligands. Bimetallic **11** and **12** contain only one additional aryloxide ligand, which is a terminal ligand on a six-coordinate europium. Complex **5** shows that Eu(II) can accommodate two additional 2,6-dimethylphenoxide ligands and achieve six-coordination with six bridging aryloxide ligands surrounding a Eu(II) center.

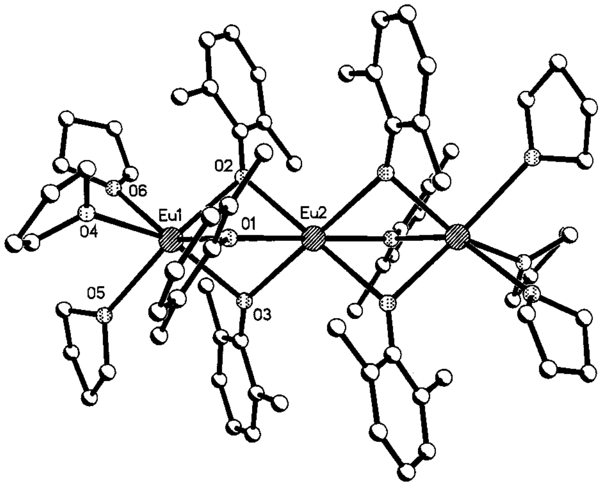

Figure 3. Ball and stick plot of $[Eu(OC_6H_3Me_2\text{-}2,6)_2(THF)_2]_3$, **5**, with hydrogen atoms omitted for clarity.

The coordination geometry of the central europium atom, Eu(2), in **5** is best described as triangular antiprismatic rather than octahedral, since the 3.08−3.12 Å O(OAr)−O(OAr) distances forming the end triangles of the antiprism are much shorter than 4.05−4.09 Å distance between the vertexes of the triangles on opposite ends. The outer Eu atoms, Eu(1) and Eu(1a), have an identical coordination geometry by virtue of symmetry, which is closer to triangular prismatic than triangular antiprismatic. The twist angle involving these two triangles is 16°, compared to 0° for a triangular prism and 60° for a triangular antiprism. In comparison, the coordination geometries of the metal atoms in **11** and **12** are irregular.

The 2.444(13)−2.581(12) Å Eu−O(μ-OAr) distances in **5** are in the range of those in **2**, **11**, and **12**. Similarly, the 2.573(15)−2.647(13) Å Eu(1)−O(THF) distances in **5** are normal compared to the 2.515(6)−2.590(5) Å Eu−O(THF) distances in divalent $Eu(OC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)_2(THF)_3$, **13**.[25]

$H_{10}[Eu_8O_8(OC_6H_3Me_2\text{-}2,6)_{10}(O^iPr)_2(THF)_6]$, 6. When crystals of **5** are left in their mother liquor for several weeks, they change color from yellow to orange. After 2 months, an entire crystalline sample turns orange and the orange crystals have a very different morphology than those of **5**. Elemental analysis of the orange product revealed a noticeably higher europium content (37%) than in **5** (28%). A slight decrease in the effective magnetic moment from 7.6 to 6.7 μ_B suggested that the product was no longer solely Eu(II) ($\mu_{eff}{}^{298K} = 7.8\ \mu_B$) and contained some Eu(III) ($\mu_{eff}{}^{298K} = 4.0\ \mu_B$).[26] Single-crystal X-ray diffraction revealed an octametallic cubic structure (Figure 4) to which, on the basis of elemental analysis, magnetic moment, IR spectroscopy, and bond lengths, we assign the formula $H_{10}[Eu_8O_8(OC_6H_3Me_2\text{-}2,6)_{10}(O^iPr)_2(THF)_6]$, **6**, a mixed valence complex containing a 3:1 Eu(II)/Eu(III) mixture.

The distorted cubic arrangement of eight europium atoms in **6** is situated about a crystallographic inversion center. The

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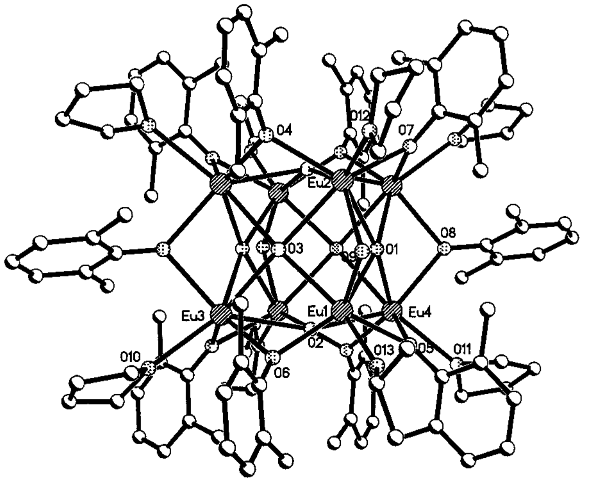

Figure 4. Ball and stick plot of $H_{10}[Eu_8O_8(OC_6H_3Me_2\text{-}2,6)_{10}(O^iPr)_2(THF)_6]$, **6**, with hydrogens omitted for clarity.

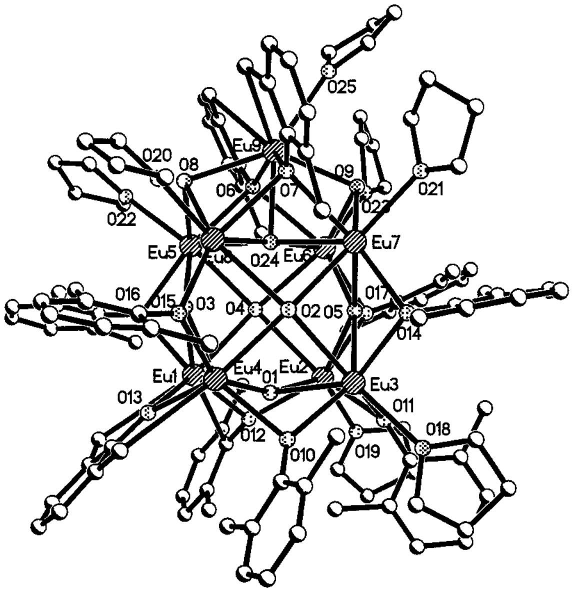

Figure 5. Ball and stick plot of the $[Eu_9O_8(OC_6H_3Me_2\text{-}2,6)_{10}(THF)_7]$ unit "A" in $H_{18}\{[Eu_9O_8(OC_6H_3Me_2\text{-}2,6)_{10}(THF)_7][Eu_9O_9(OC_6H_3Me_2\text{-}2,6)_{10}(THF)_6]\}$, **7**, with hydrogen atoms omitted for clarity.

3.6029(5)−3.7193(5) Å range of Eu···Eu distances and the 86.347(10)−94.337(11)° range of Eu−Eu−Eu angles reflect the distortions from ideal cubic symmetry in **6**. As discussed below, the bond lengths involving Eu(1) are consistently shorter than the bond lengths of the other three europium atoms. The differences in bond lengths between Eu(1) and Eu(2)−Eu(4) to comparable ligands are consistent with the 0.19 Å difference in Shannon radii between seven-coordinate Eu(II) and Eu(III).[24] The structural evidence thus indicates that Eu(1) is trivalent and that Eu(2)−Eu(4) is divalent, which is consistent with the magnetic data, which are based on X_G values from the average observed values for Eu(II) and Eu(III).[26]

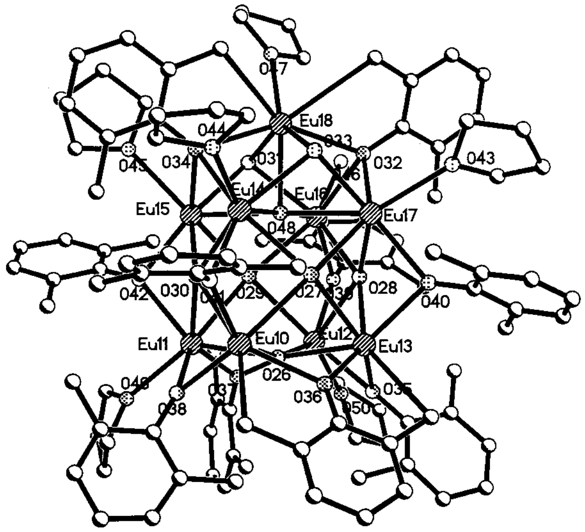

Figure 6. Ball and stick plot of the $[Eu_9O_9(OC_6H_3Me_2\text{-}2,6)_{10}(THF)_6]$ unit "B" in **7**, with hydrogen atoms omitted for clarity.

This oxidation state assignment requires 10 protons for charge balance. Unfortunately, none of these hydrogen atoms were located in the X-ray structure. Two of the protons are likely associated with the isopropoxide ligands, as discussed below, but the positions of the other eight protons cannot be specified with certainty. If they are symmetrically located, they could be associated with the eight bridging oxygen atoms, which makes these bridging hydroxide rather than oxide ligands. The protons might also bridge two oxygen atoms, as was postulated in **9** and **10**.[6]

Six μ_4-oxygen atoms bridge the faces of the cubic array of europium atoms; i.e., it has a face-centered cubic core. The average of the 2.455(4)−2.474(4) Å range of Eu(1)−O(μ_4-O) distances is 0.21 Å shorter than the average of the 2.637(5)−2.684(5) Å range of Eu−O(μ_4-O) distances involving Eu(2), Eu(3), and Eu(4). The latter range agrees well with the corresponding Eu(II)−O(μ_4-O) distances in **2**, as previously discussed, and in **7**, described below. Ten of the edges of the cubic array of europium atoms are bridged by 2,6-dimethylphenoxide ligands, and oxygens bridge the other two edges. The average of the 2.342(5)−2.369(5) Å range of Eu(1)−O(μ-OAr) distances is 0.15 Å shorter than the average of the 2.478(5)−2.594(5) Å range of Eu−O(μ-OAr) distances involving Eu(2), Eu(3), and Eu(4). The 2.276(5) Å Eu(1)−O(μ-O) distance is also shorter than the 2.446(5) Å Eu(2)−O(μ-O) bond distance.

Terminal THF ligands are coordinated to Eu(2), Eu(3), and Eu(4), while a terminal isopropoxide ligand is coordinated to Eu(1). The 2.609(5)−2.641(5) Å Eu−O(THF) distances in **6** are in the range of the corresponding distances in divalent **5** (2.573(15)−2.647(13) Å) and are generally longer but within the range of those in divalent **13** (2.515(6)−2.590(5) Å). The 2.521(5) Å Eu(1)−O(O^iPr) distance is longer than the 2.121(9)−2.184(16) Å Nd−O(O^iPr) distances in trivalent $[Nd_5O(O^iPr)_{13}(HO^iPr)_2]$ [27] but corresponds well to the 2.511(10) Å Nd−O(HO^iPr) distances. This suggests that the terminal isopropoxide moieties are present as 2-propanol ligands.

$H_{18}\{[Eu_9O_8(OC_6H_3Me_2\text{-}2,6)_{10}(THF)_7][Eu_9O_9(OC_6H_3Me_2\text{-}2,6)_{10}(THF)_6]\}$, 7. Compound **4** was heated under vacuum in order to determine whether it could be thermally converted to **6**. The yellow/orange solid product obtained from this thermolysis was found to have a μ_{eff}^{298K} of 7.5 μ_B, a value close to that of divalent europium and higher than that observed for **6**. Attempts to grow single crystals of the solid were hampered by gel formation from solutions, although in one case a few small single crystals were isolated from a toluene/THF mixture. The structure consisted of two crystallographically independent and chemically nonequivalent nonametallic europium complexes per asymmetric unit that have the formula $H_{18}\{[Eu_9O_8(OC_6H_3Me_2\text{-}2,6)_{10}(THF)_7][Eu_9O_9(OC_6H_3Me_2\text{-}2,6)_{10}(THF)_6]\}$, **7**, Figures

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5 and 6. Although this complex was not prepared in high yield, it is included here because it provides another example of the Eu_8O_6 core found in **1** and **6**.

The europium atoms in each nonametallic unit of **7** form a distorted capped cubic arrangement. In general, the cube portions of these units are similar to those of **1** and **6** with face-bridging oxygen atoms and edge-bridging 2,6-dimethylphenoxide ligands. No specific europium atoms in **7** have shorter bond lengths than the rest of the metals, which is consistent with the magnetic data, which indicate that the europium atoms in **6** are all divalent. To achieve charge balance in complex **7**, 18 protons must be associated with the two nonametallic units. As in the previous complexes, these protons could not be located by X-ray crystallography but are likely associated with bridging oxygen atoms.

In each of the nonametallic units, one face of the cube is capped by a europium atom, which is ligated by a terminal THF. The europium cap is bridged to the cube through two triply bridging oxygen atoms and two triply bridging 2,6-dimethylphenoxide groups.

In the nonametallic unit $[Eu_9O_8(OC_6H_3Me_2\text{-}2,6)_{10}(THF)_7]$, which we shall label A, only the Eu atoms numbered 2, 3, 5, 6, 7, 8, and 9 have terminal THF. This differs from complexes **1** and **6** in which there are terminal ligands on every corner of the cube (THF or isopropoxide/2-propanol). Although europium atoms 1 and 4 have no terminal ligands, they appear to have additional ligation via 3.203 and 3.254 Å Eu···Me agostic interactions involving the methyl groups of nearby 2,6-dimethylphenoxide ligands. Eu···Me agostic interactions of 3.085 and 3.160 Å are also found with the capping europium atom Eu(9). These values are in the range of agostic Eu−C distances in divalent $[(Me_3Si)_2N]Eu[\mu\text{-}N(SiMe_3)_2]_2Na$ (2.97−3.44 Å).[28]

In nonametallic unit B, $[Eu_9O_9(OC_6H_3Me_2\text{-}2,6)_{10}(THF)_6]$, terminal THF ligands are found on the Eu atoms numbered 11, 12, 14, 15, 17, and 18. As in unit A, agostic Eu···Me interactions fill out the coordination sphere of the other europium centers. Eu(10) and Eu(13) have 3.164 and 3.226 Å Eu···Me agostic interactions, and Eu(18) has 3.102 and 3.160 Å Eu···Me agostic interactions. For Eu(16), only an oxygen atom was located at a terminal position. This oxygen is likely attached to protons as well, but this could not be determined from the crystal structure.

The 3.5488(13)−3.7784(13) Å range of Eu···Eu distances in the cubic portions of **7** is larger than the 3.6029(5)−3.7193(5) Å range of distances in **6**, which may be a result of the lower symmetry of the capped cubic arrangement. In the square pyramid formed by the europium cap in each nonametallic unit in **7**, the μ_5-O ligands form longer bonds with the basal europium atoms (2.634(10)−2.683(11) Å) than with the apical europium atoms (2.459(11), 2.462(11) Å). This situation is between those of trivalent $Y_5O(O^iPr)_{13}$[29] and $Yb_5O(O^iPr)_{13}$[31] in which all of the lanthanide-O(μ_5-O) distances are equivalent within experimental error, and that of **2**, in which only the basal europium atoms interact with the oxygen bridging the basal face. A similar trend of longer basal-O and shorter apical-O distances has been observed in $Y_5O(OMe)_8(C_5H_5)_5$.[30] The 2.549(10)−2.71(1) Å Eu−O(μ_4-O) distances in **7** are longer than the 2.455(4)−2.474(4) Å Eu(1)−O(μ_4-O) distances involving trivalent europium atoms in **6**, and they are closer to the 2.637(5)−2.684(5) Å distances involving divalent europium atoms in **6**. The 2.470(11)−2.592(12) Å Eu−O(μ_3-O) distances in **7** are in good agreement with the 2.473(6)−2.521(5) Å distances reported for divalent **8**.

The 2.450(13)−2.550(14) Å range of Eu−O(μ-OAr) distances in **7** is similar to the 2.478(5)−2.594(5) Å range of Eu−O(μ-OAr) distances involving divalent europium in **6**. The 2.560(11)−2.682(11) Å Eu−O(μ_3-OAr) distances in **7** are generally longer than the edge-bridging aryloxide ligands, as expected. The 2.563(12)−2.717(16) Å range of Eu−O(THF) distances in **7** is larger but overlaps with those in **5** (2.573(15)−2.647(13) Å), **6** (2.609(5)−2.641(5) Å), and **13** (2.515(6)−2.590(5) Å).

Discussion

The direct reaction of europium with 2-propanol has proven to be a challenging system to analyze. Following the initial report in 1970 that europium would react with 2-propanol at reflux in the presence of mercuric salts,[11] it has subsequently been determined that the reaction will also proceed without the mercury additives. This product has not been proven to give crystalline, fully characterizable products, however. The addition of phenols to the 2-propanol reflux reaction did lead to polymetallic europium complexes, $H_x[Eu_8O_6(OC_6H_3Me_2\text{-}2,6)_{12}(O^iPr)_8]$, **1**, and $H_5[Eu_5O_5(OC_6H_3{}^iPr_2\text{-}2,6)_6(NCCH_3)_8]$, **2**, and showed that the direct reaction of Eu with ^{i}PrOH could provide a synthetic approach to the desired polymetallic europium complexes. However, the low yields of **1** and **2** and the fact that **2** was mixed valence suggested that milder conditions might be necessary to generate single fully characterizable products in high yield.

Examination of the europium/2-propanol reaction under milder conditions showed that europium reacts directly with 2-propanol even at room temperature. The product of this reaction is probably a Eu(II) bis(isopropoxide) complex, i.e., something related to "$Eu(O^iPr)_2$", but full characterization of this species has proven to be difficult. Given the large size of the lanthanide metals and their tendency to exhibit high coordination numbers, one would expect "$Eu(O^iPr)_2$" to exist in some oligomer and to be solvated. The fact that this Eu/2-propanol product is isolated as an orange paste could be explained by the presence of several types of oligomers and 2-propanol adducts. This is consistent with the $Nd/HO^iPr/HgCl_2/Hg(O_2CCH_3)_2$ system in which $[Nd(O^iPr)_3(HO^iPr)]_4$ and $Nd_5O(O^iPr)_{13}(HO^iPr)_2$ are formed.[27] The addition of THF to "$Eu(O^iPr)_2$" provides a more tractable material that is analyzed to be a THF solvate, namely, $[Eu(O^iPr)_2(THF)_x]_n$, **3**. However, even this compound does not readily crystallize. Only by addition of aryl alcohols have crystalline products been obtained.

The addition of phenols to the room temperature europium/2-propanol reaction product has proven to be a successful approach to provide fully characterizable products from this system. A similar result was observed with $Eu/HOCH_2CH_2OCH_3$, although the systems differ substantially in detail.[6] The isolation of the crystalline divalent THF adduct $[Eu(OC_6H_3Me_2\text{-}2,6)_2(THF)_2]_3$, **5**, confirms the presence of divalent europium in **3**. Hence, this europium/2-propanol system differs from other lanthanide isopropoxide systems in which mercury catalysts are required and trivalent lanthanide products are isolated from 2-propanol. Even the lanthanide with the next most stable divalent state, ytterbium, forms trivalent products when reacted with 2-propanol.[31]

The isolation of a trimetallic, linear (terminal ligand)$_n$Eu(μ-OAr)$_3$Eu(μ-OAr)$_3$Eu(terminal ligand)$_n$ structure for **5** is also unusual. It is much more common to find bimetallic (terminal

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ligand)$_n$Eu(μ-OAr)$_3$Eu(terminal ligand)$_n$ complexes such as (DME)$_2$Eu(μ-OC$_6$H$_3$Me$_2$-2,6)$_3$Eu(OC$_6$H$_3$Me$_2$-2,6)(DME), **11**, and (*N*-methylimidazole)$_3$Eu(μ-OC$_6$H$_3$Me$_2$-2,6)$_3$Eu(*N*-methylimidazole)$_2$(OC$_6$H$_3$Me$_2$-2,6), **12**. This is common not only for Eu(II) but for other divalent metals such as (Ph$_3$SiO)(H$_3$N)Ca(μ-OSiPh$_3$)$_3$Ca(NH$_3$)$_3$[32] and (Ph$_3$CO)(THF)Ba(μ-OCPh$_3$)$_3$Ba(THF)$_2$.[33] The structure of **3** shows that divalent europium can accommodate a coordination environment composed of six bridging aryloxide ligands. This suggests that **11** and **12** could also form trimetallic structures, e.g., (DME)$_2$Eu(μ-OAr)$_3$Eu(μ-OAr)$_3$Eu(DME)$_2$ and (*N*-methylimidazole)$_3$Eu(μ-OAr)$_3$Eu(μ-OAr)$_3$Eu(*N*-methylimidazole)$_3$ (Ar = C$_6$H$_3$Me$_2$-2,6), but these compositions are apparently not the favored in the solid state. Indeed, the option to form mono-, bi-, *and* trimetallic structures could be one reason oils instead of single crystals may result in some systems. Fortunately, in **5**, the crystallization conditions were optimum for a single product.

For a trimetallic complex of divalent metal ions with six bridging anionic ligands, the charge is balanced if all of the terminal ligands are neutral as in **5**. This may explain why further oligomerization does not occur. Oligomeric structures such as (terminal ligand)$_3$Eu[(μ-OAr)$_3$Eu]$_n$(terminal ligand)$_3$ seem reasonable as far as the coordination geometry of the individual europium atoms is concerned, but for $n = 3$, the overall charge of the complex becomes -1. Such a structure would require a trivalent metal at one end, and $n = 4$ would require trivalent metals at both ends. Although these possibilities are structurally reasonable, synthetic approaches are not currently known.

Beyond the simple "[Eu(OR)$_2$(solvate)$_n$]$_m$" and "[Eu(OAr)$_2$(solvate)$_n$]$_m$" complexes such as **3**−**5**, there appear to be a variety of more complicated polymetallic complexes that have incorporated oxide or hydroxide ligands and have a more compact polyhedral structure than the linear structures of **3**, **11**, and **12**. Pentametallic, octametallic, and nonametallic examples were found in this study, but a variety of others are likely to be accessible under the proper synthetic conditions. The isolation of the nonametallic **7**, which is a capped cubic variation of cubic **1** and **6**, and the ease by which new polyhedra can be generated by capping suggest that many structural types should be able to meet the coordination requirements of polymetallic assemblies of europium. Since europium can exist in two oxidation states in these complexes and hence can have two different radial sizes, there is even an extra parameter available with europium in addition to the variations possible with fixed oxidation state metals.

The isolation of complexes **1**, **6**, and **7** suggests that the M$_8$O$_6$ core is a rather favorable polymetallic unit for these europium oxides. This is reasonable because these structures effectively have a face-centered cubic arrangement of metals and oxygen atoms, which is common in solid-state chemistry. Recently, several similar molecular octametallic lanthanide complexes with face-centered ligands have been reported by Brennan and coworkers.[34] In these cases the face-centered ligands are sulfur and tellurium and, to our knowledge, no oxo-based molecular complexes such as **1**, **6**, and **7** have previously been reported. The square pyramidal unit in **2** is also common and has been seen in a variety of other polymetallic lanthanide complexes including Ln$_5$O(O^{i}Pr)$_{13}$ (Ln = Y, Yb)[29,31] and Y$_5$O(OMe)$_8$(C$_5$H$_5$)$_5$.[30]

Crucial to the formation of these larger polymetallic species are small bridging ligands such as hydroxide and oxide. Combining these small multiply bridging ligands with bulky alkoxide/alcohol and/or aryloxide/phenol ligands can lead to soluble, fully chacterizable species. Synthetically these smaller bridging ligands, and hence larger polymetallic europium species, can be accessed through more forcing conditions—primarily by heating. The decomposition of **5** in the presence of ^{i}PrOH to form the cubic polymetallic europium complex **6** and the thermolysis of **4** to form **7** is consistent with the behavior of trivalent lanthanide isopropoxides, which readily form polymetallic oxoalkoxide complexes.[27,29,31] Unfortunately, accompanying these higher temperature conditions are apparently an increase in the number of possible reaction pathways and concomitant formation of mixtures. Hence, one of the synthetic challenges in the future is to control the reactivity under conditions in which oxides and hydroxides are readily formed. Reactions involving soluble forms of these small bridging ligands may provide a good alternative to the high-temperature conditions.

Conclusion

We have demonstrated that fully characterizable polymetallic europium complexes can be obtained from the europium 2-propanol reaction system by using the proper reaction conditions and the addition of phenols. A variety of polymetallic species are accessible in this system, and neither the reflux temperature conditions nor the mercury catalysts originally reported for this reaction are needed to generate europium isopropoxides. Room temperature reactions are effective at generating an oxide and hydroxide-free divalent species, which, although structurally elusive, can be considered for synthetic purposes as the equivalent of "Eu(O^{i}Pr)$_2$". This complex is a good soluble Eu(II) alkoxide precursor that can be readily converted to fully characterizable divalent europium complexes in the presence of phenols. These species can be oxidized to mixed valent polymetallics under the proper conditions with 2-propanol and heat. Controlled synthesis of these polymetallics remains to be accomplished, but reasonable routes to representative examples now are available so that the chemistry and spectroscopy of this class of compounds can be investigated.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1**, **2**, and **5**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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