Direct Synthesis of Heterometallic Europium/Barium Complexes: $H_2[Eu_2Ba_6O_2(O\textit{i}Pr)_{16}(THF)_4]$ and $EuBa_2(OC_6H_4Me\text{-}4)_7(diglyme)_2(DME)$

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Convenient syntheses of mixed-metal Eu/Ba complexes starting from the elemental metals have been explored. A mixture of europium and barium ingots reacts in boiling 2-propanol to form a product which crystallizes from THF as the heterometallic complex formulated as $H_2[Eu_2Ba_6O_2(O\textit{i}Pr)_{16}(THF)_4]$ (**1**). An analogous reaction in the presence of *p*-cresol (HOC_6H_4Me-4) forms trimetallic $EuBa_2(OC_6H_4Me_4)_7(diglyme)_2(DME)$ (**2**), after recrystallization from THF/DME/diglyme (DME = 1,2-dimethoxyethane). Complex **1** exhibits an octametallic geometry comprised of two square pyramids with coplanar bases which share a basal edge and have apices on opposite sides. The six barium atoms occupy the basal positions and the two europium atoms are at the apices. Complex **2** exhibits a triangular arrangement of metal atoms with both terminal and bridging aryloxide ligands coordinated to the europium atom and bridging aryloxide and terminal ether ligands coordinated to the barium atoms.

Introduction

One approach to improve the performance of multi-metallic solid-state materials is to construct them from molecular precursors which have the metal components mixed with a predetermined stoichiometry at the molecular level.[1] To use this method to improve phosphors[2,3] that depend on the special fluorescent properties of europium,[4] convenient syntheses of heterometallic europium complexes are needed. Alkoxide or aryloxide complexes are desirable since they could be converted into oxide materials by sol-gel and thermal methods.[5] Preparation of such complexes directly from the metals is preferable, since it avoids the problems of drying and potential anion contamination which accompany the use of metal salts as precursors.

Although several routes to well-defined homometallic europium alkoxide complexes have been reported,[6–15] heterometallic species have remained elusive. For example, attempts to produce heterometallic Eu/alkaline earth species by direct reaction of the metal ingots with aryl alcohols in liquid ammonia were unsuccessful and produced only mixtures of homometallic species.[16]

We report here the direct synthesis of well-defined heterometallic europium alkoxide complexes by reaction of mixtures of europium and barium metal ingots with 2-propanol at reflux. Barium was chosen since it is a frequent heterocomponent in europium-based phosphors.[17–19] We also describe the variation in structure and metal stoichiometry induced in the isolated products by addition of *p*-cresol to the reaction mixture.

Results and Discussion

Synthesis

Mixtures of metallic europium and barium react with 2-propanol at reflux to form an ether-soluble product. Structural details could not be elucidated from the NMR spectra of the product due to the broadness and shifts in resonances caused by the paramagnetism of europium in this product. To unambiguously determine the nature of reaction products, crystallization was attempted from a variety of coordinating solvents and mixtures of solvents.

Single crystals of **1** could only be obtained from THF. Crystallization of the europium/barium/2-propanol reaction product from THF yielded single crystals which were found by X-ray diffraction to be $H_2[Eu_2Ba_6O_2(O\textit{i}Pr)_{16}(THF)_4]$ (**1**), see Figure 1. The magnetic moment of

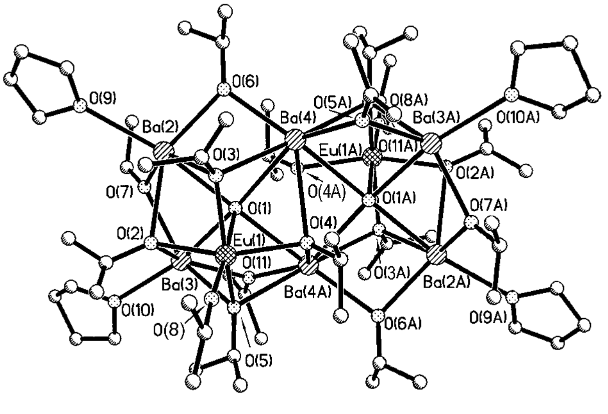

Figure 1. Ball-and-stick diagram of $H_2[Eu_2Ba_6O_2(O\textit{i}Pr)_{16}(THF)_4]$ (**1**); hydrogen atoms are omitted for the sake of clarity

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1434–1948/02/0202–0453 $ 17.50+.50/0

this complex was consistent with the presence of trivalent, rather than divalent, europium.[20]

Reactions containing aryl alcohols were also examined, since they had previously been shown to be effective in generating crystalline polymetallic lanthanide complexes.[6,7,11−13,21] After heating a mixture of *p*-cresol and europium and barium metals in 2-propanol at reflux, removal of solvent resulted in a yellow solid. The solid failed to crystallize from THF, diglyme, diethyl ether, and DME, but formed crystals from a mixture of ethers (THF, DME, diglyme, 6:1:1). The fact that **2** crystallized only from a mixture of ethers, but not from any single ether suggested that there may be more than one type of ether in the product. IR data indicated that the product contained arlyoxide ligands. The effective magnetic moment of **2** was also consistent with the presence of Eu^{III}.[20] Elemental analysis was consistent with a 2:1 ratio of Ba/Eu. The structure was determined by X-ray diffraction to be $EuBa_2(OC_6H_4Me\text{-}4)_7(diglyme)_2(DME)$ (**2**), Figure 2.

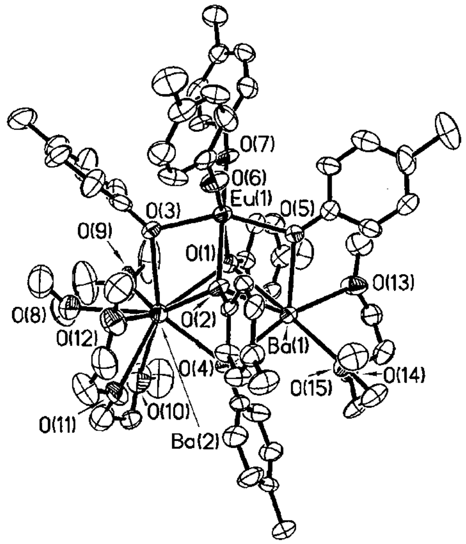

Figure 2. ORTEP diagram of the molecular structure of $EuBa_2(OC_6H_4Me\text{-}4)_7(diglyme)_2(DME)$ **(2)**; thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are omitted for the sake of clarity

Structure of $H_2[Eu_2Ba_6O_2(OiPr)_{16}(THF)_4]$ (1)

Due to the limited quality of the data, only the atomic connectivity in this structure can be described. The metal atoms in **1** do not adopt a conventional eight-coordinate geometry, but rather form the vertices of two square pyramids which share an edge and have their apices on the opposite sides of the basal plane (Figure 3). This geometry is not unique to **1** and has been observed in $H_2[Ba_8O_2(OC_6H_5)_{14}(HMPA)_6]$ (**3**), and $H_2[Ba_2Sr_6O_2(OC_6H_5)_{14}(HMPA)_6]$ (**4**), both of which have the same general formula as **1**, namely $H_2[M_8O_2(ligand)_{20}]$.[22]

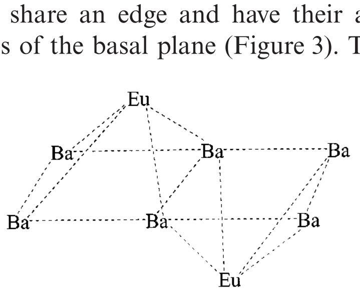

Figure 3. Metal framework in $H_2[Eu_2Ba_6O_2(OiPr)_{16}(THF)_4]$ (**1**)

The two apical positions of the square pyramids in **1** are occupied by europium atoms and the six basal positions are occupied by barium atoms. Complex **4** also has a 3:1 ratio of metals (Sr/Ba) in the same geometry as **1**, but the set of two Ba atoms occupy the shared basal edge positions in **4** instead of the apical positions occupied by the set of two europium atoms in **1**. Both square-pyramidal units in **1** are symmetry-related due to a center of symmetry located between the two europium atoms. The metal···metal distances are given in Table 1.

Table 1. Metal−metal bond lengths [Å] in $H_2[Eu_2Ba_6O_2(OiPr)_{16}(THF)_4]$ (**1**)

Bond	1
Eu(1)···Ba(3)	3.737(1)
Eu(1)···Ba(2)	3.738(1)
Eu(1)···Ba(4A)	3.895(1)
Eu(1)···Ba(4)	3.896(1)
Ba(2)···Ba(3)	3.836(1)
Ba(2)···Ba(4)	3.892(1)
Ba(3)···Ba(4A)	3.886(1)
Ba(4)···Ba(3A)	3.886(1)
Ba(4)···Eu(1A)	3.895(1)

The five metal atoms of each square pyramid are connected by one μ_5-oxygen, four μ_3-O*i*Pr ligands bridging the triangular faces, and three μ-O*i*Pr ligands bridging the unshared basal edges of the square pyramid. In addition, there is one terminal isopropoxide ligand on each of the two europium atoms and there is one THF ligand attached to each of the four unshared basal corners of the square pyramids. This generates a six-coordinate europium atom and six- and eight-coordinate barium atoms. Two THF ligands also co-crystallize with each molecule of **1**, but do not interact with the metal centers. In addition to the components described so far, the presence of two protons is required to balance the charge between the observed cations and anions. Hydrogen atoms were not located in the X-ray study and there are no structural anomalies in **1** that would indicate their exact position, in contrast to the situation in **3** and **4**.[22]

Structure of $EuBa_2(OC_6H_4Me\text{-}4)_7(diglyme)_2(DME)$ (2)

The three metal atoms in **2** occupy a triangular arrangement with 4.1316(14) Å Ba(1)···Ba(2) nonbonding distances and 3.8440(13) and 3.8934(13) Å Eu(1)···Ba nonbonding distances. The metal atoms in **2** are connected by two μ_3-aryloxide ligands above and below the triangular plane and three μ_2-aryloxide ligands, each bridging one edge of the triangle. The europium atom has two additional terminal aryloxide ligands, which lead to a formal coordination number of six. The barium atoms have dissimilar coordination environments: each atom has one tridentate diglyme coordinated to it, but Ba(2) also has a bidentate DME. This gives a formal coordination number of seven for Ba(1) and nine for Ba(2), with respect to the oxygen donor atoms, but further ligation is present, as described below. Bond lengths in **2** are shown in Table 2.

Table 2. Bond lengths [Å] in $EuBa_2(OC_6H_4Me\text{-}4)_7(diglyme)_2(DME)$ (**2**)

Eu(1)−O(1)	2.432(9)	Ba(1)−O(15)	2.815(10)
Eu(1)−O(2)	2.412(9)	Ba(2)−O(1)	2.822(9)
Eu(1)−O(3)	2.299(10)	Ba(2)−O(2)	2.829(9)
Eu(1)−O(5)	2.343(9)	Ba(2)−O(3)	2.751(9)
Eu(1)−O(6)	2.161(10)	Ba(2)−O(4)	2.675(9)
Eu(1)−O(7)	2.193(9)	Ba(2)−O(8)	2.918(11)
Ba(1)−O(1)	2.770(9)	Ba(2)−O(9)	2.909(11)
Ba(1)−O(2)	2.780(9)	Ba(2)−O(10)	2.893(12)
Ba(1)−O(4)	2.630(10)	Ba(2)−O(11)	2.943(11)
Ba(1)−O(5)	2.672(9)	Ba(2)−O(12)	2.815(11)
Ba(1)−O(13)	2.849(10)	Eu(1)···Ba(1)	3.844(1)
Ba(1)−O(14)	2.837(10)	Eu(1)···Ba(2)	3.893(1)

The 2.412(9) and 2.432(9) Å Eu−μ_3-O (OAr) (OAr = OC_6H_4Me-4) distances and the 2.161(10) and 2.193(9) Å Eu−O (terminal OAr) distances in **2** are in the range of those in the trivalent lanthanum 4-methylphenoxide complex $[Me_4N][La_2Na_2(\mu_4\text{-}OAr)(\mu_3\text{-}OAr)_2(\mu\text{-}OAr)_4(OAr)_2(THF)_5]$ [2.284(3) and 2.296(3) Å],[21] considering the differences in Shannon radii,[23] but they are shorter than the corresponding 2.350(5) Å distance in divalent $Eu_2(OC_6H_3Me_2\text{-}2,6)_4(DME)_3$.[6] The 2.299(10) and 2.343(9) Å Eu−μ-O (OAr) distances in **2** are also reasonable compared to those in trivalent $K_3Nd_2(\mu\text{-}OAr)_6(\mu_4\text{-}OAr)_3(THF)_7$ [24] and $\{[La_2Na_2(\mu_4\text{-}OAr)_3(\mu\text{-}OAr)_6(dioxane)_5](dioxane)\}_n$,[17] but they are shorter than the 2.479(3)−2.632(3), 2.447(5)−2.597(5), and 2.444(13)−2.581(12) Å Eu−O (μ-$OC_6H_3Me_2$-2,6) distances in the divalent complexes $Eu_2(OC_6H_3Me_2\text{-}2,6)_4$(*N*-methylimidazole)$_5$,[12] $Eu_2(OC_6H_3Me_2\text{-}2,6)_4(DME)_3$,[6] and $Eu_3(OC_6H_3Me_2\text{-}2,6)_6(THF)_6$,[14] respectively. In general, the differences in Eu−O bond lengths between **2** and divalent europium aryloxides in the literature correspond to the difference in Shannon radii between Eu^{III} and Eu^{II}.[23] This is in agreement with the magnetic data on **2** which indicate that the europium atom is trivalent.

The 2.630(10)−2.751(9) Å Ba−O (μ-OAr) and 2.770(9)−2.829(9) Å Ba−O (μ_3-OAr) distances in **2** are also similar to the corresponding average distances in $HBa_5(O)(OC_6H_5)_9(THF)_8$ [2.65(3) and 2.75(2) Å],[25] **3** [2.65(6) and 2.76(9) Å],[22] and those in $Ba_5(OH)(OC_6H_3Me_2\text{-}3,5)_9(THF)_5$ [26] [2.61(5) and 2.70(3) Å]. The 2.815(11)−2.943(11) Å Ba−O (ether) distances in **2** are in good agreement with the 2.814(6)−2.900(6) Å and 2.826(7)−2.919(8) Å distances in Ba(tetramethylheptanedionate)$_2$(triglyme)[27] and $KBa_2(OSiPh_3)_5(DME)_2$.[28]

In addition to coordination from oxygen atoms, Ba(1) exhibits close contacts with the *ipso*-carbon atoms, C(8) and C(1), from both μ_3-aryloxide ligands, with 3.229(13) and 3.254(14) Å Ba−C (*ipso*-Ar) distances, respectively. These distances are in the range of similar 2.981(6)−3.193(7) Å Ba−C (Ar) contacts in $[Ph_2P(4\text{-}methylbenzylide)_2]_2Ba$.[29] The Ba−O−C (Ar) angles in **2** involving these two ligands also suggest that both phenyl rings are canted towards Ba(1): the angles involving Ba(1) [97.0(7) and 98.7(8)°] are more acute than those involving Ba(2) [127.5(8) and 128.3(8)]. Consideration of these two interactions increases the coordination number of Ba(1) to nine, the same as Ba(2).

Conclusion

Mixed metal complexes of europium and barium can be readily synthesized directly from the metals in 2-propanol at reflux. Varying Eu/Ba stoichiometries have been identified in crystalline systems depending on the crystallization conditions.

Experimental Section

General: All reactions were performed in a glovebox under nitrogen or by using standard Schlenk and vacuum line techniques under nitrogen. Europium and barium ingots 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 equivalent of 2-propanol at 20° C, followed by vacuum transfer of the alcohol from this mixture into the reaction flasks. 4-Methylphenol (Aldrich) was dried and vacuum-distilled from molecular sieves (3 Å). Other solvents were dried and physical measurements were made as previously described.[15] Magnetic moments were measured by the method of Evans[30] with a General Electric QE300 NMR spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ with metal analyses done by atomic absorption spectroscopy.

$H_2[Eu_2Ba_6O_2(O\mathit{i}Pr)_{16}(THF)_4]$ (1): Mixtures of europium (0.166 g, 1.1 mmol) and barium (0.408 g, 3 mmol) ingots, typically 0.5 mm in diameter, were combined in a round-bottom flask equipped with a stir bar and a Schlenk adapter. 2-Propanol (25 mL) was vacuum-transferred into the flask. The mixture was heated at reflux for 4 h and the solvent was removed under vacuum with slight heating to give an orange-brown solid (0.51 g, 50% yield based on Eu). A portion of this material (110 mg) was then dissolved in hot THF and centrifuged. Yellow crystals formed overnight at −31 °C (75 mg, 68%). $C_{64}H_{146}Ba_6Eu_2O_{22}$ (2395.74): calcd. C 32.08, H 6.14, Ba 34.39, Eu 12.69; found C 31.86, H 6.28, Ba 34.25, Eu 12.45. Magnetic susceptibility: $\chi_g^{298K} = 5.4 \times 10^{-6}$, $\mu_{eff}^{298K} = 4.2\ \mu_B$. IR (KBr): $\tilde{\nu}$ = 2948 s, 2858 m, 2770 m, 2670 w, 2581 m, 2353 w, 2104 w, 1933 w, 1731 w, 1457 m, 1368 m, 1348 m, 1239 w, 1150 s, 1040 w, 966 s, 902 w, 812 m, 763 w, 728 w, 510 m cm^{-1}. Space group: *C*2/*c*. Unit cell: a = 27.853(5), b = 24.263(3), c = 17.097(4) Å, β = 108.496(12)°, V = 10958(4) Å^3, Z = 4.

X-ray Data Collection and Solution and Refinement for $H_2[Eu_2Ba_6O_2(O\mathit{i}Pr)_{16}(THF)_4]$ (1): A yellow crystal of approximate dimensions 0.30 × 0.23 × 0.23 mm was mounted on a glass fiber and transferred to the Siemens P4 diffractometer. The determination of symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out according to standard procedures.[31] Intensity data were collected at 163 K using the 2θ/ω scan technique with Mo-K_α radiation. The raw data were processed with a local version of CARESS[32] which employs a modified version of the Lehman−Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. All 7818 data were corrected for absorption and Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the centrosymmetric monoclinic space group *C*2/*c*. All calculations were carried out using the SHELXL program.[33] The analytical scattering factors for neutral atoms were used throughout the analysis.[34] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model. Two molecules of THF were located per octametallic molecule of **1**. Only heteroatoms were refined anisotropically because of unacceptable thermal parameters for several carbon atoms after anisotropic refinement was attempted. Hence, only connectivity could be determined from these data.

$EuBa_2(OC_6H_4Me\text{-}4)_7(diglyme)_2(DME)$ (2): Europium (117 mg, 0.77 mmol) and barium (210 mg, 1.53 mmol) ingots and *p*-cresol (592 mg, 5.47 mmol) were combined in a round-bottom flask equipped with a stir bar and a Schlenk adapter. 2-Propanol (15 mL) was vacuum-transferred into the flask and the mixture was heated at reflux for 24 h. After the solvent was removed under vacuum with slight heating, 30 mL of THF, 5 mL of DME, and 5 mL of diglyme were added to the flask. After heating for 30 min, the entire product was soluble. Reduction of the solution volume to 5 mL by rotary evaporation led, over a period of 12 h, to the formation of crystals of **2** suitable for single-crystal X-ray diffraction (910 mg, 80%). $C_{65}H_{87}Ba_2EuO_{15}$ (1534.99): calcd. C 50.9, H 5.7, Eu 9.9; found C 50.8, H 5.9, Eu 10.4. Magnetic susceptibility: $\chi_g^{298K} = 3.5 \times 10^{-6}$, $\mu_{eff}^{298K} = 3.5\ \mu_B$. IR (KBr): $\tilde{\nu} = 3010$ w, 2916 m, 2860 w, 1604 m, 1557 w, 1501 s, 1454 m, 1318 m, 1266 s, 1201 w, 1167 m, 1097 w, 1065 m, 1013 m, 933 w, 858 m, 824 s, 753 m, 580 w cm^{-1}. Temperature: 163 K. Crystal system: monoclinic. Space group: $P2_1/n$. Unit cell: $a = 12.269(3)$, $b = 24.750(5)$, $c = 23.570(4)$ Å, $\beta = 98.685(10)°$, $V = 7076(2)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.441$ Mg/m^3, $\mu = 2.035$ mm^{-1}.

X-ray Data Collection and Solution and Refinement for 2: A yellow crystal of approximate dimensions 0.20 × 0.10 × 0.10 mm was handled and raw data were processed as described above for **1**. All 9756 data were corrected for absorption and Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$. All calculations were as described for **1** above. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Minor disorder in the diglyme molecules was modeled by assigning partial occupancy to components of the disordered groups. Hydrogen atoms were included using a riding model. At convergence, $wR2 = 0.1705$ and GOF = 1.066 for 748 variables refined against all 9248 unique data [for refinement on *F*, $R1 = 0.0631$ for those 5757 data with $F > 4.0\sigma(F)$].

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-171956 (**1**) and -171957 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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