The utility of *N*-methylimidazole and acetonitrile as solvents for the direct reaction of europium with alcohols including the first example of acetonitrile as a μ-$\eta^1:\eta^1$-bridging ligand

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N-Methylimidazole and acetonitrile are suitable solvents for the direct reactions of europium metal with $2,6\text{-}Me_2C_6H_3OH$ and $2,6\text{-}Pr^i{}_2C_6H_3OH$, which lead to crystallographically characterizable (N-methylimidazole)$_3$Eu(μ-$OC_6H_3Me_2$-2,6)$_3$Eu(N-methylimidazole)$_2$($OC_6H_3Me_2$-2,6) 1 and [(MeCN)$_2$(2,6-$Pr^i{}_2C_6H_3O$)Eu]$_2$(μ-$OC_6H_3Me_2$-2,6)$_2$(μ-NCMe) 2, a complex which contains a μ-η^1-acetonitrile ligand.

Owing to the special fluorescent properties of europium,[1] it is desirable to be able to synthetically manipulate this element in a variety of ways in order to optimize its incorporation into devices of practical utility.[2] Syntheses starting from the metal are best since they avoid the preparation of starting materials, such as chlorides or nitrates, require no drying of these materials, and eliminate the possibility of incorporating some of the starting material ligands into the final product. Europium alkoxide and aryloxide complexes, potentially useful in sol-gel processing,[3] can be made by direct reaction of europium with alcohols and phenols in liquid ammonia,[4–6] by reaction of europium with $Hg(C_6F_5)_2$ in phenols,[7] by reaction of europium with Tl(OAr) in THF,[7] and by reaction of europium with Pr^iOH in the presence of Hg^{II} catalysts,[8] but more convenient are the direct reactions of europium solely with liquid alcohols.[9,10] However, the latter route is not as suitable for solid 2,6-dialkylphenols, which provide good ligands for stabilizing and solubilizing europium ions and for making polyeuropium complexes.[4–6,9] We report here that by using *N*-methylimidazole and acetonitrile as solvents, direct reactions of europium with 2,6-dialkylphenols can be achieved to form fully characterizable europium aryloxide complexes. In addition, we report a new type of bonding mode for acetonitrile.

Europium reacts slowly with $2,6\text{-}Me_2C_6H_3OH$ and $2,6\text{-}Pr^i{}_2C_6H_3OH$ at room temperature in *N*-methylimidazole or acetonitrile to form yellow solutions of paramagnetic divalent europium complexes.† Each $2,6\text{-}R_2C_6H_3OH$ reacts in each solvent, but the R = Me/*N*-methylimidazole and R = Pr^i/MeCN combinations readily provide crystallographically characterizable complexes.‡ (*N*-methylimidazole)$_3$Eu(μ-$OC_6H_3Me_2$-2,6)$_3$Eu(*N*-methylimidazole)$_2$($OC_6H_3Me_2$-2,6) **1** (Fig. 1) and [(MeCN)$_2$(2,6-$Pr^i{}_2C_6H_3O$)Eu]$_2$(μ-$OC_6H_3Me_2$-2,6)$_2$(μ-NCMe) **2** (Fig. 2).

The bimetallic nature of **1** and the arrangement of the anionic ligands are identical to those reported for (DME)$_2$Eu(μ-$OC_6H_3Me_2$-2,6)$_3$Eu($OC_6H_3Me_2$-2,6)(DME) **3** (DME = 1,2-dimethoxyethane), isolated from a Eu/$HOC_6H_3Me_2$-2,6 liquid ammonia reaction.[4] This unsymmetrical arrangement has also been observed in some calcium and barium alkoxide and siloxide complexes.[11] The structures of **1** and **3** differ in that three *N*-methylimidazole ligands in **1** take the place of two bidentate DME ligands in **3** and hence both europium atoms in **1** are six coordinate, whereas **3** contains one six- and one seven-coordinate europium atom.

Each europium atom in **1** is surrounded by a distorted face sharing bioctahedral arrangement of oxygen and nitrogen donor atoms with the shared face consisting of anionic oxygen atoms. The 2.365(3) Å Eu–O(terminal) and 2.479(3)–2.632(3) Å Eu–O(bridging) bond lengths in **1** are in the range of analogous bond lengths in the literature.[4,12]

Complex **2**, like **1**, is also bimetallic and has a face sharing bioctahedral arrangement of ligand donor atoms. However, its structure differs in that each metal atom has the same set of ligands. Although reactions in liquid ammonia and coordinating solvent yielded structurally similar complexes **1** and **3**, complex **2** is substantially different from the product obtained from europium and $HOC_6H_3Pr^i{}_2$-2,6 in liquid ammonia, Eu$_4$(μ-$OC_6H_3Pr^i{}_2$-2,6)$_4$($OC_6H_3Pr^i{}_2$-2,6)$_2$(μ_3-OH)$_2$($NCMe_3$)$_6$ **4**.[5] The 2.286(6) and 2.289(5) Eu–O(terminal), 2.438(6), 2.463(5), 2.487(5) and 2.494(6) Eu–O(bridging), and the 2.625(9)–2.667(9) Å Eu–N(terminal) bond lengths in **2** are not unusual for europium(II) aryloxide complexes.[5,12]

The most remarkable feature in **2** is that it contains a μ-$\eta^1:\eta^1$-acetonitrile ligand, which, to our knowledge, is the first observation of this binding mode for acetonitrile. The 2.847(8) and 2.913(9) Å Eu–N bond lengths of the bridging acetonitrile are longer than the Eu–N(terminal) distances in **2**, as expected.

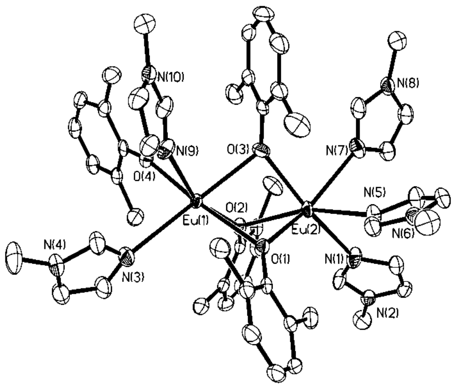

Fig. 1 Plot of Eu$_2$($OC_6H_3Me_2$-2,6)$_4$(*N*-methylimidizole)$_5$ **1** with thermal ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity.

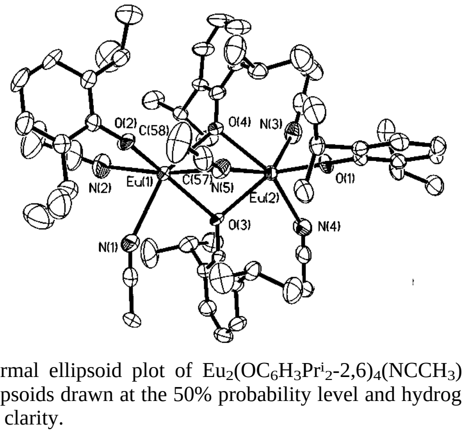

Fig. 2 Thermal ellipsoid plot of Eu$_2$($OC_6H_3Pr^i{}_2$-2,6)$_4$($NCCH_3$)$_5$ **2** with thermal ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity.

The bridging is unsymmetrical with 164.5(8) and 105.0(7)° Eu–N(5)–C(57) angles. This places C(57) closer to Eu(1) than Eu(2), but the 3.391 Å Eu(1)–C(57) distance is too long to constitute a Eu–C bond. Structurally characterized by μ-η^2-acetonitrile ligands have M–C(nitrile) interactions in the range of 1.876(9) to 2.114(7) Å.[13] The Eu(1)–N(5)–Eu(2) angle is 79.9(2)° and the Eu(1)–C(57)–Eu(2) angle is 59.9°. A space filling model of **2** suggests that the μ-$\eta^1:\eta^1$-nature of this ligand and the inequivalence of the Eu–N(5)–C(57) angles arise because there is only a limited space available for the acetonitrile to fit between the bulky 2,6-diisopropylphenoxide ligands.

The results to date on divalent europium aryloxide chemistry suggest that isolable, crystalline complexes more readily form with either a combination of larger 2,6-dialkyl substituents, such as isopropyl groups, and relatively small ligands, such as acetonitrile, or with a combination of smaller 2,6-dialkyl substituents, such as methyl groups, and larger ligands, such as *N*-methylimidazole or 1,2-dimethoxyethane. Variable binding modes are undoubtedly helpful in accommodating crowded ligand environments and the structure of **2** demonstrates another variation in the binding capacity of acetonitrile.

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Notes and references

† Compounds **1** and **2** are obtained by reaction of europium ingots (typically 5–10 mm in diameter) with $HOC_6H_3Me_2$-2,6 in *N*-methylimidazole or $HOC_6H_3Pr^i_2$-2,6 in acetonitrile, respectively, over 2 days at room temperature followed by centrifugation and recrystallization from the supernatant. Single crystals of complex **2** were isolated in 40% yield from the concentrated acetonitrile solution after several days. Single crystals of complex **1** was isolated from the *N*-methylimidazole solution. However, since the yield was low and the high boiling point of *N*-methylimidazole made solvent removal tedious, an alternate procedure was developed. The direct reaction of europium metal with $HOC_6H_3Me_2$-2,6 in a dilute solution of *N*-methylimidazole (0.5 ml) in toluene (7.0 ml), followed by centrifugation and removal of the toluene under vacuum, forms crystalline **1** in 20% yield, based on reacted Eu. Both **1** and **2** give satisfactory elemental analyses and the effective magnetic moments of 7.5 and 8.0 μ_B for **1** and **2**, respectively, are consistent with Eu^{II}.

‡ *Crystal data* for **1**: $C_{52}H_{66}Eu_2N_{10}O_4$, M = 1199, triclinic, space group $P\bar{1}$, a = 12.142(2), b = 12.763(9), c = 18.906(5) Å, α = 71.60(4), β = 73.718(10), γ = 76.48(3)°, V = 2634.3(20) Å, Z = 2, T = 158 K, μ = 2.412 mm^{-1}, Mo-Kα radiation, graphite monochromator. The raw data were processed with a local version of CARESS. All 9678 data points were corrected for Lorentz and polarization effects and were placed on an approximately absolute scale. All calculations were carried out using the SHELXL program. 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. At convergence, $wR2$ = 0.0787 and GOF = 1.036 for 613 variables refined against all 9199 unique data [in comparison, for refinement on F, $R1$ = 0.0282 for those 7984 data with $F > 4.0\sigma(F)$]. For **2**: $C_{58}H_{83}Eu_2N_5O_4$, M = 1218, monoclinic, space group Pn, a = 11.8317(12), b = 21.6202(16), c = 12.9773(13) Å, β = 112.917(7)°, V = 3057.6(5) Å, Z = 2, T = 158 K, μ = 2.077 mm^{-1}, Mo-Kα radiation, graphite monochromator. All 7348 data were collected using a Siemens P4 diffractometer, and handled as described for **1**. All calculations were carried out as described for **1** above and hydrogen atoms were included using a riding model. At convergence, $wR2$ = 0.1141 and GOF = 0.766 for 627 variables refined against all 7348 unique data [in comparison, for refinement on F, $R1$ = 0.0382 for those 6939 data with $F > 4.0\sigma(F)$]. CCDC 182/1031.

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