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Substituent effects in the formation of aryloxide-bridged europium complexes†

William J. Evans,* Michael A. Greci and Joseph W. Ziller

Department of Chemistry, University of California, Irvine, CA 92697-2025, USA

The reactivity of europium in liquid ammonia with 2,6-disubstituted phenols has been surveyed and the effect of the 2,6 substituents on the bridging ability of the aryloxides has been examined. Monomeric and tetrameric complexes of Eu^{II} have been isolated with *tert*-butyl and isopropyl substituents, $Eu(OC_6H_3Bu^t{}_2\text{-}2,6)_2(NCMe)_4$ **1** and $Eu_4(\mu\text{-}OC_6H_3Pr^i{}_2\text{-}2,6)_4(OC_6H_3Pr^i{}_2\text{-}2,6)_2(\mu_3\text{-}OH)_2(NCMe)_6$ **2**, respectively, which can be compared to the previously reported bimetallic complex, $(dme)_2Eu(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_3Eu(OC_6H_3Me_2\text{-}2,6)(dme)$ **3**, isolated with methyl substituents (dme = 1,2-dimethoxyethane). Acetonitrile has been found to be an excellent solvating ligand for the formation of crystalline complexes in this series. Complex **1** crystallizes from acetonitrile in the monoclinic space group $P2_1/c$ with $a = 11.7117(14)$, $b = 17.616(2)$, $c = 18.263(2)$ Å, $\beta = 91.318(8)°$, $U = 3766.8(7)$ Å^3 and $D_c = 1.282$ Mg m^{-3} for $Z = 4$. Complex **2** crystallizes from acetonitrile in the monoclinic space group $P2_1/n$ with $a = 13.676(3)$, $b = 20.325(4)$, $c = 32.632(6)$ Å, $\beta = 91.068(12)°$, $U = 9069(3)$ Å^3 and $D_c = 1.429$ Mg m^{-3} for $Z = 4$.

As a result of its special fluorescent properties, europium is a desirable component in several types of solid-state materials with important practical applications ranging from television picture tubes to light bulb filaments.[1] The europium-containing materials are typically made by mixing a small amount of a europium salt with a less expensive matrix and processing the mixture to the final product. An alternative route to solid-state materials which is potentially more efficient and offers the possibility of more homogeneous products involves the use of molecular precursors containing the component metals.[2]

Studies of lanthanide aryloxide chemistry have shown that aryloxides are good ligands for stabilizing and solubilizing lanthanide metal ions[3] and for making polymetallic lanthanides.[4] Among the attractive features of these ligands is the fact that steric bulk can be manipulated through the substituents without large changes in the electronic features of the metal/donor atom chemistry. In this report, we examine the effect of varying alkyl substituents at the 2 and 6 positions on the bridging ability of the aryloxide ligands in europium(II) complexes. Two new structures with *tert*-butyl and isopropyl substituents are reported and these results are compared with the earlier studies of the $OC_6H_3Me_2$-2,6 and the OC_6H_4Me-4 ligands.[4a] We also describe the utility of the Eu–NH_3(l) system for synthesis and the superiority of acetonitrile over common ether solvents (tetrahydrofuran, 1,2-dimethoxyethane, diglyme, *etc.*) in obtaining crystalline products.

Experimental

All compounds described below were handled under nitrogen using standard Schlenk, vacuum line and glove box techniques. 2,6-Di-*tert*-butylphenol (Aldrich) was thrice sublimed before use. 2,6-Diisopropylphenol (Aldrich) was dried and vacuum distilled from 3Å molecular sieves. Pieces of europium ingot (Rhone-Poulenc) were filed to a bright finish in the glovebox before use. Anhydrous liquid ammonia (99.9%, Matheson) was used as received. Other solvents were dried and physical measurements were made as previously described.[5] Magnetic moments were measured by the method of Evans[6] on a GE GN500 or QE300 NMR spectrometer; C, H and N analyses were performed on a Carlo Erba EA 108 instrument and Eu analysis was performed by complexometric titration with H_4EDTA (ethylenedinitrilotetraacetic acid) and a xylenol orange indicator.[7]

$Eu(OC_6H_3Bu^t{}_2\text{-}2,6)_2(NCMe)_4$ 1

A europium ingot (0.193 g, 1.27 mmol) and 2,6-di-*tert*-butylphenol (0.527 g, 2.55 mmol) were combined in a Schlenk flask containing a magnetic stir bar under nitrogen. Liquid ammonia was condensed into the flask at −41 °C using a dry ice–acetonitrile bath and condenser and the solution was stirred. The characteristic blue color of metal ammonia solutions was observed.[8] After approximately 6 cm^3 of liquid ammonia were collected, the reaction vessel was removed from the cold bath and the ammonia was evaporated yielding a canary yellow powder. The vessel was put under dynamic vacuum for 5 min and brought into the glovebox. Unreacted 2,6-di-*tert*-butylphenol (66 mg, 0.3 mmol) was obtained from a hexane extraction. Three extractions of the remaining yellow solid with 4, 2 and 1 cm^3 of MeCN, respectively, followed by centrifugation and rotary evaporation of the MeCN led to complex **1** (0.858 mg, 93% on the basis of Eu) as a yellow powder. X-Ray quality crystals were grown from a solution of **1** in MeCN over 7 d at ambient temperature in the glovebox. Magnetic susceptibility: $\chi_G{}^{298K} = 3.5 \times 10^{-5}$, $\mu_{eff}{}^{298K} = 7.8\ \mu_B$. IR (KBr): 3054w, 2952s, 2922m, 2871m, 2366w, 2300w, 2264m, 1580m, 1481 (sh), 1455m, 1426s, 1407s, 1378m, 1364w, 1348w, 1314w, 1294 (sh), 1280m, 1260s, 1230m, 1198m, 1145w, 1120 (sh), 1100m, 1021w, 932w, 920w, 881w, 860m, 815m, 806m, 794m, 761w, 747s, 637w, 587w, 569w, 554w, 531m cm^{-1}. UV/VIS (MeCN) 350w, 300w nm (Found: C, 57.04; H, 7.00; Eu, 20.45; N, 6.58. Calc. for $C_{36}H_{54}EuN_4O_2$: C, 59.49; H, 7.49; Eu, 20.91; N, 7.71%).

X-Ray data collection and solution and refinement for $Eu(OC_6H_3Bu^t{}_2\text{-}2,6)_2(NCMe)_4$ 1

A yellow crystal of approximate dimensions 0.33 × 0.20 × 0.10 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.[9] Intensity data were collected at 158 K using a 2θ–ω scan technique with Mo-Kα radiation. The raw data were processed with a local version of CARESS[10] which employs a modified version of the Lehman–Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles.

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† *Non-SI unit employed*: $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

All 2101 data were corrected for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was 2/m with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/c$ (C^5_{2h}; no. 14) is therefore uniquely defined.

All calculations were carried out using the SHELXTL program.[11] The analytical scattering factors for neutral atoms were used throughout the analysis.[12] 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, $wR2 = 0.1131$ and $S = 1.115$ for 179 variables refined against all 1819 unique data [as a comparison, for refinement on F, $R1 = 0.0428$ for those 1443 data with $F > 4.0\sigma(F)$] (see Table 1).

$Eu_4(\mu\text{-}OC_6H_3Pr^i_2\text{-}2,6)_4(OC_6H_3Pr^i_2\text{-}2,6)_2(\mu_3\text{-}OH)_2(NCMe)_6$ **2**

A europium ingot (0.740 g, 4.86 mmol) and 2,6-diisopropylphenol (1.74 g, 9.76 mmol) were combined as described for **1** above. The characteristic blue color of metal ammonia solutions was observed initially, but a yellow solid precipitated out within 3 min of the condensation of ammonia. After approximately 10 cm^3 of liquid ammonia were collected, the reaction vessel was removed from the cold bath and the ammonia evaporated, yielding a yellow powder. The flask was put under dynamic vacuum for 5 min and the color of the powder changed to orange. The flask was then transferred to the glovebox and the orange powder was extracted with hexanes to separate the unreacted $HOC_6H_3Pr^i_2$-2,6 (45 mg, 0.25 mmol). The solids were dried and extracted with 6, 4 and 2 cm^3 portions of hot MeCN and centrifuged to give an orange solution. Rotary evaporation yielded **2** as an orange powder (0.532 g, 92% based on Eu). X-Ray quality crystals were grown from a solution of **2** in MeCN over 2 d at ambient temperature in the glovebox. Magnetic susceptibility: $\chi_G^{298K} = 4.6 \times 10^{-5}$, $\mu_{eff}^{298K} = 7.4\ \mu_B$. IR (KBr): 3217w, 3182w, 3055m, 3013m, 2961s, 2863s, 2563w, 1585s, 1460 (sh), 1427s, 1345m, 1258m, 1200m, 1107m, 1041m, 932w, 885m, 853m, 839m, 746s, 681s, 533m cm^{-1}. UV/VIS (MeCN) 344 nm (Found: C, 51.55; H, 6.22; Eu, 29.00; N, 3.41. Calc. for $C_{84}H_{122}Eu_4N_6O_8$: C, 51.69; H, 6.30; Eu, 31.14; N, 4.31%).

X-Ray data collection and solution and refinement for $Eu_4(\mu\text{-}OC_6H_3Pr^i_2\text{-}2,6)_4(OC_6H_3Pr^i_2\text{-}2,6)_2(\mu_3\text{-}OH)_2(NCMe)_6$ 2

An orange crystal of approximate dimensions 0.26 × 0.17 × 0.16 mm was handled as described above for **1**. All 14 496 data were corrected for absorption and Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was 2/m with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$, a non-standard setting of $P2_1/c$ [C^5_{2h}; no. 14], is therefore uniquely defined.

All calculations were carried out as described for **1** above and hydrogen atoms were included using a riding model. At convergence, $wR2 = 0.1353$ and $S = 1.060$ for 926 variables refined against all 13 379 unique data [as comparison, for refinement on F, $R1 = 0.0472$ for those 9689 data with $F > 4.0\sigma(F)$] (see Table 1).

CCDC reference number 186/619.

Results

Europium reacts in liquid ammonia with 2,6-di-*tert*-butylphenol and 2,6-diisopropylphenol to form ether soluble yellow and orange products, **1** and **2**, respectively, which were not readily identified by common spectroscopic methods. The ^{1}H NMR spectra of **1** and **2** contained broad peaks in the aromatic region, indicating the presence of either co-ordinated phenols or aryloxides in the products. The broadness of the peaks was due to the high magnetic moments of Eu in these compounds, 7.8 and 7.4 μ_B, respectively. These values are consistent with the presence of divalent europium.[4,13] The IR spectra were also consistent with the presence of aryloxide ligands.

Table 1 Experimental data for the X-ray diffraction studies of $Eu(OC_6H_3Bu^t_2\text{-}2,6)_2(NCMe)_4$ **1** and $Eu_4(\mu\text{-}OC_6H_3Pr^i_2\text{-}2,6)_4(OC_6H_3Pr^i_2\text{-}2,6)_2(\mu_3\text{-}OH)_2(NCMe)_6$ **2**

	1	**2**
Formula	$C_{36}H_{54}EuN_4O_2$	$C_{84}H_{122}Eu_4N_6O_8$
M	726.79	1951.72
T/K	158	158
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	11.7117(14)	13.676(3)
b/Å	17.616(2)	20.325(4)
c/Å	18.263(2)	32.632(6)
β/°	91.318(8)	91.068(12)
U/Å^3	3666.8(7)	9068.8(33)
Z	4	4
D_c/Mg m^{-3}	1.282	1.429
Diffractometer	Siemens P4	Siemens P4
Data collected	$+h, +k, \pm l$	$+h, +k, \pm l$
Scan type	2θ–ω	2θ–ω
Scan range/°	1.2–plus Kα-separation	1.2–plus Kα-separation
Scan speed/° min^{-1} (in ω)	3.0	3.0
2θ Range/°	4.0 to 45.0	4.0 to 47.0
μ(Mo-Kα)/mm^{-1}	1.698	2.780
Reflections	2101	14 496
Collected reflections with [$F > 4\sigma(F)$]	1443	9689
No. of variables	179	926
$R1$, $wR2$	0.0428, 0.1131	0.0472, 0.1353
Goodness of fit	1.115	1.060

Details in common: radiation Mo-Kα (λ = 0.710730 Å); monochromator highly oriented graphite; absorption correction semiempirical (ψ-scan method).

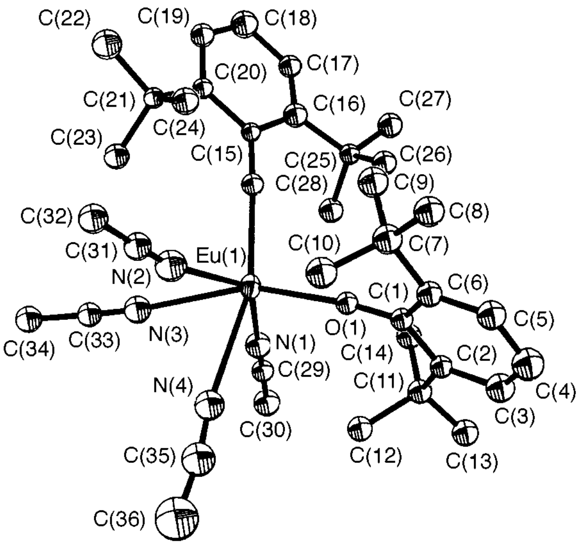

Fig. 1 Thermal ellipsoid plot of $Eu(OC_6H_3Bu^t_2\text{-}2,6)_2(NCMe)_4$ **1**, drawn at the 50% probability level

Since the spectroscopic data were not structurally definitive, it was necessary to characterize these products by X-ray crystallography. Acetonitrile was found to be a good solvent for obtaining crystalline solids in the 2,6-diisopropylphenol and 2,6-di-*tert*-butylphenol cases and these products are reported as the acetonitrile adducts.

Crystallization of the Eu–2,6-di-*tert*-butylphenol–NH_3 reaction product in the presence of MeCN forms $Eu(OC_6H_3Bu^t_2\text{-}2,6)_2(NCMe)_4$ **1** Fig. 1, in >90% yield. Complex **1** is a monometallic complex that has a distorted octahedral co-ordination

Table 2 Selected bond distances (Å) and angles (°) for $\mathrm{Eu(OC_6H_3Bu^t_2\text{-}2,6)_2(NCMe)_4}$ **1** and $\mathrm{Eu_4(\mu\text{-}OC_6H_3Pr^i_2\text{-}2,6)_4(OC_6H_3Pr^i_2\text{-}2,6)_2(\mu_3\text{-}OH)_2(NCMe)_6}$ **2**

1		**2**	
Eu(1)–O(1)	2.313(12)	Eu–O (terminal)	2.284(6)–2.299(6)
Eu(1)–O(2)	2.35(2)		
Eu(1)–N(1)	2.748(9)	Eu–(μ-O)	2.403(6)–2.543(6)
Eu(1)–N(2)	2.665(10)		
Eu(1)–N(3)	2.760(11)	Eu–(μ_3-O)	2.473(6)–2.521(5)
Eu(1)–N(4)	2.80(2)		
		Eu–N	2.662(10)–2.751(9)
O(1)–Eu(1)–O(2)	105.2(4)		
Eu(1)–O(1)–C(1)	173.6(12)		
Eu(1)–O(2)–C(15)	174.5(11)	Eu(1)–N(1)–C(1)	174.0(9)
Eu(1)–N(1)–C(29)	175(2)	Eu(1)–N(2)–C(3)	150.5(9)
Eu(1)–N(2)–C(31)	170(2)	Eu(2)–N(3)–C(5)	165.9(12)
Eu(1)–N(3)–C(33)	171.7(9)	Eu(3)–N(4)–C(7)	178.7(9)
Eu(1)–N(4)–C(35)	169(2)	Eu(3)–N(5)–C(9)	149.9(10)
		Eu(4)–N(6)–C(11)	138.4(8)
		Eu(1)–O(3)–C(13)	139.1(5)
		Eu(2)–O(3)–C(13)	116.3(5)
		Eu(2)–O(4)–C(25)	139.7(5)
		Eu(3)–O(4)–C(25)	121.8(5)
		Eu(3)–O(5)–C(37)	158.1(6)
		Eu(4)–O(5)–C(37)	97.0(5)
		Eu(4)–O(6)–C(49)	129.4(5)
		Eu(1)–O(6)–C(49)	129.3(5)

environment with the 2,6-di-*tert*-butylphenoxide ligands in the *cis* positions. To our knowledge, this is the first crystallographically characterized example of a monomeric six-co-ordinate lanthanide(II) aryloxide: four- and five-co-ordinate structures are much more common. The 105.2(4)° O–Eu–O angle in **1** is the smallest angle for any divalent lanthanide 2,6-di-*tert*-butylphenoxide complex: $\mathrm{Eu(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3}$ (thf = tetrahydrofuran), 150.3(2)°;[3a] $\mathrm{Sm(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3}$, 151.1(4)°;[3b] $\mathrm{Yb(OC_6H_2Bu^t_2\text{-}2,4\text{-}Me\text{-}6)_2L_2}$ (L = hexamethylphosphoramide), 110.3(3)°;[3c] $\mathrm{Yb(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_2}$, 118.7(3)°;[3d] $\mathrm{Yb(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(OEt_2)_2}$, 119.8(3)°;[3d] $\mathrm{Yb(OC_6H_2Bu^t_3\text{-}2,4,6)_2(thf)_3}$, 149.0(6)°;[3e] $\mathrm{Yb(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3}$, 154.8(10)°.[3d] A *cis* arrangement of the 2,6-di-*tert*-butylphenoxide ligands with a smaller O–Ln–O angle has previously been observed in the trivalent complex $\mathrm{Ce(OC_6H_3Bu^t_2\text{-}2,6)_3(CNCMe_3)_2}$,[14] which has a trigonal-bipyramidal geometry with one axial and two equatorial phenoxide ligands and 108.9°(2) and 98.4°(3) *cis* ligand O–Ce–O angles.

The 2.313(12) and 2.35(2) Å Eu–O bond lengths in **1** (see Table 2) lie within the range of other $\mathrm{Eu^{II}}$ terminal aryloxide bond lengths in the literature: 2.350(5) Å for $\mathrm{(dme)_2Eu(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_3Eu(OC_6H_3Me_2\text{-}2,6)(dme)}$ (dme = 1,2-dimethoxyethane) **3**;[4a] 2.321(5) and 2.337(5) Å for $\mathrm{Eu(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3}$.[3a] The 2.665(10)–2.80(2) Å Eu–N distances in **1** are generally shorter than those of other $\mathrm{Ln}_m\mathrm{(OR)}_{3m}\mathrm{(NCMe)}_n$ complexes ($m = 1$ or 2, $n = 1$ or 2) when corrections for the difference in ionic radii[15] are considered. In the following examples, the numbers in brackets are extrapolated Ln–N (MeCN) distances obtained by adding the differences between six-co-ordinate $\mathrm{Ln^{III}}$ and six-co-ordinate $\mathrm{Eu^{II}}$ ionic radii to the observed $\mathrm{Ln^{III}}$–N (MeCN) average distances. These bracketed distances may be compared directly to the Eu–N (MeCN) distances in **1**: $\mathrm{Dy[OCH(CMe_3)_2]_3(NCMe)_2}$, 2.536(7)[16a] [2.794(7)] Å; $\mathrm{Nd_2[OCH(CMe_3)_2]_6(NCMe)}$, 2.706(5)[16a] [2.893(5)] Å; $\mathrm{Nd[OC(CMe_3)_3]_3(NCMe)_2}$ 2.634(7)[16b] [2.821(7)] Å. The shorter distances in **1** may be due to less steric crowding at the metal center, which is consistent with the 105.2(4)° O–Ln–O angle in **1** as compared to those in the $\mathrm{Ln}_m\mathrm{(OR)}_{3m}\mathrm{(NCMe)}_n$ complexes [116.9(2)–123.8(2)°]. The Ln–N distances in **1** are slightly longer than those in polymeric $\mathrm{[SmI_2(NCCMe_3)_2]}_n$, 2.596(8).[17]

Crystallization of the Eu–2,6-diisopropylphenol–$\mathrm{NH_3}$(l) reaction product in the presence of MeCN formed $\mathrm{Eu_4(\mu\text{-}OC_6H_3Pr^i_2,\text{-}2,6)_4(OC_6H_3Pr^i_2\text{-}2,6)_2(\mu_3\text{-}OH)_2(NCMe)_6}$ **2**, Figs. 2 and 3, in >90% yield. In this case, the complex contains not only 2,6-diisopropylphenoxide and acetonitrile ligands, but also two hydroxide ligands. The structure has similarities to that of the previously reported complex $\mathrm{Nd_4(\mu_3\text{-}OH)_2(acac)_6(acac)_4}$ (acac = acetylacetonate).[18] As in that paper, the origin of the hydroxide is not certain. In the past, hydrolysis was usually suspected when oxide and hydroxide ligands were found in lanthanide products of reactions involving alkoxide, aryloxide and related ligands,[19] although, in some cases the isolation of ether by-products suggests that the alkoxide ligands are providing the oxide atoms.[18,20] It is worth noting that **2** can be reproducibly obtained in good yields using the same source of ammonia and the same experimental procedures as reactions leading to **1** and **3**.[4] If systematic sources of water were present in the experiment, **1** might be expected to form a hydroxide complex, similar to the hydrolysis side product $\mathrm{[Yb(OC_6H_2Bu^t_3\text{-}2,4,6)_2(\mu\text{-}OH)(thf)]_2}$ reported by Deacon *et al.*[19b]

A difference between the reactions leading to **1**–**3** is that only in the case of **2** does the color change from yellow to orange when the reaction vessel is evacuated to remove ammonia. Although all the products are yellow immediately following evaporation of the ammonia, only **1** and **3** remain yellow after the reaction flask is evacuated. The color change is possibly occurring with loss of co-ordinated $\mathrm{NH_3}$ under vacuum. Loss of solvent from the europium centers would lead to steric

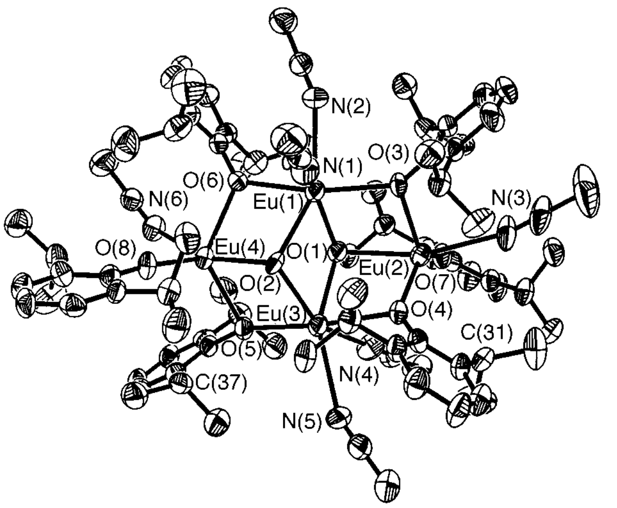

Fig. 2 Thermal ellipsoid plot of $\mathrm{Eu_4(\mu\text{-}OC_6H_3Pr^i_2\text{-}2,6)_4(OC_6H_3Pr^i_2\text{-}2,6)_2(\mu_3\text{-}OH)_2(NCMe)_6}$ **2**, drawn at the 50% probability level

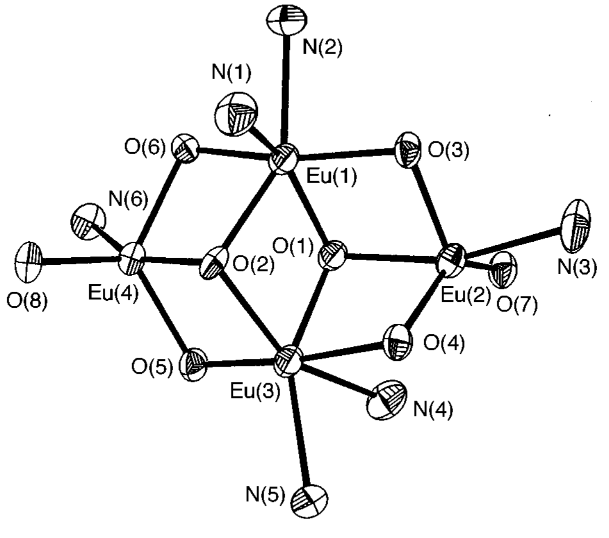

Fig. 3 Thermal ellipsoid plot of $\mathrm{Eu_4(\mu\text{-}OC_6H_3Pr^i_2\text{-}2,6)_4(OC_6H_3Pr^i_2\text{-}2,6)_2(\mu_3\text{-}OH)_2(NCMe)_6}$ **2**, drawn at the 50% probability level with hydrogen and carbon atoms omitted for clarity

unsaturation and further reactions leading to the hydroxide ligands.

The four metal centers in **2** do not adopt the most compact arrangement, namely a tetrahedral geometry, but instead have a butterfly orientation, in which the Eu(1)–Eu(3) vector is the backbone and there is a 22° angle between the Eu(1)–Eu(2)–Eu(3) and the Eu(1)–Eu(3)–Eu(4) planes. The Eu(1)–Eu(3) 3.9372(9) Å separation is the longest Eu–Eu distance in the butterfly structure of **2**. The edge Eu–Eu distances are 3.7631(9)–3.8715(9) Å.

The triply bridging hydroxide ligands lie on opposite sides of the Eu(1)–Eu(2)–Eu(3) and the Eu(1)–Eu(3)–Eu(4) planes. Atom O(1) is 1.138 Å above the first plane and O(2) is 1.110 Å off the latter plane. The Eu–O (μ_3-OH) distances in **2** are 2.473(6)–2.521(5) Å. These can be compared to the 2.363(7)–2.412(7) Å distances in $Gd_4(\mu_3\text{-}OH)_4(\mu_2\text{-}H_2O)_2(hfpd)_8\cdot H_2O$ (hfpd = 1,1,1,3,3,3-hexafluoropentane-2,4-dionate),[21] which has a tetrahedral geometry with face-capping hydroxides, the 2.207–2.413 Å distances in $Er_8(\mu_3\text{-}OH)_{12}(\mu_4\text{-}O)(thd)_8$ (thd = 2,2,6,6-tetramethylheptane-3,5-dionate),[22] which has a fairly regular dodecahedral geometry with a central μ_4-oxide anion and face-capping hydroxides, and the 2.428(6) and 2.459(5) Å distances in the structurally related $Nd_4(\mu_3\text{-}OH)_2(acac)_6(acac)_4$.[18] When differences in ionic radii[15] between Eu^{II} and Ln^{III} are added to the Ln^{III}–OH bond distances in these systems so that direct comparisons with the Eu–OH distances can be made, the Eu–OH distances are (*a*) in the range of the corrected Gd–OH distances of 2.426(7)–2.475(7) Å and the corrected Er–OH distances of 2.373–2.603 Å and (*b*) almost identical to the corrected Nd–OH distances of 2.489(6) and 2.520(5) Å.

The 2.403(6)–2.543(6) Å range of Eu–μ-O (OR) distances in **2** overlaps with that of **3**, 2.447(5)–2.597(5) Å. The aryloxide ligands involving O(3) and O(6) bridge symmetrically with sets of Eu–μ-O (OR) distances of 2.447(5) and 2.449(6) Å for O(3) and 2.474(6) and 2.482(6) Å for O(6). The ligands with O(4) and O(5) as donor atoms are asymmetrically arranged with sets of Eu–μ-O (OR) distances of 2.466(6) and 2.543(6) Å for O(4) and 2.403(6) and 2.512(6) Å for O(5). The C(37)–O(5)–Eu(3/4) angles are also unsymmetrical: they differ by 61.1°. In contrast, the other doubly bridging aryloxides in **2** have C(R)–(μ-O)–Eu angles that differ by 0.1–22.8° and the doubly bridging aryloxides in **3** have C(R)–(μ-O)–Eu(1/2) angles that differ by 16.1–27.1°. The 61.1° value in **2** reflects the high degree to which the phenyl ring containing C(37) is tilted towards Eu(4), as described below.

Associated with the asymmetry in **2** are some long-range interactions involving Eu(2) and Eu(4) with *ipso* carbons and hydrogen atoms. Atoms Eu(2) and Eu(4) are formally five-co-ordinate, while Eu(1) and Eu(3) are formally six-co-ordinate. The C(37)–Eu(4) distance of 2.987(9) Å is comparable to the Ln–C (OR) distances reported for the $[Ln(OC_6H_3\text{-}2,6\text{-}Pr^i{}_2)_3]_2$ dimers which have η^6-R–Ln interactions [Ln = Sm, 2.824(7)–3.160(8) Å, average = 3.015 Å; Ln = Nd, 2.898(12)–3.183(10) Å, average = 3.035 Å],[4e] and the 2.982(9) Å *ipso* C–Ce distance in $[Ce(OSiPh_3)_2(\mu\text{-}OSiPh_3)]_2$.[23] When the differences between the ionic radii of divalent europium and those of Sm or Nd[15] are added to the above Ln–C (R) distances for direct comparison to the distances in **2**, the corrected average Sm– and Nd–C (R) distances are 3.228 and 3.222 Å, respectively, *i.e.* the C(37)–Eu(4) distance in **2** is much shorter.

The *ipso* interaction in **2** also causes one of the co-ordinated acetonitriles to have an unusually small Eu(4)–N(6)–C(11) angle of 138.4(8)°. The other Eu–N–C angles in **2** are in the range of 149.9(10)–178.7(9)°. This orientation of the Eu(4)–N(6)–C(11) angle moves it away from one of the phenyl rings involved in an *ipso* interaction. In general, the Eu–N–C angles in **2** exhibit a greater range than those reported for the alkoxides $Dy[OCH(OCMe_3)_2]_3(NCMe)_2$, $Nd[OC(CH_3)_3]_3(NCMe)_2$ and $Nd_2[OCH(OCMe_3)_2]_6(NCMe)$ [154.9(5)–171.5(6)°][16a,b] and $SmI_2(NCCMe_3)_2$ [151.3(6)°],[17] attesting to the diverse structural features in **2**. The Eu–N distances in **2** are in the range of those mentioned for **1** and are normal.

The closest carbon atom to Eu(2) is C(31) located at a distance of 3.667 Å. Although this is well within the sum of the 1.995 Å metallic radius of Eu[24] and the 2.00 Å van der Waals radius of a methyl group,[25] it is longer than the Eu(4)–C(37) distance and is beyond the range of agostic Eu–C distances in $[N(SiMe_3)_2]Eu[\mu\text{-}N(SiMe_3)_2]_2Na$ (2.97–3.44 Å).[26] However, an agostic interaction between the hydrogen on C(31) and Eu(2) could exist.

Discussion

The reaction of europium in liquid ammonia with 2,6-disubstituted phenols provides a convenient route to europium aryloxide complexes. With 2,6-dimethylphenol, 2,6-diisopropylphenol and 2,6-di-*tert*-butylphenol, orange to yellow ether soluble products are formed which in each case are divalent. This is an asset in constructing more complex europium-containing compounds, since it provides a basis for subsequent reaction chemistry.

Structural data are now available on four different 2,6-disubstituted Eu^{II} aryloxides. With 2,6-di-*tert*-butylphenol, monomeric $Eu(OC_6H_3Bu^t{}_2\text{-}2,6)_2(NCMe)_4$ **1** was obtained. This is consistent with most other lanthanide(II) 2,6-di-*tert*-butylphenoxide complexes that have been crystallographically characterized.[3a–d] In all of these cases where co-ordinating solvents are used, monomers are isolated. However, in the absence of co-ordinating solvent, the bridged bimetallic complex $[Yb(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)(\mu\text{-}OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)]_2$ is isolated.[4d]

The product of the 2,6-diisopropylphenol reaction, $Eu_4(\mu\text{-}OC_6H_3Pr^i{}_2\text{-}2,6)_4(OC_6H_3Pr^i{}_2\text{-}2,6)_2(\mu_3\text{-}OH)_2(NCMe)_6$ **2**, on the other hand, is a tetrametallic species which shows that with the isopropyl substituents, bridging is possible in co-ordinating solvents. Bridging by the 2,6-diisopropylphenoxide ligand is facilitated by the fact that the isopropyl groups can adopt an orientation such that the methyl groups are positioned away from the metal centers.

When the size of the 2,6 substituents is decreased to methyl, the bridging ability of the phenoxides is so enhanced that there is room for three doubly bridging phenoxides to bridge two Eu^{II} centers, as in bimetallic $(dme)_2Eu(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_3\text{-}Eu(OC_6H_3Me_2\text{-}2,6)(dme)$ **3**. When the 2,6-unsubstituted 4-methylphenol is used, the isolation of a square pyramidal pentametallic cluster with face- and edge-bridging aryloxides shows that three Eu^{II} cations can be bridged by this ligand.[4a]

These data are consistent with the general expectation that bridging will be facilitated by less steric bulk, but they show that there is not necessarily a direct correlation between the size of the 2,6 substituents and the nuclearity to the polymetallic product. Hence, it appears that 2,6-phenoxide substituents smaller than *tert*-butyl are necessary to get bridging in co-ordinating solvents and that high nuclearity europium systems can be obtained with hydrogen in the 2,6 positions. This is normal. However, the next smallest substituent, methyl, did not give such a high nuclearity product, presumably because with 2,6-dimethylphenoxide, three bridging ligands can fit between two europium centers and the aggregation could stop at two metals. In addition, the more bulky 2,6-diisopropyl substituted system generated a tetrametallic product. In this case, the formation of the higher nuclearity product was facilitated by the presence of the small hydroxide bridges, whose formation appears to be specific to the isopropyl system in this series.

Acetonitrile has proven to be an excellent ligand for obtaining single crystals with these complexes. This may be due to the similarity of MeCN to ammonia. Both of these nitrogen-donor atom ligands are softer than ethers and this may favor interaction with the divalent lanthanide systems, which are relatively softer than the trivalent analogs. In addition the acetonitrile ligand is small, like ammonia. The rod-like acetonitrile can easily replace an ammonia in the co-ordination sphere of the metal without significant interference with other donor atoms. This may help to stabilize the initially formed products of the liquid ammonia reactions.

Conclusion

Liquid ammonia syntheses appear to be a general synthetic route to divalent europium aryloxide complexes. The structural data suggest that the ability of 2,6-disubstituted aryloxides to bridge metal centers in these complexes depends on substituent size and solvent and that the polynuclearity of the product can be tuned by the proper choice. In these systems, crystallization seems to be enhanced by the presence of acetonitrile.

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