Direct Syntheses and Structural Novelty of Lanthanoid Aryloxides with Flexible Radial Arms

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Direct treatment of excess lanthanum, europium or ytterbium metal with 2,6-dibenzylphenol (HOdbp) at 150 °C afforded $[La_2(Odbp)_6]$, $[Eu_2(Odbp)_4]$ and $[Yb(Odbp)_2]_n$, respectively, in high yields. Alternatively, treatment of Yb metal with excess HOdbp gave an ytterbium(III) species $[Yb_2(Odbp)_6]$, similar to the lanthanum analogue. X-ray crystal structures were obtained for $[La_2(Odbp)_6]$, $[Eu_2(Odbp)_4]$ and $[Yb_2(Odbp)_6]$. $[La_2(Odbp)_6]$ and $[Yb_2(Odbp)_6]$ are pseudo-centrosymmetric dimers with two terminal and four bridging $Odbp^-$ ligands and $[Eu_2(Odbp)_4]$ crystallizes as a centrosymmetric dimer with further organization in a polymeric form through supramolecular interactions. All three structurally characterized compounds achieve coordination saturation by Ln–π-arene interactions.

Introduction

Lanthanoid aryloxides are accessible by a wide array of synthetic routes and exhibit an enormous structural variety.[1] Use of bulky aryloxides has provided a range of exciting low-coordinate complexes for both Ln^{II} and Ln^{III} oxidation states.[1] Whilst most of these have additional neutral ligands, e.g. $[Ln(OAr)_3(THF)_n]$ (n = 1–3), (where OAr = 2,6-diphenylphenolate,[2] 2,6-diisopropylphenolate,[3] 3,5-dimethyl-2,6-diphenylphenolate,[4a] 3,5-di-*tert*-butyl-2,6-diphenylphenolate[4a] and 3,5-di-*tert*-butylphenolate[4b]), there has been increasing interest in homoleptic complexes, both neutral $[Ln(OAr)_n]$ (n = 2 or 3, where OAr = 2,6-diphenylphenolate[5] and 2,6-di-*tert*-butylphenolates[6]) and anionic $[Ln(OAr)_4]^-$ (where OAr = 2,6-diphenylphenolate[5a,7] 2,6-diisopropylphenolate,[8,9] 2,6-di-*tert*-butyl-4-methylphenolate[10]). Homoleptic complexes of the bulkiest aryloxides (OAr = $OC_6H_2tBu_2$-2,6-X-4, where X = H, Me) are normally coordinatively and sterically saturated with solely oxygen donors. However, less bulky phenolates, e.g. OAr = $OC_6H_3Ph_2$-2,6,[5,7] $OC_6H_3iPr_2$-2,6,[8,9] give rise to additional π-arene–Ln interactions ranging from η^1 to η^6. These can involve either the pendant groups as with $OC_6H_3Ph_2$-2,6[5,7] or the central arene as with $OC_6H_3iPr_2$-2,6.[8,9] Use of more flexible side arms presents opportunities for optimal π-arene–Ln coordination geometry provided that the interaction is strong enough to overcome the capacity of the aryl group to rotate away. We now report novel lanthanoid complexes obtained from the direct reactions of La, Eu or Yb metal with 2,6-dibenzylphenol (HOdbp) and find extensive π-arene–Ln interactions in the solid state. These are the first lanthanoid benzylphenolates to show such interactions, which do not appear to be exhibited by related calixarenes.[11]

Results and Discussion

Direct treatment of excess lanthanum, europium or ytterbium metal with 2,6-dibenzylphenol (HOdbp), in an evacuated Carius tube at 170 °C for 4 d, afforded crystalline material comprising $[Ln(Odbp)_n]_2$ [Ln = La, n = 3 (**1**); Ln = Eu, n = 2 (**2**)] or $[Yb(Odbp)_2]_n$ (**3**) [Equations (1) and (2)]. Initially, several drops of mercury were added to the reaction mixture to form a reactive lanthanoid amalgam. In previous related syntheses,[4,5] this was found to be essential for complete reaction. However, subsequently, it was found that the reactions occurred cleanly and in significant but lower yield without mercury for **1** and **2**, but not for **3** or **4**. In all cases crystals were obtained directly from the reaction tube. Low solubility in non-coordinating solvents (e.g. hexane and toluene) necessitated separation of crystalline products from excess metal by hand-picking under a microscope. In an attempt to improve the method of isolation, experiments were performed in the presence of excess ligand (rather than metal), followed by sublimation or washing out of the residual ligand from the product. In the cases of compounds **1** and **2**, this presented no apparent problems, but

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for Ln = Yb, a $\mathrm{Yb^{III}}$ species, $[\mathrm{Yb_2(Odbp)_6}]$ (**4**), was obtained rather than the $\mathrm{Yb^{II}}$ compound **3**. This is not surprising since previously we have found that excess lanthanoid metal in redox transmetallation reactions,[12] as well as in direct Ln metal/phenol reactions,[5a] aids in formation of the lower oxidation state product. Excess metal acts as a reductant if any $\mathrm{Ln^{III}}$ species is formed for Ln = Yb. The formation of compound **4** rather than **3** contrasts with the chemistry of compound **2**, where the $\mathrm{Eu^{II}}$ species is obtained when either excess metal or ligand is used. The results are consistent with Eu having the most stable divalent state of the lanthanoids.

$$\mathrm{Ln_{(metal)}} + 2n\,\mathrm{HOdbp} \xrightarrow{170^{\circ}\mathrm{C}} [\mathrm{Ln(Odbp)}_n]_2 + n\,\mathrm{H_2}$$

Ln = La, n = 3 (**1**); Ln = Eu, n = 2 (**2**)
Ln = Yb, n = 3 (**4**) (1)

$$\mathrm{Yb_{(metal)}} + 2n\,\mathrm{HOdbp} \xrightarrow{170^{\circ}\mathrm{C}} [\mathrm{Yb(Odbp)_2}]_n + n\,\mathrm{H_2} \quad (2)$$

The infrared spectra of all compounds showed the absence of an OH stretching band at around 3560 $\mathrm{cm^{-1}}$ establishing complete deprotonation of the phenol. Furthermore, in the ^{1}H NMR spectrum ($\mathrm{C_6D_6}$) of compounds **1** and **3**, there was no appreciable resonance at $\delta \approx 4.6$ ppm for the OH protons (however, products consistently showed small amounts of phenol detectable in the IR and NMR spectra perhaps arising from slight decomposition during measurement). Unfortunately, compounds **2** and **4** were too insoluble in $\mathrm{C_6D_6}$ to afford reasonable ^{1}H NMR spectroscopic data. The low solubility of all compounds in the same solvent precluded recording of ^{13}C NMR spectra. The ^{1}H NMR spectra of compounds **1** and **3** had reasonably sharp peaks. The methylene resonances were slightly shifted in both compounds, from $\delta = 4.0$ ppm in the parent phenol, to $\delta = 3.78$ and 3.72 ppm in compounds **1** and **3**, respectively. Compounds **1**–**4** were all analytically pure based on lanthanoid analyses as determined by complexometric titrations. For compounds **1**, **2** and **4**, crystals suitable for X-ray crystal structure determination were obtained directly from the reaction tube, however, for compound **3** no such crystals resulted; nor could crystals be grown from non-coordinating solvents such as toluene or hexane due to insolubility. The aggregation of compound **3** is therefore unknown.

Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with one whole dimer comprising the asymmetric unit. Aside from La–π-arene interactions (see below) each La center is four-coordinate, being bound by two terminal and two bridging phenolate ligands. The $\mathrm{La–O_{(bridging)}}$ distances range from 2.402(4) to 2.565(5) Å, while the $\mathrm{La–O_{(terminal)}}$ distances [range 2.172(6)–2.227(5) Å] are expectedly shorter than the former and comparable with those of mononuclear $[\mathrm{La(OC_6H_3Ph_2\text{-}2,6)_3}]$,[5b] which exhibits solely terminal $\mathrm{OC_6H_3Ph_2\text{-}2,6}$ ligands (though there are additional π-arene–Ln interactions). The La···La distance of 4.031(4) Å rules out any metal–metal interactions, being well in excess of the sum of the ionic radii of two four-coordinate $\mathrm{La^{3+}}$ ions.[13] Compared with monomeric $[\mathrm{La(OC_6H_3Ph_2\text{-}2,6)_3}]$,[5b] the presence of the methylene linker in compound **1** allows for increased steric freedom about the metal center owing to the rotational ability about the Ph–$\mathrm{CH_2}$ bond as well as the ability of the Ph group to swing away from the metal centres about the $\mathrm{CH_2}$ linker. This creates more space about the La centers resulting in dimerisation, and a higher O-donor coordination number.

To compensate for the coordinatively unsaturated four-coordinate La center in compound **1**, the metal atom is also involved in La···π-arene interactions. This mode of interaction has been a common feature of other lanthanoid aryloxide chemistry that we have presented previously,[2,5,7] and the possibility arises due to the synthesis being performed in a donor-solvent-free manner. Thus, each La center interacts with an adjacent aromatic ring of an *O*-bridged ligand in an η^6-fashion through carbon atoms C(28) to C(33) for La(1) and C(8) to C(13) for La(2) (see Figure 1a). Therefore, the four-coordination about La (O only) expands to a formal coordination number of seven. If the centroid of the η^6-attachment is regarded as a coordination site, then the geometry about La is a distorted square pyramid with the arene ring seated at the apex (see Figure 1a). The La···C distances [for La(1) 3.057(8) to 3.277(8), for La(2) 3.043(8) to 3.300(8) Å] are all within the parameters defined for $[\mathrm{La(OC_6H_3Ph_2\text{-}2,6)_3}]$[5b] (>3.5 Å is considered non-bonding for this compound) and similar to those in $[\mathrm{La_2(OC_6H_3\mathit{i}Pr\text{-}2,6)_6}]$[3b] (av. La···C 3.06 Å) where there are η^6-π-arene bridges. Thus, given there is only a small spread in La···C(π-arene) interactions for this compound, and there is no obvious cut-off in La···C distances, the interactions can only be regarded as η^6-binding. The π-arene bridges are from *O*-bridging ligands which thus bind in a μ-η^6:η^1:η^1-manner and contrast the arrangement in $\mathrm{La(OC_6H_3Ph_2\text{-}2,6)_3}$ where an arene arm from one terminal ligand binds in an η^6-fashion whilst a Ph from another binds η^3 to the metal atom.

Compound **4** is structurally similar to compound **1** in that it is also a dimer with Yb–π-arene interactions. Unfortunately, all attempts to determine a high-precision X-ray crystal structure were thwarted by consistent twinning of crystals. However, the low-precision structure leaves no doubt as to the connectivity of the compound, and the structure is similar to that of its La analogue **1**. One pertinent and clear feature of the structure is a reduction in coordination number about the metal center through reduced π-arene connectivity. In compound **3**, Yb(1) is bound in an η^3-manner, while Yb(2) is η^2-bound (Figure 2), lowered from η^6:η^6 in **1**. For Yb(1) there are three $\mathrm{Yb\cdots C_{arene}}$ distances of 2.719(13), 2.997(12) and 3.174(13) Å, while there is a drastic increase (well outside error limits) to the next closest carbon atom on the same aromatic ring [Yb(1)–C(33) 3.610(12) Å], and for Yb(2) there are two $\mathrm{Yb\cdots C_{arene}}$ distances of 2.837(12) and 2.894(12) Å, and the next closest approach is Yb(2)–C(10), 3.358(12) Å, thus defining a cut-off for potential bonding. These "bonding" distances compare well with previously established $\mathrm{Yb^{III}\cdots C}$ bond lengths

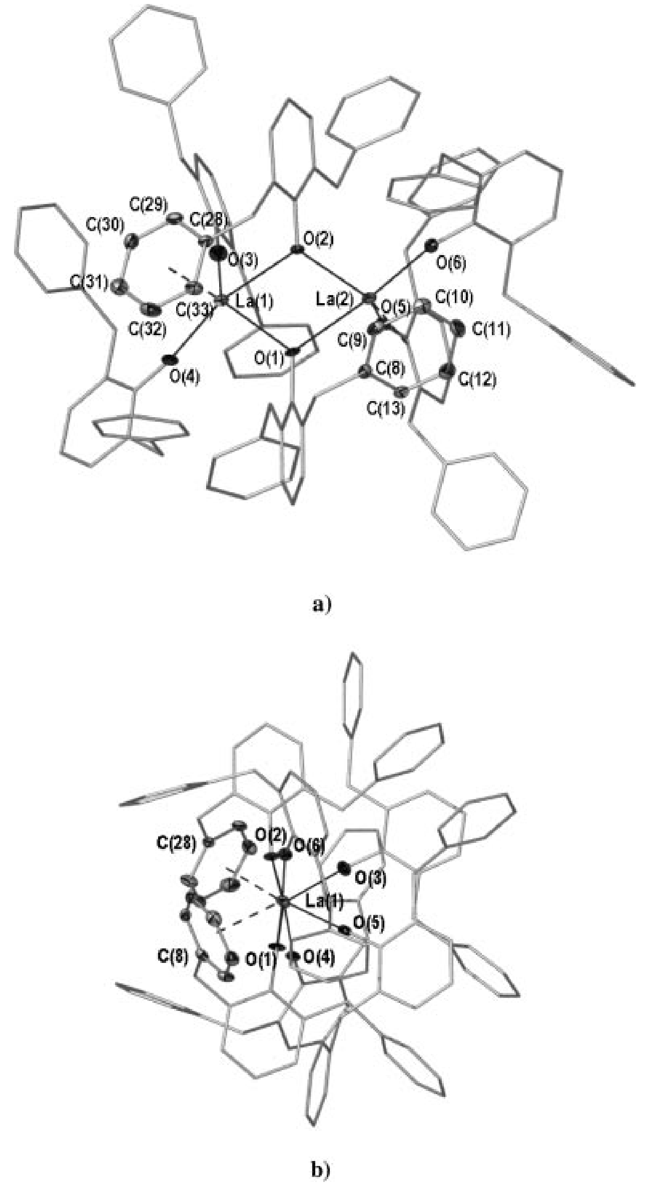

Figure 1. Molecular structure of [{La(μ-Odbp)(Odbp)$_2$}$_2$] (**1**) (40% thermal ellipsoids): all hydrogen atoms omitted for clarity and non-coordinating hydrocarbon groups depicted as wireframes. a) Normal to La$_2$O$_2$ fragment and b) along the La···La vector. Selected bond lengths [Å] and angles [°]: La(1)–O(1) 2.402(4), La(1)–O(2) 2.565(5), La(1)–O(3) 2.172(6), La(1)–O(4) 2.218(5), La(1)···C(28) 3.057(8), La(1)···C(29) 3.058(8), La(1)···C(30) 3.182(8), La(1)···C(31) 3.277(8), La(1)···C(32) 3.258(9), La(1)···C(33) 3.127(9), La(2)–O(1) 2.549(5), La(2)–O(2) 2.417(4), La(2)–O(5) 2.189(6), La(2)–O(6) 2.227(5), La(2)···C(8) 3.043(8), La(2)···C(9) 3.080(8), La(2)···C(10) 3.216(8), La(2)···C(11) 3.300(8), La(2)···C(12) 3.236(7), La(2)···C(13) 3.100(7); O1–La1–O2 69.90(16), O(1)–La(1)–O(3) 114.37(19), O(1)–La(1)–O(4) 95.18(17), O(2)–La(1)–O(3) 84.36(18), O(2)–La(1)–O(4) 165.07(16), O(3)–La(1)–O(4) 103.1(2), O(1)–La(2)–O(2) 69.94(16), O(1)–La(2)–O(5) 87.17(18), O(1)–La(2)–O(6) 174.38(16), O(2)–La(2)–O(5) 120.47(17), O(2)–La(2)–O(6) 104.52(17), O(5)–La(2)–O(6) 96.72(19).

in [Yb(OC$_6$H$_3$Ph$_2$-2,6)$_3$] and are consistent (after allowance for ionic radius differences) with the more extensive data for Yb^{II}···arene interactions.[2,5a,14] A consequence of this binding is that the capping aromatic ring does not sit flatly above the Ln center but is rather much more angled. Thus, in compound **1** the La–centroid–C$_{ipso}$ angles are 85.0° and 84.3° for La(1) and La(2), while in compound **4** the corresponding angles are much more acute, at 72° and 69° for Yb(1) and Yb(2), respectively. The Yb–O(bridging) distances are asymmetric with two short [Yb(1)–O(1) 2.198(7) and Yb(2)–O(1) 2.209(8) Å] and two long [Yb(1)–O(2) 2.317(8) and Yb(2)–O(1) 2.378(7) Å] interactions, as is observed in compound **1**. In each case, the longer Ln–O bond is *cisoid* to a bonding phenyl group.

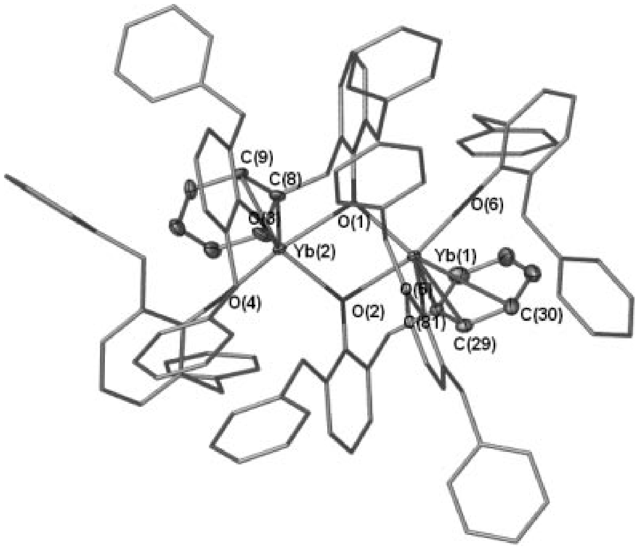

Figure 2. Molecular structure of [{Yb(μ-Odbp)(Odbp)$_2$}$_2$] (**4**) showing η^3-coordination to Yb(1) and η^2-coordination to Yb(2); all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Yb(1)–O(1) 2.198(7), Yb(1)–O(2) 2.317(8), Yb(1)–O(5) 2.031(9), Yb(1)–O(6) 2.055(10), Yb(2)–O(1) 2.378(7), Yb(2)–O(2) 2.209(8), Yb(2)–O(3) 2.056(8), Yb(2)–O(4)2.049(10), Yb(1)–C(28) 2.997(12), Yb(1)–C(29) 2.719(13), Yb(1)–C(30)3.174(13), Yb(2)–C(8) 2.894(12), Yb(2)–C(9) 2.837(12); O(1)–Yb(1)–O(2) 73.1(3), O(1)–Yb(1)–O(5) 121.3(3), O(1)–Yb(1)–O(6) 92.4(3), O(2)–Yb(1)–O(5) 89.2(3), O(2)–Yb(1)–O(6) 163.0(4), O(5)–Yb(1)–O(6) 106.2(4), O(1)–Yb(2)–O(2) 71.7(3), O(1)–Yb(2)–O(3) 90.5(3), O(1)–Yb(2)–O(4) 168.0(3), O(2)–Yb(2)–O(3) 120.6(3), O(2)–Yb(2)–O(4) 99.3(3), O(3)–Yb(2)–O(4) 101.0(4), Yb(1)–O(1)–Yb(2) 105.4(3), Yb(1)–O(2)–Yb(2) 107.1(3).

Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with two unique half dimers in the asymmetric unit. Each unique europium(II) center is bound by oxygen atoms of a terminal and two bridging phenolate groups, thereby giving an oxygen donor coordination number about Eu^{II} of three. The Eu–O bond lengths (av. 2.46 Å for bridging and av. 2.29 Å for terminal) are unexceptional, being similar to Eu–O bridging and terminal distances of 2.48 (av.) and 2.361(3) Å, respectively, in [Eu(OC$_6$H$_3$Ph$_2$-2,6)$_2$]$_2$ where there are only one terminal and three bridging ligands.[5a] The longer Eu–O$_{terminal}$ distance in [Eu(OC$_6$H$_3$Ph$_2$-2,6)$_2$]$_2$ is consistent with a lower coordination number in compound **2**. Each dimer is structurally similar but with some significant differences, one being a discrete dimer and the other a polymer of dimers, involving extended nuclearity through inter- and intramolecular Eu–π-arene interactions (see below) that increase the coordination number of Eu

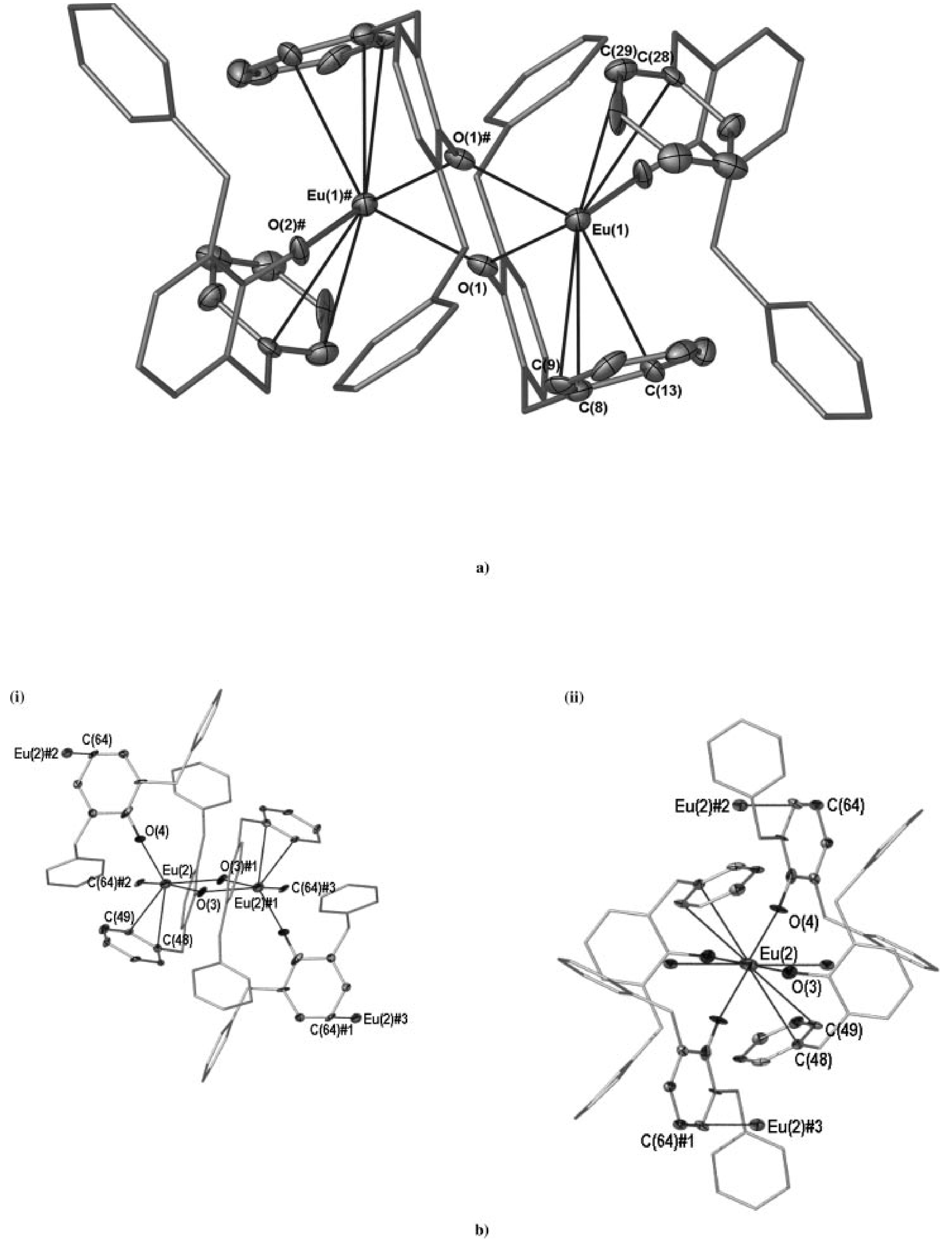

Figure 3. Molecular structure of [{Eu(μ-Odbp)(Odbp)}$_2$]/[{Eu(μ-Odbp)(Odbp)}$_2$]$_\infty$ (**2**) (40% thermal ellipsoids); all hydrogen atoms omitted for clarity and non-coordinating hydrocarbon groups depicted as wireframes. a) [{Eu(μ-Odbp)(Odbp)}$_2$] normal to Eu$_2$O$_2$ metallacycle; b) [{Eu(μ-Odbp)(Odbp)}$_2$]$_\infty$ (i) side-on and (ii) along Eu···Eu vector. Selected bond lengths [Å] and angles [°]: Eu(1)–O(2) 2.287(10), Eu(1)–O(1) 2.463(11), Eu(1)–O(1)#1 2.491(12), Eu(1)–C(8) 3.130(16), Eu(1)–C(9) 3.150(17), Eu(1)–C(13) 3.187(16), Eu(1)–C(28) 3.171(16), Eu(1)–C(29) 3.153(19), Eu(2)–O(3) 2.446(10), Eu(2)–O(3)#2 2.461(11), Eu(2)–O(4) 2.294(10), Eu(2)–C(49) 3.196(16), Eu(2)–C(48) 3.197(15), Eu(2)–C(64)#3 3.136(16); O(1)–Eu(1)–O(2) 90.5(4), O(1)–Eu(1)–O(1)#1 71.7(4), O(2)–Eu(1)–O(1)#1 117.4(4), O(3)–Eu(2)–O(3)#2 69.6(4), O(3)–Eu(2)–O(4) 97.3(4), O(4)–Eu(2)–O(3)#2 119.0(4), Eu(1)–O(1)–Eu(1)#1 108.3(4), Eu(2)–O(3)–Eu(2)#2 110.4(4). Symmetry transformations used to generate equivalent atoms: #1: $-x + 1$, $-y + 1$, $-z$; #2: $-x + 1$, $-y + 2$, $-z + 1$; #3: $-x$, $-y + 2$, $-z + 1$.

significantly. In the true dinuclear molecule the Eu centers are capped on two sides by an η^2- and an η^3-bound arene ring arising from one terminal and one bridging ligand (Figure 3a). In the other molecule, each Eu has one η^2-bound π-arene interaction with an arene group from *only* the bridging group of the dimer while an arene from the terminal groups (involved in π-interactions in the true dimer) swings away from the Eu atom with a closest Eu···C distance of 4.72(1) Å. This leaves a vacancy in the coordination sphere of Eu(2) which allows a further π-arene interaction between Eu(2) and (symmetry-generated) C(64)#1 of 3.136(16) Å [C(64) is the *p*-C atom of the central (phenolate) group of a terminal ligand rather than a radial group]. This forms a single-stranded polymer, where "dimers" are linked by Eu(2)···C(64)(arene) interactions (Figure 3b). This structure is drastically different from the stoichiometrically related $[Eu_2(OC_6H_3Ph_2\text{-}2,6)_4]$ which possesses a remarkable three bridging phenolate groups and one terminal phenolate ligand.

Conclusion

The direct reaction of lanthanoid metals (Ln = La, Eu, Yb) with 2,6-dibenzylphenol at 170°C provides the corresponding homoleptic lanthanoid phenolates in good yield. For Ln = Yb, use of either excess metal or excess phenol gives Yb^{II} or Yb^{III} complexes. All structures feature oxygen-bridged dimeric units with coordination saturation effected by intra- or intermolecular π-phenyl···Ln coordination.

Experimental Section

General: 2,6-Dibenzylphenol (HOdbp) was prepared by a literature method.[15] The lanthanoid metals used were purchased either from Strem chemicals, Tianjiao (Baotou, China), Rhône–Poulenc or Santoku, either as fine powders or as metal ingots, which were manually filed under an inert gas into metal powder for use in reactions. Toluene and hexane were dried with sodium/benzophenone and freeze-thaw-degassed prior to use. All manipulations were performed using conventional Schlenk or glovebox techniques under high-purity argon or dinitrogen in flame-dried glassware. Infrared spectra were recorded as Nujol mulls using sodium chloride plates with a Nicolet Nexus FTIR spectrophotometer. ^{1}H NMR spectra were recorded at 300.13 MHz using a Bruker BZH 300/52 spectrometer and chemical shifts were referenced to the residual ^{1}H resonances of the deuteriobenzene solvent employed. NMR and IR spectra of compounds **1** and **3** showed slight impurities of phenol due to decomposition of the rare earth phenolate compounds in the process of measurement. Compounds **2** and **4** had insufficient solubility in common non-coordinating solvents to obtain NMR spectra. Melting points were determined in sealed glass capillaries under dinitrogen. The metal analyses were adapted from the method described in a previous paper.[16]

$[La_2(Odbp)_6]$ (1). Method A: 2,6-Dibenzylphenol (0.60 g, 2.19 mmol) was treated directly with lanthanum metal (0.10 g, 0.73 mmol) in the presence of 2 drops of mercury and sealed under vacuum in a Carius tube. After 4 d of heating at 170 °C, a white crystalline material formed upon cooling. Unreacted ligand was removed by sublimation. Crystals suitable for XRD analysis were obtained. Yield: 0.58 g (82%). M.p. 184–187 °C. $C_{60}H_{51}LaO_3$ (958.92): calcd. La 14.48; found La 14.30. ^{1}H NMR (C_6D_6): δ = 3.78 (s, 12 H, CH_2), 6.67–6.70 (m, 3 H, ArH), 6.73–6.87 (m, 6 H, ArH), 6.88–7.12 (m, 30 H, ArH) ppm. IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1589 m, 1452 s, 1262 s, 1191 m, 1081 s, 1029 m, 937 w, 859 m, 819 w, 754 s, 697 s, 559 w, 515 w.

$[La(Odbp)_3]_2$. Method B (Without Mercury): HOdbp (0.25 g, 0.91 mmol) was treated with excess lanthanum metal (0.10 g, 0.72 mmol) in an evacuated sealed glass Carius tube. The reaction mixture was heated at 250 °C for 5 d, forming a clear glassy solid upon cooling. Unreacted ligand was removed by a hexane wash. The product was identical to the compound **1** synthesised in the presence of mercury. Yield: 0.12 g (41%). M.p.183–187 °C. IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1601 m, 1453 s, 1260 s, 1202 m, 1074 s, 1029 m, 950 w, 869 m, 820 w, 755 s, 698 s, 601 w, 515 w.

$[La(Odbp)_3]_2$. Method C (Excess Ligand): HOdbp (0.60 g, 2.18 mmol) and lanthanum metal (0.08 g, 0.55 mmol) were sealed under vacuum in the presence of 2 drops of mercury in a glass Carius tube. A white oil formed after heating at 210 °C for 2 d and all of the lanthanum metal was consumed. The remaining (excess) ligand was sublimed to one end of the tube (HOdbp sublimes at 240 °C). The product was identical with that obtained in Methods A and B above. Yield: 0.35 g (66%). M.p. 184–186 °C. IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1594 m, 1456 s, 1259 s, 1200 m, 1072 s, 1029 m, 950 w, 865 m, 819 w, 755 s, 699 s, 600 w, 510 w.

$[Eu_2(Odbp)_4]$ (2). Method A: 2,6-Dibenzylphenol (0.53 g, 1.93 mmol) was treated directly with europium metal (0.15 g, 0.97 mmol) in the presence of 2 drops of mercury in an evacuated Carius tube. After 4 d of heating at 170 °C, an orange molten/crystalline material formed upon cooling. Unreacted excess ligand was removed by sublimation. Crystals suitable for XRD analysis were obtained. Yield: 0.56 g (83%). M.p. 198–200 °C. $C_{40}H_{34}EuO_2$ (698.63): calcd. Eu 22.81; found Eu 22.58. IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1587 m, 1458 s, 1310 m, 1286 m, 1258 m, 1231 s, 1200 m, 1157 m, 1081 m, 1028 m, 933 w, 885 w, 854 m/w, 815 w, 748 s, 698 s, 601 w.

$[Eu(Odbp)_2]_2$ (2). Method B (Without Mercury): HOdbp (0.30 g, 1.09 mmol) was treated with excess europium metal (0.11 g, 0.72 mmol) in an evacuated glass Carius tube. The reaction was heated for 5 d at 250 °C, forming a glassy orange solid upon cooling. The residue was washed with hexane to remove any unreacted ligand. The product was identical to compound **2** from Method A. Yield: 0.19 g (49%). M.p. 197–200 °C. IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1586 m, 1458 s, 1305 m, 1281 m, 1252 m, 1230 s, 1155 m, 1078 m, 1026 m, 971 w, 888 w, 850 m/w, 754 s, 696 s, 595 w.

$[Eu(Odbp)_2]_2$ (2). Method C (Excess Ligand): HOdbp (0.50 g, 1.82 mmol) and europium metal (0.09 g, 0.61 mmol) were sealed under vacuum in the presence of 2 drops of mercury in a glass Carius tube. An orange oil formed after heating at 210 °C overnight. All of the europium metal had reacted; the remaining excess ligand was sublimed to one end of the tube (HOdbp sublimes at 240°). The product was identical with that obtained from Methods A and B above. Yield: 0.32 g (77%). M.p. 197–200 °C. IR (Nujol): $\tilde{\nu}$ = 1600 m, 1453 s, 1347 m, 1286 m, 1231 m, 1200 m, 1150 m, 1075 m, 1026 m, 934 w, 885 w, 852 m/w, 755 s, 698 s, 590 w.

$[Yb(Odbp)_2]$ (3): 2,6-Dibenzylphenol (0.60 g, 2.19 mmol) was treated directly with excess ytterbium metal (0.40 g, 2.30 mmol) in the presence of 2 drops of mercury in a sealed, evacuated Carius tube. After 4 d of heating at 170 °C, a red glassy material formed upon cooling. Yield: 0.53 g (67%). M.p. 125–128 °C. $C_{40}H_{34}O_2Yb$ (719.75): calcd. Yb 23.99; found Yb 23.80. ^{1}H NMR (C_6D_6): δ =

3.72 (s, 8 H, CH_2), 6.72–6.77 (m, 2 H, ArH), 6.82–6.87 (m, 4 H, ArH), 6.89–7.13 (m, 20 H, ArH) ppm. IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1601 m, 1456 s, 1363 s, 1230 s, 1074 w, 1028 w, 1006 w, 950 m, 923 m, 889 w, 830 w, 820 w, 794 w, 755 s, 698 s. Attempts to form this compound in the absence of mercury with heating up to 250 °C (2,6-dibenzylphenol slowly decomposes above 260 °C, so was not heated any further) resulted in the isolation of unreacted starting material.

[$Yb_2(Odbp)_6$] (4): 2,6-Dibenzylphenol (0.30 g, 1.09 mmol) was treated directly with ytterbium metal (0.04 g, 0.23 mmol) in the presence of 2 drops of mercury. The reactants were sealed under vacuum in a glass Carius tube. After 2 d of heating at 150 °C, deep orange/red crystals were grown upon cooling. Unreacted ligand was removed by a hexane wash and the remaining material characterised. Yield: 0.18 g (78%). M.p. 78–80 °C. $C_{60}H_{51}O_3Yb$ (993.05): calcd. Yb 17.42; found 18.11. IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1601 m, 1459 s, 1365 s, 1230 s, 1074 w, 1029 w, 950 m, 923 m, 889 w, 829 w, 820 w, 794 w, 755 s, 698 s. Attempts to form this compound in the absence of mercury with heating up to 250 °C (2,6-dibenzylphenol slowly decomposes above 260 °C, so was not heated any further) resulted in the isolation of unreacted starting material.

X-ray Crystallography: Crystalline samples of compounds **1**, **2** and **4** were mounted on glass fibres in viscous paraffin oil at –150 °C (123 K). Crystal data were obtained using an Enraf–Nonius Kappa CCD. An empirical absorption correction (SORTAV)[17] was applied to all data. Structural solution and refinement were carried out using SHELXL-97[18] and SHELXS-97[19] utilising the graphical interface X-Seed.[20] Crystal data and refinement parameters for all complexes are compiled below.

[$La_2(Odbp)_6$] (1): $C_{120}H_{102}La_2O_6$, M = 1917.84, 0.25 × 0.20 × 0.20 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 13.4374(5), b = 13.9358(5), c = 26.7937(12) Å, α = 98.976(1), β = 95.312(2), γ = 108.065(4)°, V = 4658.3(3) Å^3, Z = 2, D_c = 1.367 g/cm^3, F_{000} = 1968, Nonius Kappa CCD, Mo-K_α radiation, λ = 0.71073 Å, T = 123(2) K, $2\theta_{max}$ = 56.5°, 53379 reflections collected, 21478 unique (R_{int} = 0.2204). Final $GooF$ = 0.872, R_1 = 0.0748, wR_2 = 0.1217, R indices based on 7518 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1147 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.963 mm^{-1}.

[$Eu_2(Odbp)_4$] (2): $C_{80}H_{68}Eu_2O_4$, M = 1397.26, 0.10 × 0.10 × 0.10 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 10.0458(12), b = 13.136(2), c = 23.773(3) Å, α = 103.448(11), β = 94.188(9), γ = 94.379(7)°, V = 3028.9(8) Å^3, Z = 2, D_c = 1.532 g/cm^3, F_{000} = 1412, Nonius Kappa CCD, Mo-K_α radiation, λ = 0.71073 Å, T = 123(2) K, $2\theta_{max}$ = 55.9°, 19023 reflections collected, 10992 unique (R_{int} = 0.1653). Final $GooF$ = 0.930, R_1 = 0.0993, wR_2 = 0.2022, R indices based on 4255 reflections with $I > 2\sigma(I)$ (refinement on F^2), 775 parameters, 66 restraints. Lp and absorption corrections applied, μ = 2.106 mm^{-1}.

[$Yb_2(Odbp)_6$] (4): $C_{120}H_{102}O_6Yb_2$, M = 1986.10, orange, rectangular, 0.20 × 0.10 × 0.10 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 13.364(3), b = 13.475(3), c = 26.927(5) Å, α = 98.44(3), β = 97.42(3), γ = 104.68(3)°, V = 4569.2(16) Å^3, Z = 2, D_c = 1.444 g/cm^3, F_{000} = 2020, Nonius Kappa CCD, Mo-K_α radiation, λ = 0.71073 Å, T = 123(2) K, $2\theta_{max}$ = 56.5°, 57274 reflections collected, 21355 unique (R_{int} = 0.0743). Final $GooF$ = 1.108, R_1 = 0.0993, wR_2 = 0.2751, R indices based on 16207 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1153 parameters, 42 restraints. Lp and absorption corrections applied, μ = 2.094 mm^{-1}.

CCDC-274466 (**1**), -274467 (**2**) and -274468 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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