Organoamido- and Aryloxo-Lanthanoids, 17[◇]

Novel Low-Coordinate Lanthanoid(II) and -(III) Aryloxide Complexes – the X-ray Structures of Bis(2,6-diphenylphenolato)tris(tetrahydrofuran)-ytterbium(II), Bis(1,2-dimethoxyethane)bis(2,6-diphenylphenolato)ytterbium(II), and 1,2-Dimethoxyethanetris(2,6-diphenylphenolato)ytterbium(III) and -neodymium(III)

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Reduction of $[Yb(Odpp)_3(THF)_2]$ (HOdpp = 2,6-diphenylphenol; THF = tetrahydrofuran) with ytterbium powder and mercury metal yields $[Yb(Odpp)_2(THF)_3]$ (**1**) which on crystallization from DME gives $[Yb(Odpp)_2(DME)_2]$ (**2**) (DME = 1,2-dimethoxyethane). Crystallization of the reactant $[Yb(Odpp)_3(THF)_2]$ from DME yields $[Yb(Odpp)_3(DME)] \cdot (DME)_{0.5}$ (**3**) and of $[Nd(Odpp)_3(THF)_2]$ from DME/THF the analogous $[Nd(Odpp)_3(DME)] \cdot (THF)$ (**4**). The X-ray crystal structure of **1** reveals distorted trigonal bipyramidal five-coordinate ytterbium with axial Odpp ligands [O–Yb–O 164.6(3)°], and unsymmetrically distributed equatorial THF ligands [O–Yb–O 137.5(3), 138.8(3), 83.7(4)°] owing to two close H(Ph)···Yb approaches (3.1–3.2 Å). In **2**, there is trigonal prismatic six-coordination with an Odpp ligand on each triangular face and DME ligands bridging the triangular faces. Both **3** and **4** have distorted square planar five-coordination for the lanthanoid metals with an apical Odpp ligand and *cisoid* Odpp ligands and a chelating DME in the square plane.

Introduction

In the family of lanthanoid(III) complexes with bulky aryloxide ligands[2–6], which include 2,6-di-*tert*-butyl-4-X-phenolates (e.g. X = H, *t*Bu, Me)[7], 2,6-diisopropylphenolates[8] and 2,6-dimethylphenolates[9], lanthanoid tris(2,6-diphenylphenolates) $Ln(Odpp)_3$ occupy a distinctive position. They are readily prepared by redox transmetallation/ligand exchange from lanthanoid metals [equation (1)][10–12], they provide examples of both near square pyramidal $[Yb(Odpp)_3(THF)_2]$[10], (THF = tetrahydrofuran) and trigonal bipyramidal five coordination $[Ln(Odpp)_3(THF)_2]$ (Ln = La, Nd)[11,12], and they include complexes with intramolecular π-Ph–Ln coordination (η^1-,η^3-, and η^6-)[10,12]. Recently, homoleptic anionic complexes have also been obtained, e.g. $\{Na[Nd(Odpp)_4]\}$[1,13], including discrete homoleptic complexes, e.g. $[Na(diglyme)_2][Nd(Odpp)_4]$[1,13] [diglyme = bis(2-methoxyethyl) ether]. No lanthanoid(II) complexes have been prepared with this ligand, and the preparations of $Ln(Odpp)_3$ (Ln = Sm, Yb) were carried out with the stoichiometry [equation (2)] appropriate for formation of Ln^{II} complexes[10].

$$2\,Ln + 3\,Hg(C_6F_5)_2 + 6\,HOdpp \rightarrow 2\,Ln(Odpp)_3 + 6\,C_6F_5H + 3\,Hg \quad (1)$$

$$Ln + Hg(C_6F_5)_2 + 2\,HOdpp \nrightarrow Ln(Odpp)_2 \quad (2)$$

We now report the synthesis of ytterbium(II) 2,6-diphenylphenolate by reduction of $Yb(Odpp)_3$, and the X-ray crystal structures of $[Yb(Odpp)_2(THF)_3]$ and $[Yb(Odpp)_2(DME)_2]$, (DME = 1,2-dimethoxyethane). In addition, the structures of the novel five-coordinate lanthanoid(III) complexes $[Ln(Odpp)_3(DME)]$ (Ln = Nd or Yb) have also been determined.

Results and Discussion

Synthesis

Reduction of tris(2,6-diphenylphenolato)ytterbium(III) to the ytterbium(II) complex was achieved by prolonged

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treatment of the former with ytterbium powder and mercury metal, [equation (3)].

$$2\ Yb(Odpp)_3 + Yb(Hg) \rightarrow 3\ Yb(Odpp)_2 + Hg \quad (3)$$

Satisfactory reaction could *not* be achieved with ytterbium metal alone. This contrasts the reduction of $YbCp_3$ (Cp = cyclopentadienyl) by Yb alone[14] and may suggest the role of mercury extends beyond surface cleaning. Crystallization from the reaction mixture yielded $[Yb(Odpp)_2(THF)_3]$ (**1**), which was obtained analytically pure with an infrared spectrum characteristic of 2,6-diphenylphenolates[10,12]. It is not possible to establish the presence of coordinated THF from the infrared spectrum owing to Odpp absorption in the 900–800 cm^{-1} region. The red colour of the complex is associated with M → L charge transfer absorption near 400 nm. A very weak parent ion of the unsolvated $Yb(Odpp)_2$ was observed in the mass spectrum. The X-ray structure is discussed below.

Crystallization of the complex from DME/THF/pentane yielded $[Yb(Odpp)_2(DME)_2]$ (**2**), [equation (4)].

$$[Yb(Odpp)_2(THF)_3] + 2\ DME \rightarrow [Yb(Odpp)_2(DME)_2] + 3\ THF \quad (4)$$

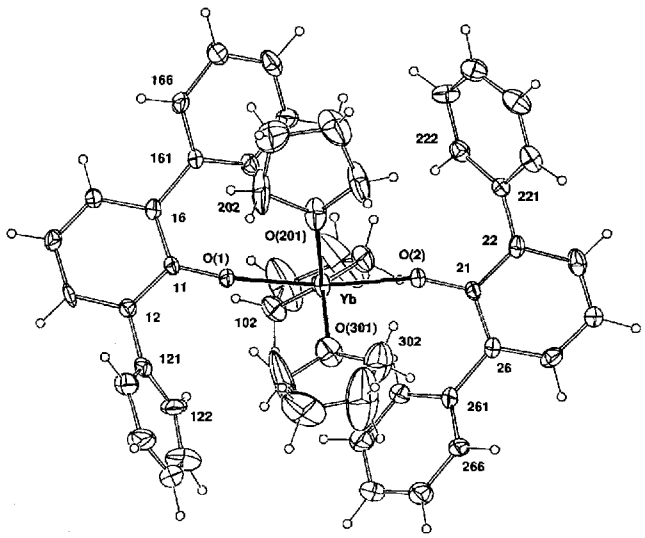
Besides the typical Odpp infrared absorptions, a strong band attributable to ν(C–O) of coordinated DME was observed at 1074 cm^{-1}, shifted as expected from the free ligand value (1106 cm^{-1})[15]. This complex was unambiguously defined by a single crystal X-ray study (see below). It was also obtained by addition of DME to the filtrate from the preparation of **1** and subsequent crystallization. The reduction reaction [equation (3)] is not entirely complete, as indicated by crystallization of yellow $[Yb(Odpp)_3(DME)].(DME)_{0.5}$ (**3**) from the filtrate after isolation of **1** and **2** (see Experimental Section). Single crystals of **3** were obtained by crystallization of $[Yb(Odpp)_3(THF)_2]$ from DME [equation (5); Ln = Yb]. Satisfactory microanalyses could not be obtained for the compound but it also was unambiguously identified by an X-ray study (see below). Coordinated DME was indicated by strong absorption at 1052 cm^{-1}, whilst a band at 1098 cm^{-1}, not observed for **1** and **2**, may be attributed to DME of solvation. Because of the problem in obtaining **3** analytically pure, $[Nd(Odpp)_3(THF)_2]$[10] was crystallized from DME/THF yielding single crystals of $[Nd(Odpp)_3(DME)].(THF)$ (**4**), (equation (5), Ln = Nd), which was obtained analytically pure. It showed ν(C–O) of coordinated DME at 1060–1050 cm^{-1}, but, unlike **3**, had no absorption near 1100 cm^{-1}. This result is consistent with assignment of the latter band to DME of solvation for **3**. No feature of the spectrum of **4** could be unequivocally attributed to the THF of solvation.

$$[Ln(Odpp)_3(THF)_2] + DME \rightarrow [Ln(Odpp)_3(DME)] + 2\ THF \quad (5)$$

Crystal Structure Analyses

Complex **1**: The molecular structure of **1** is displayed in Figure 1 with selected bond distances and angles given in the caption. The molecule has approximate *2*-symmetry. Ytterbium is five-coordinate with *transoid* aryloxide oxygens [O(1)–Yb–O(2) 164.6(3)°] and three THF oxygens. Although the best fit polyhedron[16] is a trigonal bipyramid, the arrangement of the equatorial THF ligands is considerably distorted from triangular with O–Yb–O angles of 83.7(4), 137.5(3), and 138.8(3)°. The pronounced distortion can be attributed to close Yb···H(Ph) contacts within the larger equatorial O–Yb–O angles. Thus Yb···*o*-H(162) [within O(101)–Yb–O(201)] is 3.1 Å and Yb···*o*-H(262) [within O(101)–Yb–O(301)] is 3.2 Å. These distances are too long (Σ metallic radius of Yb[17] and the Van der Waals[18] radius of H is 3.1 Å) to be seriously considered as agostic Yb–H interactions, and instead they result from the steric interactions between phenyl substituents and THF ligands.

Figure 1. Molecular structure of five-coordinate $[Yb(Odpp)_2(THF)_3]$ (**1**), projected through the equatorial plane of the ytterbium and three O(THF) atoms, along the approximate *2*-axis; in this and the other Figures, non-hydrogen atoms are shown with 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å. Carbon atoms are denoted by number only[a]



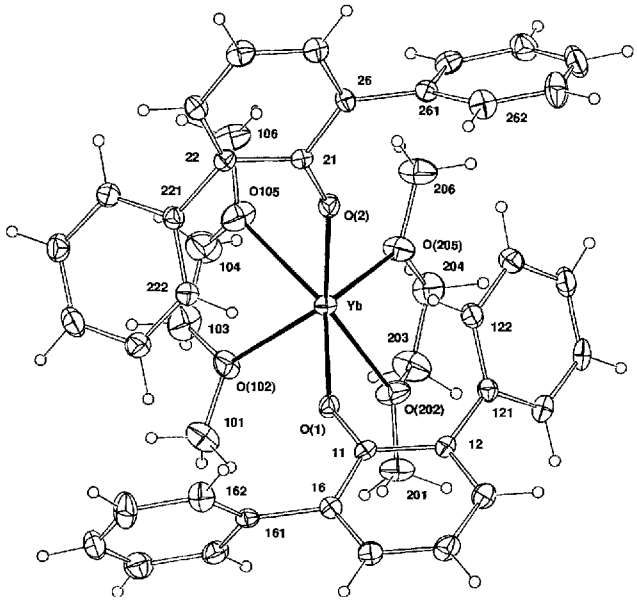
[a] Selected bond lengths [Å] and angles [°]: Yb–O(1) 2.211(8), Yb–O(2) 2.202(9), Yb–O(101) 2.496(9), Yb–O(201) 2.406(9), Yb–O(301) 2.35(1), Yb···H(162) 3.1, Yb···H(262) 3.2; O(1)–Yb–O(2) 164.6(3), O(1)–Yb–O(101) 82.6(3), O(1)–Yb–O(201) 88.4(3), O(1)–Yb–O(301) 101.5(4), O(2)–Yb–O(101) 84.3(3), O(2)–Yb–O(201) 96.0(3), O(2)–Yb–O(301) 93.6(4), O(101)–Yb–O(201) 137.5(3), O(101)–Yb–O(301) 138.8(3), O(201)–Yb–O(301) 83.7(4), Yb–O(1)–C(11) 170.5(8), Yb–O(2)–C(21) 163.5(8).

Previous examples of crystallographically characterized five-coordinate lanthanoid(II) aryloxides all involve 2,6-di-*tert*-butyl-4-(methyl or *tert*-butyl)phenolate ligands, viz, $[Ln(OC_6H_2Me\text{-}4\text{-}tBu_2\text{-}2,6)_2(THF)_3] \cdot (THF)$ (Ln = Yb **5**[19], Sm **6**[20], or Eu **7**[21]) and $[Yb(OC_6H_2tBu_3\text{-}2,4,6)_2(THF)_3] \cdot (THF)$ (**8**)[22]. Although the structures have variously been described as trigonal bipyramidal and square pyramidal[19–22], the best polyhedron[16] is square pyramidal with *transoid* aryloxides and *transoid* THF ligands in the square plane and an apical THF (the most borderline case is **7**[21]). The failure to coordinate a further THF to give octahedral stereochemistry may be attributed to blocking of the sixth position by one[19] or more[22] close methyl groups.

The Yb–OAr distances of **1** (Figure 1) are closely comparable with those of **5**[19] and **8**[22] consistent with the axial (**1**) or *transoid* (**5** and **8**) relationship of the two aryloxide ligands. Subtraction of an ionic radius for five-coordinate Yb^{2+} (0.96 Å from extrapolation of data for higher coordination numbers[23]) gives 1.25 Å for all three structures. This is somewhat larger than values derived for **6** (1.18 Å) and **7** (1.21 Å), and may reflect greater steric crowding with the smallest of these Ln^{2+} ions. In trigonal bipyramidal **1**, the ArO–Yb–OAr angle is significantly larger than in square pyramidal **5**–**8** [149.0(6)–156.7(6)][19–22]. The Yb–O(THF) distances of **1** (Figure 1) cover a wider range (maximum difference 0.15 Å) than in **5**–**8** (maximum difference 0.03–0.075 Å)[19–22] with one distance notably shorter than any for **5** and **8** [2.44(1)–2.51(2) Å]. Subtraction of the five-coordinate ionic radius gives 1.39–1.54 Å for **1** compared with 1.48–1.55 Å for the Yb complexes **5** and **8**, but with 1.40–1.44 Å for **6** and **7**. Lower values (1.25–1.39 Å; ave 1.34(5) Å)[24] are derived from Ln–O(ether) distances of formally eight- to ten-coordinate THF complexes of di- and tri-(cyclopentadienyl)lanthanoid(II or III) compounds illustrating the hindered nature of **1**. A noteworthy difference between the structure of trigonal bipyramidal **1** and square pyramidal **5**–**8** is that for the former the largest O(THF)–Yb–O(THF) angle is 138.8(3)° whereas in the latter group this angle has values of 163.8(7)° (**5**), 175.7(5)°, (**6**), 178.6(2)° (**7**), and 177.3(5)° (**8**). The sum of the steric coordination numbers of the ligands[25] for **5** to **8** is 8.4 compared with 7.4 for **1**. Since this difference in crowding is not reflected significantly in bond length differences, it may be associated with the difference in stereochemistry.

Complex **2**: The molecular structure of **2** is displayed in Figure 2, with selected bond distances and angles given in the caption. As with **1**, the molecule has approximate *2*-symmetry. Ytterbium is six-coordinate, but this is still a low coordination number for a lanthanoid metal. The increase in coordination number from **1** may be attributed to the lower steric requirements of chelating DME rather than two THF ligands[26] and the preference for chelating vis-a-vis unidentate DME[15] (see, however, recent examples of unidentate DME[27], even as a ligand to Ln elements[15,28]). The arrangement of the donor atoms is best described[16] as trigonal prismatic with one aryloxide oxygen on each of the triangular faces, giving rise to a much smaller bond angle between the bulky aryloxide ligands [105.4(2)°] than in **1** [164.6(3)°]. The near equal Yb–OAr distances are longer than those of **1** by an amount consistent[23] with the higher coordination number. Subtraction of an ionic radius for six-coordinate Yb^{2+} (1.02 Å)[23] gives 1.24 Å, comparable with the value for **1**. Likewise, Yb–O(DME) distances are significantly larger than Yb–O(THF) of **1** (ave. 2.42 Å, **1**; 2.54 Å, **2**), but in this case by an amount exceeding somewhat the difference expected from the coordination number difference. Subtraction of the ionic radius from ⟨Yb–O(DME)⟩ gives 1.52 Å compared with 1.46 Å from ⟨Yb–O(THF)⟩ of **1**. Interestingly, the two longest Yb–O(DME) distances are associated with the largest O(DME)–Yb–O(DME) angle. The structure of **2** differs significantly from that of six-coordinate $Yb(SC_6H_2tBu_3\text{-}2,4,6)_2(DME)_2$ (**9**)[29] and markedly from that of $Eu[N(SiMe_3)_2]_2(DME)_2$ (**10**)[30]. In **9** and **10**, the S–Yb–S and N–Eu–N angles [124.4(2) and 134.5(2)° respectively][29,30] are considerably larger than ArO–Yb–OAr of **2** (Figure 2), and there are O–Ln–O angles of 133.0(7)° for **9** and 135.2(7)° and 162.7(2)° for **10** compared with the largest O(DME)–Yb–O(DME) angle of 110.5(2)° for **2**. The Yb–O(DME) distances of **9** [2.41(2), 2.66(2) Å] cover a wider range than those of **2** [2.496(6)–2.594(4) Å] though ⟨Yb–O(DME)⟩ values are virtually the same. Subtraction of the ionic radius of six-coordinate Eu^{2+} from ⟨Eu–O⟩ gives 1.53 Å, close to the value derived from ⟨Yb–O(DME)⟩ of **2** (above). Both are much larger than the 1.34(5) Å derived from Ln–O of ether complexes of organolanthanoids[24]. Values derived from ⟨Ln–O(DME)⟩ of eight-coordinate $Ln(THD)_2(DME)_2$ [H(THD) = 2,2,6,6-tetramethylheptane-3,5-dione][31], viz 1.32 Å (Ln = Sm), 1.42 Å (Ln = Eu) are also much smaller than the value for **2**. Steric crowding is greater in **10** than **2** for which the sum of the respective ligand steric coordination numbers are 7.9 and 7.4[26]. In relation to the different coordination numbers of **1** and **2**, it should be noted that the sum of the steric coordination numbers for two DME ligands is approximately that for three THF ligands[26].

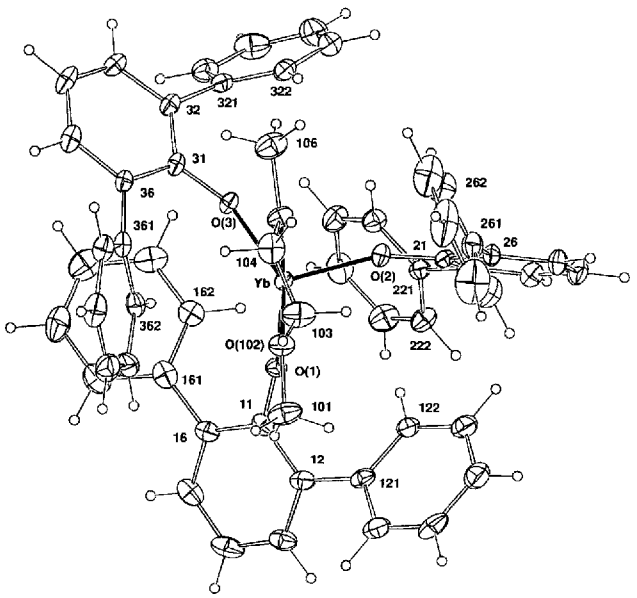
Figure 2. Molecular structure of six-coordinate $[Yb(Odpp)_2(DME)_2]$ (**2**), projected down its approximate *2*-axis[a]



[a] Selected bond lengths [Å] and angles [°]: Yb–O(1) 2.259(5), Yb–O(2) 2.258(5), Yb–O(102) 2.496(6), Yb–O(105) 2.563(7), Yb–O(202) 2.594(5), Yb–O(205) 2.498(5); O(1)–Yb–O(2) 105.4(2), O(1)–Yb–O(102) 90.3(2), O(1)–Yb–O(105) 143.8(2), O(1)–Yb–O(202) 82.5(2), O(1)–Yb–O(205) 138.3(2), O(2)–Yb–O(102) 134.4(2), O(2)–Yb–O(105) 80.7(2), O(2)–Yb–O(202) 149.6(2), O(2)–Yb–O(205) 98.0(2), O(102)–Yb–O(105) 63.4(2), O(102)–Yb–O(202) 73.6(2), O(102)–Yb–O(205) 97.5(2), O(105)–Yb–O(202) 110.5(2), O(105)–Yb–O(205) 73.1(2), O(202)–Yb–O(205) 61.1(2), Yb–O(1)–C(11) 150.4(4), Yb–O(2)–C(21) 155.5(4).

Complexes **3** *and* **4**: The complexes have very similar structures (Figures 3 and 4), the lanthanoid metals being five-coordinate with three aryloxide ligands and a chelating DME. However, with the same arrangement of the Odpp ligands for **3** and **4** the DME has a λ configuration in **3** and δ in **4**, (Figures 3 and 4). The best fit polyhedron[16] is a square pyramid with O(2) as the apex and *cisoid* aryloxides and a chelating DME in the square plane. Since the ArO−Ln−OAr angles lie close to tetrahedral values, there is an approximately tetrahedral array of aryloxide oxygens and the centre of the DME ligand. Selected bond distances and angles for both **3** and **4** are given with the Figures. Corresponding bond angles are in reasonable agreement between the structures, the differences ranging from 0° [O(1)−Ln−O(102)] to 10.9° [O(2)−Ln−O(102)]. For ⟨Ln−OAr⟩, the bond distance difference (0.13 Å) corresponds closely to that between the ionic radii of Nd^{3+} and Yb^{3+}[23], but for ⟨Ln−O(DME)⟩ there is a larger difference (0.17 Å).

Figure 3. Molecular structure of five-coordinate $[Yb(Odpp)_3(DME)] \cdot (DME)_{0.5}$ (**3**) (the DME of solvation is not shown)[a]



[a] Selected bond lengths [Å] and angles [°]: Yb−O(1) 2.062(5), Yb−O(2) 2.051(5), Yb−O(3) 2.084(4), Yb−O(102) 2.341(5), Yb−O(105) 2.367(5); O(1)−Yb−O(2) 104.1(2), O(1)−Yb−O(3) 113.8(2), O(1)−Yb−O(102) 87.9(2), O(1)−Yb−O(105) 153.5(2), O(2)−Yb−O(3) 107.8(2), O(2)−Yb−O(102) 102.8(2), O(2)−Yb−O(105) 87.9(2), O(3)−Yb−O(102) 135.9(2), O(3)−Yb−O(105) 83.7(2), O(102)−Yb−O(105) 66.2(2), Yb−O(1)−C(11) 171.2(5), Yb−O(2)−C(21) 161.0(5), Yb−O(3)−C(31) 148.3(4).

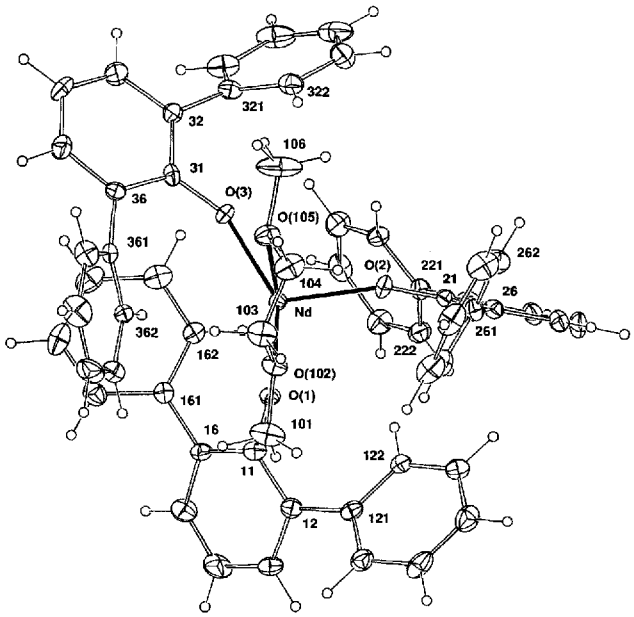
The structure of **3** is related to that of $[Yb(Odpp)_3(THF)_2] \cdot (THF)$ (**11**)[10,32], where ytterbium has square pyramidal stereochemistry but with *transoid* Odpp ligands in the square plane by contrast with *cisoid* for **3**. Despite this difference, ⟨Yb−Odpp⟩ for **3** (2.062 Å) is very similar to that of **11** (2.078[10], 2.062[32] Å). Although ⟨Yb−O(DME)⟩ of **3** (2.354 Å) is marginally longer than ⟨Yb−O(THF)⟩ (2.305[10], 2.324[32] Å) of **11**, a similar relationship has been observed between **1** and **2**, where ⟨Yb−O(DME)⟩ of **2** exceeds ⟨Yb−O(THF)⟩ of **1** by an amount greater than expected for the change in coordination number. Subtraction of an ionic radius for five coordinate Yb^{3+} (0.81 Å extrapolated from data for higher coordination numbers[23]) from ⟨Yb−Odpp⟩ gives 1.25 Å in agreement with values derived from Yb−Odpp of **1** and **2**, despite the difference in oxidation state, and in general agrees with values (e.g.[33]) derived from ⟨Ln−OAr⟩ of a number of complexes with bulky aryloxide ligands. A similar subtraction from ⟨Yb−O(DME)⟩ gives 1.54 Å, close to the value for **2**, but larger than the value for the THF complexes **1** (1.46 Å) and **11** (1.50[10], 1.51[33] Å). Comparisons can also be made with values derived from ⟨Ln−O(DME)⟩ of higher coordinate (i.e. more typical) lanthanoid complexes. Thus, from ⟨Ln−O(DME)⟩ of seven-coordinate $[DyCl_3(DME)_2]$[34], and eight-coordinate $[Gd(THD)_3(DME)]$[35], appropriate subtractions give 1.47 and 1.52 Å, the latter approaching the value for **3** and perhaps suggesting comparable degrees of steric crowding. Indeed, the sum of the steric coordination numbers for both **3** and $[Gd(THD)_3(DME)]$ is 7.5.

Five-coordination has also been observed for other bulky $Ln(OAr)_3(L)_n$ complexes of elements of a similar size to Yb, but with different structural or stereochemical features[8b,9a]. In $[Y(OAr)_3THF]_2$ (Ar = 2,6-$Me_2C_6H_3$) (**12**), the yttrium ions have square planar stereochemistry but there are both bridging and terminal OAr ligands[9a], whilst in $[Ln(OAr)_3(THF)_2]$ (Ln = Er (**13**) or Lu (**14**), Ar = 2,6-$iPr_2C_6H_3$), there is distorted trigonal bipyramidal stereochemistry with axial THF ligands[8b]. In the dimer **12**, terminal ⟨Y−OAr⟩ (2.060 Å) and Y−O(THF) (2.348(6) Å) one very close to ⟨Yb−Odpp⟩ and ⟨Yb−O(DME)⟩ of **3** (Figure 3), whilst the ionic radii of Y^{3+} and Yb^{3+} differ by only 0.03 Å. In the case of **13** and **14**, the respective ⟨Ln−OAr⟩ (Ln = Er or Lu) and ⟨Ln−O(THF)⟩ distances [2.078 (**13**); 2.044 (**14**); 2.346 (**13**); 2.296 (**14**) Å] are also similar to those of **3**.

The Nd−Odpp distances of **4** (Figure 4) are comparable with Nd−OAr of five-coordinate $[Nd(Odpp)_3(THF)_2]$ (**15**) (⟨Nd−O⟩ 2.190 Å)[12] and $[Nd(OAr)_3(THF)_2]$ (Ar = 2,6-$iPr_2C_6H_3$) (**16**) (⟨Nd−O⟩ 2.171 Å)[8b], both of which have distorted trigonal bipyramidal stereochemistry, the former with both axial and equatorial Yb−O(THF) bonds[12] and the latter with only axial THF ligands[8b]. Likewise, ⟨Nd−O(DME)⟩ of **4** is similar to ⟨Nd−O(THF)⟩ of **15** (2.52 Å) and **16** (2.48 Å), but the former correspondence is misleading owing to the marked difference (0.18 Å) in the Nd−O(THF) bond lengths of **15**[12]. Subtraction of an extrapolated ionic radius for five-coordinate Nd^{3+} (0.91 Å) from ⟨Nd−Odpp⟩ gives 1.28 Å, a normal value for complexes of bulky aryloxides[33]. However, the value derived from ⟨Nd−O(DME)⟩ (1.61 Å) is one of the highest for Ln−O(ether) bonds[12,24,33] (but see below).

Five-coordination has also been established in some comparable bulky tris(alkoxides), viz $[Nd(OCH_2\text{-}tBu)_3]_4$ (**17**)[36], and $[Nd_2(OCH\text{-}iPr_2)_6L_2]$ [L = THF (**18**), pyridine (**19**), L_2 = DME (**20**)][37]. In all of these complexes, terminal ⟨Nd−OR⟩ (R = CH_2tBu or $CHiPr_2$) distances are shorter

Figure 4. Molecular structure of five-coordination [Nd(Odpp)$_3$(DME)] · (THF) (**4**) (the THF of solvation is not shown)[a]



[a] Selected bond lengths [Å] and angles [°]: Nd–O(1) 2.198(5), Nd–O(2) 2.179(5), Nd–O(3) 2.197(5), Nd–O(102) 2.502(6), Nd–O(105) 2.546(5); O(1)–Nd–O(2) 102.9(2), O(1)–Nd–O(3) 120.3(2), O(1)–Nd–O(102) 87.9(2), O(1)–Nd–O(105) 149.8(2), O(2)–Nd–O(3) 113.4(2), O(2)–Nd–O(102) 91.9(2), O(2)–Nd–O(105) 87.1(2), O(3)–Nd–O(102) 133.6(2), O(3)–Nd–O(105) 79.4(2), O(102)–Nd–O(105) 63.1(2), Nd–O(1)–C(11) 170.5(5), Nd–O(2)–C(21) 154.4(5), Nd–O(3)–C(31) 149.7(5).

[2.138 (**17**), 2.153 (**18**), 2.146 (**19**), 2.144 (**20**) Å][36,37] than ⟨Nd–Odpp⟩ of **4**, though bridging ⟨Nd–OR⟩ is considerably larger (ca. 2.32–2.39 Å)[36,37] as expected. The shortening of Nd–OR(ter) could suggest lower steric repulsion for the terminal alkoxide ligands. By contrast, Nd–O(THF) [2.552(4) Å] cf **18**[37] is marginally longer, and Nd–O(DME) [2.604(6) Å] of **20**[37] is considerably longer than ⟨Nd–O(DME)⟩ of **4**. However, in **20** DME is unusually present as a bridging ligand and bond lengthening can be associated with this, as has been shown for bridging DME in a lanthanoid tris(η^2-pyrazolate)[15]. Indeed, subtraction of an ionic radius for five-coordinate Nd^{3+} from Nd–O(DME) of **20** gives 1.69 Å, as large as the 1.70 Å similarly derived for the abnormally long axial Ln–O(THF) bonds of [Ln(Odpp)$_3$(THF)$_2$][12] (Ln = La or Nd). Both are larger (ca. 0.1 Å) than the otherwise large value (1.61 Å) for **4**.

Thus, the first lanthanoid(II) 2,6-diphenylphenolates have been prepared and use of the bulky Odpp ligand has provided new examples of low-coordinate lanthanoid complexes in both the II and III oxidation states. The Odpp ligand is surprisingly flexible and versatile given the steric constraints imposed by the aromatic rings. In the present structures, five- and six-coordinate Yb^{II} and five-coordinated Yb^{III} are all accommodated in structures in which the sums of the steric coordination numbers of the ligands[25,26] are 7.4–7.5. A similar steric coordination number (7.6) is observed for the homoleptic anion in [Na(diglyme)$_2$][Nd(Odpp)$_4$][1]. More crowding can be tolerated, since the sum of the ligand steric coordination numbers in [Yb(Odpp)$_3$(THF)$_2$] (**11**)[10] is 8.1. Possibly, the transoid arrangement of the Odpp ligands in the square plane (cf. *cis* in **3** and **4**) mitigates repulsion between pendant phenyl groups. Remarkably, in the Nd analogue **15** of the Yb complex **11**, there is distorted trigonal bipyramidal stereochemistry with severe elongation of an axial Nd–O(THF) bond. Given that Nd is larger than Yb by ca. 0.14 Å, this bond lengthening may be electronic in origin, viz. a strong *trans* influence of the axial Odpp ligand *trans* to the weakly bound THF[12]. Even more variety in ligand behaviour is shown in the apparently three-and four-coordinate [Ln(Odpp)$_3$] (Ln = Nd or Yb)[10,12] and [Nd(Odpp)$_3$(THF)][12], which have apparent steric coordination number sums of 5.7 and 6.9 respectively[25,26]. Because of coordination unsaturation, intramolecular π-Ph–Ln coordination occurs[10,12] and can be accomodated within reasonable steric repulsion limits by η^6- and η^1-Ph–Ln bonding in the former and η^3-Ph–Nd in the latter.

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Experimental Section

The compounds described here are extremely air- and moisture-sensitive and consequently all operations were carried out in an inert atmosphere (argon, nitrogen) environment. Handling methods and solvent purification were as described previously[12,14,38]. – IR data (4000–550 cm^{-1}) were obtained for Nujol mulls sandwiched between NaCl plates with a Perkin Elmer 1600 FTIR spectrometer. – Metal analyses were by EDTA titration with xylenol orange indicator and hexamine buffer of solutions prepared by digestion of accurately weighed samples in concentrated HNO_3/2% concentrated H_2SO_4 followed by dilution with water. – Microanalytical data (C, H, N) were determined by the Campbell Microanalytical Service, University of Otago, New Zealand. – Ytterbium metal powder was obtained from Rhône-Poulenc, Phoenix Plant, USA. It was produced by mechanical abraiding, and was sieved to ca. 35 mesh. It was supplied under argon, and has been stored in a drybox under argon or nitrogen since initial use. – 2,6-Diphenylphenol was obtained from Aldrich and was used without further purification. [Ln(Odpp)$_3$(thf)$_2$] (Ln = Nd, Yb) were prepared according to the literature procedure[10]. DME, pentane, and THF were freshly distilled from sodium/benzophenone prior to use.

Attempted Preparation of Yb(Odpp)$_2$: A mixture of ytterbium powder (0.50 g, 2.9 mmol), Hg(C_6F_5)$_2$ (1.55 g, 2.9 mmol), and 2,6-diphenylphenol (1.07 g, 4.35 mmol) was stirred in THF for 16 h and a yellow solution was obtained. Addition of further ytterbium powder (0.50 g, 2.9 mmol) to the reaction mixture resulted in no further colour change after prolonged stirring and yellow crystals of [Yb(Odpp)$_3$(THF)$_2$] were obtained.

Bis(2,6-diphenylphenolato)tris(tetrahydrofuran)ytterbium(II) (**1**): Ytterbium powder (0.52 g, 3.0 mmol) and mercury metal (0.20 g, 1.0 mmol) were added to a THF (30 ml) solution of Yb(Odpp)$_3$(THF)$_2$, prepared in situ from ytterbium powder (0.50 g, 2.9 mmol), Hg(C_6F_5)$_2$ (1.55 g, 2.9 mmol), and 2,6-diphenylphenol (1.07 g, 4.35 mmol)[10], and then rapidly stirred for three days. The reaction mixture was then filtered and the mother liquor reduced to 5 ml, followed by addition of *n*-pentane (20 ml). Deep red crystals of the title compound deposited from solution overnight, (yield 1.5 g, 79%). – IR: $\tilde{\nu}$ = 1596 w, 1581 w, 1554 w, 1495

Table 1. Crystal and refinement parameters

	$Yb(Odpp)_2(THF)_3$ (1)	$Yb(Odpp)_2(DME)_2$ (2)	$[Yb(Odpp)_3(DME)] \cdot (DME)_{0.5}$ (3)	$[Nd(Odpp)_3(DME)] \cdot (THF)$ (4)
formula	$C_{48}H_{50}O_5Yb$	$C_{44}H_{46}O_6Yb$	$C_{60}H_{54}O_6Yb$	$C_{62}H_{57}NdO_6$
mol. wt.	880.0	843.9	1044.1	1042.4
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a [Å]	19.403(6)	8.813(2)	13.443(2)	9.902(6)
b [Å]	11.516(5)	21.258(9)	17.389(3)	25.09(1)
c [Å]	9.465(7)	21.279(8)	22.567(4)	20.693(4)
α [deg]	82.10(6)	90	90	90
β [deg]	77.34(5)	109.32(3)	104.60(1)	95.93(4)
γ [deg]	83.04(3)	90	90	90
V [Å^3]	2035	3762	5105	5114
Z	2	4	4	4
D_c [g cm^{-3}]	1.44	1.49	1.36	1.35
$F(000)$	896	1712	2128	2148
μ [cm^{-1}]	22.3	25.3	18.8	10.7
crystal dim [mm]	0.30 × 0.10 × 0.40	0.12 × 0.32 × 0.50	0.52 × 0.42 × 0.21	0.38 × 0.17 × 0.27
$A^*_{min,max}$	1.24, 1.88	1.26, 1.88	1.76, 2.13	1.19, 1.32
N	5428	8620	8975	8982
No	3784	4316	5813	4697
R	0.060	0.037	0.040	0.047
R_w	0.064	0.038	0.047	0.042

[a] *In* **1**, high thermal motion on the THF ligands may be a foil for unresolved disorder, and is probably the principal cause of rather high residuals; in **4**, the population of the lattice THF was set at 1.0 after trial refinement.

w, 1412 m, 1295 m, 1247 w, 1172 w, 1086 w, 1069 w, 1030 s, 1010 w, 913 w, 857 m, 765 w, 750 s, 741 sh, 701 s, 608 w, 590 m cm^{-1}. – UV/Vis/near IR (THF): λ_{max} (ε, 1 mol^{-1} cm^{-1}), 410 (1800). – MS; *m/z* (%): 664 (0.1) [$^{174}Yb(ArO)_2^+$], 419 (4) [$^{174}Yb(ArO)^+$], 246 (100) [$ArOH^+$]. – $C_{48}H_{50}O_5Yb$ (880.0): calcd. C 65.5, H 5.7, Yb 19.7; found C 65.2, H 5.6, Yb 19.6%.

Bis(1,2-dimethoxyethane)bis(2,6-diphenylphenolato)-ytterbium(II) (**2**): (i) Crystallization of $Yb(Odpp)_2(THF)_3$ (**1**) from DME/THF/*n*-pentane (1:1:1) yielded dark red crystals of compound **2**. – IR: $\tilde{\nu}$ = 1596 w, 1579 w, 1552 w, 1491 w, 1415 m, 1300 s, 1280 w, 1251 m, 1192 w, 1172 w, 1112 m, 1074 s, 1026 m, 1010 m, 993 w, 939 w, 919 w, 872 m, 855 s, 764 s, 749 s, 711 m, 702 s, 627 w, 610 w, 596 m, 586 w cm^{-1}. – $C_{44}H_{46}O_6Yb$ (843.9): calcd. Yb, 20.5; found: Yb, 20.4%.

(ii) To the filtrate from the preparation of **1** was added DME (2 ml). After evaporation to 5 ml, *n*-pentane (5 ml) was added. Crystals of **2** deposited after 2 days.

1,2-Dimethoxyethanetris(2,6-diphenylphenolato)-ytterbium(III)–1,2-Dimethoxyethane(1/0.5) (**3**): (i) Crystallization of $[Yb(Odpp)_3(THF)_2]$ from DME yielded large crystals of the title compound. – IR: $\tilde{\nu}$ = 1595 m, 1582 w, 1494 m, 1407 s, 1306 m, 1285 s, 1264 s, 1190 w, 1156 w, 1098 m, 1070 m, 1052 s, 1010 w, 865 vs, 804 m, 756 s, 703 vs, 620 m, 606 m, 590 w cm^{-1}. – Satisfactory microanalyses could not be obtained, e.g. $C_{60}H_{54}O_6Yb$ (1044.1): calcd. C 69.0, H 5.2; found C 65.3, H 5.5%.

(ii) The mother liquor from preparation (ii) of **2** was evaporated to dryness, and the residue extracted with DME/pentane (1:1). Concentration to near dryness and standing for 2 days gave the title compound.

1,2-Dimethoxyethanetris(2,6-diphenylphenolato)neodymium(III)–Tetrahydrofuran(1/1) (**4**): Crystallization of $[Nd(Odpp)_3(THF)_2]$[10] from DME/THF yielded large blue crystals of the title compound. – IR: $\tilde{\nu}$ = 1595 m, 1406 s, 1308 w, 1281 s, 1264 s, 1086 m, 1070 m, 1057 s, 859 s, 804 w, 750 s, 702 s, 602 m cm^{-1}. – UV/Vis (toluene): λ_{max} = 482, 590, 716, 750 nm. – $C_{62}H_{57}NdO_6$ (1042.4): calcd. C 71.4, H 5.5, Nd, 13.8; found C 71.0, H 5.4, Nd 13.5%.

X-Ray Crystallography: Unique room-temperature diffractometer data sets were measured (2Θ/Θ scan mode, $2\Theta_{max}$ = 50°; monochromatic Mo-K_α radiation, λ = 0.7107(3) Å; $T \approx 298$ K) on capillary mounted specimens, N independent reflections, N_0 of these with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinements after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals on $|F|$, R, R_w [statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$], are quoted at convergence. Neutral atom complex scattering factors were employed, computation using the XTAL 3.2 program system implemented by S. R. Hall[39]. Pertinent results are given in the Figures and Tables; material deposited comprises atomic coordinates and thermal parameters, full non-hydrogen geometries and structure factor amplitudes. Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100237. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@chemcrys.cam.ac.uk].

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