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Homoleptic anionic aryloxolanthanoid(III) complexes

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Several anionic complexes of lanthanoid metals with the 2,6-diphenylphenolate ligand have been synthesized and their room-temperature single-crystal structures determined. In novel reactions of anhydrous $LnCl_3$ (Ln = Nd or Er) with $NaOC_6H_3Ph_2$-2,6·0.5thf (thf = tetrahydrofuran) in 1,3,5-tri-*tert*-butylbenzene at 300 °C, complexes of the type [Na{Ln($OC_6H_3Ph_2$-2,6$)_4$}] were obtained. Crystallisation of [Na{Nd($OC_6H_3Ph_2$-2,6$)_4$}] from bis(2-methoxyethyl) ether (diglyme) or 1,2-dimethoxyethane (dme) afforded the corresponding solvated complexes [Na(diglyme$)_2$][Nd($OC_6H_3Ph_2$-2,6$)_4$] or [Na(dme$)_3$][Nd($OC_6H_3Ph_2$-2,6$)_4$] respectively, and from an analogous reaction for Ln = Er [Na(diglyme$)_2$][Er($OC_6H_3Ph_2$-2,6$)_4$] was isolated. The complexes [Na(diglyme$)_2$]-[Ln($OC_6H_3Ph_2$-2,6$)_4$] (Ln = Nd or Er) are isomorphous. Their structures revealed novel discrete homoleptic tetrakis(aryloxo)lanthanoid(III) anions, well separated from the solvated sodium cations. Annealing the reaction mixture for the synthesis of [Na{Nd($OC_6H_3Ph_2$-2,6$)_4$}] at 120 °C gave single crystals of a monomeric bimetallic in which the sodium ion is encapsulated by three aryloxide oxygens as well as by three phenyl rings of the phenolate ligand, and neodymium is surrounded by a highly distorted tetrahedral arrangement of aryloxide oxygens. There are also intramolecular π-Ph−M (M = Na or Nd) interactions.

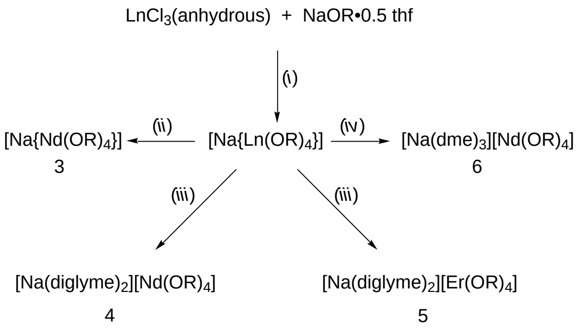
The use of sterically bulky ligands in preparing lanthanoid tris(aryloxides) and tris(alkoxides) provides examples of low-co-ordinate species,[1,2] metal-organic chemical vapour deposition precursors,[1a,e,3] and intra-[2f,g,4] and inter-molecular[4,5] π-bonded complexes. Similar approaches have been used for low-co-ordinate aryloxolanthanoid(II) species.[6] Such complexes, including solvent-free derivatives, are now well established[1] and are of considerable continuing interest. However, structurally characterised compounds containing low-co-ordinate, *homoleptic* anionic complexes of the type $[Ln(OR)_n]^{(3-n)-}$ (R = aryl or alkyl) are limited to [{K[Ln($OC_6H_3Pr^i_2$-2,6$)_4$]$\}_n$] **1** (Ln = La, Nd, Er or Lu),[7a–c] [{Cs_2[La($OC_6H_3Pr^i_2$-2,6$)_5$]$\}_n$] **2**[7d] and [Na{Nd($OC_6H_3Ph_2$-2,6$)_4$}] **3**,[7d] the latter being the topic of a preliminary communication of our current work. In each of these complexes the alkali-metal ion is involved in π-arene and oxygen bridging interactions with the anion, resulting in bimetallic complex structures of either one-dimensional chains (**1**, Ln = Nd, Er or Lu),[7a,b] two-dimensional sheets (**1**, Ln = La),[7c] an extended three-dimensional structure (**2**)[7d] or a monomer (**3**).[7d] These complexes reveal a common feature in lanthanoid chemistry, *viz.* the retention of an alkali-metal reagent from the metathesis synthetic pathway in the lanthanoid co-ordination sphere.

In this paper we report the synthesis and crystal structures of [Na(diglyme$)_2$][Nd($OC_6H_3Ph_2$-2,6$)_4$] **4** [diglyme = bis(2-methoxyethyl) ether], [Na(diglyme$)_2$][Er($OC_6H_3Ph_2$-2,6$)_4$] **5** and [Na(dme$)_3$][Nd($OC_6H_3Ph_2$-2,6$)_4$] **6** (dme = 1,2-dimethoxyethane). These have discrete homoleptic aryloxolanthanoid(III) anions with the alkali-metal cations separated fully from the lanthanoid co-ordination sphere. We also record a full account of the synthesis and crystal structure of the unsolvated [Na{Nd($OC_6H_3Ph_2$-2,6$)_4$}] **3**.

Results and Discussion

Syntheses

The key step in the synthesis of compounds **3**–**6** was a metathesis reaction between anhydrous lanthanoid trichlorides and sodium 2,6-diphenylphenolate at elevated temperature in 1,3,5-tri-*tert*-butylbenzene [Scheme 1, step (*i*)]. In the preparation of [Na{Nd($OC_6H_3Ph_2$-2,6$)_4$}] **3** subsequent annealing at 120 °C [Scheme 1, step (*ii*)] provided single crystals in a tri-*tert*-butylbenzene matrix, from which the compound was readily extracted. Similar syntheses followed by treatment of the reaction mixture with the tri- or bi-dentate co-ordinating solvents bis(2-methoxyethyl) ether and 1,2-dimethoxyethane afforded complexes **4**–**6** [Scheme 1, (*iii*)–(*v*)]. This approach has allowed us to isolate compounds in which the co-ordinating solvent successfully competes with co-ordination sites in the anions for complexation of the cation (see structural section). Previous compounds of this type were prepared in the unidentate co-ordinating solvent tetrahydrofuran (thf), or non-co-ordinating solvents such as toluene or pentane. In these complexes the anions evidently offer a more favourable co-ordinating environment for the cations.[7]



Scheme 1 R = $C_6H_3Ph_2$-2,6. (*i*) 1,3,5-Tri-*tert*-butylbenzene, 240–300 °C; (*ii*) annealing at 120 °C giving single crystals; (*iii*) recrystallisation from diglyme; (*iv*) recrystallisation from dme

Infrared and UV/VIS spectra of compounds **3**–**6** show features expected for the ligands and Nd^{3+} or Er^{3+} respectively. Compound **4** behaves as a 1 : 1 electrolyte in methylene chloride (see ref. 8 for characteristic values), implying that the compound exists as discrete cations and anions in solution.

Structures

The molecular structures of compounds **3**–**6** were determined by room-temperature single-crystal studies. Pertinent bond distances and angles are shown in Tables 1–3. The determination for compound **6** was of rather low precision due to a poor

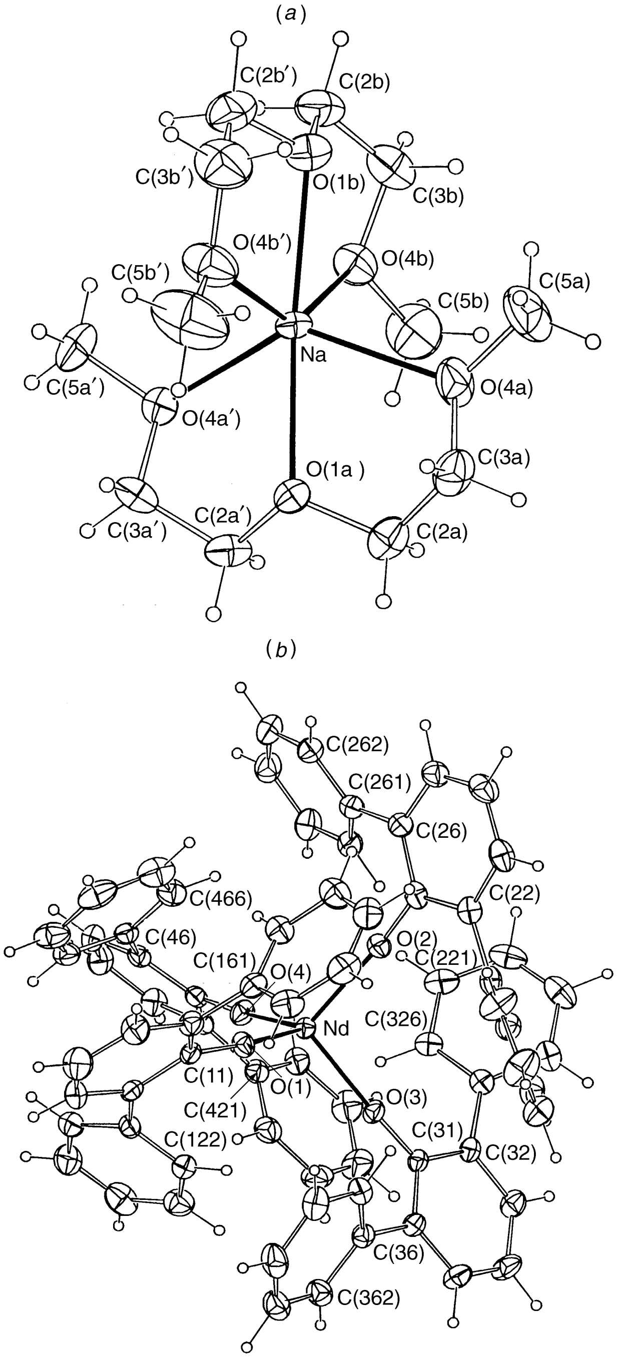


Fig. 1 Structure of $[Na(diglyme)_2][Nd(OC_6H_3Ph_2\text{-}2,6)_4]$ **4**. Compound **5** is isostructural. (*a*) The cation, (*b*) the anion

quality, poorly diffracting, decomposing specimen and the structure is not discussed in detail.

Discrete homoleptic anionic complexes. Compounds **4** and **5** are isostructural and crystallise in the triclinic space group $P\bar{1}$ with one formula unit in the asymmetric unit existing as discrete $[Na(diglyme)_2]^+$ cations and $[Ln(OC_6H_3Ph_2\text{-}2,6)_4]^-$ anions (Fig. 1). The determination for **6** likewise clearly indicated the presence of discrete $[Na(dme)_3]^+$ and $[Nd(OC_6H_3Ph_2\text{-}2,6)_4]^-$ ions. These are the first examples of low-co-ordinate, homoleptic aryloxolanthanoid(III) anions existing separate from their counter ions. The few previous examples of such complexes have structures where the cations are involved in *O*-co-ordination and/or π-arene intractions with the anion (Introduction).[7]

The anions found in compounds **4** and **5** have very similar structural features. In each case the metal exists in a slightly distorted tetrahedral environment of four phenolate ligands [Fig. 1(*b*), Table 1]. The Nd–O distances in **4** range from 2.175(4) to 2.207(4) Å. These are comparable with Nd–O in $[\{K[Nd(OR)_4]\}_n]$ (R = 2,6-$Pr^i_2C_6H_3$) (average = 2.21 Å),[7a,b] despite the presence of K–O–Nd bridging in the latter, and of $Nd–O_{ter}$ in $[Na\{Nd(OC_6H_3Ph_2\text{-}2,6)_4\}]$ **3** (2.20 Å) where the co-ordination number of Nd may be considered to be enhanced by π bonding of the aryl groups (below). The Nd–O distances are also similar to the $Nd–O(OC_6H_3Ph_2\text{-}2,6)$ distances of 2.160(2) to 2.233(3) Å in the four-co-ordinate $[Nd(OC_6H_3Ph_2\text{-}2,6)_3(thf)]$ and slightly longer than those in the three-co-ordinate $[Nd(OC_6H_3Ph_2\text{-}2,6)_3]$ [2.140(3)–2.193(5) Å], but again, in both these complexes, the formal co-ordination number of neodymium is higher due to neodymium–π-aryl interactions.[2g] They also lie between $\langle Nd–O_{ter}\rangle$ (2.122 Å) and $\langle Nd–O_{br}\rangle$ (2.211 Å) of $[\{Nd(OR)_3\}_2]$ (R = 2,6-$Pr^i_2C_6H_3$) where the formal co-ordination number of neodymium is six owing to η^6-Ph–Nd bridging.[5] The Nd–O distances are longer than the average terminal Nd–O distances (2.05–2.174 Å) found in alkoxide complexes $[Nd_2(OCHPr^i_2)_6(thf)_2]$,[9] $[Nd_2(OCHPr^i_2)_6(py)_2]$ (py = pyridine),[9] $[Nd_2(OCHPr^i_2)_6(\mu\text{-}dme)]$,[9] $[Nd_6(OPr^i)_{17}Cl]$,[10] $[Nd(OCBu^t_2CH_2PMe_2)_3]$,[11] $[Nd_5O(OPr^i)_{13}(HOPr^i)_2]$,[12] $[Nd_4(OCH_2Bu^t)_{12}]$[13] and $[Nd(OCBu^t_3)_3(MeCN)_2]$,[14] suggesting greater bulkiness of the $OC_6H_3Ph_2$-2,6 ligand *vis-à-vis* the alkoxides. The Er–O distances in compound **5** [2.068(6) to 2.090(6) Å] are shorter than the Nd–O distances in **4** to an extent reasonably consistent with the differences in ionic radii between Nd^{3+} and Er^{3+}.[15] They are also similar to those of $[\{K[Er(OR)_4]\}_n]$ (R = $C_6H_3Pr^i_2$-2,6) [2.053(6)–2.115(6) Å,[7b] where oxygen bridges K and Er, and of *five*-co-ordinate $[Er(OR)_3(thf)_2]$ (R = $C_6H_3Pr^i_2$-2,6) [2.07(1)–2.09(1) Å].[5a] It is noteworthy that in the homoleptic phenolato anionic complexes **4** and **5** there are no intramolecular Ln–C (aryl) contacts of any significance, by contrast with **3** (below) as well as **1** and **2**.[7]

The structures of the cations in compounds **4** and **5** reveal a discrete sodium ion six-co-ordinated by two diglyme molecules. The stereochemistry about the sodium centres is best described as a distorted trigonal prism (polyhedron fitting basis[16]) with O–Na–O angles ranging from 68.7(2) to 165.4(2)° for **4** and 68.4(3) to 167.9(3)° for **5**. This arrangement has been previously observed in $[Na(diglyme)_2][Lu(C_5H_5)_2(C_{14}H_{10})]$[17] ($C_{14}H_{10}{}^{2-}$ = anthracene dianion) and $[Na(diglyme)_2]_2[C_{20}H_{12}]$ ($C_{20}H_{12}{}^{2-}$ = perylene dianion),[18] where the O–Na–O angles range from 69.0(2) to 163.2(2) and from 68 to 157° respectively. The Na–O distances [2.337(5)–2.401(5) for **4**, 2.343(7)–2.406(8) Å for **5**] are similar to those in previous examples of $[Na(diglyme)_2]^+$ ions, where the average Na–O distance is 2.39 Å in $[Na(diglyme)_2]_2[C_{20}H_{12}]$,[18] 2.35 Å in $[Na(diglyme)_2][Mn_2(CO)_6(CF_3CNNNN)_3]$[19] and 2.40 Å in the foregoing lutetium complex.[17]

While complexes **4**–**6** are a new class of low-co-ordinate, homoleptic aryloxolanthanoid anions, and there are no analogous homoleptic anionic alkoxolanthanoid derivatives, it should be noted that two tetra(alkanethiolato)lanthanoid(III) anions have been structurally authenticated.[20] In addition, the water-soluble anionic lanthanoid catecholates $Na_5[Gd(C_6H_4O_2)_4]\cdot 19.2H_2O$ and $Na_6[Ln(C_6H_4O_2)_3]_2\cdot 20H_2O$ (Ln = Gd or Ho), can be regarded as high-co-ordinate homoleptic anionic aryloxolanthanoid complexes.[21] In these cases the highly negatively charged environment provided by the small bite chelating aryloxide ligands stabilises the complexes to hydrolysis, in dramatic contrast to the extreme water sensitivity of the present complexes. This contrast in properties is more striking since substraction of the ionic radius for seven- or eight-co-ordinate (as appropriate) Gd^{3+} from the Gd–O distances, gives *ca.* 1.34–1.38 Å, comparable with the range 1.31–1.35 Å for water-sensitive **4** and **5**, and both are larger than the range (1.26–1.28 Å) derived from Ln–OR distances of low-co-ordinate neutral lanthanoid aryloxides.[2f,g,h,22]

Table 1 Lanthanoid environments (distances in Å, angles in °)

(*a*) [Na{Nd($OC_6H_3Ph_2$-2,6)$_4$}] **3** [values for molecule 1 (**3a**) followed by those for molecule 2 (**3b**)]

O(11)–Nd	2.244(5)	O(11)–Nd–O(12)	81.8(2)
O(21)–Nd	2.278(4)	O(21)–Nd–O(22)	80.2(2)
O(12)–Nd	2.236(5)	O(11)–Nd–O(13)	88.1(2)
O(22)–Nd	2.257(5)	O(21)–Nd–O(23)	91.6(2)
O(13)–Nd	2.236(4)	O(12)–Nd–O(13)	87.8(2)
O(23)–Nd	2.199(6)	O(22)–Nd–O(23)	92.4(2)
O(14)–Nd	2.208(4)	O(11)–Nd–O(14)	125.7(2)
O(24)–Nd	2.181(6)	O(21)–Nd–O(24)	132.9(2)
C(1166)···Nd	[3.34(1)]*	O(12)–Nd–O(14)	122.5(2)
C(2166)–Nd	3.233(7)	O(22)–Nd–O(24)	126.3(2)
C(1222)–Nd	3.246(7)	O(13)–Nd–O(14)	134.9(1)
C(2222)–Nd	3.049(9)	O(23)–Nd–O(24)	120.9(2)
C(1462)–Nd	3.131(9)		
C(2462)–Nd	3.157(6)		

(*b*) [Na(diglyme)$_2$][Ln($OC_6H_3Ph_2$-2,6)$_4$] [Ln = Nd **4** or Er **5** (in square brackets)]

O(1)–Nd	2.175(4) [2.068(6)]	O(1)–Nd–O(2)	108.1(1) [109.0(2)]
O(2)–Nd	2.207(4) [2.090(6)]	O(1)–Nd–O(3)	113.6(1) [112.7(2)]
O(3)–Nd	2.176(4) [2.088(6)]	O(2)–Nd–O(3)	101.7(1) [102.9(2)]
O(4)–Nd	2.191(4) [2.080(6)]	O(1)–Nd–O(4)	111.7(1) [110.5(2)]
		O(2)–Nd–O(4)	115.4(1) [114.0(2)]
		O(3)–Nd–O(4)	106.0(1) [107.6(2)]

* Considered non-bonding.

[Na{Nd($OC_6H_3Ph_2$-2,6)$_4$}]. The crystal structure of [Na{Nd($OC_6H_3Ph_2$-2,6)$_4$}] **3** reveals two independent, but closely related monomeric molecules **3a**, **3b** (Fig. 2); **3a** was displayed in simpler form in the preliminary communication.[7d] Each neodymium is co-ordinated by the oxygens of one terminal [O(*n*4)] and three bridging [O(*n*1–*n*3)] (Nd–O–Na) ligands (*n* = 1 or 2) in a highly distorted tetrahedral array [O–Nd–O 80.2(2)–134.9(1)°], while the sodium is surrounded by three bridging oxygen and three phenyl groups, one from each of the bridging $OC_6H_3Ph_2$-2,6 ligands. The three encapsulating phenyl groups not only block association through intermolecular interactions, but also allow intramolecular π-Ph–Na interactions (below). This is in contrast to reported examples of $M_{3-n}[Ln(OR)_n]$ (R = 2,6-$Pr^i_2C_6H_3$) complexes, all of which have polymeric structures where the alkali-metal cations are involved in intermolecular *O*-co-ordination and/or π-arene interactions with the anions.[7] While the structures of the two independent molecules in **3** appear very similar, there are significant differences upon close inspection. The most notable is in the sodium environment. In **3a** the sodium is co-ordinated by three aryloxide oxygens at 2.343(6), 2.614(7) and 2.722(5) Å, whereas in **3b** there are two close contacts at 2.337(7) and 2.438(7) Å and a much longer Na···O separation of 3.183(6) Å. Bridging Na–O–Ln distances have been reported from 2.298(4) to 2.842(5) Å, though these incorporate μ-, μ_3- and μ_4-O binding.[23] In this context it is difficult to defend Na···O(23) [3.183(6) Å] as bonding, except from the viewpoint of the similar topology of **3a** and **3b** and the similarity of the NdO_4 environments. Other more subtle differences between these molecules emerge from consideration of the Na–π-Ph interactions.

Of the C···Na separations in molecules **3a** and **3b** respectively, five of the former [average 2.92; range 2.814(9) to 2.99(1) Å] and six of the latter [average 3.00; range 2.783(9)–3.11(1) Å] are considered Na–π-Ph interactions. These correspond closely to reported average Na–C distances (2.94 Å) for η^6-Ph–Na interactions in $(NaOC_6H_4Me\text{-}4)_n$,[23] Na–C(Ph) π bonding for the unsolvated (only π-Ph bonded) sodium of [{$Na_2(C_2Ph_4)(OEt_2)_2$}$_n$] (average 2.91 Å, upper limit 3.0–3.1 Å),[24] and Na–C (Ph) of Na($Ph_2CCHCPh_2$) (average 2.88 Å).[25] Thus, in **3a**, rings 12, 26 and 36 are η^1, η^2 and η^2 bonded, whereas in **3b** they are all η^2 bonded.

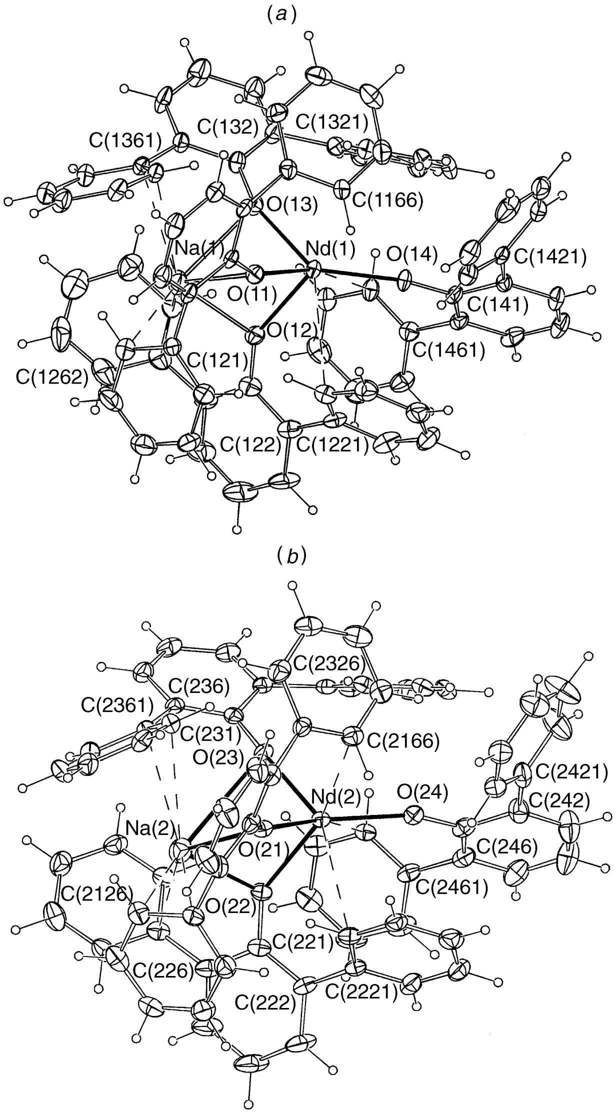


Fig. 2 Structure [Na{Nd($OC_6H_3Ph_2$-2,6)$_4$}] **3**, (*a*) molecule 1 (**3a**), (*b*) molecule 2 (**3b**). 20% Thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. The conformation of molecule 1 is portrayed in a more schematic form for simplicity in the preliminary communication[7d]

In molecule **3a**, the neodymium is contacted by four aryloxide oxygens at distances ranging from 2.208(4) to 2.244(5) Å and *two* aryl carbon atoms at 3.131(9) and 3.246(7) Å respectively. Intra- and inter-molecular C (Ph)–Nd distances in [{K[Nd(OR)$_4$]}$_n$] (R = $C_6H_3Pr^i_2$-2,6),[7a] [Nd($OC_6H_3Ph_2$-2,6)$_3$(thf)],[2g] [Nd($OC_6H_3Ph_2$-2,6)$_3$][2g] and [{Nd(OR)$_3$}$_2$][5a] (R = $C_6H_3Pr^i_2$-2,6) of 2.898(12)–3.183(10) Å are considered significant π-Ph–Nd interactions. (For a review of such interactions see ref. 4.) For **3b** the co-ordination sphere of the neodymium atom consists of four aryloxide oxygens [2.181(6)–2.278(4) Å] and *three* aryl carbon atoms [3.049(9)–3.233(7) Å]. The arrangement of the four aryloxide groups about the neodymium is distorted from tetrahedral owing to Na–O–Nd bridging of three oxygens and intervention of π-Ph–Nd interactions. Oxygen bridging between Nd and Na leads to small O_{br}–Nd–O_{br} angles and large O_{br}–Nd–O_{ter} angles [Table 1(*a*)]. π-Ph–Nd Interactions are accommodated within the large O–Nd–O angles. For molecule **3a**, Nd–O_{ter} [2.208(4) Å] is similar to Nd–O_{br} (average 2.239 Å), whereas for **3b** the difference may be significant [Nd–O_{ter} 2.181(6), Nd–O_{br} average 2.245 Å]. The Nd–O_{br} distances are

Table 2 Sodium environments (distances in Å, angles in °)

(*a*) [Na{Nd($OC_6H_3Ph_2$-2,6)$_4$}] **3** [values for molecule 1 (**3a**) followed by those for molecule 2 (**3b**)]

O(11)–Na	2.614(7)	C(1121) · · · Na	[3.290(1)]*	C(1266)–Na	2.92(1)	O(11)–Na–O(12)	72.3(2)
O(21)–Na	2.438(7)	C(2121)–Na	3.11(1)	C(2266)–Na	3.046(8)	O(21)–Na–O(22)	75.4(2)
O(12)–Na	2.343(6)	C(1126)–Na	2.929(9)	C(1361)–Na	2.955(8)	O(11)–Na–O(13)	71.4(2)
O(22)–Na	2.337(7)	C(2126)–Na	2.783(9)	C(2361)–Na	2.976(9)	O(21)–Na–O(23)	68.2(2)
O(13)–Na	2.722(5)	C(1261)–Na	2.99(1)	C(1362)–Na	2.814(9)	O(12)–Na–O(13)	75.1(2)
O(23) · · · Na	3.183(6)	C(2261)–Na	3.045(5)	C(2362)–Na	3.023(8)	O(22)–Na–O(23)	69.3(2)

(*b*) [Na(diglyme)$_2$][Ln($OC_6H_3Ph_2$-2,6)$_4$] [Ln = Nd **4** or Er **5** (in square brackets)]

O(1a)–Na	2.383(4) [2.342(7)]	O(1a)–Na–O(4a)	68.7(2) [71.3(3)]	O(1a)–Na–O(4b)	121.7(2) [121.4(3)]
O(4a)–Na	2.396(5) [2.379(9)]	O(4a)–Na–O(4a′)	132.4(2) [135.4(3)]	O(4a)–Na–O(4b)	92.7(2) [91.2(3)]
O(4a′)–Na	2.401(5) [2.381(8)]	O(4a′)–Na–O(1b)	122.0(2) [118.4(3)]	O(4a′)–Na–O(4b)	90.5(2) [89.4(3)]
O(1b)–Na	2.337(5) [2.401(8)]	O(1b)–Na–O(4b)	69.7(2) [68.4(3)]	O(1a)–Na–O(4b′)	99.5(2) [101.8(3)]
O(4b)–Na	2.366(5) [2.406(8)]	O(4b)–Na–O(4b′)	138.5(2) [136.4(3)]	O(4a)–Na–O(4b′)	108.2(2) [109.1(3)]
O(4b′)–Na	2.347(6) [2.368(9)]	O(1a)–Na–O(4a′)	69.4(2) [70.6(3)]	O(4a′)–Na–O(4b′)	100.0(2) [100.6(3)]
		O(1a)–Na–O(1b)	165.4(2) [167.9(3)]	O(1b)–Na–O(4b′)	70.7(2) [69.6(3)]
		O(4a)–Na–O(1b)	103.4(2) [103.1(3)]		

* Considered non-bonding.

Table 3 Parameters of $OC_6H_3Ph_2$-2,6 ligands: δ/Å is the deviation of the Ln atom from the central C_6 phenyl ring plane, τ° the Ln–O–C(1)–C(2) torsion, φ_2, φ_6/° the dihedral angles between the central ring C_6 plane and those of the peripheral phenyl ring planes and Σ_n° is the sum of the angles about the O(*n*) centre

	Complex			
Parameter	**3a**	**3b**	**4**	**5**
δ_1	0.17(2)	0.61(2)	0.59(1)	0.61(2)
δ_2	0.74(2)	0.38(2)	0.90(1)	0.79(2)
δ_3	0.16(2)	0.73(2)	0.14(1)	0.09(1)
δ_4	0.04(2)	0.23(2)	0.10(1)	0.09(2)
τ_1	−179.4(8)	−141.9(9)	38(1)	48(2)
τ_2	28(1)	18(1)	80(2)	75(3)
τ_3	6(2)	−43(2)	−14(8)	−53(9)
τ_4	173.7(6)	−173.1(8)	−177(2)	−167(3)
φ_{12}	78.8(3)	88.1(3)	45.8(2)	46.8(4)
φ_{16}	49.2(3)	58.2(3)	58.2(2)	58.8(4)
φ_{22}	42.2(3)	46.5(3)	49.0(2)	51.7(4)
φ_{26}	54.7(4)	49.3(3)	37.9(2)	38.1(4)
φ_{32}	49.7(3)	37.2(3)	49.3(2)	48.8(6)
φ_{36}	44.8(2)	44.0(3)	50.2(2)	50.2(3)
φ_{42}	50.6(3)	50.8(4)	50.8(2)	50.3(4)
φ_{46}	46.0(3)	45.3(3)	62.0(2)	62.6(4)
Ln–O(1)–C(1)	157.8(4)	152.9(5)	163.4(4)	162.1(6)
Ln–O(2)–C(2)	146.4(5)	144.8(6)	166.6(4)	166.1(6)
Ln–O(3)–C(3)	159.9(4)	167.7(4)	177.3(4)	176.2(5)
Ln–O(4)–C(4)	155.8(6)	154.3(4)	169.5(4)	171.3(6)
Na–O(1)–C(1)	109.1(4)	117.8(5)		
Na–O(2)–C(2)	123.2(4)	119.0(5)		
Na–O(3)–C(3)	118.2(4)	111.0(5)		
Nd–O(1)–Na	83.3(2)	88.8(2)		
Nd–O(2)–Na	90.2(2)	91.9(2)		
Nd–O(3)–Na	81.0(1)	73.2(2)		
Σ_1	$350._1$	$359._5$		
Σ_2	$359._6$	$355._8$		
Σ_3	$359._1$	$352._4$		

very similar to Nd–O_{br}(K) (average 2.211 Å) of [{K[Nd(OR)$_4$]}$_n$] (R = 2,6-$Pr^i_2C_6H_3$),[7a] whilst Nd–O_{ter} are similar to Nd–O [2.175(4)–2.207(4) Å] of **4**. Thus, the π-Ph–Nd interactions appear to have little effect on the Nd–O_{ter} distances. Likewise, in [{Nd(OR)$_3$}$_2$] (R = 2,6-$Pr^i_2C_6H_3$), where there is formal six-co-ordination for Nd because of η^6-Ph–Nd bridging, Nd–O_{br} (average 2.211 Å)[6] is similar to Nd–O_{br} (average 2.211 Å) of four-co-ordinate Nd in [{K[Nd(OR)$_4$]}$_n$][7a] whilst Nd–O_{ter} (average 2.122 Å) are shorter than Nd–O of the isolated four-co-ordinate [Nd($OC_6H_3Ph_2$-2,6)$_4$]$^-$ anion in **4**. However, π-Ph–Nd interactions (η^6, η^1) in [Nd($OC_6H_3Ph_2$-2,6)$_3$] do lengthen the Nd–O distances [2.140(3)–2.193(5) Å] beyond what would be expected for three-co-ordinate neodymium.

The angle sums at the bridging oxygen atoms are all above 350° (Table 3), which indicates substantial delocalisation of the oxygen lone pairs into the aromatic ring. Further, the C–O distances [1.327(8)–1.347(8) Å] are well below single bond C–O lengths (1.43 Å)[26] and shorter than in $HOC_6H_3Ph_2$-2,6 [1.381(4) Å].[27]

Experimental

2,6-Diphenylphenol was obtained from Aldrich Chemical Co., and anhydrous neodymium and erbium chlorides from Cerac Incorporated, Milwaukee, WI and were used without further purification. 1,2-Dimethoxyethane, diglyme, pentane and thf were freshly distilled from sodium–benzophenone prior to use. The lanthanoid complexes **3**–**6** are highly air- and moisture-sensitive and all preparations were conducted under an inert atmosphere (purified N_2 or Ar) involving conventional glove-box and Schlenk techniques. The compound $NaOC_6H_3Ph_2$-2,6·0.5thf was prepared by stirring $HOC_6H_3Ph_2$-2,6 (1.0 g, 4.06 mmol) and NaOH (1.5 g, 37.5 mmol) in thf (50 cm^3) for 10 h at room temperature, followed by filtration and evaporation to dryness. The product was then dissolved in toluene and evaporated to dryness, and the ratio of thf : $NaOC_6H_3Ph_2$-2,6 determined by ^{1}H NMR spectroscopy.

Preparations

[Na{Nd($OC_6H_3Ph_2$-2,6)$_4$}] 3. Anhydrous $NdCl_3$ (0.10 g, 0.40 mmol), $NaOC_6H_3Ph_2$-2,6·0.5thf (0.46 g, 1.60 mmol) and 1,3,5-tri-*tert*-butylbenzene (1.0 g, 4.05 mmol) were heated *in vacuo* in a sealed tube at 240 °C for 3 h, at 300 °C for 2 h, and then overnight at 120 °C, giving blue crystals of complex **3** in the $C_6H_3Bu^t_3$ matrix. The bulk solid was washed with pentane to remove $C_6H_3Bu^t_3$, and the residue extracted with toluene (3 × 10 cm^3), filtered and evaporated to dryness giving **3** (yield 92%) (Found: C, 75.5; H, 4.9; Nd, 12.35. $C_{72}H_{52}NaNdO_4$ requires C, 75.3; H, 4.55; Nd, 12.55%). Infrared (Nujol, $\tilde{\nu}$/cm^{-1}):

Table 4 Crystal and refinement parameters[a]

	$[Na\{Nd(OC_6H_3Ph_2\text{-}2,6)_4\}]$ **3**	$[Na(diglyme)_2][Nd(OC_6H_3Ph_2\text{-}2,6)_4]$ **4**	$[Na(diglyme)_2][Er(OC_6H_3Ph_2\text{-}2,6)_4]$ **5**
Formula	$C_{72}H_{52}NaNdO_4$	$C_{84}H_{80}NaNdO_{10}$	$C_{84}H_{80}ErNaO_{10}$
M	1148.4	1416.8	1439.8
Crystal symmetry	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	21.232(6)	18.760(2)	18.67(1)
b/Å	21.250(8)	15.192(5)	15.206(7)
c/Å	13.912(4)	12.749(3)	12.71(1)
α/°	81.32(3)	90.97(2)	91.03(5)
β/°	80.82(2)	90.20(2)	90.55(6)
γ/°	63.85(3)	92.51(2)	92.11(4)
U/Å^3	5539	3629	3604
Z	4	2	2
D_c/g cm^{-3}	1.38	1.30	1.33
F(000)	2348	1470	1486
μ/cm^{-1}	10.0	7.8	12.3
Crystal dimensions/mm	0.18 × 0.42 × 0.42	0.25 × 0.15 × 0.33	0.14 × 0.30 × 0.40
A^*_{min}, A^*_{max}	1.28, 1.48	1.12, 1.19	1.18, 1.36
N	19 462	12 505	12 634
N_o	9896	7822	7039
R	0.048	0.049	0.061
R'[b]	0.044	0.045	0.056

[a] $[Na(dme)_3][Nd(OC_6H_3Ph_2\text{-}2,6)_4]$ **6**: $C_{84}H_{82}NaNdO_{10}$, $M = 1418.8$, triclinic, space group $P\bar{1}$, $a = 30.26(2)$, $b = 17.13(1)$, $c = 16.99(2)$ Å, $\alpha = 61.57(8)$, $\beta = 73.80(3)$, $\gamma = 89.71(5)°$, $U = 7351$ Å^{-3}, D_c ($Z = 4$) = 1.28 g cm^{-3}; $\mu_{Mo} = 7.7$ cm^{-1}, specimen 0.25 × 0.25 × 0.20 mm, $2\theta_{max} = 45°$, $N = 19\,235$, $N_o = 4326$, $R = 0.10$, $R' = 0.09$. This is an inferior determination, recorded on a decomposing (*ca.* 20%) specimen, refined as pseudo-symmetric triclinic, which, with better material, may be found to be truly of higher symmetry. Anisotropic thermal parameters were refined for Na and Nd only, with non-hydrogen cation geometry constrained. There are two molecules in the asymmetric unit with one of the cations disposed about an inversion centre. This particular cation was modelled as disordered over two sites. [b] Statistical weights.

1594m, 1577m, 1405m, 1309m, 1282s, 1256s, 1070s, 854vs, 800m, 763m, 750vs, 705vs and 600s. UV/VIS (CH_2Cl_2), λ/nm (ε/l mol^{-1} cm^{-1}): 530 (83), 576 (84), 586 (84) and 748 (57).

$[Na(diglyme)_2][Nd(OC_6H_3Ph_2\text{-}2,6)_4]$ 4. Anhydrous $NdCl_3$ (0.10 g, 0.40 mmol) and $NaOC_6H_3Ph_2$-2,6·0.5thf (0.49 g, 1.60 mmol) were heated at 300 °C for 3 h in a sealed glass tube. After cooling to room temperature, the resulting blue solid was extracted with thf (20 cm^3) and filtered. The solvent diglyme (2 cm^3) and then pentane (10 cm^3) were added yielding a blue solid and a light blue solution from which single *crystals* of the complex grew over several days (total yield 93%) (Found: C, 70.8; H, 4.7; Nd, 9.75. $C_{84}H_{80}NaNdO_{10}$ requires C, 71.2; H, 5.7; Nd, 10.15%). Infrared (Nujol, $\tilde{\nu}$/cm^{-1}): 1596m, 1580m, 1496m, 1407s, 1288s, 1269m, 1244m, 1200s, 1161s (sh, br), 1135s (sh, br), 1111vs, 1081m, 862vs, 764m, 754m, 745vs, 701vs and 600s. UV/VIS (CH_2Cl_2): λ/nm (ε/l mol^{-1} cm^{-1}): 534 (77), 582 (78), 593 (68) and 751 (30). Λ_m(CH_2Cl_2): 22 S cm^2 mol^{-1} (5.31 × 10^{-3} mol dm^{-3}).

$[Na(diglyme)_2][Er(OC_6H_3Ph_2\text{-}2,6)_4]$ 5. Anhydrous $ErCl_3$ (0.11 g, 0.40 mmol) and $NaOC_6H_3Ph_2$-2,6·0.5thf (0.49 g, 1.60 mmol) and 1,3,5-tri-*tert*-butylbenzene (1.0 g, 4.05 mmol) were heated at 280 °C for 3 h in a sealed glass tube. After cooling to room temperature, the resulting pink solid was extracted with thf (20 cm^3) and filtered. The solvent diglyme (2 cm^3) and then pentane (10 cm^3) were then added yielding a pink solid and a light pink solution from which *crystals* of the complex were isolated (yield 89%) (Found: C, 69.8; H, 5.5; Er, 11.25. $C_{84}H_{80}ErNaO_{10}$ requires C, 70.1; H, 5.6; Er, 11.6%). Infrared (Nujol, $\tilde{\nu}$/cm^{-1}): 1598m, 1582w, 1497w, 1411s, 1352w, 1291s, 1272w, 1200s, 1109s, 1084m, 1026m, 870s, 754w, 747s, 701s and 607w.

$[Na(dme)_3][Nd(OC_6H_3Ph_2\text{-}2,6)_4]$ 6. Anhydrous $NdCl_3$ (0.10 g, 0.40 mmol), $NaOC_6H_3Ph_2$-2,6·0.5thf (0.49 g, 1.60 mmol) and 1,3,5-tri-*tert*-butylbenzene (1.0 g, 4.05 mmol) were heated *in vacuo* at 240 °C for 3 h, 300 °C for 2 h, then overnight at 120 °C, giving a blue solid in a matrix of 1,3,5-tri-*tert*-butylbenzene. After cooling to room temperature, the resulting blue $[Na\{Nd(OC_6H_3Ph_2\text{-}2,6)_4\}]$ was washed with pentane (3 × 5 cm^3) to remove 1,3,5-tri-*tert*-butylbenzene. Recrystallisation from dme–pentane gave blue *crystals* of the complex (Found: C, 70.85; H, 6.05; Nd, 10.1%. $C_{84}H_{82}NaNdO_{10}$ requires C, 71.1; H, 5.8; Nd, 10.15%). Infrared (Nujol, $\tilde{\nu}$/cm^{-1}): 1596w, 1578w, 1560w, 1407m, 1308w, 1287s, 1264s, 1248w, 1082s, 859s, 745s, 702m and 600w. UV/VIS (CH_2Cl_2), λ/nm (ε/l mol^{-1} cm^{-1}): 534 (38), 580 (39), 587 (40), 593 (39) and 749 (29).

Crystallography

Unique room-temperature diffractometer data sets were measured on an Enraf-Nonius CAD-4 diffractometer (2θ–θ scan mode, $2\theta_{max}$ 50°; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; $T \approx 298$ K) on capillary mounted specimens, yielding N independent reflections, N_o of which with $I > 3\sigma(I)$ were considered 'observed' and used in the large-block 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' are quoted at convergence. Neutral atom complex scattering factors were employed, computation using the XTAL 3.2 program system implemented by S. R. Hall.[28]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/393.

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