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The preparation and crystal structure of bis(cyclopentadienyl)(2,6-diphenylphenoxy)-bis(tetrahydrofuran)neodymium(III); an unexpected example of formal nine coordination

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Abstract

Reaction of NdCp_3 (Cp = cyclopentadienyl) with an equimolar amount of 2,6-diphenylphenol (HOdpp) in tetrahydrofuran (thf) yields the formally nine-coordinate $[\text{NdCp}_2(\text{Odpp})(\text{thf})_2]$. The crystal structure shows a distorted trigonal bipyramidal arrangement of oxygen donor atoms and cyclopentadienyl ring centroids, with the thf oxygens in the axial positions and a two-fold axis along the Nd–Odpp bond

Crystallization of bis(cyclopentadienyl)lanthanoid(III) complexes, LnCp_2X (X = halogen, hydrocarbyl, OR etc) from tetrahydrofuran (thf) usually gives pseudo-tetrahedral formally eight-coordinate complexes $\text{LnCp}_2\text{X}(\text{thf})$ [1–3]. We now report the synthesis and crystal structure of the formally nine-coordinate complex $[\text{NdCp}_2(\text{Odpp})(\text{thf})_2]$ (Odpp = 2,6- $\text{Ph}_2\text{C}_6\text{H}_3\text{O}$), where this coordination number is attained despite the presence of the bulky 2,6-diphenylphenoxy ligand. Previous crystal structures of $\text{LnCp}_2(\text{OR})$ (R = alkyl or aryl) derivatives or substituted cyclopentadienyl analogues, and their complexes with thf [4–8] reveal eight coordination of the lanthanoid, apart from the seven-coordinate $[\text{Sm}(\text{C}_5\text{Me}_5)_2(\text{OC}_6\text{HMe}_4-2,3,5,6)]$ [4].

Reaction of equimolar amounts of tris(cyclopentadienyl)neodymium(III) and 2,6-diphenylphenol in tetrahydrofuran for 16 h at room temperature was accompanied by a colour change from blue to red-blue. Filtration and evaporation to dryness gave a red-blue oil. Stirring with pentane gave a suspension of light blue powder, which was slightly soluble in this solvent, and residual oil. The suspension was decanted and the oil was treated a further three times with pentane followed by decantation. Evaporation of the suspensions gave a blue solid, which was dissolved in tetrahydrofuran. The solid obtained on evaporation contained some $\text{Nd}(\text{Odpp})_3$ [9] (MS identification). Further extraction with pentane, decantation, evaporation,

and crystallization from tetrahydrofuran gave air-sensitive $[\text{NdCp}_2(\text{Odpp})(\text{thf})_2]$ in 58% yield. Variable microanalyses were obtained (Found: C, 67.3, 62.95, ave, 65.1; H, 5.7, 5.0, ave, 5.35; $\text{C}_{36}\text{H}_{39}\text{NdO}_3$ Calcd.: C, 65.1; H, 5.9%). The mass spectrum showed a low intensity parent ion cluster with the correct isotope pattern for $\text{NdCp}_2(\text{Odpp})^+$, and features attributable to $\text{NdCp}(\text{Odpp})^+$, $\text{Nd}(\text{Odpp} - \text{H})^+$, NdCp_2^+ , and HOdpp^+ (base peak). Infrared spectroscopy provided no clear evidence for the presence of coordinated thf, but the characteristic ring stretching mode [10] at $900\text{--}800\text{ cm}^{-1}$ may be obscured by intense Odpp absorption [9] in this region. To fully identify the compound, an X-ray crystal structure was carried out.

Crystallography

Intensity data for 2547 reflections ($\theta_{\text{max}} 22.5^\circ$) were measured at room temperature on an Enraf–Nonius CAD4F diffractometer fitted with graphite monochromatized Mo-K_α radiation, $\lambda = 0.7107\text{ \AA}$ using the $\omega\text{--}2\theta$ scan technique. The unit cell was found to contain four molecules of the compound each situated about a crystallographic 2-fold axis of symmetry. The data were corrected for Lorentz and polarization effects but not for absorption. Crystal data: $[\text{C}_{36}\text{H}_{39}\text{NdO}_3]$, $M = 663.9$, orthorhombic, space group $Pbcn$, $a = 12.015(2)$, $b = 19.445(3)$, $c = 13.182(1)\text{ \AA}$, $V = 3079.7\text{ \AA}^3$, $D_c = 1.432\text{ g cm}^{-3}$, 1958 unique reflections and 1188 satisfied $I \geq 2.5\sigma(I)$. The structure was solved by the Patterson method and refined by a full-matrix least-squares procedure based on $F[11]$. The phenyl ring was refined as an hexagonal rigid group with individual isotropic thermal parameters; all remaining non-H atoms were refined anisotropically. Hydrogen atoms were included in the model at their calculated positions. After the inclusion of a weighting scheme of the form, $w = k/[\sigma^2(F) + g|F|^2]$, the refinement was continued until convergence; $R = 0.045$, $k = 1.76$, $g = 0.0008$, $R_w = 0.048$. The numbering scheme employed is shown in Fig. 1 drawn with ORTEP [12] at 15% probability ellipsoids. Selected bond lengths and angles are given with Fig. 1. A list of atomic coordinates, and a complete table of bond distances and angles is available from the Cambridge Crystallographic Data Centre.

X-Ray crystallography revealed monomeric, formally nine-coordinate, $[\text{NdCp}_2(\text{Odpp})(\text{thf})_2]$ (**1**) with, unexpectedly, two coordinated thf ligands (Fig. 1). The stereochemistry described by the three oxygen donor atoms and the centroids (Cp, Cp') of the cyclopentadienyl rings is distorted trigonal bipyramidal, and there is a two-fold axis along the Nd–Odpp bond (Nd–O(1)–C(6) linear—Fig. 1). The equatorial bond angles involving O(1), Cp, Cp' are close to 120° , and their sum is exactly 360° . Distortion from trigonal bipyramidal is most evident in the O(2)–Nd–O(2') angle of the axial donor atoms. Coordinated thf in ideal axial positions would be too close to Cp, hence the ether ligands are tilted away towards the Odpp group (Fig. 1). Resulting steric repulsion by the *ortho* phenyl groups is minimised by the linearity of Nd–O(1)–C(6).

By contrast with the present complex, $[\text{Sm}(\text{C}_5\text{Me}_5)_2(\text{OC}_6\text{HMe}_4\text{-}2,3,5,6)]$ (**2**) has been isolated from hexane as a seven-coordinate monomer [4]. Other crystallographically characterized $\text{LnCp}'_2(\text{OR})$ (Cp' = Cp, MeC_5H_4 , or C_5Me_5) complexes and their thf adducts are eight coordinate [5–8]. Thus, $[\text{Y}(\text{MeC}_5\text{H}_4)_2(\mu\text{-OCH}=\text{CH}_2)]_2$ (**3**) [5] and $[\text{LuCp}_2(\mu\text{-O}(\text{CH}_2)_4\text{PPh}_2)]_2$ (**4**) [8] are alkoxo-bridged dimers. The latter has uncoordinated diphenylphosphino groups. It is plausible that

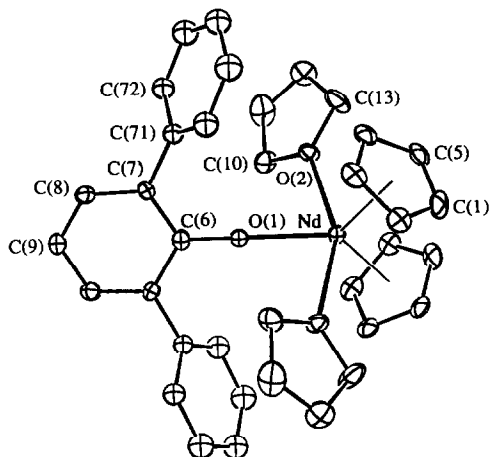


Fig. 1. Crystal structure of $[\text{NdCp}_2(\text{Odpp})(\text{thf})_2]$. Selected bond distances (\AA) and angles ($^\circ$) (Cp denotes the centroid of a cyclopentadienyl ligand): Nd–C(1) 2.82(1), Nd–C(2) 2.83(1), Nd–C(3) 2.81(1), Nd–C(4) 2.77(1), Nd–C(5) 2.76(1), $\langle \text{Nd–C}(1\text{--}5) \rangle$ 2.80, Nd–Cp 2.54(1), Nd–O(1) 2.239(8), Nd–O(2) 2.543(6), O(1)–Nd–O(2) 77.7(2), O(1)–Nd–Cp 121.4(4), O(2)–Nd–O(2') 155.5(3), O(2)–Nd–Cp 94.9(4), Cp–Nd–Cp' 117.2(5), Nd–O(1)–C(6) 180.

sublimable $\text{ErCp}_2(\text{OMe})$ and $\text{YbCp}_2(\text{OPh})$ [13] are also organo-oxo bridged dimers, as seven-coordinate monomers would be sterically unsaturated. Eight coordination in related thf complexes has been established in $[\text{Sm}(\text{C}_5\text{Me}_5)_2(\text{thf})_2](\mu\text{-O}_2\text{C}_{16}\text{H}_{10})$ ($\text{O}_2\text{C}_{16}\text{H}_{10}$ = dihydroindenoidene diolate) [6] and $\text{Sm}(\text{C}_5\text{Me}_5)_2[\text{O}(\text{CH}_2)_4\text{-C}_3\text{Me}_5](\text{thf}) \cdot (5)$ [7], and is also likely in $\text{Lu}(\text{C}_5\text{Me}_5)_2(\text{O}^t\text{Bu})(\text{thf}) (6)$ [14]. One consequence of the higher coordination number in **1** is that the centroid–Ln–centroid angle ($117.2(5)^\circ$) is much lower than values ($127\text{--}128^\circ$) for eight-coordinate **3** [5] and **4** [8], and is similar to angles ($117\text{--}119^\circ$) for ten-coordinate $\text{LnCp}_3(\text{py})$ (Ln = Sm or Nd) [15]. An increase in this angle for **1** would increase Cp : thf steric repulsion, which already leads to bending of O(2)–Nd–O(2') away from the Cp rings.

Subtraction of ionic radii for nine-coordinate neodymium and seven-coordinate samarium [16] for $\langle \text{Ln–C} \rangle$ of **1** and **2** gives 1.64 and 1.66 \AA , respectively, in good agreement with the effective ionic radius ($1.64 \pm 0.04 \text{\AA}$) of the cyclopentadienide ion [17]. Similar subtraction from the Ln–OAr bond lengths gives 1.08 and 1.11 \AA for **1** and **2** respectively. Thus, nine coordination in **1** does not appear to cause bond lengthening due to steric crowding above that in seven-coordinate **2**, despite the presence of a bulkier aryl oxide. This may support the view that C_5Me_5 groups have the dominant steric influence in **2** [4]. By contrast, subtraction of appropriate ionic radii [16] from $\langle \text{Ln–OAr} \rangle$ for a range of complexes with two or more bulky aryl oxide ligands, e.g. $\text{Yb}(\text{Odpp})_3(\text{thf})_2$, gives values of 1.25–1.30 \AA [9], indicative of considerable steric repulsion relative to **1** and **2**. Subtraction of the ionic radius for nine-coordinate Nd^{3+} from Nd–O(thf) gives 1.38 \AA , in reasonable agreement with the average value, 1.34(5) \AA for a series of lanthanoid-ether complexes [18] and

* The $\text{C}_5\text{Me}_5(\text{CH}_2)_4\text{O}^-$ ligand coordinates solely through oxygen [7].

much smaller than the value (1.50 Å) derived from $\langle \text{Yb}-\text{O}(\text{thf}) \rangle$ of $\text{Yb}(\text{Odpp})_3(\text{thf})_2$ [9].

Steric coordination numbers * for 1–6 are estimated to be 8.9 (maximum), 6.6, < 6.8, < 6.6, < 7.5 and 7.6 respectively, assuming 6 to be monomeric (see above). These values do not exceed the formal coordination numbers, confirming that the complexes are not highly crowded sterically. By contrast, five-coordinate $[\text{Yb}(\text{Odpp})_3(\text{thf})_2]$ has a steric coordination number approaching 10 [9].

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* This recently defined term, which provides an estimate of the steric demands of a ligand in terms of coordination site occupancy relative to chloride as 1.0, is based on the solid angle comprising the van der Waals radii of all atoms of the ligands [19]. The value for 2,6-diphenylphenoxide is considered [9] to approach that (2.4) for 2,6-di-*t*-butylphenoxide [19], whilst values for bridging $\text{CH}_2=\text{CHO}^-$ and $\text{Z}(\text{CH}_2)_4\text{O}^-$ ($\text{Z} = \text{PPh}_2$ or C_5Me_5) should be significantly less than that (1.28) [19] for terminal $^- \text{OPh}$.