

Synthesis and structure of a new organolanthanide oxide complex, $(\text{CH}_3\text{C}_5\text{H}_4)_3\text{Yb}_4(\mu\text{-Cl})_6(\mu_3\text{-Cl})(\mu_4\text{-O})(\text{THF})_3$

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Abstract

Reaction of NaCp' ($\text{Cp}' = \text{C}_5\text{H}_4\text{CH}_3$) with YbCl_3 and YbOCl in THF results in the formation of a new complex, $\text{Cp}'_3\text{Yb}_4(\mu\text{-Cl})_6(\mu_3\text{-Cl})(\mu_4\text{-O})(\text{THF})_3$ (**1**). The X-ray crystal structure of **1** reveals an oxygen-centred tetrahedral arrangement of ytterbium atoms which has $\mu\text{-Cl}$ groups bridging each edge and a $\mu_3\text{-Cl}$ ligand over the triangular face composed of Yb atoms with Cp' groups.

Keywords: Ytterbium

1. Introduction

One of the most important aspects of the organometallic chemistry of yttrium and lanthanides, which indicates the general behaviour of these metals, is their strongly oxophilic character. The formation of oxide ligands in yttrium and lanthanides reactions has frequently been observed [1–14]. An extensive chemistry has been developed for polynuclear cyclopentadienyl oxide complexes of yttrium and lanthanides in which oxygen acts as a multiple bridging ligand and various structural dispositions have been observed.

Oxidation of low-valent cyclopentadienyllanthanide complexes was the first defined preparative method for biscyclopentadienyl oxo derivatives [1,2]. However, most of the other cyclopentadienyl oxo derivatives of yttrium and lanthanides known so far are incidentally obtained and the origin of the oxide ligands is often ill-defined [3–12]. Adventitious water or the alkoxide ligand is sometimes discussed as the source of oxides [3–5,9–12]. Since the organometallic oxide complexes of yttrium and lanthanides may exploit an unusual chemistry [1–11], we were interested in developing a

method for their synthesis with the features higher yield, higher in product purity, simpler manipulations and more distinct mechanism of formation. We report here the synthesis and structure of a new organolanthanide oxide complex, $\text{Cp}'_3\text{Yb}_4(\mu\text{-Cl})_6(\mu_3\text{-Cl})(\mu_4\text{-O})(\text{THF})_3$.

2. Experimental and results

Anhydrous YbCl_3 (10 mmol) and YbOCl (2.0 mmol) were dissolved in THF (60 ml). Addition of $\text{Cp}'\text{Na}$ (5.0 mmol) to this suspension caused immediate formation of a red–brown solution. After stirring for 48 h at room temperature, the reaction mixture was centrifuged to remove the precipitate. The solution was concentrated to ca. 15 ml by reducing the pressure and then slowly cooled to ca. -20°C for 48 h to produce the pale-red crystalline $\text{YbCl}_3(\text{THF})_3$ (**2**) (5% yield based on Yb). The mother liquor was again concentrated to ca. 10 ml by reducing the pressure and cooled to ca. -40°C . A mixture containing primarily red crystals of $\text{Cp}'_3\text{Yb}_4(\mu\text{-Cl})_6(\mu_3\text{-Cl})(\mu_4\text{-O})(\text{THF})_3$ (**1**) (40% yield based on Cp' group) and a small amount of **2** (total yield 6%) was obtained. These were separated by picking large crystals, and the pure compounds were used for characteri-

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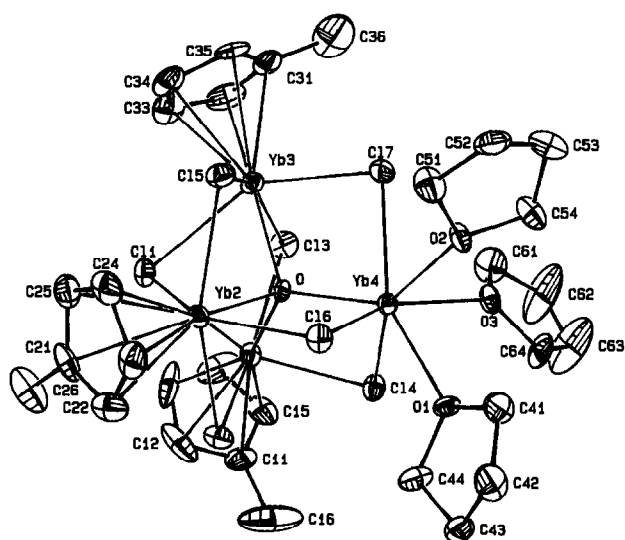


Fig. 1. Molecular structure of $\text{Cp}'_3\text{Yb}_4(\mu\text{-Cl})_6(\mu_3\text{-Cl})(\mu_4\text{-O})(\text{THF})_3$. Selected bond lengths (Å) and angles ($^\circ$): Yb(1)–O 2.28(1), Yb(2)–O 2.28(1), Yb(3)–O 2.29(1), Yb(4)–O 2.13(1), Yb(1)–Cl(1) 2.81(1), Yb(2)–Cl(1) 2.81(1), Yb(3)–Cl(1) 2.79(1), (Yb(4)–Cl) $_{\text{av}}$ 2.70(1), (Yb–C(ring)) $_{\text{av}}$ 2.59(2), (Yb–O(THF)) $_{\text{av}}$ 2.38(1), Yb(1)–Yb(2) 3.57(1), Yb(1)–Yb(3) 3.57(1), Yb(2)–Yb(3) 3.57(1), Yb(1)–Yb(4) 3.73(1), Yb(2)–Yb(4) 3.73(1), Yb(3)–Yb(4) 3.74(1), Yb(1)–O–Yb(2) 103.1(3), Yb(1)–O–Yb(3) 102.5(3), Yb(1)–O–Yb(4) 115.2(4), Yb(2)–O–Yb(3) 102.9(3), Yb(2)–O–Yb(4) 115.6(3), Yb(3)–O–Yb(4) 115.7(4), O(1)–Yb(4)–O(2) 85.0(3), O(1)–Yb(4)–O(3) 79.5(3), O(2)–Yb(4)–O(3) 81.0(3).

zation purposes. The complexes **1** and **2** have been characterized by elemental analysis, IR and MS spectra [15] and X-ray crystallography [16].

The structure of **1**, shown in Fig. 1, is an interesting variation of the structures of the polymetallic cyclopentadienyl oxo complexes of yttrium and lanthanides characterized previously [3–8]. The four Yb centres form a distorted tetrahedron, connected by six $\mu\text{-Cl}$ ligands along each of the edges of the tetrahedron, a $\mu_3\text{-Cl}$ ligand over the triangular face and an internal $\mu_4\text{-O}$. The oxygen ligand is closer to the Yb(4) atom. The $\mu_3\text{-Cl}$ ligand caps the face of the triangle plane of Yb(1)–Yb(3) and extends away from the apical Yb(4) with a distance of 1.9 Å. The four Yb atoms are located in two different coordinate environments. Atoms Yb(1), Yb(2) Yb(3) are coordinated by one bridging oxygen atom, four bridging chlorine atoms and Cp' group, respectively, to form a distorted octahedral geometry, while Yb(4) is coordinated by one bridging oxygen atom, three bridging chlorine atoms and three tetrahydrofuran ligands. The molecule has a threefold rotation axis such that the three ytterbium atoms at the base of the tetrahedron are crystallographically equivalent, as are the three THF ligands. The overall structure of **1** resembles that of $\text{YCl}_3(\text{THF})_3\text{Y}_3(\text{OR})_7\text{O}$ [12].

The average Yb–C(ring) distance of 2.59(2) Å in **1** is in good agreement with that found in $[\text{Cp}'_2\text{YbCl}]_3$ (2.58 Å) [17], but is slightly shorter than those observed in the

related compounds $[\text{Cp}'_2\text{Yb}(\text{THF})_2\text{O}]_2$ (2.66 Å) [9], $\text{Cp}'_3\text{Yb}$ (2.64 Å) [18] and $\text{CpYbCl}_2(\text{THF})_3$ (2.64 Å) [19]. This result may be understood by a decrease in the intraligand repulsions since the Cp' groups are at apexes of the tetrahedron and are far from each other.

In **1** the triple bridging Yb–Cl distances of 2.79(4)–2.81(4) Å are longer than the doubly bridging Yb–Cl lengths of 2.60(4)–2.71(4) Å. The Cp' Yb units have longer bridging Yb–O distances than the $\text{Yb}(\text{THF})_3$ part; however, in the latter the Yb–Cl distances (average 2.69 Å) are longer than the analogous distances (average 2.61 Å) in the former.

The Yb–O($\mu_4\text{-oxide}$) distances of 2.13(1)–2.29(1) Å are longer than that observed for the $\mu\text{-oxide}$ group in $[\text{Cp}'_2\text{Yb}(\text{THF})_2\text{O}]_2$ [9], 2.02(1) Å. They are comparable to the range of values found for Y–O($\mu_4\text{-oxide}$) distances in $[\text{Y}_7(\mu_3\text{-OCMe}_3)_2(\mu_3\text{-Cl})(\mu_4\text{-O})(\mu\text{-OCMe}_3)_7(\text{OCMe}_3)_5(\mu\text{-Cl})_4(\text{THF})_2]_2$ [20], 2.13(2)–2.37(2) Å. However, the Yb(4)–O($\mu_4\text{-oxide}$) distance is still shorter than those found in $[\text{Li}(\text{DME})_3]_2[\text{Cp}'_4\text{Nd}_4(\mu\text{-CH}_3)_2(\mu\text{-Cl})_6(\mu_4\text{-O})]$ [6] and $[\text{Li}(\text{THF})_4]_2[\text{Cp}'_4\text{Nd}_4\text{Cl}_6(\mu\text{-Cl})_2(\mu_4\text{-O})]$ [7], even after the difference in the ionic radii is considered, and is even shorter than the Yb–O distances of $\mu_3\text{-oxide}$ and $\mu_5\text{-oxide}$ groups [8,11]. The Yb–O(THF) distances of 2.35–2.40 Å in **1** fall within the range of values observed in $\text{CpYbCl}_2(\text{THF})_3$ (2.34–2.42 Å) [19], but are longer than those in $\text{YbCl}_3(\text{THF})_3$ (2.25–2.34 Å) [21]. Interestingly, either the differences between Yb–O(THF) bond lengths or the differences between O(THF)–Yb–O(THF) bond angles in **1** are all much smaller than those observed in the other three-THF coordinated complexes [19,21] owing to the rigid tetrahedron structure, which causes the steric crowding of the three THF ligands to be similar.

The title compound is also obtained from the reaction of $\text{Cp}'_3\text{Yb}$ and YbCl_3 and YbOCl , but the reaction rate is slow. Attempts to synthesize Cp analogues by the above methods were unsuccessful.

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- [15] Elemental analysis and spectroscopic data. For **1**: m.p. 70–72 °C. Found: C, 25.18; H, 3.07; Yb, 48.87. Calcd. for $C_{30}H_{45}O_4Cl_7Yb_4$: C, 25.56; H, 3.22; Yb, 49.09%. IR (KBr, cm^{-1}): 2923s, 1622m, 1463s, 1379s, 1076m, 888m, 722m, 615m, 481m, 217m. MS (EI): m/z 72 (THF, 5%), 79 (Cp', 38%). For **2**: found: C, 29.00; H, 4.73; Yb, 35.12. Calcd. for $YbCl_3(THF)_3$: C, 29.08; H, 4.88; Yb, 34.90%.
- [16] Crystal data for $(MeCp)_3Yb_4OCl_7(THF)_3$: $M_r = 1410.01$, monoclinic, $P2_1/n$, $a = 11.760(6)$, $b = 18.421(5)$, $c = 18.508(3)$ Å, $\beta = 100.97(3)^\circ$, $V = 3936(2)$ Å³, $Z = 4$, $D_c = 2.38$ g cm⁻⁵, $F(000) = 2624$, $\mu = 99.06$ cm⁻¹. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 296 K, using graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å), $\omega - 2\theta$ scan mode; 7518 reflections were measured in the range $2 \leq 2\theta \leq 49.9^\circ$, 4590 unique reflections, 4351 of which with $I > 3\sigma(I)$ were used for refinement. Intensities were corrected for Lorentz polarization effects and empirical absorption. The structure was solved by direct methods using the program TEXSAN and Fourier techniques, refined on F , 406 parameters. $R = 0.040$, $R_w = 0.045$ for $w = 1/\delta^2(|F_o|)$. Final difference maps showed no peaks higher than 1.54 or less than -1.31 e Å⁻³, all Δ/δ values < 0.18 . The H atoms were placed at calculated positions 0.95 Å from the bonded C atom. All the calculations were performed on a MICRO VAX 3100 computer. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. The crystal structure of **2** was described previously in [21].
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