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Synthesis, thermal stability and X-ray crystal structure of the bis(cyclopentadienyl)ytterbium naphthoxide derivative (C_5H_5)₂Yb(OC₁₀H₇)(THF)

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Abstract

Cp₃Yb (Cp = C₅H₅) reacts with α -naphthol (HNP) in THF to form Cp₂Yb(NP)(THF) (1), which crystallizes in the space group $P2_1/n$ with unit cell dimensions $a = 8.084(2)$, $b = 15.996(6)$, $c = 15.973(7)$ Å, $\beta = 98.95(3)^\circ$, $V = 2040.3$ Å³ and $D_{\text{calc.}} = 1.69$ g cm⁻³ for $Z = 4$. Least-squares refinement based on 2242 observed reflections converged to a final R value of 0.081. The average Yb–C(Cp) distance is 2.60(2) Å and Yb–O(THF) and Yb–O(NP) distances are 2.30(1) and 2.06(1) Å, respectively. The title compound loses the coordinated THF molecule readily by heating under vacuum to give dimeric [Cp₂Yb(NP)]₂ (2), which undergoes disproportionation to give Cp₃Yb and Yb(NP)₃ on heating above 230°C.

Introduction

The chemistry of organolanthanide alkoxide complexes has been of interest for many years. Despite many synthetic studies [1–6], relatively little is known of the reactivity of these complexes. Recently, we have reported studies on the thermal stability of unsolvated organolanthanide alkoxides [6–8] and found that they are thermally unstable and tend to disproportionate at moderately high temperatures. In continuation of our previous studies, we report here the synthesis, thermal

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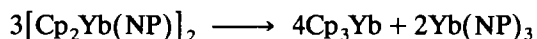
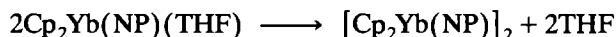
stability and crystallographic characterization of a monomeric, solvated bis(cyclopentadienyl)ytterbium α -naphthoxide derivative, $\text{Cp}_2\text{Yb}(\text{NP})(\text{THF})$.

Results and discussion

The very versatile method of liberating cyclopentadiene from a Cp_3Ln moiety by the action of protonic acid stronger than C_5H_6 was adopted [3,6,8]. $\text{Cp}_2\text{Yb}(\text{NP})(\text{THF})$ (**1**) was prepared by reaction of Cp_3Yb with α -naphthol (HNP) in THF at room temperature. Thermolysis of **1** gave $[\text{Cp}_2\text{Yb}(\text{NP})]_2$ (**2**).

The IR spectra of **1** and **2** contain the bands interpretable primarily in terms of coordinated cyclopentadienyl and the α -naphthoxide group. Comparison of the IR spectra of **1** and **2** shows that the $\nu(\text{Yb}-\text{O}(\text{NP}))$ vibration in **1** occurs at 393 cm^{-1} [9], while in **2** this vibration is shifted to a lower wave number at 380 cm^{-1} . This shift may show that the $\text{Yb}-\text{O}(\text{NP})$ bond order decreases going from nonbridging to bridging. In addition, the IR spectra also exhibit the characteristic absorption peaks for coordinated THF at 1065 and 915 cm^{-1} in **1**, which are absent in **2**.

For the purpose of studying the thermal stability of **1** and **2**, their mass spectra were recorded at different vaporization temperatures and the main peaks are reported in the Experimental section. It is interesting to note that when the vaporization temperature of a sample is below 120°C , the feature of fragment peaks for **1** is only to lose the coordinated THF molecule. In the spectra of **2**, however, no fragment peak is observed. When the vaporization temperature reaches 200°C , both the spectra of **1** and **2** exhibit fragment peaks corresponding to $[\text{Cp}_2\text{Yb}(\text{NP})]_2$. When the vaporization temperature exceeds 230°C , not only are the fragment peaks of $[\text{Cp}_2\text{Yb}(\text{NP})]_2^+$ observed in both spectra, but the peaks corresponding to $[\text{Cp}_3\text{Yb}]^+$ and its fragments are also observed. On raising the vaporization temperature further, the fragment peaks of $[\text{Cp}_2\text{Yb}(\text{NP})]_2^+$ gradually reduce and the intensity of the peaks which are characteristic of $[\text{Cp}_3\text{Yb}]^+$ is obviously enhanced. Thus, based on the above results, we deduce that complexes **1** and **2** may undergo the following rearrangement reactions during the course of raising the temperature [6–8]:



These reactions have been confirmed by sublimating the samples of **1** and **2**. We found that when **1** was heated to about 120°C under vacuum for 2 h, a THF-free product analyzed as $[\text{Cp}_2\text{Yb}(\text{NP})]_2$ (**2**), was obtained. By increasing the sublimation temperature (230°C), a dark-green sublimate and a grey residue were obtained. The sublimate was identified as Cp_3Yb by elemental and spectroscopic analysis and the residue as $\text{Yb}(\text{NP})_3$. Similarly, when complex **2** was sublimed, just the same sublimate and residue were obtained. Moreover, the reversibility of the above two reactions was also verified by the fact that $[\text{Cp}_2\text{Yb}(\text{NP})]_2$ could be formed by reaction of $\text{Yb}(\text{NP})_3$ with two equivalents of Cp_3Yb .

The molecular structure of $\text{Cp}_2\text{Yb}(\text{NP})(\text{THF})$ is shown in Fig. 1. Selected bond lengths and angles are listed in Tables 1 and 2. The molecule crystallizes in monomeric units. The ytterbium ion is coordinated in a distorted tetrahedral geometry by two cyclopentadienyl ring centroids and two oxygen atoms, one from

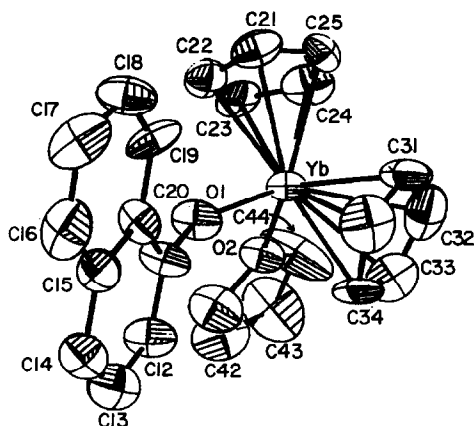


Fig. 1. The structure of $(C_5H_5)_2Yb(NP)(THF)$.

Table 1

Selected bond distances (Å)

Yb–O(1)	2.06(1)	Yb–O(2)	2.30(1)
Yb–C(21)	2.58(2)	Yb–C(22)	2.60(2)
Yb–C(23)	2.64(2)	Yb–C(24)	2.64(2)
Yb–C(25)	2.60(2)	Yb–C(31)	2.50(2)
Yb–C(32)	2.61(2)	Yb–C(33)	2.60(2)
Yb–C(34)	2.62(2)	Yb–C(35)	2.59(2)
O(1)–C(11)	1.31(2)	[Yb–C(Cp)] _{av.}	2.60(2)
Yb–Cent1 ^a	2.33	Yb–Cent2	2.30

^a Cent = cyclopentadienyl ring centroid.

the THF molecule and another from the naphthoxide group. The average Yb–C(Cp) distance of 2.60(2) Å is comparable to those usually found in related compounds, $Cp_2Yb(CH_3)(THF)$ (3) [10], 2.60(2) Å; $[Cp_2YbOCH_2CH=CH_2]_2$ (4) [11], 2.60(2) Å, and $[Cp_2YbOCH_2CH_2CH_3]_2$ (5) [11], 2.60(2) Å. The Yb–O(THF) distance of 2.31(2) Å is similar to the analogous ytterbium–oxygen (THF) distance in 3, 2.31(1) Å. The Yb–O(NP) distance of 2.06(1) Å is similar to the distances of the terminal Ln–O bonds found in *cis*- and *trans*- $[(C_5Me_5)_2Sm(OPPh_3)]_2$ (OCH=CHO) [12], 2.16(1) and 2.12(1) Å; $(C_5Me_5)_2Sm(OC_6HMe_4-2,3,5,6)$ (6) [1], 2.13(1) Å, when the difference in the metallic radii is considered [13], but is shorter than the known Yb–O distances in dimeric $[Cp_2YbOR]_2$ [11], in which the oxygen atoms are in bridging positions. This shortening of 0.128–0.145 Å is quite normal

Table 2

Selected bond angles (°)

Yb–O(1)–C(11)	150(1)	O(1)–Yb–O(2)	90(1)
Cent1–Yb–Cent2	131	Cent1–Yb–O(1)	110
Cent1–Yb–O(2)	103	Cent2–Yb–O(1)	106
Cent2–Yb–O(2)	106		

going from bridging to nonbridging and is in the range observed for organolanthanide alkyl (0.12–0.25 Å) [10] and chloride complexes (0.04–0.27 Å) [14].

Taking into account that the radii of Yb^{3+} is 0.106 Å less than that of Sm^{3+} [13], the Yb–O(NP) distance in **1** is longer than the analogous distance in $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{OC}_4\text{H}_8\text{C}_5\text{Me}_5)(\text{THF})$ (**7**) [4], 2.08(1) Å. Evidently, this difference results from the fact that the steric bulk of $\text{O}(\text{CH}_2)_4\text{C}_5\text{Me}_5$ in **7** is not so large at the oxygen atom coordinated to ytterbium as to cause Sm– $\text{O}(\text{CH}_2)_4\text{C}_5\text{Me}_5$ to decrease. In contrast, the shorter Yb–O(THF) distance compared to the analogous distance in **7**, 2.49(1) Å, can be explained by unfavourable THF– C_5R_5 (R = H, Me) interaction, which would be diminished along with diminution of the size of R.

It is interesting that **4** and **5** are reported to be stable up to about 280°C [11], whereas the α -naphthoxide analogue $[\text{Cp}_2\text{Yb}(\text{NP})]_2$ thermally decomposes to Cp_3Yb and $\text{Yb}(\text{NP})_3$ at 230°C. Furthermore, a similar divergence exists in solvent effects: the former crystallized from THF solvent-free and appeared to have bridged structures, the latter crystallized from THF to give solvated complex **1**. Since the main difference between these complexes is the size of ligands, these results suggest that there can be considerable variation in structure and stability due to small changes in steric crowding. In other words, by varying the size of R, a $[\text{Cp}_2\text{LnOR}]_2$ system can be changed from steric unsaturation to steric saturation, and to steric oversaturation with changes in structure and stability. The size of the α -naphthoxide group is larger than that of the propoxide or allyloxide ligand; this difference in size leads **2** to be more sterically crowded and to decompose more readily. Moreover, it also enhances a bridged cleavage of **2** leading to $\text{Cp}_2\text{Yb}(\text{NP})(\text{THF})$, in which steric crowding around the metal center can be minimized. Consistent with this, the absence of a dimeric structure for **6** can be attributed to the steric effect of the bulky pentamethylcyclopentadienyl and 2,3,5,6-tetramethylphenoxy group which might present attack at Sm^{3+} by the bridged phenoxide oxygen atom.

Although the size of 8-quinolinolate is similar to that of α -naphthoxide, the unsolvated biscyclopentadienyl ytterbium 8-quinolinolate complex is reported to be a monomeric structure and to be thermally stable below 250°C [6], presumably because an intramolecular coordination from the nitrogen atom should satisfy the demand of coordination saturation of ytterbium instead of bridged aryloxide. Moreover, this intramolecular coordination is then favourable to minimize steric crowding. All the results discussed clearly demonstrate the importance of steric crowding in the organolanthanide structure and stability.

Experimental

The complexes described below are extremely air- and moisture-sensitive. Therefore, both the syntheses and subsequent manipulation of these compounds were conducted under purified argon with rigorous exclusion of air and water by using Schlenk and glovebox techniques. All solvents were refluxed and distilled over finely divided LiAlH_4 or sodium benzophenone ketyl immediately before use. YbCl_3 [15] and Cp_3Yb [16] were prepared according to the literature methods. Infrared spectra were obtained on a PE 983G spectrometer. Samples were prepared as Nujol and Fluoroluble mulls between CsI plates. Mass spectra were recorded on a MAT 312 mass spectrometer operating in EI mode. The sample was

protected under argon and introduced by direct inlet techniques with a source temperature of 150°C and sample evaporation temperature in the range of 50–350°C. Melting points were determined in sealed capillaries filled with argon and not corrected. Elemental analyses for carbon and hydrogen were performed on a PE 2400 analyzer. Metal analyses for lanthanides were accomplished using the literature method [17]. The molecular weights were determined cryoscopically in toluene.

Preparation of Cp₂Yb(NP)(THF) (1)

A solution of HNP (0.216 g, 1.5 mmol) in 20 ml of THF was added dropwise to a stirred solution of Cp₃Yb (0.552 g, 1.5 mmol) in 30 ml of THF at room temperature. The colour of the solution slowly changed from dark-green to orange-red. After stirring for 48 h, the reaction solution was concentrated under reduced pressure to *ca.* 10 ml and n-hexane (40 ml) was added. The resulting mixture was centrifuged and the solution was decanted. The resultant orange-yellow solid was redissolved in THF. The solvent was removed from the solution leaving an orange solid (0.622 g, 80%). X-Ray quality crystals were grown from a concentrated solution in THF at –30°C. Anal. Found: Yb, 33.78; C, 54.20; H, 4.78. C₂₄H₂₅O₂Yb calc.: Yb, 33.37; C, 55.59; H, 4.86%. IR (CsI): 3060m, 1614w, 1567m, 1501m, 1440m, 1400s, 1015m, 770s, 735m, 393w, 220w cm⁻¹. MS (v.t. = 200°C): *m/e* = 829 [M – Cp, 10%], 764 [M – 2Cp, 8%], 447 [M', 55%], 382 [M' – Cp, 40%], 304 [Cp₂Yb, 22%]; MS (v.t. = 280°C): *m/e* = 829 [M – Cp, 4%], 764 [M – 2Cp, 3%], 507 [M – 4Cp – C₁₀H₇, 2%], 447 [M', 30%], 382 [M' – Cp, 18%], 369 [Cp₃Yb, 24%], 317 [Yb(NP), 22%], 304 [Cp₂Yb, 85%], 239 [CpYb, 100%], 222 [Yb(NP)₃ – 3C₁₀H₇, 3%] {v.t., vaporization temperature; M = [Cp₂Yb(NP)]₂; M' = Cp₂Yb(NP)}.

Preparation of [Cp₂Yb(NP)]₂ (2)

(a) Following the procedure described above, a concentrated solution of **1** in THF was treated with n-hexane, an orange-yellow powder was obtained in 70% yield, m.p. 230–234°C (dec.). Anal. Found: Yb, 38.68; C, 53.20; H, 3.86. C₄₀H₃₄O₂Yb₂ calc.: Yb, 38.76; C, 53.81; H, 3.84%. IR (CsI): 3050m, 1595w, 1567m, 1502m, 1440m, 1091m, 1015m, 773m, 740m, 380w, 230w cm⁻¹. MS (v.t. = 200°C): *m/e* = 829 [M – Cp, 15%], 764 [M – 2Cp, 10%], 699 [M – 3Cp, 9%], 634 [M – 4Cp, 6%], 447 [M', 50%], 382 [M' – Cp, 32%], 304 [M' – NP, 20%]; MS (v.t. = 280°C): *m/e* = 829 [M – Cp, 3%], 764 [M – 2Cp, 3%], 447 [M', 24%], 369 [Cp₃Yb, 30%], 317 [Yb(NP), 25%], 304 [Cp₂Yb, 90%]. Molecular weight measured: 820 (C₄₀H₃₄O₂Yb₂ calc.: 892.75).

(b) To a suspension of Cp₃Yb (0.442 g, 1.20 mmol) in toluene (50 ml) was added a sample of HNP (0.173 g, 1.20 mmol). The dark-green solution slowly turned orange-red with the formation of an orange precipitate. After stirring for 48 h at room temperature, the mixture was centrifuged, the solution was decanted and the precipitate was dried under reduced pressure to give an orange-yellow powder (0.428 g, 80%); m.p. 231–234°C (dec.). Anal. Found: Yb, 38.32; C, 53.12; H, 3.78. C₄₀H₃₄O₂Yb₂ calc.: Yb, 38.76; C, 53.81; H, 3.86%. Spectral properties were similar to those described above. Molecular weight measured: 815 (C₄₀H₃₄O₂Yb₂ calc.: 892.75).

Table 3

Crystal and data collection parameters

Formula	C ₂₄ H ₂₅ O ₂ Yb
MW	518.48
Crystal size (mm)	0.22 × 0.34 × 0.48
Space group	P2 ₁ /n
Cell constants	
<i>a</i> (Å)	8.084(2)
<i>b</i> (Å)	15.996(6)
<i>c</i> (Å)	15.973(7)
β (deg)	98.95(3)
<i>V</i> (Å ³)	2040.3
<i>D</i> _{calc.} (g cm ⁻³),	1.69
<i>Z</i>	4
2 θ range (deg)	3–50
Scan speed (deg/min)	7.0 fixed
μ_c (cm ⁻¹)	48.4
Radiation (Å)	Mo-K α , 0.71069
No. of reflections measured	3660
No. of unique reflections observed	2535
No. of reflections observed $I > 3\sigma(I)$	2242
<i>F</i> (000)	1024
GOOF	0.102
$R = \Sigma(F_o - F_c) / \Sigma F_o$	0.081
$R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w(F_c)^2]^{1/2}$	0.080
<i>w</i>	1/ $[\sigma^2(F)]$

Transformation of 1 into 2

Crystals of **1** were pulverized and heated to *ca.* 120°C in a vacuum for 2 h, giving powder that was identical with the product **2** described above by elemental analysis, IR and MS.

Thermolysis of 2

[Cp₂Yb(NP)]₂ (0.383 g, 0.429 mmol) was placed in a sublimation apparatus and heated to 235°C at 10⁻³ Torr. A dark-green sublimate slowly appeared around the upper part of the tube (0.19 g). The sublimate was identified as Cp₃Yb by elemental analysis and IR. The residue analysis indicated that it was naphtholate (0.17 g).

X-Ray crystallography of Cp₂Yb(NP)(THF)

A single crystal (0.22 mm × 0.34 mm × 0.48 mm) was sealed under argon in a thin-walled glass capillary. The intensity data were collected at ambient temperature (22–24°C) on a Nicolet R3m/E diffractometer with graphite-monochromated Mo-K α radiation (0.71069 Å). A total of 3660 intensities within the range of 3° < 2 θ < 50° were measured by the ω -scan technique. A summary of the data collection parameters is given in Table 3

The intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by the heavy-atom method. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found in the differ-

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	$U (\text{\AA}^2)^a$
Yb	3742(1)	7229(1)	174(1)	38(1)
O(1)	4757(12)	6202(7)	864(6)	57(4)
O(2)	4956(14)	6936(7)	-1004(6)	56(4)
C(11)	5816(17)	5876(10)	1461(8)	48(5)
C(12)	7477(21)	5701(11)	1368(10)	60(6)
C(13)	8633(25)	5360(11)	2058(11)	70(7)
C(14)	8154(21)	5125(10)	2795(9)	54(5)
C(15)	6489(20)	5302(9)	2919(10)	50(5)
C(16)	5927(25)	5075(11)	3683(10)	69(7)
C(17)	4317(24)	5224(11)	3795(9)	64(6)
C(18)	3155(20)	5623(11)	3173(9)	59(6)
C(19)	3677(18)	5835(10)	2425(9)	56(5)
C(20)	5297(19)	5667(9)	2265(8)	46(5)
C(21)	722(20)	6906(12)	403(10)	62(6)
C(22)	1081(18)	6294(12)	-139(10)	62(6)
C(23)	1181(19)	6667(10)	-903(12)	65(6)
C(24)	901(24)	7522(14)	-839(12)	75(7)
C(25)	603(22)	7665(9)	-11(11)	51(5)
C(31)	3871(20)	8542(11)	1028(12)	68(7)
C(32)	4456(27)	8821(12)	303(14)	95(8)
C(33)	5924(24)	8427(13)	235(12)	79(8)
C(34)	6427(21)	7991(12)	937(16)	82(8)
C(35)	5120(28)	8077(13)	1478(11)	81(8)
C(41)	6266(29)	6352(15)	-1016(12)	91(9)
C(42)	6733(29)	6381(16)	-1858(11)	100(9)
C(43)	5959(46)	7065(18)	-2283(16)	148(16)
C(44)	4705(39)	7366(20)	-1809(14)	136(14)

ence Fourier map but added to the structure model on the calculated positions ($d_{C-H} = 0.96 \text{ \AA}$). The final $R = 0.081$, $R_w = 0.080$. All calculations were carried out with the SHELXTL program. The final positional parameters are given in Table 4.

Acknowledgement

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