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Syntheses and crystal structures of $(\eta^5\text{-}C_5H_5)_3Ln(THF)$ (Ln = Ce, Er)

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Abstract

Brown crystalline tricyclopentadienyl cerium tetrahydrofuranate (THF) complex $(\eta^5\text{-}C_5H_5)_3Ce(THF)$ was prepared by the reaction of $(NH_4)_2Ce(NO_3)_6$ with sodium cyclopentadienide (C_5H_5Na) in THF at molar ratio of 1:6. $ErCl_3 \cdot 4THF$ reacts with potassium cyclooctadienide ($C_8H_{11}K$) at −78°C and then with C_5H_5Na at room temperature in THF at a molar ratio of 1:1:2 to give pink crystals of $(\eta^5\text{-}C_5H_5)_3Er(THF)$. The crystal structure determination of both these complexes shows that both belong to monoclinic space group $P2_1/n$, but their structures differ in that the Ce complex is not isostructural with $(\eta^5\text{-}C_5H_5)_3Ln(THF)$ (Ln = La, Pr, Nd, Gd, Dy, Y and Lu). However, the Er complex structure is isostructural. There are two discontinuity points at Ce and Dy but no "gadolinium break phenomenon" in the regularity of lanthanide contraction.

Key words: Cerium; Erbium

1. Introduction

The rare earth triscyclopentadienides were the first well-characterized organolanthanide compounds to be prepared [1]. Eight crystal structures of $(\eta^5\text{-}C_5H_5)_3Ln(THF)$ (Ln = La [2], Pr [3], Nd [3], Gd [4], Dy [5], Y [2], and Lu [6]) have so far been reported; these are isostructural. However, the Dy complex is not in agreement as regards the lanthanide contraction regularity, to be called "gadolinium break phenomenon" [5]. In order to study the reality of this phenomenon, we have determined the crystal structures of $(\eta^5\text{-}C_5H_5)_3Ce(THF)$ and of $(\eta^5\text{-}C_5H_5)_3Er(THF)$.

2. Experimental section

Since the complexes described below were extremely air- and moisture-sensitive, all experiments were conducted under pure nitrogen by Schlenk techniques. All solvents were predried with NaOH and metal sodium and then distilled from sodium benzophenoneketyl. Anhydrous erbium trichloride [7], cyclopentadienyl sodium [8] and cyclooctadienyl potassium [9] were prepared by a published procedure.

2.1. *Preparation of* $(\eta^5\text{-}C_5H_5)_3Ce(THF)$

Solid $(NH_4)_2Ce(NO_3)_6$ (2.0 g, 3.65 mol) and THF (50 ml) were mixed, then the solution was stirred for 2 h and NaC_5H_5 (21.89 mmol) in THF was added at −70°C with stirring. After 24 h, the solution was centrifuged to remove solids. The filtrate was evaporated in vacuum to give a brown solid. Hexane (10 ml) and then THF (10 ml) were used to extract the solid. After centrifugation and concentration of the THF extract, brown crystals of $(\eta^5\text{-}C_5H_5)_3Ce(THF)$ crystallized in a refrigerator in 56% yield. Anal. Found: Ce, 34.74. $CeC_{19}H_{23}O$ Calcd: Ce 34.38%.

2.2. *Preparation of* $(\eta^5\text{-}C_5H_5)_3Er(THF)$

$ErCl_3 \cdot 4THF$ (2.70 mmol) reacted with $C_8H_{11}K$ (2.70 mmol) in THF at −78°C and then C_5H_5Na (5.40 mmol) in THF was added at room temperature. After 24 h, the solution was treated by the same procedure as in the preparation of $(\eta^5\text{-}C_5H_5)_3Ce(THF)$. Pink crystals could be obtained in 35% yield.

2.3. *Determination of the crystal structures*

Crystals of dimensions 0.12 × 0.54 × 0.60 (Ce complex) and 0.18 × 0.32 × 0.46 (Er complex) mm^3 were selected and sealed in thin-walled glass capillaries under nitrogen for X-ray diffraction. The intensity data

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TABLE 1. Crystal data

	$(\eta^5\text{-}C_5H_5)Ce(THF)$	$(\eta^5\text{-}C_5H_5)Er(THF)$
M.W.	407.6	434.75
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Cell constants:		
a, Å	8.349(2)	8.258(5)
b, Å	24.658(6)	24.674(10)
c, Å	8.423(3)	8.170(6)
β, deg	101.67(2)	101.45(4)
V, Å^3	1698.20(0.82)	1613.60(1.20)
Z	4	4
D_c g/cm^3	1.59	1.77
μ (Mo Kα), cm^{-1}	27.1	53.3
F(000)	812	852
R	0.052	0.031
R_w	0.058	0.033
G	0.00134	0.00045

were collected on a Nicolet R3m/E four circle diffractometer at room temperature using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å), scan speed of 7°/min and scan range of 1.4°. One check reflection was measured after every 69 reflections. Totals of 3349 reflections for Ce and 6341 for Er were collected within the range $3° < 2\theta < 50°$, of which 2404 reflections with $I \geqslant 3\sigma(I)$ for Ce (2417 for Er) were considered observed. Systematic absences in $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$ indicated space group $P2_1/n$. The intensities were corrected for Lp factors and empirical absorption. Both structures were solved by the heavy atom method and refined by the block-matrix least-squares method.

All non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced at theoretical positions. Further refinements led to final convergence at $R = \Sigma(|F_o - F_c|)/\Sigma F_o = 0.0519$ for Ce (0.0307 for Er); $R_w = \Sigma w^{1/2}(|F_o - F_c|)/\Sigma(F_o)w^{1/2} = 0.0580$ (0.0326), where $w = [\sigma^2|F_o| + 0.00134$ (or 0.00045) $|F_o|^2]^{-1}$.

All calculations were performed with an Eclipse S/140 computer and the SHELXTL program system.

The cell parameters of $(\eta^5\text{-}C_5H_5)_3Ce(THF)$ and $(\eta^5\text{-}C_5H_5)_3Er(THF)$ are given in Table 1.

3. Results and discussion

3.1. Syntheses

We let anhydrous $(NH_4)_2Ce(NO_3)_6$ react with C_5H_5Na in THF at −70°C in the hope of synthesizing the compound of $(C_5H_5)_4Ce$. However, we obtained $(C_5H_5)_3Ce(THF)$ instead of $(C_5H_5)_4Ce$. The attempts to synthesize cyclooctadienyl biscyclopentadienyl erbium $C_8H_{11}Er(C_5H_5)_2$ by the reaction of $ErCl_3 \cdot 4THF$ with $C_8H_{11}K$ and then with C_5H_5Na failed, and $(C_5H_5)_3Er(THF)$ was formed instead.

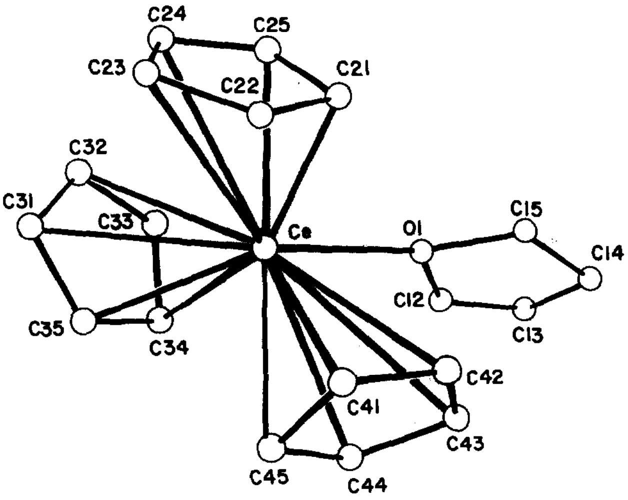

Fig. 1. The crystal structure of $(\eta^5\text{-}C_5H_5)_3Ce(THF)$.

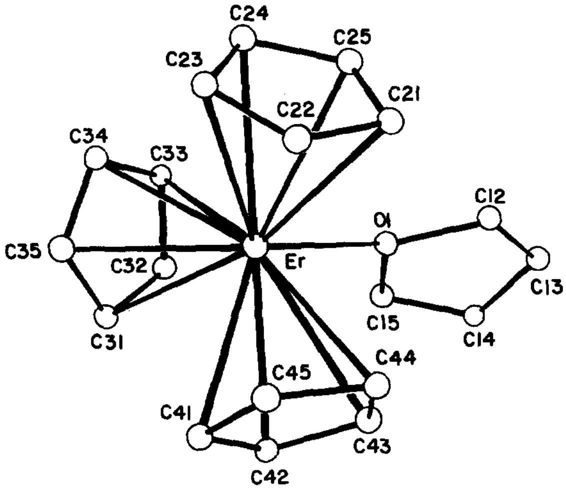

Fig. 2. The crystal structure of $(\eta^5\text{-}C_5H_5)_3Er(THF)$.

3.2. Molecular structures

The crystal structures of $(\eta^5\text{-}C_5H_5)_3Ce(THF)$ and $(\eta^5\text{-}C_5H_5)_3Er(THF)$ are shown in Fig. 1 and Fig. 2. Selected bond lengths and angles are listed in Tables 2–5.

TABLE 2. Bond lengths (Å)

Ce–O(1)	2.956(5)	Ce–C(21)	2.367(10)
Ce–C(22)	2.364(15)	Ce–C(23)	2.792(13)
Ce–C(24)	3.000(11)	Ce–C(25)	2.660(10)
Ce–C(31)	3.013(10)	Ce–C(32)	2.967(10)
Ce–C(33)	2.576(10)	Ce–C(34)	2.313(10)
Ce–C(35)	2.534(10)	Ce–C(41)	2.787(9)
Ce–C(42)	2.981(9)	Ce–C(44)	2.905(10)
Ce–C(45)	2.787(10)	Ce–C(43)	3.263(10)

TABLE 3. Bond angles (°)

C(22)–C(21)–C(25)	95.7(11)	C(21)–C(22)–C(23)	117.3(12)
C(22)–C(23)–C(24)	105.3(12)	C(23)–C(24)–C(25)	102.7(11)
C(21)–C(25)–C(24)	118.9(10)	C(32)–C(31)–C(35)	100.0(10)
C(31)–C(32)–C(33)	113.5(10)	C(32)–C(33)–C(34)	108.8(10)
C(33)–C(34)–C(35)	101.4(9)	C(31)–C(35)–C(34)	116.4(10)
C(42)–C(41)–C(45)	104.1(8)	C(41)–C(42)–C(43)	121.6(7)
C(42)–C(43)–C(44)	90.2(7)	C(43)–C(44)–C(45)	122.0(7)
C(41)–C(45)–C(44)	101.9(8)	Cent(4)–Ce–O(1)	85.6
Cent(3)–Ce–O(1)	111.1	Cent(2)–Ce–O(1)	108.9
Cent(4)–Ce–Cent(3)	126.8	Cent(4)–Ce–Cent(2)	126.6
Cent(3)–Ce–Cent(2)	96.3		

TABLE 4. Bond lengths (Å)

Er–O(1)	2.437(4)	Er–C(21)	2.712(9)
Er–C(22)	2.674(9)	Er–C(23)	2.695(7)
Er–C(24)	2.776(10)	Er–C(25)	2.735(12)
Er–C(31)	2.716(10)	Er–C(32)	2.744(9)
Er–C(33)	2.729(9)	Er–C(34)	2.716(8)
Er–C(35)	2.650(10)	Er–C(41)	2.692(8)
Er–C(42)	2.714(8)	Er–C(43)	2.713(7)
Er–C(44)	2.722(9)	Er–C(45)	2.708(8)

TABLE 5. Bond angles (°)

C(22)–C(21)–C(25)	106.4(8)	C(21)–C(22)–C(23)	107.8(8)
C(22)–C(23)–C(24)	109.0(9)	C(23)–C(24)–C(25)	107.5(10)
C(21)–C(25)–C(24)	109.2(9)	C(32)–C(31)–C(35)	107.5(7)
C(31)–C(32)–C(33)	108.4(7)	C(32)–C(33)–C(34)	107.7(7)
C(33)–C(34)–C(35)	107.7(7)	C(31)–C(35)–C(34)	108.6(7)
C(42)–C(41)–C(45)	107.1(7)	C(41)–C(42)–C(43)	107.2(7)
C(42)–C(43)–C(44)	109.7(7)	C(43)–C(44)–C(45)	105.7(8)
C(41)–C(45)–C(44)	110.1(7)	Cent(4)–Er–O(1)	96.5
Cent(3)–Er–O(1)	100.6	Cent(2)–Er–O(1)	100.7
Cent(4)–Er–Cent(3)	118.1	Cent(4)–Er–Cent(2)	118.8
Cent(3)–Er–Cent(2)	115.5		

From Table 2 it can be seen that the differences are great among the five Ce–C bond lengths in each cyclopentadienyl ring. For example, the largest distance Ce–C(43) is 3.263(10) Å and the smallest Ce–C(41) is 2.787(10) Å; the average is 2.945(8) Å. The average Ce–C(η^5) bond lengths in the two other cyclopentadienyl rings are 2.681(10) and 2.637(12) Å, respectively. The average Ce–C(η^5) bond length in all three rings is 2.754(10) Å. The distance Ce–Cent(4), Ce–Cent(3), Ce–Cent(2) (Cent represents the centroid of cyclopentadienyl ring) are 2.685, 2.395 and 2.360 Å, respectively.

The cyclopentadienyl ring is seriously distorted. For example, the five inner angles in the fourth ring are 104.1(8)°, 121.6(7)°, 90.2(7)°, 122.0(7)°, 101.9(8)°, respectively, and the average is 108.7(7)°.

The three Ln–Cent distances in $(\eta^5\text{-}C_5H_5)_3$Er(THF) are almost equal (Table 6) and the three cyclopentadienyl rings are not twisted (Table 5). The dihedral angles among three carbon rings in $(\eta^5\text{-}C_5H_5)_3$Ce(THF) are 71.2°, 68.4° and 46.6° while the corresponding angles in $(\eta^5\text{-}C_5H_5)_3$Er(THF) are 63.4°, 63.5° and 62.9°, respectively. The differences of the dihedral angles among three rings in the former are considerable, but those in the latter are almost equal. In $(\eta^5\text{-}C_5H_5)_3$Er(THF) each plane of three carbon rings is perpendicular to the plane linking the central ion and ring centroid (92.5°, 92.1° and 90.6°); in $(\eta^5\text{-}C_5H_5)_3$Ce(THF) the angles between each plane of three rings and the plane linking the central ion and the ring centroid are 71.8°, 70.3° and 79.0°, respectively. On the whole, the structural parameters of $(\eta^5\text{-}C_5H_5)_3$Ce(THF) are considerably different from those of $(\eta^5\text{-}C_5H_5)_3$Ln(THF) (Ln = La, Pr, Nd, Gd, Dy, Y and Lu). In $(\eta^5\text{-}C_5H_5)_3$Ce(THF) the bond lengths of Ce–O and Ce–C (η^5), and the distance Ce–Cent(2–4 ring) are not in accordance with the regularity of the Ln elements (Table 6).

From Table 6 and the above discussion it can be concluded that the crystal of $(\eta^5\text{-}C_5H_5)_3$Er(THF) is isostructural with that of $(\eta^5\text{-}C_5H_5)_3$Ln(THF) (Ln = La, Pr, Nd, Gd, Dy, Y and Lu). On the other hand, there are two discontinuity points at Ce and Dy and no "gadolinium break phenomenon" in the series $(\eta^5\text{-}$

TABLE 6. Significant structural parameters in the series of $(C_5H_5)_3$Ln(THF)

Atom	Ln^{3+} radius (Å) [12]	Ln–O (Å)	Ln–Cent(2) (Å)	Ln–Cent(3) (Å)	Ln–Cent(4) (Å)	Ln–C(av.) (Å)	Ref.
La	1.216	2.57	2.575	2.576	2.576	2.82(4)	[4]
Ce	1.196	2.956(5)	2.360	2.395	2.685	2.75(1)	
Pr	1.179	2.56(1)	2.51	2.54	2.55	2.80(2)	[5]
Nd	1.163	2.54(1)	2.51	2.51	2.51	2.78(2)	[5]
Gd	1.107	2.494(7)	2.47	2.49	2.49	2.74(3)	[6]
Dy	1.083	2.522(5)	2.477	2.508	2.516	2.74(3)	[7]
Y	1.075	2.451(4)	2.438	2.453	2.454	2.71(3)	[8]
Er	1.062	2.437(4)	2.427	2.439	2.440	2.70(1)	
Lu	1.032	2.39(2)	2.40	2.42	2.43	2.69(4)	[9]

$C_5H_5)_3$Ln(THF) because the bond lengths of Ln–O and Ln–C(η^5) and the Ln–Centroid distances of the elements (Y, Er and Lu) are shorter than those of Gd.

In $(\eta^5\text{-}C_5H_5)_3$Er(THF) the bond angles of Cent(2)–Er–O(1), Cent(3)–Er–O(1) and Cent(4)–Er–O(1) are 100.7°, 100.6° and 96.5°, while Cent(2)–Er–Cent(3), Cent(2)–Er–Cent(4) and Cent(3)–Er–Cent(4) are 115.5°, 118.8° and 118.1°, respectively, *i.e.* almost 120°.

In $(\eta^5\text{-}C_5H_5)_3$Ce(THF) the bond angles Cent(2)–Ce–O(1), Cent(3)–Ce–O(1) and Cent(4)–Ce–O(1) are 108.9°, 111.0° and 85.6°; Cent(2)–Ce–Cent(3), Cent(2)–Ce–Cent(4) and Cent(3)–Ce–Cent(4) are 96.3°, 126.6° and 126.8°. The differences between these corresponding angles in Er and Ce complexes are therefore very large.

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