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Syntheses and molecular structure of $(C_8H_8)Ln(2,4\text{-}C_7H_{11}) \cdot THF$ $(Ln = Nd, Er)$

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Abstract

$LnCl_3$ (Ln = Nd, Er) reacts with $K_2C_8H_8$ to yield the complex $(C_8H_8)LnCl \cdot 2THF$, which reacts with $K(2,4\text{-}C_7H_{11})$ $(2,4\text{-}C_7H_{11}$ = 2,4-dimethylpentadienyl) to form $(C_8H_8)Ln(2,4\text{-}C_7H_{11}) \cdot THF$. The compound $(C_8H_8)Nd(2,4\text{-}C_7H_{11}) \cdot THF$(1) crystallizes from the mixed solvents hexane and THF in monoclinic space group $P2_1$ with $a = 8.734(1)$, $b = 10.915(4)$, $c = 9.786(2)$ Å, $\beta = 104.13(1)°$, $V = 904.8(4)$ Å^3, $D_c = 1.53$ g cm^{-3} and $Z = 2$. The crystal of $(C_8H_8)Er(2,4\text{-}C_7H_{11}) \cdot THF$ (2) belongs to monoclinic space group $P21/m$ with $a = 7.776(2)$, $b = 13.030(5)$, $c = 8.729(3)$ Å, $\beta = 101.21(2)°$, $V = 867.59(0.46)$ Å^3, $D_c = 1.73$ g cm^{-3} and $Z = 2$. Because of the difference between the radii of Nd and Er, **2** is not isostructural with **1**. The THF molecule in **2** is situated against the open jaws of the pentadienyl ligand, and in compound **1**, it is situated by the back of the pentadienyl ligand.

Keywords: Neodymium; Erbium; Cyclooctatetraenyl; 2,4-Dimethylpentadienyl; Crystal structure

1. Introduction

Acyclic pentadienyl complexes of transition metals have been studied extensively in recent years [1], but less attention has been given to the development of pentadienyl lanthanide complexes. So far, only a few crystal structures of 2,4-dimethylpentadienyl lanthanide complexes, $(2,4\text{-}C_7H_{11})_3Ln$ (Ln = Nd [2], Gd [3]) and $[Nd_6(2,4\text{-}C_7H_{11})_6Cl_{12}(THF)]$ [4] have been determined. In an earlier paper, we reported the synthesis and crystal structure of $(C_8H_8)Sm(2,4\text{-}C_7H_{11}) \cdot THF$ [5]. It has been found that since the radii of Ln^{3+} in the complexes $(C_8H_8)LnCp'$ $(Cp' = C_6H_5CH_2C_5H_4)$ [6] are different, the space arrangements of the ligands in the molecules are diverse. In order to study the effects of Ln radii on spatial arrangements in the molecules we determined the crystal structures of $(C_8H_8)Ln(2,4\text{-}C_7H_{11}) \cdot THF$ for neodymium and erbium. At the same time we attempted to establish some significant structural parameters for (C_8H_8)-$Sm(2,4\text{-}C_7H_{11}) \cdot THF$.

2. Experimental section

All experiments were conducted under pure argon by Schlenk techniques. THF and hexane were predried over $CaCl_2$ and distilled from sodium benzophenone ketyl. Anhydrous $LnCl_3$ was prepared by Taylor's method [7]. Cyclooctatetraene (Merck) was degassed by vacuum, transferred and stored over molecular sieves (4 Å) under argon. 2,4-Dimethylpentadienyl potassium was prepared by a procedure published previously [8]. Metal analysis was carried out by complexometric titration. Infrared spectra were recorded on an Digilab FTS-20E spectrometer as KBr pellets. Mass spectra were recorded on a Finnigan 4021 spectrometer.

2.1. $(C_8H_8)Nd(2,4\text{-}C_7H_{11}) \cdot THF$ (1)

To a suspension of $NdCl_3$ (0.9 g, 3.6 mmol) in 30 ml of THF was added a solution of $K_2C_8H_8$ (3.6 mmol) in THF at −78°C. After stirring for 12 h, $K(2,4\text{-}C_7H_{11})$ (3.6 mmol) was added at room temperature and the stirring was continued for 10 h. The solution was centrifuged to remove the solid mass, and hexane was added to the clear solution. The resulting solution

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Table 1
Crystal data

Compound	$(C_8H_8)Nd(2,4\text{-}C_7H_{11})\cdot THF$	$(C_8H_8)Er(2,4\text{-}C_7H_{11})\cdot THF$
Mol wt.	415.7	450.75
Crystal size	0.44 × 0.28 × 0.48	0.36 × 0.52 × 0.6
Cell constants		
a, Å	8.734(1)	7.776(2)
b, Å	10.915(4)	13.030(5)
c, Å	9.786(2)	8.729(3)
β, deg	104.13(1)	101.21(2)
V, Å^3	904.67	867.50(0.46)
Scan range, 2θ	3–56	3–56
Reflections	2402	2396
Reflections for $I > 3\sigma(I)$	2063	1948
Space group	$P2_1$	$P2_1/m$
Z	2	2
D_c g cm^{-3}	1.53	1.73
R	0.034	0.032
$F(000)$	418	446

crystallized at −5°C. Green crystals (0.76 g) were obtained in 51% yield. Anal. Found: Nd, 34.8; $C_{19}H_{27}ONd$ Calcd.: 34.73%; IR (KBr): 3090w, 2880m, 1580w, 1535m, 1455m, 1380s, 1225w, 1065m, 890m, 800s, 670s, 625m cm^{-1}. m/e: 343(22), 248(100), 239(9), 104(20), 95(20), 77(30).

2.2. $(C_8H_8)Er(2,4\text{-}C_7H_{11})\cdot THF$

This compound was prepared from 0.8 g of $ErCl_3$ (2.9 mmol), 2.9 mmol of $K_2C_8H_8$ and 2.9 mmol of $K(2,4\text{-}C_7H_{11})$ using the same precedure as described above. Deep-red crystals (0.5 g) of $(C_8H_8)Er(2,4\text{-}C_7H_{11})\cdot THF$ were obtained in 38% yield. Anal. Found: Er, 38.31; $C_{19}H_{27}OEr$ Calcd.: Er, 38.16%; IR (KBr): 3079w, 3002s, 2967m, 2870m, 1630m, 1595s, 1555w, 1448m, 1372m, 1262w, 1076s, 1056s, 1028m, 892s, 800m, 776w, 673s, 628s cm^{-1}. m/e: 364(28), 270(100), 260(9), 104(14), 95(24), 77(40).

2.3. X-ray crystallography of compounds 1 and 2

A suitable crystal was sealed in a glass capillary. Intensity data were collected on a Nicolet R3m/E diffractometer with Mo Kα radiation ($\lambda = 0.71069$ Å) in the ω-scan mode. Experimental details are given in Table 1. The intensities were corrected for Lorentz, polarization and absorption effects. The structures were solved by Patterson and Fourier techniques. The atomic coordinates and anisotropic temperature factors for all nonhydrogen atoms were refined by block-diagonal least-squares method. The coordinates of hydrogen atoms were obtained according to theoretical calculations.

All calculations were performed on an Eclipse S/140 computer with the SHELXTL program system. The atomic coordinates for compounds **1** and **2** are listed in Tables 2 and 3.

Table 2
Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$ Å^2) for compound **1**

	x	y	z	U_{eq} [a]
Nd	869(1)	2222(4)	2781(1)	33(1)
O	2884(9)	2743(9)	1373(8)	58(3)
C(1)	−1781(27)	1463(12)	3372(35)	247(26)
C(2)	−1747(14)	2738(12)	3552(10)	137(15)
C(3)	−1939(15)	3258(15)	2208(7)	105(9)
C(4)	−1587(14)	3121(8)	890(12)	76(6)
C(5)	−1115(12)	2087(8)	258(11)	77(6)
C(6)	−714(15)	873(9)	626(8)	73(6)
C(7)	−644(17)	173(10)	1834(8)	67(6)
C(8)	−981(16)	399(15)	3138(13)	83(7)
C(11)	1586(15)	−250(13)	3614(14)	53(4)
C(12)	3005(13)	273(12)	3604(12)	46(4)
C(13)	3681(13)	1398(12)	4347(12)	45(4)
C(14)	3139(12)	2154(22)	5407(10)	54(4)
C(15)	1767(14)	1950(23)	5848(12)	72(9)
C(16)	3990(17)	−170(16)	2591(16)	70(6)
C(17)	4199(20)	3212(16)	5903(17)	83(7)
C(21)	2853(14)	2042(22)	−51(12)	52(6)
C(22)	4365(17)	2689(17)	−322(17)	87(8)
C(23)	4840(16)	3868(16)	589(15)	70(6)
C(24)	4172(17)	3644(16)	1917(16)	69(6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

3. Results and discussion

Complexes **1** and **2** were synthesized by the following reactions:

$$LnCl_3 + K_2C_8H_8 \longrightarrow (C_8H_8)LnCl\cdot 2THF$$

$$(C_8H_8)LnCl\cdot 2THF + K(2,4\text{-}C_7H_{11})$$

$$\longrightarrow (C_8H_8)Ln(2,4\text{-}C_7H_{11})\cdot THF$$

The reaction of $LnCl_3$ with $K(2,4\text{-}C_7H_{11})$ at a molar

Table 3
Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$ Å^2) for compound **2**

	x	y	z	U_{eq} [a]
Er	7120(1)	2500	1590(1)	35(1)
O	4296(7)	2500	−182(7)	57(2)
C(11)	7867(10)	1971(7)	−1094(8)	82(3)
C(12)	8470(11)	1199(6)	−21(11)	87(3)
C(13)	9497(11)	1212(6)	1468(11)	82(3)
C(14)	10308(8)	1955(8)	2491(9)	100(4)
C(21)	7166(10)	2500	4638(8)	50(2)
C(22)	6488(7)	1513(4)	4169(6)	49(1)
C(23)	5041(7)	1287(5)	3033(7)	59(2)
C(24)	7662(11)	634(6)	4887(10)	70(3)
C(31)	3315(11)	1609(6)	−833(9)	82(3)
C(32)	2398(15)	1967(7)	−2408(13)	132(5)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

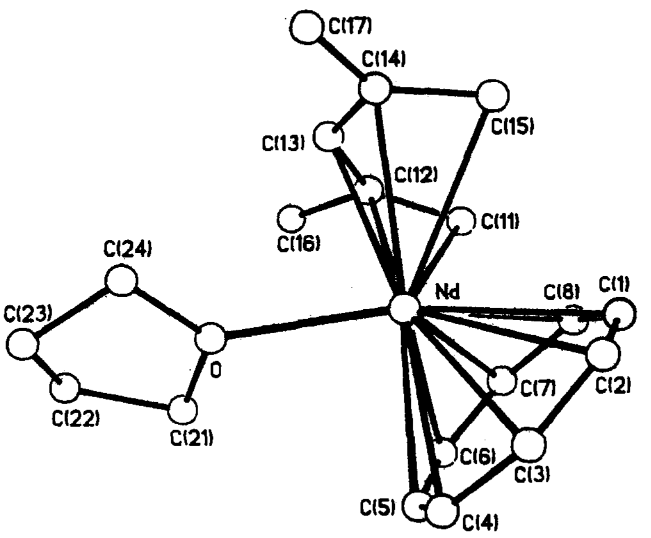

Fig. 1. Structure of $(C_8H_8)Nd(C_7H_{11})\cdot THF$.

ratio of 1:1 in THF gives $(2,4\text{-}C_7H_{11})_3Ln$ instead of $(2,4\text{-}C_7H_{11})LnCl_2\cdot 3THF$.

The IR spectra of 1 and 2 display the characteristic absorptions of the η^8-C_8H_8 group at 892, 800, 776 and 673 cm^{-1} [9], and of the η^5-2,4-C_7H_{11} group at 2967, 2880, 1448 and 1076 cm^{-1} [10].

The mass spectra of 1 and 2, recorded at $50°C < T < 350°C$, show the THF-free molecular ion peak $[M]^+$ [343 for 1, 364 for 2]. Additional peaks were observed for $[M - C_7H_{11}]^+$ [248,270], $[M - C_8H_8]^+$ [239,260], $[C_8H_8]^+$ [104], $[C_7H_{11}]^+$ [95], $[C_4H_8O]^+$ [77].

The crystal structures of compounds 1 and 2 are illustrated in Figs. 1 and 2. Selected bond lengths and angles are listed in Tables 4 and 5.

Table 4
Bond lengths (Å) and angles (°) for compound 1

Nd–O	2.550(9)	Nd–C(1)	2.652(27)
Nd–C(2)	2.536(13)	Nd–C(3)	2.633(14)
Nd–C(4)	2.665(11)	Nd–C(5)	2.652(9)
Nd–C(6)	2.655(9)	Nd–C(7)	2.648(12)
Nd–C(8)	2.640(16)	Nd–C(11)	2.844(15)
Nd–C(12)	2.814(13)	Nd–C(13)	2.712(11)
Nd–C(14)	2.838(9)	Nd–C(15)	2.927(12)
O–C(21)	1.585(18)	O–C(24)	1.491(17)
C(1)–C(2)	1.403(18)	C(1)–C(8)	1.403(25)
C(2)–C(3)	1.405(14)	C(3)–C(4)	1.405(16)
C(4)–C(5)	1.397(15)	C(5)–C(6)	1.395(13)
C(6)–C(7)	1.396(13)	C(7)–C(8)	1.400(17)
C(11)–C(12)	1.367(18)	C(12)–C(13)	1.475(18)
C(12)–C(16)	1.541(21)	C(13)–C(14)	1.490(21)
C(14)–C(15)	1.387(18)	C(14)–C(17)	1.486(26)
C(21)–C(22)	1.576(23)	C(22)–C(23)	1.563(24)
C(23)–C(24)	1.569(23)		
O–Nd–C(1)	160.4(7)	O–Nd–C(2)	150.2(4)
O–Nd–C(3)	121.3(3)	O–Nd–C(4)	95.0(3)
O–Nd–C(5)	83.7(3)	O–Nd–C(6)	89.4(3)
O–Nd–C(7)	110.5(3)	O–Nd–C(8)	139.9(4)
O–Nd–C(11)	103.5(4)	O–Nd–C(12)	80.0(3)
O–Nd–C(13)	74.3(3)	O–Nd–C(14)	94.2(3)
O–Nd–C(15)	121.9(3)	C(11)–C(12)–C(13)	126.9(12)
C(12)–C(13)–C(14)	130.3(12)	C(13)–C(14)–C(15)	125.0(17)
COT [a]–Nd–C [b]	133.0	COT [a]–Nd–O	125.5
C [b]–Nd–O	86.5		

[a] COT indicates the centroid of cyclooctateraenyl.
[b] C indicates the centroid C(11) to C(17).

As shown in Figs. 1 and 2, complex 1 is not isostructural with complex 2. The central ion $Nd^{3+}[Er^{3+}]$ is coordinated by the cyclooctatetraenyl in η^8 mode and by the 2,4-dimethylpentadienyl in η^5 bonding fashion. In addition, the O atom of THF is bonded to the central metal and situated against the open jaws of the pentadienyl ligand in the case of the $(C_8H_8)Er(2,4\text{-}C_7H_{11})\cdot THF$ complex, while it is situated by the back of the pentadienyl ligand in the $(C_8H_8)Nd(2,4\text{-}C_7H_{11})\cdot THF$, which is similar to the structure of $(C_8H_8)Sm(2,4\text{-}C_7H_{11})\cdot THF$ [4]. In the molecule of $(C_5H_5)Ti(2,4\text{-}C_7H_{11})PEt_3$ [11] and $(C_5H_5)V(2,4\text{-}$

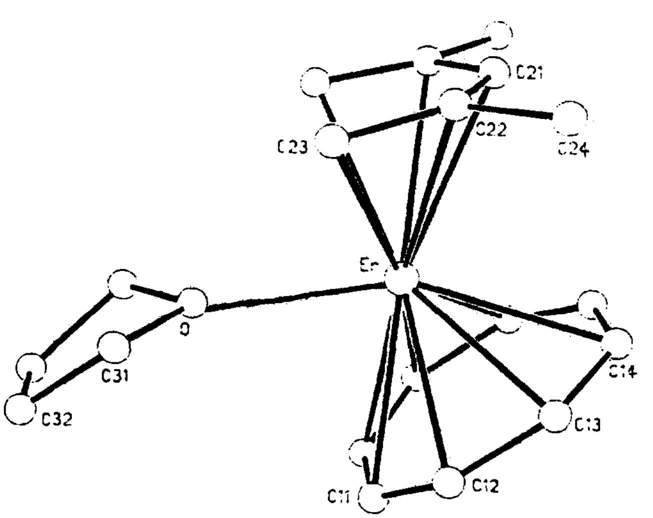

Fig. 2. Structure of $(C_8H_8)Er(C_7H_{11})\cdot THF$.

Table 5
Bond lengths (Å) and angle (°) for compound 2

Er–O	2.427(5)	Er–C(11)	2.614(8)
Er–C(12)	2.555(9)	Er–C(13)	2.515(8)
Er–C(14)	2.552(6)	Er–C(21)	2.653(7)
Er–C(22)	2.719(5)	Er–C(23)	2.736(6)
Er–C(11a)	2.614(8)	Er–C(12a)	2.555(9)
Er–C(13a)	2.515(8)	Er–C(14a)	2.552(6)
Er–C(22a)	2.719(5)	Er–C(23a)	2.736(6)
O–C(31)	1.444(8)	O–C(31a)	1.444(8)
C(11)–C(12)	1.391(12)	C(11)–C(11a)	1.380(19)
C(12)–C(13)	1.387(12)	C(13)–C(14)	1.384(12)
C(14)–C(14a)	1.420(21)	C(21)–C(22)	1.420(6)
C(21)–C(22a)	1.420(6)	C(22)–C(23)	1.379(7)
C(22)–C(24)	1.522(9)	C(31)–C(32)	1.495(13)
C(32)–C(32a)	1.388(19)	COT [a]–Er–C [b]	147.2
COT [a]–Er–O	116.6	C [b]–Er–O	96.1

[a] COT indicates the centroid of cyclooctateraenyl.
[b] C indicates the centroid C(11) to C(17).

C_7H_{11})CO [12], the ligands of PEt_3 and CO are situated against the open jaws of the pentadienyl groups, which is similar to the case of (C_8H_8)Er(2,4-C_7H_{11})·THF. This is probably dependent on the radii of the central ions in the complexes. Because the radii of Nd and Sm are greater than those of Er, Ti and V, the O atom of THF is situated by the back of the pentadienyl ligand in (C_8H_8)Ln(2,4-C_7H_{11})·THF (Ln = Nd, Sm) without steric hindrance. If the complexes of Er, Ti and V adopt the same space arrangement as that of the molecules of Nd and Sm, their ligands exhibit steric hindrance. The average Nd–C(C_8H_8)[Er–C(C_8H_8)] distance of 2.65(7) Å (2.55(9) Å) is comparable to that of 2.65(9) Å in (C_8H_8)Sm(2,4-C_7H_{11})·THF, when corrections are made for differences in ionic radii.

The Nd–C(2,4-C_7H_{11}) distances vary in the range 2.712(11) to 2.927(12) Å. The Nd–C(13) distance is the shortest (2.712(11) Å), and the average Nd–C(11,15) distance is the longest (2.885(6) Å). This rank order is comparable to that of complex **2** with Er–C(21) (2.653(7) Å < Er–C(22,22a) (2.719(5) Å) < Er–C(23,23a) (2.736(6) Å), although the space arrangements of the pentadienyl ligand in complexes **1** and **2** are different.

For compounds **1** and **2**, the C–C bond distances within the pentadienyl ligand fall essentially in two sets. The external C–C bond [C(11)–C(12) and C(14)–C(15)] distances are 1.39 (Å) (compound **1**) and 1.38 Å (compound **2**) and internal C–C bond [C(12)–C(13) and C(13)–C(14)] distances are 1.48 Å (compound **1**) and 1.42 Å (compound **2**).

The angle of centroid (C_8H_8)–Nd[Sm]–centroid (2,4-C_7H_{11}) is 133.0° (131.1°), which is smaller than that of (C_8H_8)Er(2,4-C_7H_{11})·THF (147.2°). This is due to the repulsion of the THF ligand by the two methyl groups in the pentadienyl moiety (Ln = Nd, Sm) and the absence of this repulsion in the case of compound **2**, which has a plane of symmetry through the C(21), Er and O atoms.

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