

Syntheses and crystal structures of triindenyl lanthanide complexes ($\eta^5\text{-C}_9\text{H}_7$)₃Ln · OC₄H₈ (Ln = Nd, Gd, Er)

Jusong Xia, Zhongshen Jin, Guanyang Lin and Wenqi Chen *

*Changchun Institute of Applied Chemistry, Academia Sinica,
Changchun 130022 (People's Republic of China)*

(Received October 5th, 1990)

Abstract

The complexes named in the title ($\eta^5\text{-C}_9\text{H}_7$)₃Ln · OC₄H₈ (Ln = Nd, Gd, Er) were synthesized by the reaction of anhydrous lanthanide trichlorides with indenyl potassium and cyclooctadienyl potassium (1:2:1 molar ratio) in THF. The complexes were characterized by elemental analysis, infrared and ¹H-NMR spectroscopy, and mass spectrometry. In addition, the crystal structures of ($\eta^5\text{-C}_9\text{H}_7$)₃Nd · OC₄H₈ (**1**) and ($\eta^5\text{-C}_9\text{H}_7$)₃Gd · OC₄H₈ (**2**) were determined by an X-ray diffraction study. Complexes **1** and **2** belong to hexagonal space group *P*6₃ with unit cell parameters $a = b = 11.843(3)$, $c = 10.304(4)$ Å, $V = 1251.7(9)$ Å³, $D_c = 1.49$ g · cm⁻³, $Z = 2$ for **1**, and $a = b = 11.805(2)$, $c = 10.236(2)$ Å, $V = 1235.4(6)$ Å³, $D_c = 1.54$ g · cm⁻³, $Z = 2$ for **2**. The structures were solved by Patterson and Fourier techniques and refined by least-squares to final discrepancy indices of $R = 0.049$, $R_w = 0.053$ using 925 independent reflections with $I \geq 3\sigma(I)$ for **1**, and $R = 0.023$, $R_w = 0.025$ using 1327 independent reflections with $I \geq 3\sigma(I)$ for **2**. Coordination numbers for Nd³⁺ and Gd³⁺ are 10; the average bond lengths Nd–O and Gd–O are 2.557(21) and 2.459(13) Å, respectively. The structural studies showed the complexes to have 3-fold symmetry, but the THF molecule has no such symmetry; consequently the arrangement of carbon atoms in the THF molecule are disordered.

Introduction

In 1968, Tsutsui et al. [1] first reported the synthesis of triindenyl lanthanide complexes ($\eta^5\text{-C}_9\text{H}_7$)₃Ln · OC₄H₈ (Ln = La, Sm, Gd, Tb, Dy, Yb), and then W. Chen et al. [2,3] reported the syntheses of indenyl lanthanide dichlorides and bis(indenyl)lanthanide chlorides. So far, however, very few structures of indenyl lanthanide complexes [4] have been determined. Difficulties of separation and the unstable nature of triindenyl lanthanide complexes ($\eta^5\text{-C}_9\text{H}_7$)₃Ln · OC₄H₈ have meant there has been no work on the crystal structure of this type of complex. In this paper, we report a synthesis of ($\eta^5\text{-C}_9\text{H}_7$)₃Ln · OC₄H₈ (Ln = Nd **1**, Gd **2**, Er **3**), different from that used before [1], and determinations of crystal structures of complexes **1** and **2**.

Experimental

1. Reagents

The solvent tetrahydrofuran (THF) was treated with NaOH, refluxed over sodium strips and distilled under argon before use.

Anhydrous lanthanide trichlorides [5], indenyl potassium [2] and cyclooctadienyl potassium [6] were prepared by published procedures.

2. Preparation of $(\eta^5\text{-C}_9\text{H}_7)_3\text{Ln}\cdot\text{OC}_4\text{H}_8$

Anhydrous LnCl_3 (3.0 mmol) (Ln = Nd, Gd, Er) in a Schlenk flask was heated over a naked flame under reduced pressure for several minutes, and then cooled under argon. THF (20 ml) was added and the resulting solution was stirred overnight. The THF solutions of indenyl potassium (6.0 mmol) and of cyclooctadienyl potassium (3.0 mmol) were added to the THF solution of LnCl_3 at -78°C and stirred for several minutes, then allowed to warm to room temperature. After the mixture had been stirred for about 36 h, a yellowish clear solution was separated off by centrifugation and then placed in a refrigerator to produce green hexagonal block (Ln = Nd), pale yellow hexagonal column (Ln = Gd) or pink block (Ln = Er) crystals of the complexes under investigation. Yield 35–40%.

The elemental analyses of the complexes are shown in Table 1. IR (cm^{-1}): 550m, 690m, 715s, 760s, 860m, 910m, 1015m, 1065m, 1289w, 1325m, 1390m, 1459s, 1600m, 1680m, 2880m, 2962m, 3060m, with the absorption peaks at 1015 and 860 cm^{-1} appearing to be the characteristic absorption bands of indenyl, and thoreat 1065 and 910 cm^{-1} of THF [2,7]. The $^1\text{H-NMR}$ signals of the hydrolytic products were observed at 1.63–1.90, 3.65–3.78 ppm (THF) [1] and 3.37, 6.47–6.54, 6.82–6.88, 7.11–7.47 ppm (indene) [8]. The mass spectra of the hydrolytic products showed a parent molecular ion peak at m/e 116 [$M + 1$] $^+$ and their fragments as expected: 117, 115, 114, 89, 65, 63, 36, 18.

3. Determinations of crystal structures

Since the crystals are extremely sensitive to air and moisture a single crystal with dimensions of $0.42 \times 0.16 \times 0.36\text{ mm}$ (**1**) [$0.36 \times 0.40 \times 0.80\text{ mm}$ (**2**)] was selected and sealed in a thin-walled lithium-glass capillary tube under argon for measurement.

Table 1

Elemental analysis of complexes $(\eta^5\text{-C}_9\text{H}_7)_3\text{Ln}\cdot\text{OC}_4\text{H}_8$ (Ln = Nd, Gd, Er)

Complex	Colour	Anal. (Found (calc.) (%))		
		C	H	Ln
$(\text{C}_9\text{H}_7)_3\text{Nd}\cdot\text{OC}_4\text{H}_8$	green	66.03	5.10	25.38
		(66.29)	(5.17)	(25.69)
$(\text{C}_9\text{H}_7)_3\text{Gd}\cdot\text{OC}_4\text{H}_8$	pale yellow	63.94	4.92	27.10
		(64.77)	(5.08)	(27.35)
$(\text{C}_9\text{H}_7)_3\text{Er}\cdot\text{OC}_4\text{H}_8$	pink	62.95	4.82	28.20
		(63.67)	(4.96)	(28.63)

Table 2

Crystallographic data of complexes **1** and **2**

	1	2
Formula	C ₃₁ H ₂₉ NdO	C ₃₁ H ₂₉ GdO
Crystal system	hexagonal	hexagonal
Space group	<i>P</i> 6 ₃	<i>P</i> 6 ₃
Cell constants		
<i>a</i> , Å	11.843(3)	11.805(2)
<i>b</i> , Å	11.843(3)	11.805(2)
<i>c</i> , Å	10.304(4)	10.236(2)
$\alpha = \beta$, °	90	90
γ , °	120	120
<i>V</i> , Å ³	1251.7(9)	1235.4(6)
<i>Z</i>	2	2
<i>D</i> _c , g·cm ⁻³	1.49	1.54
μ , cm ⁻¹	21.0	27.9
<i>F</i> (000)	566	574
Radiation	Mo- <i>K</i> _α (λ = 0.71069 Å)	Mo- <i>K</i> _α (λ = 0.71069 Å)
<i>R</i>	0.049	0.023
<i>R</i> _w	0.053	0.025

The intensity data were collected on a Nicolet *R3m/E* four-circle diffractometer with Mo-*K*_α radiation (λ = 0.71069 Å) and a scan range 3 ≤ 2θ ≤ 60° (**1**) [3 ≤ 2θ ≤ 65° (**2**)]. Of the 1488 (**1**) [4979 (**2**)] reflections collected, 925 (**1**) [1327 (**2**)] reflections with *I* ≥ 3σ(*I*) were considered to have been observed.

The structures were solved by the heavy-atom method and refined by block-diagonal least-squares by the use of the SHELXTL program. The position of the heavy atom, Nd³⁺ (**1**) [Gd³⁺ (**2**)], was found from Patterson maps and the positions of other non-hydrogen atoms were found by Fourier techniques. The coordinates of hydrogen atoms were added according to theoretical models.

The crystallographic data of (η⁵-C₉H₇)₃Nd·OC₄H₈ (**1**) and (η⁵-C₉H₇)₃Gd·OC₄H₈ (**2**) are listed in Table 2.

Results and discussion

1. Synthesis

The previous method for preparing the triindenylanthanide complexes (η⁵-C₉H₇)₃Ln·OC₄H₈ involves reaction of indenylsodium with anhydrous lanthanide trichloride at a 3 : 1 molar ratio in THF [1], but it is very difficult to get suitable crystals for X-ray diffraction.

In our work, anhydrous LnCl₃ was reacted with KC₉H₇ and KC₈H₁₁ at a molar ratio of 1 : 2 : 1 in THF, and the complexes named in the title (η⁵-C₉H₁₁)₃Ln·OC₄H₈ (Ln = Nd, Gd, Er) obtained. We think this is mainly due to the instability of the intermediates (C₈H₁₁)Ln(C₉H₇)₂·*n*THF, and their disproportionation, which takes place as follows:

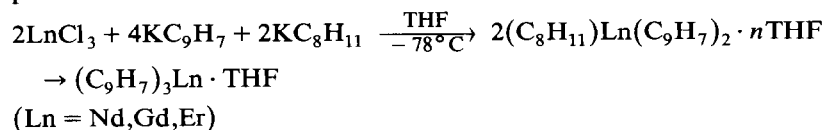


Table 3

Atomic coordinates ($\times 10^4$) and equivalent temperature factors ($\times 10^3 \text{ \AA}$) for non-hydrogen atoms of complexes **1** and **2**

Atom	x	y	z	U_{eq}^a
<i>Complex 1</i>				
Nd	6667	3333	1994	30(1)
O(1)	6667	3333	4475(20)	62(6)
C(1)	8803(13)	4644(16)	458(16)	51(6)
C(2)	9072(14)	5375(14)	1581(19)	54(6)
C(3)	9275(13)	4781(18)	2645(19)	58(7)
C(4)	9278(13)	3593(12)	2220(12)	42(6)
C(5)	8993(16)	3527(16)	781(19)	57(6)
C(6)	9100(20)	2559(16)	23(22)	70(8)
C(7)	9394(22)	1728(25)	625(36)	95(13)
C(8)	9698(20)	1848(18)	1864(41)	76(10)
C(9)	9591(21)	2703(22)	2753(25)	81(11)
<i>Complex 2</i>				
Gd	6667	3333	1994	29(1)
O(1)	6667	3333	4397(13)	57(3)
C(1)	8785(6)	4584(7)	420(9)	48(2)
C(2)	9017(6)	5330(7)	1562(11)	54(3)
C(3)	9266(6)	4759(7)	2883(9)	51(2)
C(4)	9298(6)	3611(7)	2115(15)	54(3)
C(5)	9013(6)	3510(7)	758(8)	49(2)
C(6)	9086(8)	2604(9)	-19(11)	60(4)
C(7)	9491(11)	1773(12)	579(17)	81(5)
C(8)	9719(10)	1846(11)	1981(22)	89(5)
C(9)	9605(9)	2743(9)	2717(13)	68(4)

^a U_{eq} : Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4

Selected bond lengths (\AA) for complexes **1** and **2**

	Complex 1	Complex 2
Ln–O(1)	2.557(21)	2.459(13)
Ln–C(1)	2.718(14)	2.708(7)
Ln–C(2)	2.694(12)	2.628(5)
Ln–C(3)	2.763(13)	2.728(6)
Ln–C(4)	2.960(16)	2.959(8)
Ln–C(5)	2.927(20)	2.955(8)
C(1)–C(2)	1.384(25)	1.405(13)
C(1)–C(5)	1.486(30)	1.463(13)
C(2)–C(3)	1.387(29)	1.354(14)
C(3)–C(4)	1.475(27)	1.456(14)
C(4)–C(5)	1.513(23)	1.420(18)
C(4)–C(9)	1.393(34)	1.390(17)
C(5)–C(6)	1.445(31)	1.370(15)
C(6)–C(7)	1.347(42)	1.426(21)
C(7)–C(8)	1.314(55)	1.455(26)
C(8)–C(9)	1.418(44)	1.360(21)

Table 5

Selected bond angles (deg) for complexes **1** and **2**

	Complex 1	Complex 2
O(1)–Ln–C(1)	125.6(3)	126.5(2)
O(1)–Ln–C(2)	99.1(4)	99.7(2)
C(1)–Ln–C(2)	29.6(5)	30.5(3)
O(1)–Ln–C(3)	75.9(4)	77.2(2)
C(1)–Ln–C(3)	49.8(5)	49.3(3)
C(2)–Ln–C(3)	29.4(6)	29.2(3)
O(1)–Ln–C(4)	85.5(5)	87.6(3)
C(1)–Ln–C(4)	50.2(3)	48.1(3)
C(2)–Ln–C(4)	48.5(5)	47.9(3)
C(3)–Ln–C(4)	29.6(5)	29.3(3)
O(1)–Ln–C(5)	115.3(4)	115.3(2)
C(1)–Ln–C(5)	30.2(6)	29.5(3)
C(2)–Ln–C(5)	48.0(5)	48.2(3)
C(3)–Ln–C(5)	48.6(5)	47.6(2)
C(4)–Ln–C(5)	29.8(5)	27.8(3)
C(2)–C(1)–C(5)	106.2(16)	106.5(8)
C(1)–C(2)–C(3)	112.8(17)	110.7(8)
C(2)–C(3)–C(4)	109.4(16)	108.8(9)
C(3)–C(4)–C(5)	103.5(15)	106.5(9)
C(5)–C(4)–C(9)	118.9(17)	120.7(10)
C(1)–C(5)–C(4)	107.6(15)	107.3(8)
C(4)–C(5)–C(6)	117.7(19)	121.9(9)
C(5)–C(6)–C(7)	119.2(24)	117.5(11)
C(6)–C(7)–C(8)	121.7(29)	119.9(13)
C(7)–C(8)–C(9)	125.9(28)	120.3(14)
C(4)–C(9)–C(8)	116.0(24)	119.5(14)

Under suitable conditions, the desired complexes $(C_9H_7)_3Ln \cdot THF$ were obtained by crystallization from solution. The complexes $(\eta^5-C_9H_7)_3Ln \cdot OC_4H_8$ ($Ln = Nd, Gd, Er$) were characterized by elemental analysis, IR and 1H -NMR spectroscopy and mass spectrometry of hydrolytic products.

2. Structure

The atomic coordinates, selected bond lengths and angles of all non-hydrogen atoms of complexes **1** and **2** are listed in Table 3–5. The molecular and crystal structures of complex **1** and the packing of molecules in the unit cell are shown in Figs. 1 and 2, respectively.

The crystal structure analysis shows that the two complexes **1** and **2** are isostructural. The O atom of the THF molecule and the five-membered rings of the three π -bonded indenyl moieties are arranged almost tetrahedrally around the Nd (Gd) atom, and Nd (Gd) coordination number is 10. The average bond lengths Nd–C and Gd–C are 2.812 and 2.795 Å, respectively (the Nd–O bond length is 2.557(21) Å and Gd–O is 2.459(13) Å), comparable with the Nd–C(Cp) bond length (2.849 Å) in the complex $[Na(OC_4H_8)_6][Nd(\eta^5-C_9H_7)_3(\mu-Cl)Nd(\eta^5-C_9H_7)_3]$ [7]. The tetrahedral coordination approaches regularity as illustrated by the following angles: Co–Nd(Gd)–Coa = Co–Nd(Gd)–Cob = Coa–Nd(Gd)–Cob = 116.6° (116°), Co–Nd(Gd)–O(1) = Coa–Nd(Gd)–O(1) = Cob–Nd(Gd)–O(1) = 100.7°

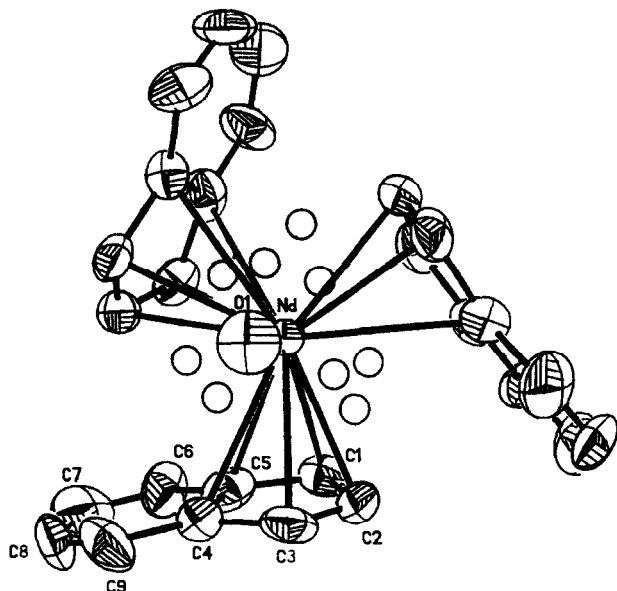


Fig. 1. Molecular structure of $(\eta^5\text{-C}_9\text{H}_7)_3\text{Nd}\cdot\text{OC}_4\text{H}_8$.

(101.7°), which are also different from the Co–Nd–Coa(Cob), Coa–Nd–Cob angles of $115.2(5)$, $114.9(6)$ and $113.7(6)^\circ$ in complex $[\text{Na}(\text{OC}_4\text{H}_8)_6][\text{Nd}(\eta^5\text{-C}_9\text{H}_7)_3(\mu\text{-Cl})\text{Nd}(\eta^5\text{-C}_9\text{H}_7)_3]$. (Cp = the five-membered rings of the three indenyl moieties; Co, Coa and Cob = centroid of the five-membered rings of the three indenyl moieties).

In Table 6, the equations of the best planes of the “five-membered rings”, their atomic deviations and torsion angles are listed.

In the crystal structures of complexes **1** and **2**, it can be seen that Nd(Gd) and O(1) are located at the special positions of the three-fold axis, and the three indenyl

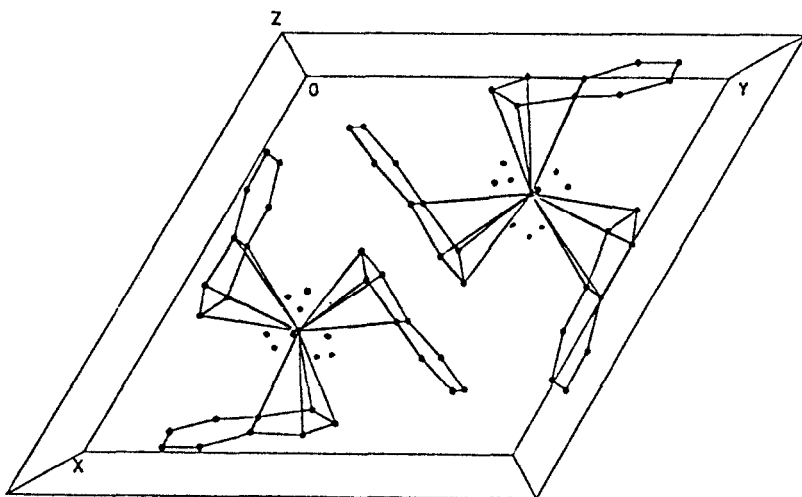


Fig. 2. The packing of $(\eta^5\text{-C}_9\text{H}_7)_3\text{Nd}\cdot\text{OC}_4\text{H}_8$ in the unit cell.

Table 6

The equations of the best planes of the "five-membered rings", atomic deviations and their torsion angles of complex 1 [complex 2]

Plan	Equation, atoms and their deviation (Å)	Torsion angle (deg)	
		P(1a)	P(1b)
P(1)	$9.742X + 0.579Y - 2.086Z = 8.7832$ $[9.478X + 0.959Y - 2.167Z = 8.6926]$ C(1) C(2) C(3) C(4) C(5) -0.033 0.036 -0.022 0.001 0.018 [-0.034] [0.036] [-0.021] [-0.001] [0.021]	64.0 [64.4]	64.0 [64.4]
P(1a)	$10.321X - 9.742Y + 2.086Z = 1.5378$ $[10.436X - 9.478Y + 2.167Z = 1.7438]$ C(1a) C(2a) C(3a) C(4a) C(5a) 0.033 -0.036 0.022 -0.001 -0.018 [0.034] [-0.036] [0.021] [0.001] [-0.021]		116.0 [115.6]
P(1b)	$-0.579X + 10.321Y + 2.086Z = 0.9587$ $[-0.959X + 10.436Y + 2.167Z = 0.7851]$ C(1b) C(2b) C(3b) C(4b) C(5b) 0.033 -0.036 0.022 -0.001 -0.018 [0.034] [-0.036] [0.021] [0.001] [-0.021]		

moieties at its general positions so the complexes have the symmetry of C_3 , but the THF molecule has no such symmetry, so the arrangement of carbon atoms in the THF molecule is disordered. Because the positions of the carbon atoms in the THF molecule are uncertain, reliable estimates of bond lengths, angles and equivalent temperature factors have not been obtained. In Fig. 1, the small loops around the Nd(Gd)-O(1) axis denote the four disordered carbon atoms of the THF molecule.

Acknowledgements

This project was supported by a grant from the Chinese National Foundation of Natural Science.

References

- 1 (a) M. Tsutsui and H.J. Gysling, *J. Am. Chem. Soc.*, 90 (1968) 6880; (b) *idem, ibid.*, 91 (1969) 3175.
- 2 W. Chen, S. Xiao, Y. Wang and G. Yu, *Kexue Tongbao*, 22 (1983) 1370.
- 3 W. Chen and X. Wang, *Acta Chim. Sin.*, 43 (1985) 295.
- 4 (a) A. Zazzetta and A. Greco, *Acta Crystallogr., Sect. B*, 35 (1979) 457; (b) J.L. Atwood, J.H. Burns and P.G. Laubereau, *J. Am. Chem. Soc.*, 95 (1973) 1830.
- 5 G.N. Papatheodorou, *J. Chem. Phys.*, 66 (1977) 2893.
- 6 S. Zhang and W. Chen, *Kexue Tongbao*, 6 (1990) 432.
- 7 (a) Y. Su, Z. Jin and W. Chen, *J. Chin. Rare Earth Soc.*, 2 (1990) 106; (b) M. Chen, G. Wu, W. Wu, S. Zhuang and Z. Huang, *Organometallics*, 7 (1988) 802.
- 8 The Sadtler Standard Spectra, $^1\text{H-NMR}$, Sadtler Research Laboratories, Inc., Philadelphia, 1971, No. 10408.