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Synthesis of phenyl lanthanide dichloride complexes and crystal structure of $C_6H_5GdCl_2 \cdot 4THF$

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Abstract

Anhydrous lanthanide trichlorides react with phenyl lithium in THF(tetrahydrofuran) to give the complexes, $C_6H_5LnCl_2 \cdot n$THF (Ln = Pr, Sm, Gd; $n = 3$, 4). The crystal structure of the $C_6H_5GdCl_2 \cdot 4$THF was determined by X-ray diffraction, orthorhombic space group $Ccm2_1$, a 12.776(6), b 12.954(6), c 15.802(3) Å, V 2615.4(1.8) Å^3, $Z = 4$. The final R is 0.0438, Rw 0.0445, Gd^{3+} coordination number 7. The length of the Gd–C bond is 2.416(24) Å, the average Gd–Cl bond length is 2.677(8) Å, that of Gd–O is 2.508(4) Å, and the C–C distance in the phenyl group is 1.378(41) Å.

Introduction

Phenyl lanthanide is a typical compound with Ln–C σ bonds. In 1970, Hart et al. [1] first reported the synthesis of $Sc(C_6H_5)_3$, $Y(C_6H_5)_3$, $LiLa(C_6H_5)_4$ and $LiPr(C_6H_5)_4$. In 1972, Cotton et al. [2] determined the crystal structure of $[Li(THF)_4]$. $[Lu(C_6H_3\text{-}2,6\text{-}CH_3)_4]$ for the first time. Because of the difficulties in separation and the unstable nature of phenyl lanthanide compounds, very few further studies were reported, and there has been no work on phenyl lanthanide chlorides. In this paper we report the synthesis of $C_6H_5LnCl_2 \cdot n$THF (Ln = Pr, Sm, Gd; $n = 3$, 4) and the determination of crystal structure of $C_6H_5GdCl_2 \cdot 4$THF.

Experimental

Reagents

The solvents, THF and Et_2O, were treated with NaOH, refluxed on sodium strips and distilled under nitrogen before use.

Anhydrous lanthanide trichlorides [3] and phenyllithium [4] were prepared by published procedures.

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Table 1

Analytical data

Complex	Color	Anal. (Found (calc.)/%)				Yield/%
		Ln	Cl	C	H	
$C_6H_5PrCl_2 \cdot 3THF$	light yellow	28.02 (27.89)	13.94 (14.03)	28.24 (42.74)	5.50 (5.78)	55–60
$C_6H_5SmCl_2 \cdot 4THF$	light yellow	24.52 (25.63)	13.01 (12.08)	30.62 (45.03)	5.80 (6.36)	50–60
$C_6H_5GdCl_2 \cdot 4THF$	white	26.02 (26.49)	11.77 (11.94)	37.42 (44.51)	5.82 (6.28)	60–65

Preparation of $C_6H_5LnCl_2 \cdot n$THF

Anhydrous $LnCl_3$ (5.0 mmol) (Ln = Pr, Sm, Gd) in a glass vessel was heated over a naked flame under reduced pressure for several minutes, and then cooled under nitrogen. THF was added and the resulting solution was stirred for several hours. An etherial solution of phenyllithium (2.5 mmol) was then allowed to react with the THF solution of $LnCl_3$. After 35 h with stirring, a yellowish clear solution was separated off. The solution was slowly concentrated under reduced pressure, and then placed in a refrigerator to produce rod-shaped crystals of the title complexes:

$$LnCl_3 + LiC_6H_5 \xrightarrow{THF} C_6H_5LnCl_2 \cdot n\text{THF}$$

(Ln = Pr, Sm, Gd; $n = 3, 4$)

The elemental analyses of the complexes are shown in Table 1. IR(cm^{-1}): 2970(s), 2870(s), 2160(s), 1592(w), 1480(m), 1455(w), 1245(w), 1175(w), 1065(m), 1040(s), 910(w), 885(m), 758(w), 700(w) and 480(w). The ^{1}H-NMR signals of the hydrolytic products were observed at 1.87, 3.72 and 7.31 ppm. The thermogravimetry data of the complexes are listed in Table 2.

Determination of crystal structure

A single crystal of dimensions 0.16 × 0.14 × 0.82 mm was sealed in a thin-walled lithium-glass capillary under nitrogen. Diffraction intensities were collected at room

Table 2

Thermogravimetry data

Complexes	Temperature °C	Weight loss/%	Referred to number of THF's (Calc./%)
$C_6H_5PrCl_2 \cdot 3THF$	100	20.8	1.5 (21.4)
	170	28.0	2 (28.5)
	320	41.5	3 (42.8)
$C_6H_5SmCl_2 \cdot 4THF$	50	10.2	1 (12.3)
	90	25.0	2 (24.6)
	140	34.0	3 (36.8)
	350	50.0	4 (49.1)
$C_6H_5GdCl_2 \cdot 4THF$	85	12.2	1 (12.1)
	160	36.5	3 (36.4)
	300	46.5	4 (48.5)

Table 3

Crystallographic data of $C_6H_5GdCl_2 \cdot 4THF$

Formula	$GdO_4C_{22}H_{37}$
Crystal system	orthorhombic
Space group	$Ccm2_1$
Cell constants	
a/Å	12.776(6)
b/Å	12.954(6)
c/Å	15.802(3)
$\alpha = \beta = \gamma$, (°)	90
V/Å^3	2615.4(1.8)
Z	4
Dc/g cm^{-3}	1.43
μc/cm^{-1}	29.3
$F(000)$	1120
R	0.0438
Rw	0.0445

temperature on a Nicolet $R3m/E$ four-circle diffractometer with Mo$K\alpha$ radiation (0.71069 Å) and a scan range $3 < 2\theta < 48°$. Of the 1246 reflections collected, 703 reflections with $I \geq 3\sigma(I)$ were considered observed.

The structure was solved by heavy-atom method by use of the SHELXTL program system. The position of the heavy atom, Gd^{3+}, was found from Patterson maps. The position of other non-hydrogen atoms were found by use of Fourier techniques. The coordinates of hydrogen atoms were added according to theoretical models.

The crystallographic data of $C_6H_5GdCl_2 \cdot 4THF$ are listed in Table 3.

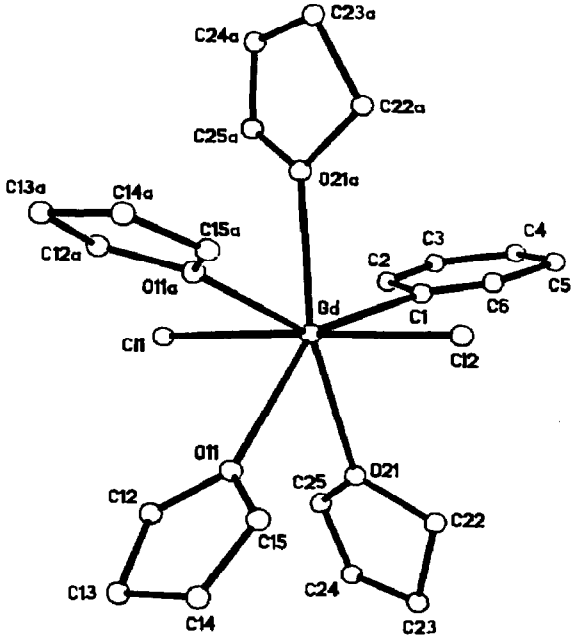

Fig. 1. Structure of $C_5H_5GdCl_2 \cdot 4THF$

Results and discussion

The elemental analysis data are consistent with calculated values except for the carbon ones. The analytical values of carbon are lower than calculated ones probably because formation of metal carbide renders the burning of carbon incomplete [1].

The IR data of the complexes indicate the absorption bands of benzene ring at 1592 and 1480 cm^{-1}, THF molecule at 1065 and 910 cm^{-1}, and Ln–Cl at 480 cm^{-1}, respectively.

The ^{1}H-NMR data of the hydrolytic products of the complexes show that the complexes contain benzene (signal at 7.31 ppm) [5]. The thermogravimetry indicates

Table 4

Bond lengths/Å

Gd–Cl(1)	2.650(7)	Gd–Cl(2)	2.694(9)
Gd–O(11)	2.584(14)	Gd–O(21)	2.432(14)
Gd–C(1)	2.412(24)	Gd–O(11a)	2.584(14)
Gd–O(21a)	2.432(14)	O(11)–C(12)	1.335(51)
O(11)–C(15)	1.308(38)	O(21)–C(22)	1.355(28)
O(21)–C(25)	1.319(61)	C(1)–C(2)	1.400(36)
C(1)–C(6)	1.309(38)	C(2)–C(3)	1.383(39)
C(3)–C(4)	1.376(45)	C(4)–C(5)	1.401(43)
C(5)–C(6)	1.400(45)	C(12)–C(13)	1.477(63)
C(13)–C(14)	1.413(48)	C(14)–C(15)	1.355(52)
C(22)–C(23)	1.446(39)	C(23)–C(24)	1.327(57)
C(24)–C(25)	1.381(52)		

Table 5

Bond angles/deg

Cl(1)–Gd–Cl(2)	171.8(2)	Cl–Gd–O(11)	87.2(3)
Cl(2)–Gd–O(11)	86.1(3)	Cl–Gd–O(21)	89.0(3)
Cl–Gd–O(21)	92.7(3)	O(11)–Gd–O(21)	67.9(4)
Cl(1)–Gd–C(1)	95.6(5)	Cl(2)–Gd–C(1)	92.6(5)
O(11)–Gd–C(1)	145.9(3)	O(21)–Gd–C(1)	78.2(3)
Cl(1)–Gd–O(11a)	87.2(3)	Cl(2)–Gd–O(11a)	86.1(3)
O(11)–Gd–O(11a)	68.1(6)	O(21)–Gd–O(11a)	135.9(4)
C(1)–Gd–O(11a)	145.9(3)	Cl(1)–Gd–O(21a)	89.0(3)
Cl(2)–Gd–O(21a)	92.7(3)	O(11)–Gd–O(21a)	135.9(4)
O(21)–Gd–O(21a)	156.0(6)	C(1)–Gd–O(21a)	78.2(3)
Gd–O(11)–C(12)	124.3(24)	Gd–O(11)–C(15)	131.4(20)
C(12)–O(11)–C(15)	104.3(31)	Gd–O(21)–C(22)	131.1(15)
Gd–O(21)–C(25)	123.2(20)	C(22)–O(21)–C(25)	103.2(27)
Gd–C(1)–C(2)	124.2(17)	Gd–C(1)–C(6)	124.1(22)
C(2)–C(1)–C(6)	111.7(27)	C(1)–C(2)–C(3)	132.6(29)
C(2)–C(3)–C(4)	110.7(28)	C(3)–C(4)–C(5)	121.4(29)
C(4)–C(5)–C(6)	120.4(30)	C(1)–C(6)–C(5)	123.2(32)
O(11)–C(12)–C(13)	108.9(36)	C(12)–C(13)–C(14)	105.8(31)
C(13)–C(14)–C(15)	101.3(29)	O(11)–C(15)–C(14)	119.5(33)
C(21)–C(22)–C(23)	107.1(23)	C(22)–C(23)–C(24)	106.0(28)
C(23)–C(24)–C(25)	104.9(39)	O(21)–C(25)–C(24)	113.7(45)

Table 6

Atomic coordinates (10^4) and equivalent temperature/Å^2 (10^3) of non-hydrogen atoms

Atom	x	y	z	U
Gd	0	5823(1)	4282	66(1)
Cl(4)	0	4963(5)	3568(5)	71(2)
Cl(2)	0	8562(7)	5216(6)	86(3)
O(11)	1132(11)	6034(11)	5473(8)	96(6)
O(21)	1862(11)	5958(11)	3982(7)	80(5)
C(1)	0	7773(18)	2969(16)	69(10)
C(2)	0	7315(25)	2167(16)	94(14)
C(3)	0	7720(25)	1358(18)	109(17)
C(4)	0	8782(24)	1383(21)	118(19)
C(5)	0	9320(25)	2152(15)	103(15)
C(6)	0	3782(24)	2920(24)	87(15)
C(12)	1540(51)	5086(36)	5450(32)	380(39)
C(13)	2112(22)	4901(28)	6244(19)	155(17)
C(14)	2068(28)	5835(28)	6703(21)	139(15)
C(15)	1489(36)	6429(29)	6176(22)	242(26)
C(22)	2543(21)	7749(16)	4091(31)	152(19)
C(23)	3570(17)	7371(32)	3863(31)	229(39)
C(24)	3410(31)	6555(25)	3372(29)	219(30)
C(25)	2352(24)	5349(47)	3444(43)	332(42)

that $C_6H_5PrCl_2 \cdot 3THF$ includes three molecules of THF, $C_6H_5SmCl_2 \cdot 4THF$ and $C_6H_5GdCl_2 \cdot 4THF$ contain four molecules of THF, respectively.

The molecule is depicted in Fig. 1. The bond lengths, angles and atomic coordinates of all non-hydrogen atoms are listed in Tables 4, 5 and 6, respectively.

Table 7

The equations of the best planes of the rings, atomic deviations and their torsion angles

Plane	Equation, atoms and their deviation/Å						Torsion angle /deg
1	$12.776X + 0.000Y + 0.000Z = 0.0000$						
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	
	0.0000	0.0000		0.0000	0.0000	0.0000	
2	$10.899X + 4.359Y - 6.301Z = 0.5183$						31.5
	O(11)	C(12)	C(13)	C(14)	C915)		
	−0.0881	0.0893	−0.0598	0.0132	0.0454		
3	$2.376X - 7.069Y + 12.912Z = 0.5471$						79.3 110.5
	O(21)	C(22)	C(23)	C(24)	C(25)		
	0.1311	−0.1293	0.0916	−0.0271	−0.0663		
4	$10.899X - 4.359Y + 6.301Z = -0.5183$						31.5 62.9
	O(11a)	C912a)	C(13a)	C(14a)	C(15)		48.1
	0.0881	−0.0893	0.0598	−0.0132	−0.0454		
5	$2.376X + 7.069Y - 12.912Z = -0.5471$						79.3 48.1
	O(21a)	C(22a)	C(23a)	C924a)	C(25a)		158.6 110.5
	−0.1311	−0.1293	0.0916	−0.0271	−0.0663		

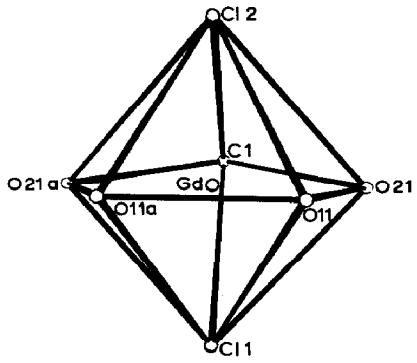

Fig. 2. Perspective drawing of the molecule, showing the pentagonal bipyramid coordination around Gd.

It can be seen from the data of Table 4 that the average bond length of C–C from phenyl group is 1.378 Å which approximates the C–C bond length in neutral benzene ring 1.39 Å.

It is known that the covalent radii of Gd^{3+} (1.11 Å) and Sm^{3+} (1.13 Å) are similar. The Gd–C(phenyl group) bond length of 2.412 Å is shorter than that of the Sm–C(phenyl group) bond of 2.511 Å in $(C_5H_5)_2Sm(C_6H_5) \cdot THF$ [6].

In Table 7 are listed the equations of the best planes of the rings, atomic deviations and their torsion angles. The phenyl group is perfectly planar. The planes are all distorted from P_2 to P_5 to different extents from the ideal model.

The coordination environment around Gd^{3+} and packing of the unit cell is depicted in Figs 2 and 3, respectively. One carbon atom of the phenyl group and four oxygen atoms from THF molecules are located in one plane with the centre of Gd^{3+} bonded to two chlorine atoms to give a bipyramid (Fig. 2). One chlorine is located at each apex of the pentagonal bipyramid.

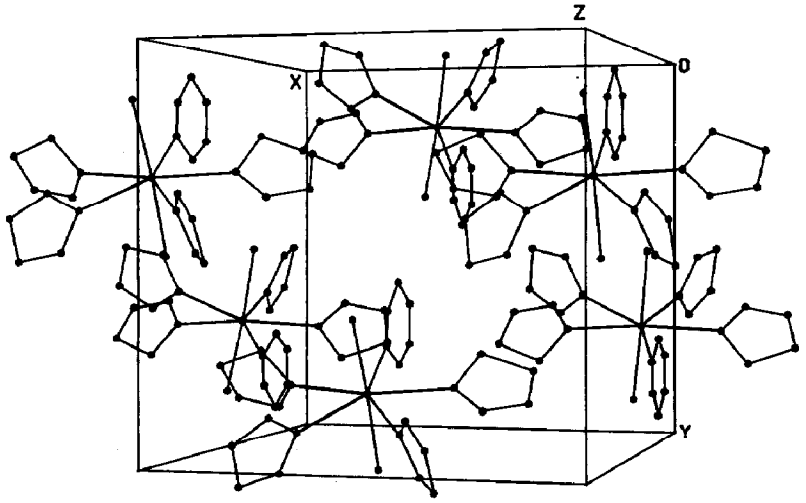

Fig. 3. The unit cell.

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