

## CRYSTAL STRUCTURE OF CYCLOPENTADIENYLNEODYMIUM DICHLORIDE

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### Summary

The compound  $\eta^5\text{-C}_5\text{H}_5\text{NdCl}_2 \cdot 3\text{THF}$  was successfully prepared from  $\text{NaC}_5\text{H}_5$  and  $\text{NdCl}_3$  in tetrahydrofuran (THF). Methods preventing disproportionation are discussed.

X-ray diffraction data of the compound were collected at low temperature (about 210 K). Crystals belong to monoclinic space group  $P2_1/n$  with  $a$  7.864(3),  $b$  17.198(7),  $c$  15.212(5) Å,  $\beta = 94.46(3)^\circ$ ,  $Z = 4$ . 1791 reflections were considered observed. The structure was solved by heavy-atom methods. Least-squares refinement converged to a final value of  $R = 0.049$ .

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### Introduction

The syntheses of cyclopentadienyl dichlorides of the heavier lanthanides ( $\eta^5\text{-C}_5\text{H}_5\text{LnCl}_2 \cdot 3\text{THF}$ ) and determination of crystal structure of  $\eta^5\text{-C}_5\text{H}_5\text{YbCl}_2 \cdot 3\text{THF}$  [1] have been reported. A 1:1 ratio of cyclopentadienyl sodium and anhydrous lanthanide trichloride gave tricyclopentadienyl neodymium instead of the desired product, cyclopentadienylneodymium dichloride, owing to disproportionation [2]. We have improved the preparative conditions to give cyclopentadienyl neodymium dichloride tetrahydrofuranates [3]. In order to verify the existence of the title compound we determined its crystal structure.

The compound acts as the main catalyst when combined with aluminum alkyls, in initiating butadiene polymerisation. The polymerisation activities [4] and kinetics [5] have been reported.

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## Experimental

### 1. Preparation of the crystal

Freshly distilled cyclopentadiene (0.41 ml (0.005 mol)) was dissolved in refined tetrahydrofuran (THF) (30 ml). To this solution was added metallic Na and the reaction mixture was left to stand for 50 min.

Solid  $\text{NdCl}_3$  (1.25 g, 0.005 mol) in a glass bottle was heated over a naked flame under reduced pressure for several minutes, then cooled by filling it with nitrogen, THF was added and the resulting solution was left to stand overnight.  $\eta^5\text{-C}_5\text{H}_5\text{NdCl}_2 \cdot 3\text{THF}$  was finally obtained by allowing the cyclopentadienyl sodium tetrahydrofuran solution to react with the  $\text{NdCl}_3$  solution with stirring for 5 h. After reaction was complete, the solution/suspension was centrifuged to remove unused solid. A certain amount of gasoline was added to the bottle until the solution went slightly turbid. The solution was then placed in a refrigerator for crystallization. Analytical data of  $\eta^5\text{-C}_5\text{H}_5\text{NdCl}_2 \cdot 3\text{THF}$  are: Found: Nd 29.90, Cl 15.07; calc: Nd 29.05, Cl 14.36%.

### 2. Determination of crystal structure

Since the compound is unstable at room temperature the sample was kept in a cooling stream of nitrogen (about 210 K) during the period of data collection. Diffracted intensities were collected on a Nicolet XRD four circle diffractometer (R3), with the use of a graphite monochromator,  $\text{Mo-K}_\alpha$  radiation (0.71069 Å), a scan range  $3 < 2\theta < 45^\circ$  and a scan mode  $\theta-2\theta$  at variable speeds. Of the 2685 reflections measured, 1791 reflections with  $I \geq 3\sigma(I)$  were considered observed.

Systematic absences for reflections,  $h0l$  with  $h+l$  odd, and  $0k0$  with  $k$  odd, fixed the space group as  $P2_1/n$ . For crystal data of  $\eta^5\text{-C}_5\text{H}_5\text{NdCl}_2 \cdot 3\text{THF}$  see Table 1.

Lp correction was applied. The structure was solved by heavy-atom methods by use of the SHELXTL program system. The position of the heavy atom was found from Patterson maps. After several cycles of electron-density calculations the coordinates of all non-hydrogen atoms were obtained and the preliminary structure model was established.

The atomic coordinates and anisotropic temperature factors for all non-hydrogen atoms were refined by block-diagonal least squares using unit weighting for each reflection in later cycles.

The coordinates of hydrogen atoms were added according to theoretical models. The refinement finally converged to  $R = 0.049$  ( $R = \Sigma(|F_o - F_c|)/F_o$ ).

TABLE 1

#### CRYSTALLOGRAPHIC DATA OF $\eta^5\text{-C}_5\text{H}_5\text{NdCl}_2 \cdot 3\text{THF}$

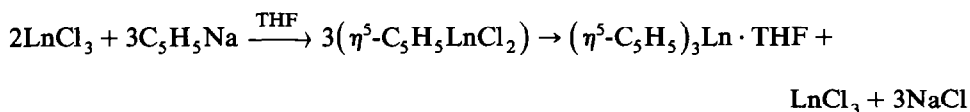
Monoclinic system	Space group $P2_1/n$
$a$ 7.864(3) Å	$b$ 17.198(7) Å
$c$ 15.212(5) Å	$\beta$ 94.46(3)°
$F(000) = 1028(e)$	$Z = 4$
$V$ 2046.52 Å <sup>3</sup>	$\mu(\text{Mo-K}_\alpha)$ 28.16 cm <sup>-1</sup>
Crystal size ca 0.35 × 0.30 × 0.13 mm <sup>3</sup>	

TABLE 2  
EFFECT OF REACTANT RATIOS ON COMPOSITION OF PRODUCTS

Central ion	Molar ratio of C <sub>5</sub> H <sub>5</sub> Na to LnCl <sub>3</sub>				
	0.25	0.5	1.0	1.5	2.0
La <sup>3+</sup>	(C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> La·OC <sub>4</sub> H <sub>8</sub>	(C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> La·OC <sub>4</sub> H <sub>8</sub>			
Ce <sup>3+</sup>		C <sub>5</sub> H <sub>5</sub> CeCl <sub>2</sub> ·OC <sub>4</sub> H <sub>8</sub>	(C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> Ce·OC <sub>4</sub> H <sub>8</sub>		
Pr <sup>3+</sup>		C <sub>5</sub> H <sub>5</sub> PrCl <sub>2</sub> ·OC <sub>4</sub> H <sub>8</sub>	uncertain	(C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> Pr·OC <sub>4</sub> H <sub>8</sub>	
Nd <sup>3+</sup>		C <sub>5</sub> H <sub>5</sub> NdCl <sub>2</sub> ·OC <sub>4</sub> H <sub>8</sub>	uncertain	uncertain	(C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> Nd·OC <sub>4</sub> H <sub>8</sub>

### Discussion of preparative methods

The previous method for preparing the cyclopentadienyl heavier lanthanide dichloride compounds involves reaction of cyclopentadienyl sodium with anhydrous lanthanide trichlorides in a 1:1 ratio in THF to give crystalline solids but not  $\eta^5\text{-C}_5\text{H}_5\text{LnCl}_2 \cdot 3\text{THF}$  (Ln = La, Ce, Pr and Nd) [1]. This is mainly due to the larger radii and coordination unsaturation of the lighter lanthanides, and the disproportionation reaction, which takes place as follows:



Three methods for the preparation of  $\eta^5\text{-C}_5\text{H}_5\text{LnCl}_2 \cdot 3\text{THF}$  (Ln = La, Ce, Pr and Nd) were used.

1. *Changing reactant ratios.* The products prepared at various reactant ratios are listed in Table 2 [3], from which it can be seen that when the molar ratios of C<sub>5</sub>H<sub>5</sub>Na to LnCl<sub>3</sub> are 1:2, cyclopentadienyl lighter-lanthanide (except lanthanum) dichlorides can be obtained.

2. *NdCl<sub>3</sub> · nTHF as starting materials.* Anhydrous lanthanide trichlorides were dissolved in THF. The solution was then centrifuged to remove suspended solids. To the solution was added a certain amount of gasoline. The resulting solution was kept below 0°C until recrystallization was complete. The Nd and Cl content of NdCl<sub>3</sub> · nTHF were determined and the values of *n* were calculated. The complex, NdCl<sub>3</sub> · nTHF, used as starting material, reacted with C<sub>5</sub>H<sub>5</sub>Na in a molar ratio of 1:1 or 1:2 in THF to give  $\eta^5\text{-C}_5\text{H}_5\text{NdCl}_2 \cdot 3\text{THF}$  or (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>NdCl · THF [6]. The yield, however, of NdCl<sub>3</sub> · nTHF obtained this way was low.

3. *Purification of anhydrous lanthanide trichlorides.* Anhydrous lanthanide trichlorides dehydrated with SOCl<sub>2</sub>, were heated over an open flame in a glass bottle in vacuo to remove the remaining HCl and SO<sub>2</sub>, THF was then added and the resulting mixture was left to stand overnight giving LnCl<sub>3</sub> · nTHF [7]. The anhydrous lanthanide trichlorides were washed twice with THF and dried under reduced pressure at room temperature giving LnCl<sub>3</sub> · nTHF.

### Description of the structure

The atomic coordinates, bond lengths and angles of all non-hydrogen atoms are listed in Tables 3, 4 and 5. The stereo-plot of the molecule and packing of the unit cell are shown in Fig. 1 and Fig. 2, respectively.

The molecule is composed of two  $\text{Cl}^-$  and one  $(\eta^5\text{-C}_5\text{H}_5\text{Nd} \cdot 3\text{THF})^{2+}$ . In the cation, the central atom  $\text{Nd}^{\text{III}}$  is bonded to the five carbon atoms of cyclopentadiene and to the oxygen atoms of the three THF molecules to form a coordination polyhedron. The five carbon atoms of  $\text{C}_5\text{H}_5$  group are coplanar and form a regular pentagon with the sum of inner angles equal to  $540^\circ$ . From Table 4 and 5 it can be seen that Nd atom is situated directly above the centre of the pentagon, i.e. with almost equal distances from the five C atoms, resulting in a 5-sided cone. Bond angles indicate that the line passing through O(2) and Nd is the axis of the 5-sided cone, while Cl(1) Cl(2) O(1) O(3) are located symmetrically around the axis. There is a  $C_{2v}$  symmetry about Nd Cl(1) Cl(2) O(1) O(2) O(3) which becomes  $C_s$  when the  $\text{C}_5\text{H}_5$  group is taken account. Obviously the mirror plane is that containing the Nd, Cl(1), Cl(2), O(2) and C(43) atoms.

The best planes and torsion angles of some atomic groups are given in Table 6. As a rule, the sum of the internal angles of a pentagon should be  $540^\circ$ , so the smaller the deviations of atoms from best planes, the closer they are to a planar configuration. In view of this, one of THF rings, labelled plane 4 in Table 6 is

TABLE 3

COORDINATES ( $\times 10^4$ ) AND EQUIVALENT TEMPERATURE FACTORS ( $\text{\AA}^2 \times 10^3$ ) OF NON-HYDROGEN ATOMS

Atom	x	y	z	U
Nd	548(1)	5506(1)	7644(1)	30(0)
Cl(1)	-2117(5)	5182(3)	8617(2)	54(1)
Cl(2)	2614(5)	5311(2)	6306(2)	52(1)
O(1)	2078(10)	4416(5)	8377(5)	38(3)
C(11)	1549(21)	3999(10)	9146(10)	63(7)
C(12)	2931(24)	3440(14)	9419(13)	89(8)
C(13)	4472(22)	3716(12)	8992(15)	92(9)
C(14)	3834(18)	4186(11)	8202(13)	77(8)
O(2)	-847(11)	4356(6)	6838(6)	53(4)
C(21)	-2637(22)	4272(16)	6528(19)	133(13)
C(22)	-2802(27)	3550(12)	6078(20)	134(13)
C(23)	-1275(28)	3089(12)	6196(12)	85(9)
C(24)	27(22)	3641(11)	6670(13)	78(8)
O(3)	-1560(11)	6106(6)	6585(6)	48(4)
C(31)	-1306(22)	6215(15)	5650(10)	97(10)
C(32)	-2956(25)	6566(15)	5231(12)	102(10)
C(33)	-3802(22)	6938(12)	5989(11)	79(8)
C(34)	-3233(19)	6463(11)	6795(11)	64(7)
C(41)	1987(20)	6248(10)	9136(11)	61(7)
C(42)	3261(20)	6315(9)	8512(11)	56(6)
C(43)	2641(19)	6813(9)	7826(11)	57(6)
C(44)	978(19)	7083(9)	8012(12)	62(7)
C(45)	571(20)	6728(9)	8829(10)	52(6)

TABLE 4  
BOND LENGTHS (Å)

Nd–Cl(1)	2.712(4)	Nd–Cl(2)	2.719(4)
Nd–O(1)	2.448(9)	Nd–O(2)	2.529(10)
Nd–O(3)	2.445(9)	Nd–C(41)	2.768(16)
Nd–C(42)	2.788(15)	Nd–C(43)	2.785(15)
Nd–C(44)	2.786(15)	Nd–C(45)	2.768(15)
O(1)–C(11)	1.460(19)	O(1)–C(14)	1.476(17)
C(11)–C(12)	1.484(27)	C(12)–C(13)	1.493(28)
C(13)–C(14)	1.502(28)	O(2)–C(21)	1.453(20)
O(2)–C(24)	1.411(21)	C(23)–C(24)	1.534(27)
C(22)–C(23)	1.437(30)	O(3)–C(34)	1.506(18)
O(3)–C(31)	1.463(18)	C(32)–C(33)	1.520(27)
C(31)–C(32)	1.522(27)	C(41)–C(42)	1.436(24)
C(33)–C(34)	1.520(24)	C(42)–C(43)	1.406(22)
C(41)–C(45)	1.432(22)	C(44)–C(45)	1.443(24)
C(43)–C(44)	1.435(22)		

TABLE 5  
MAIN BOND ANGLES (°)

Cl(1)–Nd–Cl(2)	155.9(1)	Cl(1)–Nd–O(1)	88.0(2)
Cl(1)–Nd–O(2)	77.4(2)	Cl(1)–Nd–O(3)	86.3(2)
Cl(2)–Nd–O(1)	86.9(2)	Cl(2)–Nd–O(2)	78.6(2)
Cl(2)–Nd–O(3)	88.4(2)	O(1)–Nd–O(2)	78.5(3)
O(1)–Nd–O(3)	155.0(3)	O(2)–Nd–O(3)	76.5(3)
C(41)–Nd–C(42)	29.5(5)	C(41)–Nd–C(43)	49.1(5)
C(41)–Nd–C(44)	49.5(5)	C(41)–Nd–C(45)	30.0(5)
C(42)–Nd–C(43)	29.2(5)	C(42)–Nd–C(44)	48.9(4)
C(42)–Nd–C(45)	49.2(5)	C(43)–Nd–C(44)	29.8(4)
C(43)–Nd–C(45)	49.3(5)	C(44)–Nd–C(45)	30.1(5)
O(1)–C(11)–C(12)	107.2(14)	C(11)–O(1)–C(14)	109.9(11)
C(11)–C(12)–C(13)	105.7(17)	O(1)–C(14)–C(13)	104.9(14)
C(12)–C(13)–C(14)	106.7(14)	C(21)–O(2)–C(24)	108.6(14)
C(21)–C(22)–C(23)	112.3(19)	O(2)–C(24)–C(23)	107.7(14)
O(2)–C(21)–C(22)	107.1(17)	C(22)–C(23)–C(24)	103.6(16)
O(3)–C(31)–C(32)	106.4(13)	C(31)–O(3)–C(34)	109.9(11)
C(31)–C(32)–C(33)	104.9(14)	O(3)–C(34)–C(33)	104.8(13)
C(32)–C(33)–C(34)	105.6(16)	Nd–C(41)–C(42)	75.8(9)
Nd–C(41)–C(45)	75.0(9)	Nd–C(42)–C(41)	74.2(9)
Nd–C(42)–C(43)	75.2(9)	Nd–C(43)–C(42)	75.5(9)
Nd–C(44)–C(45)	74.3(8)	Nd–C(45)–C(41)	75.0(9)
Nd–C(43)–C(44)	75.1(9)	Nd–C(44)–C(43)	75.0(9)
Nd–C(45)–C(44)	75.6(9)	C(42)–C(41)–C(45)	107.5(14)
C(41)–C(42)–C(43)	108.7(14)	C(42)–C(43)–C(44)	108.6(15)
C(41)–C(45)–C(44)	107.9(14)	C(43)–C(44)–C(45)	107.3(14)
O(2)–Nd–C(41)	153.1(4)	O(2)–Nd–C(42)	154.8(4)
O(2)–Nd–C(43)	155.3(4)	O(2)–Nd–C(44)	154.1(4)
O(2)–Nd–C(45)	152.8(5)	Cl(1)–Nd–C(41)	81.8(4)
Cl(1)–Nd–C(42)	107.9(4)	Cl(1)–Nd–C(43)	125.4(3)
Cl(1)–Nd–C(44)	107.3(4)	Cl(1)–Nd–C(45)	81.2(5)

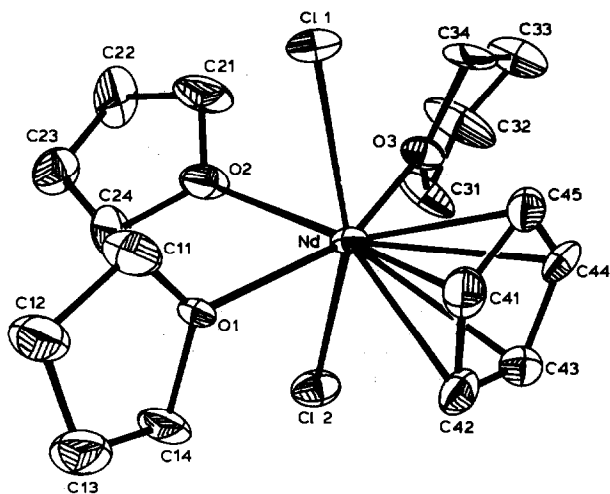
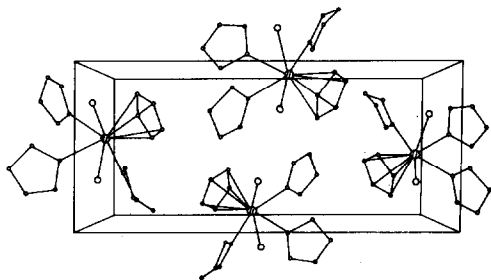
Fig. 1. Structure of  $\eta^5\text{-C}_5\text{H}_5\text{NdCl}_2 \cdot 3\text{THF}$ .

Fig. 2. Packing of the unit cell.

TABLE 6

## BEST PLANES OF RINGS AND THEIR TORSION ANGLES

Plane	Equation, atoms and deviation of atoms (Å)	Sum of inner angles	Torsion angles (°)
1	$2.872x + 13.450y + 7.216z = 15.56$ C(41) C(42) C(43) C(44) C(45) 0.01 -0.01 0.00 0.00 -0.01	$540^\circ$	
2	$1.849x + 12.679y + 9.324z = 13.79$ O(1) C(11) C(12) C(13) C(14) 0.01 0.07 -0.12 0.13 -0.08	$535.1^\circ$	10.8
3	$2.498x + 6.356y - 13.616z = -6.767$ O(2) C(21) C(22) C(23) C(24) 0.02 -0.04 0.04 -0.03 0.00	$539.5^\circ$	92.0 101.8
4	$4.143x + 14.365y + 1.698z = 9.23$ O(3) C(31) C(32) C(33) C(34) 0.01 0.12 -0.20 0.20 -0.13	$533.0^\circ$	22.5 33.1 69.9
5	$5.791x + 0.854y - 11.079z = -7.69$ Nd O(1) O(2) O(3) 0.01 -0.005 0.00 -0.005		91.7 102.4 32.8 70.8
6	$4.232x - 10.546y + 8.133z = 0.6273$ Nd Cl(1) Cl(2) 0.00 0.00 0.00		89.5, 87.8, 124.0, 98.0, 91.2

almost perfectly planar, whereas the other two THF rings are distorted to different extents from the ideal model.

Furthermore Table 6 shows that plane 4 (Nd, O(1), O(2), O(3)) makes an angle of  $91.7^\circ$  with the  $C_5H_5$  ring, while Cl(1) and Cl(2) are located on either side of the plane at the same distance normal to the plane. This indicates that it is the best geometrical arrangement in view of the stereochemistry. The orientation of THF rings seems reasonable, although there are no ideal symmetries.

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