Inorganica Chimica Acta, 130 (1987) 125–129

Crystal Structure of $NdCl_3 \cdot 4THF$ and its Catalytic Activity in Polymerization of Diene*

CHEN WENQI**, JIN ZHONGSHENG, XING YAN

Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, China

FAN YUGUO and YANG GUANGDI

Institute of Theoretical Chemistry of Jilin University, Changchun, China

(Received December 30, 1985; revised September 29, 1986)

Abstract

The crystal and molecular structures of $NdCl_3 \cdot 4THF$ have been determined by the low temperature (−60 °C) X-ray diffraction method. $NdCl_3 \cdot 4THF$ recrystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 9.404(4)$, $b = 21.591(5)$, $c = 11.751(3)$ Å, $\beta = 111.03(3)^\circ$, $Z = 4$. The final R value is 0.039. Three chlorine atoms and four oxygen atoms from THF are coordinated with the central Nd(III) ion to give a pentagonal bipyramid polyhedron with coordination number 7, the average Nd–Cl bond length is 2.674 Å and Nd–O 2.498 Å.

When combined with aluminum alkyls, $NdCl_3 \cdot 4THF$ is a highly effective catalyst for the polymerization of dienes.

Relationships between complex structures and polymerization activities are discussed and the difference in polymerization activities between $NdCl_3$ and $NdCl_3 \cdot 4THF$ is related to their crystal stabilities.

Introduction

It is known that when combined with aluminum alkyls, $NdCl_3$ is less active for the polymerization of dienes. If $NdCl_3$ is coordinated with some donors (D = ROH [1], R_3PO [2] and THF [3]) the polymerization activities of $NdCl_3 \cdot nD$ combined with aluminum alkyls will increase greatly. In order to study the relationship between polymerization activities and molecular structures we have determined the crystal structure of $NdCl_3 \cdot 4THF$.

The crystal structures of $NdCl_3 \cdot 3i\text{-}C_3H_7OH$ [4] and $NdBr_3 \cdot 4THF$ [5] have already been reported but the structure of $NdCl_3 \cdot 4THF$ has not been communicated as yet.

Experimental

Preparation of $NdCl_3 \cdot 4THF$

Anhydrous $NdCl_3$ was dissolved in THF. The solution was centrifuged to remove insoluble solid. Hexane was added to the clear solution and it was kept at a temperature below 0 °C to give a single purple crystal.

Polymerization Procedure

Reagents

Pure butadiene was purchased from Beijing Oil Co. Isoprene was freed of inhibitor by distillation and stored over active aluminum oxide prior to use. Hexane used as the polymerization solvent was purified by distilling under nitrogen and storing over active aluminum oxide.

Catalyst preparation

Into a predried and N_2 filled glass tube containing several glass beads a weighed quantity of $NdCl_3 \cdot 4THF$ was placed. A calculated quantity of solvent and $AlEt_3$ was added. The mixture was then shaken for several hours. The resulting suspension could be used for polymerization after overnight standing.

Polymerization procedure

Polymerizations were carried out in 50 ml glass bottles under N_2 atmosphere. The reagents were introduced into the bottle in the following order: the monomer, the solvent, and finally the catalyst. The polymerization reaction proceeded at 50 °C for 5 h and terminated by adding an ethanol solution containing antioxidant. The resulting polymer was precipitated with an excess of ethanol and dried to a constant weight. The conversion percent was calculated based on the quantities of monomers used and polymer obtained.

Polymer characterization

Infrared spectra of polymer films on NaCl plates were recorded on an 580B spectrophotometer. The

---

*Project supported by the Science Fund of the Chinese Academy of Sciences.

**Author to whom correspondence should be addressed.

0020-1693/87/$3.50

relative contents of *cis*-1,4-, 1,2- and *trans*-1,4-polybutadiene were calculated by the equation:

$$A = 17\,667\mathrm{D}_{738} + 3673.8\mathrm{D}_{911} + 4741.4\mathrm{D}_{967}$$

$$cis\text{-}1{,}4\ (\%) = (17\,667\mathrm{D}_{738}/A) \times 100$$

$$trans\text{-}1{,}4\ (\%) = (4741.4\mathrm{D}_{967}/A) \times 100$$

$$1{,}2\ (\%) = (3673.8\mathrm{D}_{911}/A) \times 100.$$

For polyisoprene the contents of *cis*-1,4 and 3,4 structures were calculated by the equations:

$$A = -8.82\mathrm{D}_{890} + 704.50\mathrm{D}_{1130} + 31.66\mathrm{D}_{890} - 7.43\mathrm{D}_{1130}$$

$$cis\text{-}1{,}4\ (\%) = (-8.82\mathrm{D}_{890} + 704.50\mathrm{D}_{1130}/A) \times 100$$

$$3{,}4\ (\%) = (31.66\mathrm{D}_{890} - 7.43\mathrm{D}_{1130}/A) \times 100$$

The intrinsic viscosity (η) of the polymers was determined with an Ubbelohde viscositymeter in toluene solution at 30 ℃.

Determination of Crystal Structure

Because crystals of $\mathrm{NdCl_3 \cdot 4THF}$ are unstable in air at room temperature crystal selection was carried out on a device made by ourselves under N_2 at −70 ℃. A good single crystal was chosen of size 0.40 × 0.30 × 0.04 mm.

The low temperature technique was adopted to protect the crystal and collect the X-ray diffraction data. X-ray diffraction data were collected on Nicolet XRD Corporation R3 Four Circle Diffractometer at −60 ℃ under the following conditions: Mo Kα (λ = 0.710 69 Å) radiation, graphite monochromator, scan mode θ–2θ at the speeds of 6 and 29.3 °/min, and scan range $4° \leqslant 2\theta \leqslant 40°$. Two control reflections were set and every 61 reflections a detection period was undertaken. Data for 2852 reflections were measured and 1791 reflections satisfying $I \geqslant 2.5\sigma(I)$ were accepted as being unique observations.

From the systematic absences in reflections $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ the space group was uniquely determined as monoclinic $P2_1/c$ with unit cell parameters a = 9.404(4), b = 21.591(5), c = 11.751(3) Å, β = 111.03(3)°, Z = 4, V = 2227(1) Å^3, $F(000)$ = 1148(e), μ = 27.12 cm^{-1}.

The crystal structure was solved by heavy atom methods using the SHELXTL programs. Lorentz polarization factor corrections have been made for all diffraction data. The coordinate parameters of the Nd atom were found from the Patterson map. The coordinate parameters of the carbon and oxygen atoms were obtained by the Fourier iteration technique. The coordinates of the non-hydrogen atoms and isotropic temperature factors were converged by least-square refinement R = 0.1013. After the coordinates of hydrogen atoms were added according to theoretical models, anisotropic temperature factors were refined. The structure parameters were further refined with blocked-matrix least-squares to a final R = 0.039. All calculations were carried out on an Eclipse S/250 minicomputer.

Results and Discussion

Description of the Structure

The coordinates, bond lengths and angles of non-hydrogen atoms are listed in Tables I, II and III. A perspective drawing of $\mathrm{NdCl_3 \cdot 4THF}$ is shown in Fig. 1.

The central Nd(III) ion is bonded with three chlorine and four oxygen atoms of the THF mole-

TABLE I. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3)

Atom	x	y	z	U^a
Nd	3436(1)	1164(1)	2063(1)	43(1)
Cl(1)	3212(4)	1039(1)	−248(2)	80(1)
Cl(2)	4364(4)	1329(1)	4485(2)	75(1)
Cl(3)	521(4)	1190(2)	1874(4)	111(2)
O(1)	5705(7)	1823(3)	2170(6)	64(3)
C(11)	5841(16)	2184(7)	1170(11)	109(7)
C(12)	7280(16)	2402(7)	1488(12)	102(8)
C(13)	8023(16)	2324(6)	2797(12)	94(7)
C(14)	7013(14)	1963(7)	3195(11)	102(8)
O(2)	5788(7)	504(3)	2710(6)	59(3)
C(21)	6870(14)	393(6)	2083(11)	88(6)
C(22)	8194(14)	116(6)	2967(12)	93(7)
C(23)	7843(15)	46(7)	4098(12)	101(7)
C(24)	6226(15)	86(7)	3692(12)	105(7)
O(3)	2754(8)	46(3)	1932(6)	57(3)
C(31)	2745(19)	−368(5)	996(12)	106(8)
C(32)	2486(20)	−994(6)	1411(15)	120(9)
C(33)	1697(19)	−865(6)	2248(17)	129(10)
C(34)	2005(22)	−272(6)	2598(16)	146(11)
O(4)	2676(7)	2259(3)	1571(5)	52(3)
C(41)	1549(16)	2470(6)	441(10)	90(6)
C(42)	1081(16)	3091(6)	667(11)	97(7)
C(43)	2018(25)	3219(8)	1845(12)	218(14)
C(44)	2806(19)	2704(5)	2457(11)	101(7)

^{a}Equivalent isotropic U defined as one third of the trace of the orthogonalised U tensor.

TABLE II. Bond Lengths (Å)

Nd–Cl(1)	2.664(3)	Nd–Cl(2)	2.689(3)
Nd–Cl(3)	2.666(4)	Nd–O(1)	2.530(7)
Nd–O(2)	2.509(7)	Nd–O(3)	2.493(6)
Nd–O(4)	2.485(6)		

TABLE III. Bond Angles (deg)

Cl(1)–Nd–Cl(2)	166.4(1)	Cl(1)–Nd–Cl(3)	102.2(1)
Cl(2)–Nd–Cl(3)	91.2(1)	Cl(1)–Nd–O(1)	82.3(2)
Cl(2)–Nd–O(1)	85.6(2)	Cl(3)–Nd–O(1)	144.4(2)
Cl(1)–Nd–O(2)	89.6(2)	Cl(2)–Nd–O(2)	80.6(2)
Cl(3)–Nd–O(2)	143.5(2)	O(1)–Nd–O(2)	70.8(2)
Cl(1)–Nd–O(3)	85.0(2)	Cl(2)–Nd–O(3)	100.0(2)
Cl(3)–Nd–O(3)	77.4(2)	O(1)–Nd–O(3)	183.1(2)
O(2)–Nd–O(3)	69.3(2)	Cl(1)–Nd–O(4)	86.9(2)
Cl(2)–Nd–O(4)	94.5(1)	Cl(3)–Nd–O(4)	76.0(2)
O(1)–Nd–O(4)	68.9(2)	O(2)–Nd–O(4)	139.7(2)
O(3)–Nd–O(4)	149.9(2)	Nd–O(1)–C(11)	125.3(6)
Nd–O(1)–C(14)	128.5(7)	Nd–O(2)–C(21)	129.1(6)
Nd–O(2)–C(24)	125.6(8)	Nd–O(3)–C(31)	126.3(7)
Nd–O(3)–C(34)	127.5(8)	Nd–O(4)–C(41)	124.8(6)
Nd–O(4)–C(44)	123.0(6)		

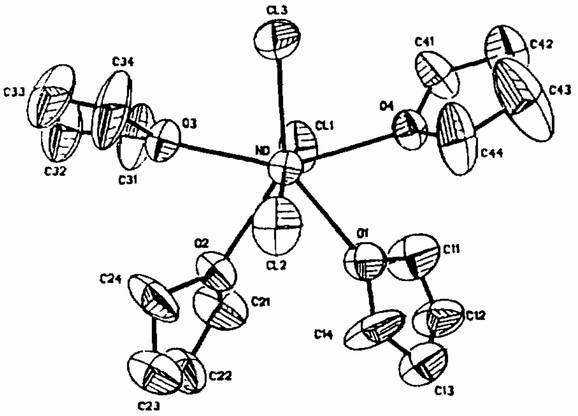

Fig. 1. Perspective drawing of $NdCl_3 \cdot 4THF$ (projected on 001 plane).

cule. The coordination number of the compound is 7. The coordination polyhedron is a pentagonal bipyramid, shown in Fig. 2. The plane (O(1) O(2) O(3) O(4) Cl(3)) equation is $-1.56x + 2.49y + 11.46z = 2.09$* with the r.m.s. deviation of –0.31 Å (O(3)). The plane (Cl(1) Cl(2) Nd) equation is $-1.03x + 21.31y - 1.04z = 1.91$. The torsion angle between the two planes is 90.1°. The bond angle of Cl_1–Nd–Cl_2 is 166.5°, which is close to 180°. The distance of Nd–Cl is in the range 2.664–2.689 Å and average value is 2.673 Å. The distance of Nd–O is in the range 2.485–2.530 Å and average value is 2.504 Å. In the pentagonal structure the average angles of Cl–Nd–O and O–Nd–O are 76.7° and 69.7°, respectively. The former is larger than the latter by 7°. This is because the chlorine atom is larger than the oxygen atom. The sum of these angles is 362.5°, which is close to 360°.

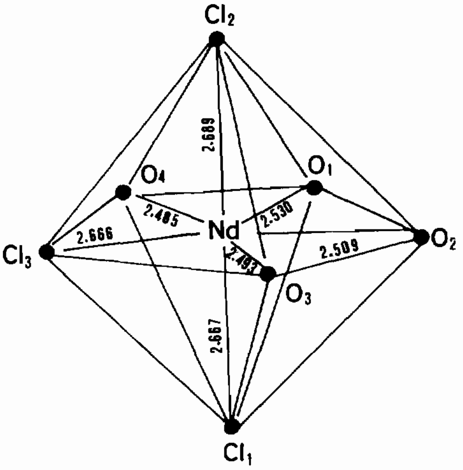

Fig. 2. Pentagonal bipyramid.

The angles of nip (O(i)) between the vectors of $Nd_{(O(i))}$ ($i = 1, 2, 3, 4$) and normals in the THF ring containing O(i) are O(1) = 112.2, O(2) = 104.7, O(3) = 90.4, O(4) = 79.8°. In Table IV the angles between the normals of the planes are as follows: P(2)–P(1) = 42.1, P(3)–P(2) = 77.2, P(3)–P(1) = 112.2, P(4)–P(3) = 68.3, P(4)–P(2) = 70.6, P(4)–P(1) = 104.9°.

From Table IV it can be seen that the plane P(2) is seriously distorted with the r.m.s. deviation of –2.6 Å. The internal angle sum of the pentagonal structure is 540° without torsion but that of P(2) is 527.3°. The planes of P(3) and P(4) are also distorted seriously with the r.m.s. deviations of 0.17 and 0.16 Å. It is interesting that the torsion is not only related to the internal angle sum but also the bond lengths of Nd–O. For example, the longest of four Nd–O bonds is 2.530 Å which is slightly distorted with the r.m.s. deviation of 0.09 Å (O(1)) from the plane (O(1) O(2) O(3) O(4) Cl(3)), of which the internal angle sum is near 540°.

Molecular Structure and Polymerization Activity

The crystal structure determination of $NdCl_3$ has been reported [6]. A comparison of molecular structure of $NdCl_3 \cdot 4THF$ with $NdCl_3$, $NdBr_3 \cdot 4THF$ and $NdCl_3 \cdot 3i\text{-}C_3H_7OH$ is very instructive. From Table V it can be seen that when different ligands are bonded with the central Nd(III) ion the space group changes greatly.

The $NdCl_3 \cdot 3i\text{-}C_3H_7OH$ molecules in the crystalline state are associated as dimers because of the coordinate unsaturation. From Table VI it can be seen that in order to satisfy coordinate saturation the molecules of $(C_5H_5)_2NdCl \cdot THF$ [7] in the crystalline state are also associated as dimers. However, all the complexes of $(C_5H_5)_3Nd \cdot THF$, $C_5H_5NdCl_2 \cdot 3THF$ [8] and $NdCl_3 \cdot 4THF$ in the crystalline state are monomer.

---

*The crystal coordinates were taken.

TABLE IV. Plane Equations of THF as well as their Average Bond Lengths (Å) and Angles (°)[a]

Plane	Equation and atomic deviation (d) (Å)	C–C	C–O	C–C–C	C–O–C	O–C–C	Internal angle sum	Average angle
P(1)	$-4.78x + 18.02y + 4.52z = 1.60$ O(1) C(11) C(12) C(13) C(14) −0.05 0.09 −0.09 0.05 0	1.428	1.442	105.1	110.1	106.1	583.3	107.7
P(2)	$1.69x + 19.40y + 3.70z = 2.75$ O(2) C(21) C(22) C(23) C(24) 0.21 −0.07 −0.07 0.20 −0.26	1.462	1.445	104.7	106.1	105.3	527.3	105.5
P(3)	$6.56x + 4.42y + 4.61z = 2.58$ O(3) C(31) C(32) C(33) C(34) 0.10 −0.17 0.17 −0.12 0.02	1.434	1.411	104.3	109.8	104.2	532.1	106.4
P(4)	$8.48x + 6.90y - 6.93z = 2.66$ O(4) C(41) C(42) C(43) C(44) 0.07 0.03 −0.12 0.16 −0.14	1.408	1.422	107.2	106.6	109.2	538.8	107.8

[a] x, y, z in the plane equations are crystal coordinates and d is the perpendicular distance deviated from plane.

TABLE V. Comparison of Molecular Structures

Complex	Space group	Molecule number for unit cell	Nd–X (1)	Nd–X (2)	Nd–X (3)	Specific gravity d (g cm^{-3})	Association state	Coordination number
$NdCl_3$	$P6_3/m$	10	2.923	2.886	–	4.139	polymer	9
$NdCl_3 \cdot 4THF$	$P2_1/c$	4	2.666	2.689	2.668	0.968	monomer	7
$NdBr_3 \cdot 4THF$	$P\bar{1}$	2	2.837	2.863	2.871	1.144	monomer	7
$NdCl_3 \cdot 3i\text{-}C_3H_7OH$	$P\bar{1}$	1	2.911	2.755	2.693	1.042	dimer	7

TABLE VI. Comparison of Crystallographic Parameters

Compound	Space group	Nd–Cl[a] (Å)	Nd–C[a] (Å)	Nd–O[a] (Å)	Coordination number	SAS
$(\eta^5\text{-}C_5H_5)_3Nd \cdot THF$ [9]	$P2_1/n$		2.79	2.54	10	0.712
$(\eta^5\text{-}C_5H_5)_2NdCl \cdot THF$	$P2_1/c$	2.83	2.76	2.55	8	0.777
$\eta^5\text{-}C_5H_5NdCl_2 \cdot 3THF$	$P2_1/n$	2.72	2.76	2.47	8	0.736
$NdCl_3 \cdot 4THF$	$P2_1/c$	2.67		2.50	7	0.748

[a] Average.

The solid angle sum (SAS) of these compounds is estimated to be near to the value of 0.73.

In order to explain the difference between polymerization activities of $NdCl_3$ and $NdCl_3 \cdot 4THF$ for diene we completed the polymerization of diene using the $NdCl_3 \cdot 4THF–AlEt_3$ system. The polymerization results are listed in Tables VII and VIII. It can be seen from Tables VII and VIII that $NdCl_3 \cdot 4THF$ is highly active for the polymerization of diene, also the polymerization activity of butadiene is greater than that of isoprene.

If the chlorine atom in $NdCl_3 \cdot 4THF$ is replaced by cyclopentadienyl group the bond lengths of Nd–Cl increase (Table VI) but the polymerization activities of $C_5H_5NdCl_2 \cdot n THF$ become close to those of $NdCl_3 \cdot 4THF$ [10]. We wonder why $NdCl_3$ is hard to react with aluminium alkyls in hydrocarbon solvent, while $NdCl_3 \cdot 4THF$ is able to react with aluminium alkyls to form highly active species. The molecules of $NdCl_3$ are bridged by two chlorine atoms to form a polyhedral crystal but the molecules of $NdCl_3 \cdot$ 4THF are associated together by the van der Waals

TABLE VII. Butadiene Polymerization Using the $NdCl_3$·4THF–$AlEt_3$ System[a]

Nd/monomer (mol/mol) × 10^5	Conversion (%)	(η) (dl/g)	Microstructure (%)		
			cis-1,4	1,2	*trans*-1,4
4.0	81.3	10.1	96.8	0.5	2.6
3.0	62.6	14.2	97.4	0.3	2.0
2.0	44.3	16.2	97.0	0.3	2.7

[a]Polymerizations were carried out at 50 °C for 5 h in hexane with the monomer concentration initially at 10% (*w*/*v*), at $AlEt_3$/$NdCl_3$·4THF (mol/mol) 30%.

TABLE VIII. Isoprene Polymerization Using the $NdCl_3$·4THF–$AlEt_3$ System[a]

Nd/monomer (mol/mol) × 10^5	Conversion (%)	(η) (dl/g)	Microstructure (%) *cis*-1,4	3,4
14.0	88.2	4.9	95.4	4.6
12.0	85.3	5.7	95.5	4.5
6.0	60.3	7.7	94.8	5.2

[a]Polymerization conditions are the same as in Table VII.

force. Of course, the intermolecular force of $NdCl_3$ is greater than that of $NdCl_3$·4THF and the crystal of $NdCl_3$ in non-polar solvent is more stable than that of $NdCl_3$·4THF.

References

1 Yang Jihua, Hu Jingyu, Feng Shufen, Pan Enli, Xie Demin, Zhong Chongqi and Ouyang Jun, *Sci. Sin., 23,* 734 (1980).

2 Fourth Laboratory, Changchun Institute of Applied Chemistry, Academia Sinica, 'Collected Papers on Synthetic Rubber Prepared With Rare Earth Catalysts', Science Press, Beijing, 1980.

3 Ji-Hua Yang, M. Tsutsui, Zonghan Chen and E. Bergbreiter, *Macromolecules, 15,* 230 (1982).

4 Jin Zhongshen, Wang Shenglong and Wang Fusong, Shen Cheng, Yang Guangdi and Fan Yiguo, *Chem. J. Chin. Univ., 6,* 735 (1985).

5 M. Zocchi, L. Depero and M. C. Gallazzi, *XVII Congresso Nazionale Chimica Inorganica, Collected Abstracts,* Cefalú, October 1984.

6 B. Morosin, *J. Chem. Phys., 49,* 3007 (1968).

7 Jin Zhingsheng, Liu Yongsheng and Chen Wenqi, *Sci. Sin., B,* in press.

8 Guangdi Yan, Yuguo Fan, Zhongsheng Jin, Yan Xing and Wenqi Chen, *J. Organomet. Chem., 322,* 57 (1987).

9 Fan Yuguo, Lu Pinzhe, Jin Zhongsheng and Chen Wenqi, *Sci. Sin., Ser. B, 27,* 993 (1984).

10 Yu Guangqian, Chen Wenqi and Wang Yuling, *Kexue Tongbao, 28,* 408 (1983).