Synthesis and Characterization of Monomeric Salicylaldiminato Lanthanide Complexes and Their Catalytic Behavior for Polymerization of ε-Caprolactone

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Anhydrous $LnCl_3$ reacts with 2 equiv. of the sodium salt of the bidentate Schiff base *N*-(2,6-diisopropylphenyl) salicylaldimine in THF to form the monomeric lanthanide chlorides [2-OC_6H_4CH = N(2,6-*i*-$Pr_2C_6H_3$)]$_2$LnCl(THF) [Ln = Yb (1), Er (2)]. Complex 1 crystallizes in *P*1 space group with a = 0.9215(2) nm, b = 1.36612(4) nm, c = 1.6899(2) nm, α = 74.83(3)°, β = 77.43(2)°, γ = 81.04(1)°, Z = 2, V = 1.9929(4) nm^3, D_c = 1.402 g/cm^3. The two complexes exhibited fairly good catalytic activity in the ring-opening polymerization of ε-caprolactone.

Keywords Schiff base, lanthanide complex, synthesis, crystal structure, polymerization of ε-caprolactone

Introduction

Schiff base ligands can be used to provide a stereochemically rigid ligand framework in homogenous precatalysts of some metals, such as salen Cr catalysts in asymmetric ring-opening reaction of epoxide[1] and salen Al in ring-opening polymerization of lactide and related cyclic esters.[2] Recently, it was reported that the bidentate Schiff base complexes of early and late transition metals can serve as promising alternatives to metallocene catalysts for the polymerization of α-olefins.[3] Therefore, the applications of Schiff base ligands in organometallic chemistry of the transition and main metals have attracted much attention.

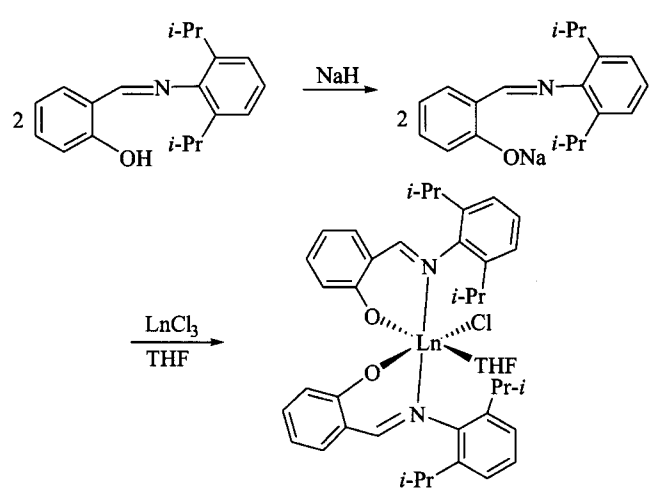
The use of flexible and tunable Schiff base ligands in the coordination chemistry of organolanthanides has also been reported in the literatures.[4] However, the study on the synthesis, characterization and catalytic activity of their monochloro derivatives of the lanthanides is still rather limited. There are only a few papers concerning the synthesis and molecular structure of this kind of complexes,[4c,4b,4g] and none dealt with their catalytic activity for the polymerization of ε-caprolactone. Herein we report the synthesis and molecular structure of monomeric lanthanide chlorides supported by the bidentate Schiff base ligand [2-OC_6H_4CH = N(2,6-*i*-$Pr_2C_6H_3$)], and their catalytic activity as a single component catalyst for the polymerization of ε-caprolactone.

Results and discussion

Synthesis

By the reaction of anhydrous $LnCl_3$ with 2 equiv. of the sodium salt of the bidentate Schiff base generated from the treatment of *N*-(2,6-diisopropylphenyl) salicylaldimine with NaH in THF, the complexes **1** and **2** were synthesized in good yields (Scheme 1).

Scheme 1



Ln = Yb (1), Et (2)

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The crystals of **1** and **2** obtained from concentrated DME (ethylene glycol dimethyl ether) solution were characterized by elemental analysis and IR spectra, and the X-ray crystal structure of **1** was determined. In their IR spectra, the bands of stretching vibration of imine groups were observed at 1622 cm^{-1} for **1** and 1646 cm^{-1} for **2**, respectively. The two complexes are soluble in THF, DME and slightly soluble in toluene. They had good thermal stability and decomposed at 220 and 217 ℃, respectively.

X-Ray crystal structure of **1**

Complex **1** crystallizes with two crystallographically independent but chemically similar molecules (**1a** and **1b**) in the unit cell; the selected bond lengths and angles are listed in Table 1 for both molecules, and the molecular structure is shown in Fig 1. The complex has a monomeric structure in solid state, which is rare. Usually, Schiff base lanthanide monochlorides tend to form dimeric structure, even when they crystallize in THF solution. The Yb ion is coordinated by one chlorine atom, two oxygen and two nitrogen atoms from two bidentate Schiff base ligands and a THF ligand in a distorted octahedral geometry. In contrast, the reported analogues $\{[(2\text{-}OC_6H_4)CH=N(2,4,6\text{-}Me_3C_6H_2)]La(\mu\text{-}Cl)(THF)\}_2$ (**3**)[4b] and $\{[(2\text{-}O\text{-}3,5\text{-}t\text{-}BuC_6H_2)HC=NCH_2CH_2N=CH(2\text{-}O\text{-}3,5\text{-}t\text{-}Bu_2C_6H_2)]Y(\mu\text{-}Cl)(THF)\}_2$ (**4**)[4c] are seven-coordinate complexes.

The Yb(1)—N(1A) and Yb(1)—N(1B) bond distances are 0.243(1) and 0.247(1) nm, respectively. The average Yb—N bond distance is 0.245 nm, which is comparable to that for **4** (0.2492 nm) and apparently shorter than that for **3** (0.2724 nm). The Yb(1)—O(1B) and Yb(1)—O(1A) bond distances are 0.2110(7) and 0.210(1) nm, respectively and the average Yb—O bond distances (0.2107 nm) is close to those in previously reported lanthanide complexes, $\{N[CH_2CH_2N=CH(2\text{-}O\text{-}3,5\text{-}t\text{-}Bu_2C_6H_2)]_3\}Sm$ (**5**) (0.2272 nm),[4e] $[(2\text{-}O\text{-}3,5\text{-}t\text{-}BuC_6H_2)HC=NCH_2CH_2N=CH(2\text{-}O\text{-}3,5\text{-}t\text{-}Bu_2C_6H_2)]YN(SiHMe_2)_2(THF)$ (0.216 nm)[4a] and **3** (0.2295 nm).[4b] The Yb—Cl bond length of 0.2497(2) nm is apparently shorter than those for **3** [0.2865 (5), 0.2996 (6) nm] and **4** [0.2734 (1), 0.2759(1) nm]. It is reasonable that the bond length for terminal Ln—Cl is shorter than that for bridged ones.

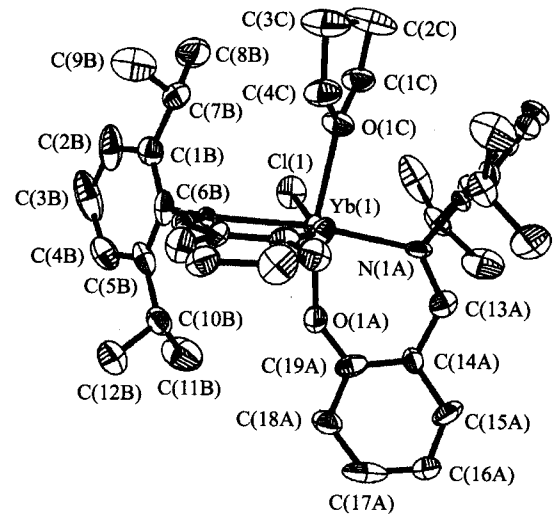

Fig. 1 Molecular structure of complex **1**.

Table 1 Selected bond distances (nm) and angles (°) for complex **1**

1a		**1b**	
	Bond distances		
Yb(1)—O(1A)	0.2110(7)	Yb(2)—O(1D)	0.2113(9)
Yb(1)—O(1B)	0.2104(10)	Yb(2)—O(1E)	0.2099(8)
Yb(1)—O(1C)	0.2385(5)	Yb(2)—O(1F)	0.2382(5)
Yb(1)—N(1A)	0.243(1)	Yb(2)—N(1D)	0.243(1)
Yb(1)—N(1B)	0.247(1)	Yb(2)—N(1E)	0.2464(9)
Yb(1)—Cl(1)	0.2497(2)	Yb(2)—Cl(2)	0.2498(2)
	Bond angles		
O(1A)-Yb(1)-O(1B)	92.1(4)	O(1D)-Yb(2)-O(1E)	92.4(4)
O(1A)-Yb(1)-O(1C)	164.9(3)	O(1D)-Yb(2)-O(1F)	163.1(3)
O(1A)-Yb(1)-N(1A)	76.9(3)	O(1D)-Yb(2)-N(1D)	74.7(4)
O(1A)-Yb(1)-N(1B)	96.2(3)	O(1D)-Yb(2)-N(1E)	95.0(3)
O(1B)-Yb(1)-O(1C)	79.2(3)	O(1E)-Yb(2)-O(1F)	80.0(3)
O(1B)-Yb(1)-N(1A)	93.9(4)	O(1E)-Yb(2)-N(1D)	95.9(4)
O(1B)-Yb(1)-N(1B)	78.2(3)	O(1E)-Yb(2)-N(1E)	76.7(3)
O(1B)-Yb(1)-Cl(1)	162.3(2)	O(1E)-Yb(2)-Cl(2)	159.8(2)
O(1C)-Yb(1)-N(1A)	91.4(3)	O(1F)-Yb(2)-N(1D)	90.9(3)
O(1C)-Yb(1)-N(1B)	94.0(3)	O(1F)-Yb(2)-N(1E)	97.9(3)

Catalytic behavior

The catalytic activity of these two complexes for the polymerization of ε-caprolactone was tested. The preliminary results are summarized in Table 2. It is interesting to note that these two complexes both exhibit good catalytic activity. Satisfactory polymerization yields were obtained at 70 ℃ over 3 h in the case of [CL]/[I] = 500/1 (molar ratio). The obtained polymers have higher molecular weight ($M_n > 10^5$) and moderate molecular distribution ($M_w/M_n < 2.0$), which are comparable to those observed for the system with $(MeC_5H_4)_2Ln[O{=}\overset{\lceil}{C}{-}N(CH_2)_4CH_2\rceil]$ as a catalyst.[5] The molecular distribution increases constantly with reaction time and temperature. This may be attributed to transesterification reactions.[6] The activity of the catalysts strongly depends on the reaction temperature (Entries 1—3). Thus, raising the temperature from 50, 70 to 100 ℃ caused an increase of polymerization yield from 11.5%, 63.7% to 98.2%, correspondingly. In addition, increasing polymerization time can also result in higher conversion, even if at lower temperature.

Table 2 Polymerization of ε-caprolactone by complex **1** and **2**

Entry	Cat.	[CL]/[I] (mol/mol)	Temperature (℃)	Time (h)	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n
1	**1**	500/1	50	3	11.5	3.77	1.21
2	**1**	500/1	100	1	98.2	20.7	1.92
3	**1**	500/1	70	3	63.7	13.2	1.41
4	**1**	500/1	70	4	77.2	17.2	1.75
5	**1**	500/1	70	6	87.4	14.9	1.67
6	**1**	500/1	70	12	100	36.5	1.92
7	**1**	1000/1	70	3	31.2	9.9	1.38
8	**2**	500/1	70	3	82.5	16.8	1.87
9	**2**	1000/1	70	3	48.5	12.8	1.74

Experimental

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. THF, toluene and DME were dried and freed of oxygen by refluxing over sodium benzophenone ketyl and distilled under argon prior to use. ε-Caprolactone was dried over CaH_2 for 4 d and stored over 3 Å molecular sieves under argon after distillation. Anhydrous $LnCl_3$ was prepared according to the reported method.[7] Metal analyses were carried out by complexometric titration[8] and chlorine analyses by the Volhard method. Carbon, hydrogen and nitrogen analyses were performed on EA 110-CHEN-O spectrometer by direct combustion. The IR spectra were obtained as KBr pellets on a Nicolet-550 FT-IR spectrometer. Molecular weight (M_n, M_w) and molecular distribution (M_w/M_n) were determined by gel permeation chromatographic analyses (GPC) which were run on a Waters 1515 GPC apparatus equipped with three columns (HR-1, HR-2 and HR-4) in THF at 30 ℃. Polystyrene standards were used to obtain the universal curve.

Preparation of $[2\text{-}OC_6H_4CH{=}N(2,6\text{-}i\text{-}Pr_2C_6H_3)]_2YbCl(THF)$ (**1**)

To a slurry of $YbCl_3$ (1.05 g, 3.75 mmol) in THF was added a THF solution of $Na[2\text{-}OC_6H_4CH{=}N(2,6\text{-}i\text{-}Pr_2C_6H_3)]$ (40 mL, 7.5 mmol). The mixture was stirred at room temperature for 48 h. After centrifugation, the THF was completely removed and an adequate amount of DME was added to dissolve the residue. Pale yellow crystals were obtained at room temperature from concentrated DME solution. Yield 1.53 g (48.5%); IR (KBr) ν: 2957 (s), 2923 (m), 2868 (m), 1622 (s), 1584 (s), 1458 (s), 1392 (m), 1345 (m), 1321 (m), 1280 (w), 1146 (s), 1096 (w), 1031 (w), 924 (m), 906 (s), 862 (m), 792 (s), 743 (s), 689 (w), 602 (m) cm^{-1}. Anal. calcd for $C_{42}H_{52}N_2O_3ClYb$: C 59.92, H 6.18, N 3.33, Cl 4.25, Yb 20.57; found C 59.85, H 6.24, N 3.28, Cl 4.16, Yb 20.51.

Preparation of $[2\text{-}OC_6H_4CH{=}N(2,6\text{-}i\text{-}Pr_2C_6H_3)]_2ErCl(THF)$ (**2**)

The complex was prepared from 1.31 g of $ErCl_3$ and 53 mL of a THF solution of NaL (9.59 mmol) according to the procedure described above. Pale orange crystals were formed. Yield 1.63 g (46.3%); IR (KBr) ν: 2964 (s), 2933 (m), 2869 (m), 1646 (s), 1575 (s), 1464 (s), 1436 (m), 1392 (m), 1320 (m), 1279 (s), 1174 (s), 1097 (w), 1038 (w), 906 (s), 843 (m), 752 (s), 694 (w) cm^{-1}. Anal. calcd for $C_{42}H_{52}N_2O_3ClEr$: C 60.39, H 6.23, N 3.35, Cl 4.25, Er 20.01; found C 59.46, H 6.17, N 3.21, Cl 4.05, Er 19.07.

Polymerization of ε-caprolactone

To a toluene solution (10 mL) of ε-caprolactone (1 mL, 9.04 mmol) was added at once the desired amount of complex **1** or **2** with vigorous magnetic stirring at the chosen temperature. After the polymerization was carried out for a predefined time, 5 mL of ethanol containing 2% HCl solution was added to terminate the reaction, and then the viscous solution mixture was poured into a large excess of petroleum ether to induce the precipitation of the polymer. The polymer was washed with petroleum ether three times and dried at 30 ℃ under vacuum.

X-*Ray crystallographic analysis of* **1**

Suitable crystals were selected and mounted in thin-walled glass capillaries for X-ray structure analysis. Diffraction data were collected at 293 K on a Rigaku AFC7R diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.071073 nm).

The structure was solved and refined using the TEXAN crystallographic software package of Molecular Structure Corporation. A summary of crystallographic data and structure refinement parameters are given in Table 3.

Table 3 Crystal data and experimental parameters for **1**

Empirical formula	$C_{42}H_{52}ClN_2O_3Yb$
Formula weight	841.35
Temperature (K)	293(2)
Crystal color and habit	Pale yellow, octahedral
Crystal system	Triclinic
Space group	*P*1
Lattice parameters	
a (nm)	0.9215(2)
b (nm)	1.36612(4)
c (nm)	1.6899(2)
α (°)	74.83(3)
β (°)	77.43(2)
γ (°)	81.04(1)
V (nm^3)	1.9929(4)
D_{calcd} ($g \cdot cm^{-3}$)	1.402
Z	2
F(000)	858
Crystal size (mm)	0.21 × 0.46 × 0.31
θ_{max} (°)	27.43
Reflections collected	8619
Independent reflections	8619
Reflections with $I \geqslant 2.0\ \sigma(I)$	7762
R	0.0271
wR_2	0.0649

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