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Synthesis and structures of amine bis(phenolate) lanthanide thiolates and their application in the polymerization of ε-caprolactone

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ABSTRACT

Reaction of anhydrous $LnCl_3$ with 1 equivalent of LNa_2 (L^{2-} = $[Me_2NCH_2CH_2CH_2N\{CH_2\text{-}(3,5\text{-}^tBu_2\text{-}C_6H_2\text{-}2\text{-}O)\}_2]^{2-}$) and 1 equivalent of CpNa (Cp^- = $C_5H_5^-$) in THF firstly, then with 1 equivalent of *p*-thiocresol, leads to the lanthanide thiolates of $LLn(SC_6H_4\text{-}p\text{-}Me)(THF)$ (Ln = Sm (**1**), Er (**2**), Yb (**3**)). They were characterized by infrared spectra, elemental analyses and X-ray crystallography. Complexes **1**–**3** are monomers. The L^{2-} dianion ligand coordinates with the lanthanide ion in an O,*N*,*N*,O-tetradentate mode. All the complexes can catalyze the ring-opening polymerization of ε-caprolactone, and the activity decreases in the order of **1**(Sm) > **2**(Er) > **3**(Yb). The polymer's polydispersity index (PDI) by complexes **1**–**3** is in the range of 1.3–1.5, less than that by $[(MeCp)_2Sm(SC_6H_5)(THF)]_2$. The initiation mechanism for the polymerization was discussed.

1. Introduction

Lanthanide thiolates are receiving increasing attention for their interesting structures [1] and their potential applications in advanced materials [2] and catalytic processes [3]. Many types of lanthanide thiolates have been reported such as $(C_5Me_5)_2Lu(\mu\text{-}S^tBu)_2Li(THF)_2$ [4], $[(C_8H_8)Sm(\mu\text{-}SC_6H_5)(THF)_2]_2$ [5], $[(MeCp)_2Nd(\mu\text{-}SC_6H_5)(THF)]_2$ [6], $(C_5Me_5)_2Sm(SC_6H_5)(THF)$ [7], $Ln(SC_6H_2\text{-}^tBu_3\text{-}2,4,6)_3$ (Ln = La, Ce, Pr, Nd) [8], $[\{(Me_3Si)_2N\}_2Ln(\mu\text{-}S^tBu)]_2$ (Ln = Pr, Sm) [9], $\{[(Me_3Si)_2NC(NC_6H_{11})_2]_2Ln(\mu\text{-}S^nBu)\}_2$ (Ln = Y, Er) [10], etc. However, the lanthanide thiolates with amine bis(phenolate) ligand have not been reported yet, although this types of ligands have been widely used in coordination chemistry [11]. Also, such ligands can be compared to the tripodal tetraamines, which display diverse coordination geometries [12].

Moreover, the study on the catalytic property of lanthanide thiolates has been limited. There are only countable examples regarding this scope, including the polymerization of methyl methacrylate (MMA) by lanthanide arenethiolate complexes [3a], polymerization and block-copolymerization of styrene and ethylene by divalent C_5Me_5/S(Arene)-ligated Sm(II) complexes [3b], oligomerization of phenyl isocyanate (PhNCO) [3c] and polymerization of ε-caprolactone (ε-CL) by $[(MeCp)_2Sm(SC_6H_5)(THF)]_2$ and $Sm(SC_6H_5)_3(hmpa)_3$ (hmpa = hexamethylphosphoric triamide) [3d]. In order to understand more about the catalytic property of lanthanide thiolates, especially the effect of lanthanide element and the coordination ligand, we began to prepare lanthanide thiolates bearing amine bis(phenolate) ligands and studied their catalytic property for the polymerization of ε-CL.

In this paper, lanthanide thiolates of $LLn(SC_6H_4\text{-}p\text{-}Me)(THF)$ (L^{2-}=$[Me_2NCH_2CH_2CH_2N\{CH_2\text{-}(3,5\text{-}^tBu_2\text{-}C_6H_2\text{-}2\text{-}O)\}_2]^{2-}$; Ln = Sm(**1**), Er(**2**), Yb(**3**)) were synthesized and characterized. All of them can catalyze the polymerization of ε-CL. It is found that the lanthanide element has great influence on the catalytic activity. Bulky amine bis(phenolate) ligand is favorable for lanthanide thiolates to prepare PCL with narrow molecular weight distribution.

2. Experimental

2.1. General

All of the manipulations were performed under an argon atmosphere, using the standard Schlenk techniques. *p*-Thiocresol (*p*-MeC_6H_4SH) was commercially available from Aladdin Reagent Database Incorporation and used without purification. Tetrahydrofuran (THF) and toluene were dried and freed of oxygen by refluxing over sodium/benzophenone ketyl and distilled prior to use. LH_2, i.e. $[Me_2NCH_2CH_2CH_2N\{CH_2\text{-}(3,5\text{-}^tBu_2\text{-}C_6H_2\text{-}2\text{-}OH)\}_2]$, was prepared according to the literature procedure [13]. LNa_2 and CpNa (Cp^- = $C_5H_5^-$) were prepared by reaction of LH_2 or CpH (freshly distilled) and metallic sodium in THF. ε-CL was purchased from Acros, dried over CaH_2 for 48 h, and then distilled under reduced pressure. Anhydrous $LnCl_3$ (Ln = Sm, Er, Yb) were prepared according to the literature procedure [14]. Lanthanide metal analyses were performed by ethylenediaminetetraacetic acid titration with a

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xylenol orange indicator and a hexamine buffer. Carbon, hydrogen and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument. The IR spectra were recorded on a Perkin Elmer Spectrum BXII spectrometer as KBr pellets. The ^{1}H NMR spectra were recorded in a $CDCl_3$ solution for oligomer of ε-CL on an Inova-400 spectrometer. The melting points of crystalline samples were determined in sealed capillaries (under argon) and uncorrected. Polymer's molecular weight and molecular weight distribution were determined against a polystyrene standard by a PL-50 gel permeation chromatography (GPC), and THF was used as an eluent at a flow rate of 1.0 mL/min at 40 °C.

2.2. Synthesis of LSm(SC_6H_4–p-CH_3)(THF) (**1**)

To a suspension of $SmCl_3$ (0.559 g, 2.18 mmol) in 20 mL of THF was added the THF solution of LNa_2 (6.5 mL, 0.335 mol/L, 2.18 mmol) dropwise. Half an hour later, a THF solution of CpNa (1.04 mL, 2.10 mol/L, 2.18 mmol) was added. The reaction was kept stirring overnight. Precipitates were then separated from the reaction mixture by centrifugation. To the clear solution was added the THF solution of *p*-thiocresol (0.271 g, 2.18 mmol). After being stirred for 24 h at room temperature, the solution was concentrated by evaporating the solvent under reduced pressure, and then stored at −20 °C. Pale-yellow powders of **1** (1.239 g, 64% yield based on Sm) were obtained. M.p. (dec.): 137 °C. *Anal.* Calc. for $C_{46}H_{71}N_2O_3SSm$: C, 62.64; H, 8.05; N, 3.17; Sm, 17.05. Found: C, 62.46; H, 7.86; N, 3.32; Sm, 17.12%. IR (KBr, cm^{-1}): 3422(w), 2953(s), 2867(m), 2365(w), 1608(w), 1475(s), 1360(w), 1301(m), 1274(m), 1237(m), 1203(w), 1166(w), 1018(w), 877(w), 836(w), 809(w), 742(w), 532(w), 443(w). The crystals suitable for X-ray diffraction analysis were acquired from the concentrated THF/toluene solution.

2.3. Synthesis of LEr(SC_6H_4–p-CH_3)(THF) (2)

Complex **2** was prepared by a procedure which was analogous to that for complex **1**, but $ErCl_3$ was used instead of $SmCl_3$. Pink powders of **2** were obtained from concentrated THF solution at −20 °C in a few days in yield of 59% (based on Er). M.p. (dec.): 185 °C. *Anal.* Calc. for $C_{46}H_{71}N_2O_3SEr$: C, 61.46; H, 7.90; N, 3.11; Er, 18.61. Found: C, 61.18; H, 7.70; N, 3.35; Er, 18.72%. IR (KBr, cm^{-1}): 3423(w), 2953(s), 2866(m), 2374(w), 1602(w), 1477(s), 1360(w), 1303(m), 1274(m), 1237(w), 1203(w), 1167(w), 1019(w), 878(w), 837(w), 814(w), 744(w), 533(w), 454(w). The crystals suitable for X-ray diffraction analysis were acquired from the concentrated THF/toluene solution.

2.4. Synthesis of LYb(SC_6H_4–p-CH_3)(THF) (**3**)

Complex **3** was prepared by a procedure which was analogous to that for complex **1**, but $YbCl_3$ was used instead of $SmCl_3$. Yellow powders of **3** were obtained from concentrated THF solution at −20 °C in a few days in yield of 73% (based on Yb). M.p. (dec.): 197 °C. *Anal.* Calc. for $C_{46}H_{71}N_2O_3SYb$: C, 61.07; H, 7.84; N, 3.09; Yb, 19.12. Found: C, 60.88; H, 7.62; N, 3.23; Yb, 19.21%. IR (KBr, cm^{-1}): 3423(w), 2953(s), 2865(m), 2366(w), 1602(w), 1478(s), 1360(w), 1303(m), 1278(m), 1237(w), 1203(w), 1167(w), 1020(w), 878(w), 837(w), 814(w), 744(w), 534(w), 452(w). The crystals suitable for X-ray diffraction analysis were acquired from the concentrated THF/toluene solution.

2.5. Crystal structure determination

Suitable single crystals of complexes **1**–**3** were sealed in thin-walled glass capillaries under argon. Intensity data were collected on a SMART APEX-II detector in the ω scan mode using Mo Kα radiation (λ = 0.71070 Å). The diffraction intensities were corrected for Lorentz/polarization effects and empirical absorption corrections. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on F^2. The atoms of C(32), C(37) and C(39) as well as C(23)–C(26) (for complex **1**) and C(27)–C(30) (for complexes **2** and **3**) were treated with disordered refinement. Twin refinement was employed for the three structures. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. The structures were solved and refined using the SHELXL-97 programs.

2.6. Typical procedure for the polymerization

A typical polymerization procedure was as follows. The lanthanide catalyst was charged in a round-bottomed flask previously flame-dried and purged with argon. Then toluene and ε-CL were added in turn. The mixture was stirred vigorously at constant temperature for a determined time. In the process an increase in viscosity was observed. The reaction mixture was quenched by the addition of methanol and was then poured into large amount of petroleum ether. The polymeric product was precipitated, washed completely with petroleum ether, filtered and finally dried in vacuum at 45 °C. The polymer yield was determined gravimetrically.

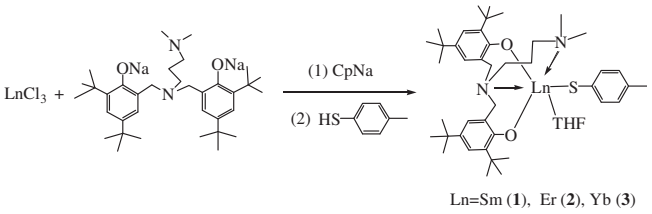
2.7. Synthesis of oligomer for end group analysis

The oligomerization of ε-CL was carried out by reaction of complex **3** (0.90 g, 0.991 mmol) in 35 mL of THF and ε-CL at a molar ratio of 1:5. The reaction proceeded first at 0 °C for 2 h, then at 25 °C for 24 h. It was terminated by addition of about 5 mL of water. When the water was added in, the solution turned turbid. After centrifugation, the obtained clear solution was evaporated to dryness. The resulting solid was washed with hot *n*-hexane completely and dried under vacuum.

3. Results and discussion

3.1. Synthesis and structures of complexes **1**–**3**

There are several synthetic approaches to lanthanide thiolates such as metathesis of a lanthanide halide with an alkali metal thiolate [15], oxidative addition of organic disulfide RSSR to lanthanide(II) complexes [7,16] or lanthanide metals under the presence of catalyst [5,17], reaction of lanthanide alkyls with elemental sulfur [10,18], and protolysis of Ln–Cp [6,19], Ln–C [4], Ln–N [8,9,20] and Grignard-analogous RLnI [21] complexes with thiols. We wished to prepare amine bis(phenolate) lanthanide thiolates by protolysis of LLnCp with *p*-thiocresol (*p*-MeC_6H_4SH). Reaction of anhydrous $LnCl_3$ with 1 equivalent of LNa_2 and 1 equivalent of CpNa in THF firstly, then with 1 equivalent of *p*-thiocresol, leads to the lanthanide thiolates of LLn(SC_6H_4–*p*-Me)(THF) (Ln = Sm(**1**), Er(**2**, Yb(**3**)) in good yields (Scheme 1).



Scheme 1.