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Synthesis and Structure of Lanthanide Aryloxo Complexes and Their Polymerization Behavior for ε-Caprolactone

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Abstract. Protic exchange reactions of bis(phenolate) lanthanide cyclopentadienyl complexes $(C_5H_5)Ln(MBMP)(THF)_2$ [$MBMP^{2-}$ = 2,2′-methylene-bis(6-*tert*-butyl-4-methyl-phenolate)] with a series of mono-phenols (including 2,6-dimethylphenol, 4-*tert*-butylphenol, and 4-methoxyphenol) produce the lanthanide aryloxo complexes $(MBMP)Ln(OC_6H_3\text{-}Me_2\text{-}2,6)(DME)_2$ [Ln = La (**1**), Nd (**2**)], $(MBMP)La(OC_6H_4\text{-}t\text{Bu-}4)(DME)_2$ (**3**), $[(MBMP)Nd(OC_6H_4\text{-}t\text{Bu-}4)(THF)_2]_2$ (**4**), and $[(MBMP)Ln(OC_6H_4\text{-}OMe\text{-}4)(THF)_2]_2$ [Ln = La (**5**), Nd (**6**)]. All of these complexes were well characterized by elemental analyses, IR spectra, and NMR in the cases of complexes **1**, **3**, and **5**. The definitive molecule structures of complexes **1**, **3**, and **4** were determined by single-crystal X-ray diffraction. The catalytic behavior of complexes **1**–**6** for the ring-opening polymerization of ε-caprolactone was explored.

Introduction

During the past decades, organolanthanide chemistry has witnessed rapid progress, because many of lanthanide complexes have interesting catalytic properties for organic transformation and polymerization.[1–5] It is well known that the catalytic properties of organolanthanide complexes depend on not only the metal itself, but also the coordination environment around the central metal atom because of the unique electron structure of the lanthanide metal. Thus, exploration of new ancillary ligands and synthesis of organolanthanide complexes with different structures to systematically study the relationship between structure and catalytic property have received considerable attention.[6–9]

In recent years, the application of bridged bis(phenolate)s as ancillary ligands has received increasing attention in organolanthanide chemistry.[10] The bridged bis(phenolate) groups can be used as dianionic ligands, which has the advantage of avoiding ligand redistribution reactions because of chelating effects. Meanwhile, these dianionic ligands have an advantage to design single-site catalysts, which is important for controlled polymerization. Indeed, some of the organolanthanide complexes stabilized by bridged bis(phenolate) groups have been found to show good catalytic activity and controllability in the polymerization of some polar monomers.[11–19] For example, the amine bridged bis(phenolate) lanthanide complexes can catalyze the controlled polymerization of L-lactide,[18] and the highly heteroselective polymerization of *rac*-lactide.[11,12,14] Recently, we also found that the lanthanide alkoxo and amido complexes stabilized by carbon bridged bis(phenolate) groups are efficient initiators for the ring-opening polymerization of ε-caprolactone, and the polymerization controllability is greatly influenced by the property of the initiating group.[20–22] To further understand the influence of the initiating group on the catalytic property of carbon bridged bis(phenolate) lanthanide complexes, some lanthanide aryloxo complexes stabilized by 2,2′-methylene-bis(6-*tert*-butyl-4-methyl-phenolate) ($MBMP^{2-}$) group were synthesized by protic exchange reaction, and their catalytic behavior for the polymerization of ε-caprolactone was explored. Herein we report these results.

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Experimental Section

Materials and General Procedures: All manipulations were performed in an argon atmosphere, using the standard Schlenk techniques. Solvents were distilled from sodium benzophenone ketyl before use. ε-Caprolactone was purchased from Acros, dried with CaH_2 for 48 h, and distilled under reduced pressure before use. Phenols and 2,2′-methylene-bis(6-*tert*-butyl-4-methyl-phenol) ($MBMPH_2$) were commercially available. $(C_5H_5)Ln(MBMP)(THF)_n$ (Ln = La, Nd) was prepared according to the literature procedures.[22,23] Lanthanide analyses were performed by EDTA titration with an xylenol orange indicator and a hexamine buffer.[24] Carbon and hydrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 FT-IR spectrometer as KBr pellets. NMR spectra were obtained with an INOVA-400MHz apparatus. Molecular weights and molecular weight distributions were determined against polystyrene standards by gel permeation chromatography (GPC) with a PL 50 apparatus, and THF was used as an eluent at a flow rate of 1.0 mL·min^{-1} at 40 °C.

Synthesis of $(MBMP)La(OC_6H_3\text{-}Me_2\text{-}2,6)(DME)_2$ (1): To a THF solution (30 mL) of $(C_5H_5)La(MBMP)(THF)_3$ (2.81 g, 3.70 mmol)

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was added HOC_6H_3-Me_2-2,6 (0.45 g, 3.70 mmol). The mixture was stirred overnight at 50 °C, and further the solvent was removed under vacuum. Toluene was added to extract the solid, and the precipitate was removed by centrifugation. The toluene extracts were concentrated to about 12 mL and about 1 mL of DME was added. Colorless microcrystals were obtained at room temperature in a few days (2.07 g, 72% based on La). $C_{39}H_{59}LaO_7$: calcd. C 60.15; H 7.64; La 17.84%; found: C 59.86; H 7.57; La 17.55%. **^{1}H NMR** (400 MHz, 25 °C $CDCl_3$): δ = 1.34 [s, 18 H, C(CH_3)$_3$], 2.13 (s, 6 H, ArCH_3), 2.27 (s, 6 H, ArCH_3), 3.24 (s, 12 H, CH_3O), 3.48 (m, 8 H, OCH_2), 3.79 (d, $^2J_{HH}$ = 14.2 Hz, 2 H, CH_2), 6.70 (m, 2 H, Ar*H*), 6.85–7.04 (m, 5 H, Ar*H*) ppm. **^{13}C NMR** (400 MHz, $CDCl_3$): δ = 15.8 (Ar*C*H$_3$), 21.4 (Ar*C*H$_3$), 30.3 [C(*C*H$_3$)$_3$], 35.1 [*C*(CH$_3$)$_3$], 35.8 (*C*H$_2$), 59.8 (*C*H$_3$O), 71.0 (O*C*H$_2$), 124.2, 125.5, 127.9, 128.6, 129.7, 130.1, 136.2, 139.3, 152.7, 161.4 (Ph) ppm. **IR** (KBr): $\tilde{\nu}$ = 2956 (s), 2915 (s), 2871 (m), 1608 (m), 1442 (s), 1232 (s), 1156 (s), 861 (m), 768 (m), 619 (m), 582 (s) cm^{-1}. Crystals suitable for an X-ray diffraction analysis were obtained by slow cooling of a hot DME solution.

Synthesis of (MBMP)Nd(OC_6H_3-Me_2-2,6)$(DME)_2$ (2): The synthesis of complex **2** was carried out in the same way as that described for complex **1**, but (C_5H_5)Nd(MBMP)$(THF)_3$ (1.93 g, 2.53 mmol) was used instead of (C_5H_5)La(MBMP)$(THF)_3$. Pale blue microcrystals were isolated from the concentrated toluene/DME (7:1) solution (8 mL) at room temperature (1.35 g, 68% based on Nd). $C_{39}H_{59}NdO_7$: calcd. C 59.82; H 7.59; Nd 18.42%; found: C 59.53; H 7.62; Nd 18.67%. **IR** (KBr): $\tilde{\nu}$ = 2955 (s), 2916 (s), 2871 (m), 1593 (m), 1442 (s), 1234 (s), 1186 (s), 861 (m), 760 (m), 582 (m) cm^{-1}.

Synthesis of (MBMP)La(OC_6H_4-*t*Bu-4)$(DME)_2$ (3): The synthesis of complex **3** was carried out in the same way as that described for complex **1**, but HOC_6H_4-*t*Bu-4 (0.32 g, 2.15 mmol) was used instead of HOC_6H_3-Me_2-2,6. Colorless microcrystals were obtained from concentrated toluene/DME solution at room temperature in a few days (1.41 g, 81% based on La). $C_{41}H_{63}LaO_7$: calcd. C 61.03; H 7.87; La 17.22%; found: C 60.59; H 7.95; La 16.89%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.30 [s, 9 H, C(CH_3)$_3$], 1.38 [s, 18 H, C(CH_3)$_3$], 2.25 (s, 6 H, ArCH_3), 3.27 (s, 12 H, CH_3O), 3.47 (m, 8 H, OCH_2), 3.88 (d, $^2J_{HH}$ = 14.4 Hz, 2 H, CH_2), 6.75–6.96 (m, 4 H, Ar*H*), 7.19 (m, 4 H, Ar*H*) ppm. **^{13}C NMR** (400 MHz, $CDCl_3$): δ = 21.6 (Ar*C*H$_3$), 30.3 [C(*C*H$_3$)$_3$], 31.2 [C(*C*H$_3$)$_3$], 35.4 [*C*(CH$_3$)$_3$], 35.7 [*C*(CH$_3$)$_3$], 36.3 (*C*H$_2$), 59.5 (*C*H$_3$O), 70.8 (O*C*H$_2$), 117.1, 126.8, 128.3, 129.5, 130.4, 136.6, 140.3, 147.1, 152.7, 161.4 (Ph) ppm. **IR** (KBr): $\tilde{\nu}$ = 2954 (s), 2915 (s), 2869 (m), 1609 (m), 1447 (s), 1363 (m), 1231 (s), 1159 (m), 860 (m), 766 (m), 617 (m) cm^{-1}. Crystals suitable for an X-ray diffraction analysis were obtained from the hot toluene/DME solution.

Synthesis of [(MBMP)Nd(OC_6H_4-*t*Bu-4)$(THF)_2$]$_2$ (4): The synthesis of complex **4** was carried out in the same way as that described for complex **2**, but HOC_6H_4-*t*Bu-4 (0.72 g, 4.80 mmol) was used instead of HOC_6H_3-Me_2-2,6. Pale blue crystals were isolated from the concentrated THF solution (8 mL) at room temperature (2.64 g, 71% based on Nd). $C_{82}H_{118}Nd_2O_{10}$: calcd. C 63.45; H 7.66; Nd 18.58%; found: C 63.86; H 7.74; Nd 18.31%. **IR** (KBr): $\tilde{\nu}$ = 2956 (s), 2912 (s), 2869 (m), 1608 (m), 1443 (s), 1234 (s), 1158 (s), 861 (m), 768 (m), 619 (m) cm^{-1}.

Synthesis of [(MBMP)La(OC_6H_4-OMe-4)$(THF)_2$]$_2$ (5): The synthesis of complex **5** was carried out in the same way as that described for complex **1**, but HOC_6H_4-OMe-4 (0.36 g, 3.00 mmol) was used instead of HOC_6H_3-Me_2-2,6. Colorless microcrystals were obtained from concentrated THF solution at room temperature in a few days (1.57 g, 70% based on La). $C_{76}H_{106}La_2O_{12}$: calcd. C 61.29; H 7.17; La 18.65%; found: C 61.67; H 7.24; La 19.11%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.24 (br., 16 H, THF), 1.38 [s, 36 H, C(CH_3)$_3$], 2.25 (s, 12 H, ArCH_3), 3.57 (d, $^2J_{HH}$ = 14.4 Hz, 4 H, CH_2), 3.68 (br., 16 H, THF), 3.89 (s, 6 H, OCH_3), 7.10–6.96 (m, 12 H, Ar*H*), 7.19 (m, 4 H, Ar*H*) ppm. **^{13}C NMR** (400 MHz, $CDCl_3$): δ = 21.2 (Ar*C*H$_3$), 25.7 (THF), 32.4 [C(*C*H$_3$)$_3$], 35.5 [*C*(CH$_3$)$_3$], 36.7 (*C*H$_2$), 57.2 (O*C*H$_3$), 71.3 (THF), 116.1, 117.5, 128.1, 129.6, 130.2, 135.8, 141.2, 150.6, 154.8, 160.2 (Ph) ppm. **IR** (KBr): $\tilde{\nu}$ = 2957 (s), 2916 (s), 2871 (m), 1606 (m), 1453 (s), 1378 (m), 1236 (s), 1090 (m), 860 (m), 762 (m), 619 (m) cm^{-1}.

Synthesis of [(MBMP)Nd(OC_6H_4-OMe-4)$(THF)_2$]$_2$ (6): The synthesis of complex **6** was carried out in the same way as that described for complex **2**, but HOC_6H_4-OMe-4 (0.43 g, 3.60 mmol) was used instead of HOC_6H_3-Me_2-2,6. Pale blue microcrystals were obtained from concentrated THF solution at room temperature in a few days (1.76 g, 65% based on Nd). $C_{76}H_{106}Nd_2O_{12}$: calcd. C 60.85; H 7.12; Nd 19.23%; found: C 60.51; H 7.48; Nd 18.91%. **IR** (KBr): $\tilde{\nu}$ = 2957 (s), 2914 (s), 2866 (m), 1615 (m), 1450 (s), 1369 (m), 1237 (s), 1082 (s), 861 (m), 765 (m), 614 (m) cm^{-1}.

Procedure for the Polymerization Reaction: The procedures for the polymerization of ε-caprolactone initiated by complexes **1** to **6** were similar, and a typical polymerization procedure is given below. A 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with a solution of initiator in toluene. To this solution was added desired amount of ε-caprolactone by syringe. The contents of the flask were stirred vigorously at 50 °C for desired time, during which time an increase in viscosity was observed. The reaction mixture was quenched by the addition of 1 M HCl/ethanol solution, and then poured into methanol to precipitate the polymer, which was dried under vacuum and weighed.

X-ray Crystallography: Suitable single crystals of complexes **1**, **3**, and **4** were sealed in a thin-walled glass capillary for determining the single-crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo-K_α radiation (λ = 0.71070 Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 1.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically (C–H bond lengths fixed at 0.95 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using the SHELEXL-97 program.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-935151 (**1**), CCDC-935152 (**3**), and CCDC-935153 (**4**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Results and Discussion

Synthesis and Characterization of Lanthanide Complexes 1–6

We previously reported that the reaction of carbon bridged bis(phenol) ($MBMPH_2$) with $(C_5H_5)_3$Ln(THF) in THF in a 1:1

Table 1. Crystallographic data for complexes **1**, **3**, and **4**.

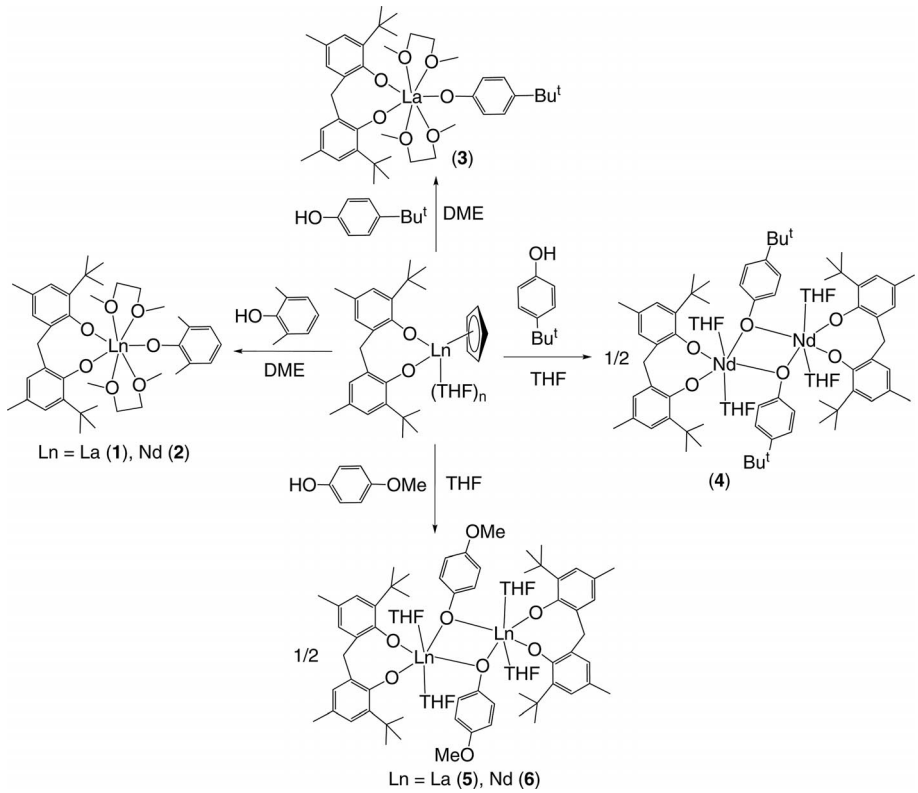
	1	**3**·0.5(C_7H_8)·0.5(C_4H_8O)	**4**·(C_4H_8O)
Formula	$C_{39}H_{59}LaO_7$	$C_{46.5}H_{71}LaO_{7.5}$	$C_{86}H_{126}Nd_2O_{11}$
Fw	778.77	878.86	1624.35
T /K	193(2)	223(2)	193(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
Crystal size /mm	0.31 × 0.29 × 0.20	0.31 × 0.22 × 0.20	0.55 × 0.36 × 0.18
a /Å	13.726(1)	15.635(2)	11.874(2)
b /Å	15.367(1)	23.143(2)	13.586(1)
c /Å	18.943(2)	26.999(3)	13.586(1)
α /°	90.00	90.00	71.145(5)
β /°	98.927(3)	101.656(3)	88.081(6)
γ /°	90.00	90.00	83.720(6)
V /Å^3	3947.3(6)	9568(2)	2061.6(4)
Z	4	8	1
$D_{calcd.}$ /g·cm^{-3}	1.310	1.220	1.308
μ /mm^{-1}	1.126	0.938	1.301
F(000)	1624	3656	850
θ_{max} /°	27.48	25.35	25.35
Collected reflections	43648	92314	20381
Unique reflections	8996	17485	7521
Observed reflections [$I > 2.0\sigma(I)$]	8158	12343	7148
No. of variables	439	908	483
GOF	1.117	1.184	1.086
R	0.0301	0.1240	0.0316
wR	0.0625	0.2451	0.0833

molar ratio gave the bis(phenolate) lanthanide cyclopentadienyl complexes (MBMP)Ln(C_5H_5)(THF)$_n$, which is a useful precursor for synthesis of neutral lanthanide alkoxo complexes stabilized by MBMP group by further proton exchange reaction.[21,22] This method has the advantage for avoiding formation of "ate" lanthanide derivatives. Therefore, we intend to expand the scope of this method, and synthesize bis(phenolate) lanthanide aryloxo complexes.

A NMR-scale reaction was conducted firstly. ^{1}H NMR monitoring reaction revealed that the reaction of (MBMP)La(C_5H_5)(THF)$_3$ with 2,6-dimethylphenol occurred in 1 h in C_6D_6 solution at room temperature, because the single sharp resonance of cyclopentadienyl group at about 6.31 ppm almost disappeared and the splitting peaks at about 6.47, 6.32, and 2.67 ppm appeared, which can be attributed to the eliminated cyclopentadiene. On a preparative scale, the expected lanthanide aryloxo complexes (MBMP)Ln(OC_6H_3-Me_2-2,6)(DME)$_2$ [Ln = La (**1**), Nd (**2**)] can be obtained in high isolated yields from toluene/DME solution. A further study revealed that the reactions of (MBMP)Ln(C_5H_5)(THF)$_n$ with 4-*tert*-butylphenol proceeds smoothly, and generated the desired lanthanide aryloxo complexes (MBMP)La(OC_6H_4-*t*Bu-4)(DME)$_2$ (**3**) and [(MBMP)Nd(OC_6H_4-*t*Bu-4)(THF)$_2$]$_2$ (**4**) from toluene/DME and THF solution, respectively. The similar reactions with 4-methoxylphenol also produced the expected bridged bis(phenolate) lanthanide aryloxo complexes [(MBMP)Ln(OC_6H_4-OMe-4)(THF)$_2$]$_2$ [Ln = La (**5**), Nd (**6**)] as shown in Scheme 1. Complexes **1**–**6** were well characterized by elemental analysis, IR spectroscopy, and NMR spectrum for the diamagnetism lanthanum complexes **1**, **3**, and **5**. Because of their paramagnetic properties, no resolvable NMR spectrum for the neodymium complexes was obtained. All of these complexes are moderate sensitive to air and moisture. These complexes are soluble in THF, DME, and toluene, and slightly soluble in hexane.

The definitive molecular structures of complexes **1**, **3**, and **4** were determined by X-ray diffraction. Crystals of complex **1** suitable for an X-ray structure determination were obtained from a concentrated DME solution. The molecular structure of complex **1** is depicted in Figure 1, and the selected bond lengths and bond angles are provided in Table 2. Complex **1** has a monomeric structure and the lanthanum atom is coordinated by two oxygen atoms from one MBMP^{2-} group, one oxygen atom from aryloxo group, and four oxygen atoms from two DME molecules. The coordination number is seven, and the coordination arrangement around lanthanum ion can be described as a distorted capped trigonal prism, with the capping atom being the oxygen atom O(5). The La(1)–O[bis(phenolate)] and the La(1)–O(Ar) bond lengths are 2.279(2), 2.302(2), and 2.259(2) Å, respectively, which is comparable with the corresponding bond lengths in complexes (MBMP)La(C_5H_5)(THF)$_3$,[23] (MBMP)$_3$La$_2$(THF)$_3$,[23] and (THF)La(O-2,6-*i*Pr$_2$$C_6H_3$)$_2$(μ-O-2,6-*i*Pr$_2$$C_6H_3$)$_2$M($THF$)$_2$ (M = Li, Na).[25]

Complex **3** crystallizes with two crystallographically independent but chemically similar molecules (**3a** and **3b**) in the unit cell, and selected bond lengths of both molecules are provided in Table 2. An ORTEP of complex **3a** is depicted in Figure 2. Complex **3** has a monomeric structure and the lanthanum ion is coordinated by two oxygen atoms from one MBMP^{2-} group, one oxygen atom from aryloxo group, and four oxygen atoms from two DME molecules. The overall coordination is similar to that in complex **1**. The La(1)–O[bis(phenolate)] and the La(1)–O(Ar) bond lengths are 2.266(7), 2.220(8), and 2.230(8) Å, respectively. These values are slightly shorter than the corresponding bond lengths in com-



Scheme 1. Synthesis of the lanthanide aryloxo complexes.

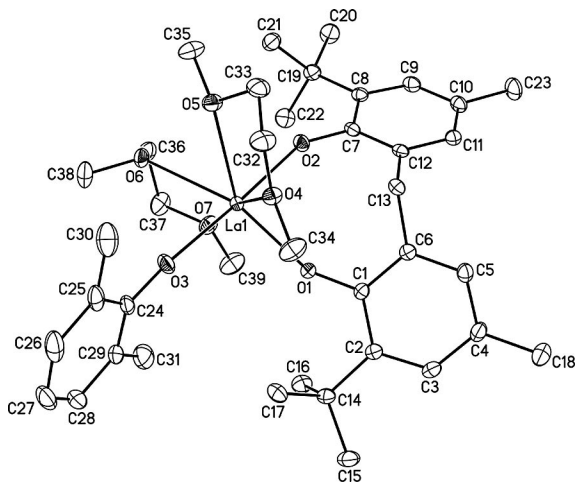


Figure 1. ORTEP diagram of complex **1** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

plex **1**, reflecting the less steric congestion around lanthanum ion resulted from the coordination of less bulky 4-*tert*-butylphenolate group.

An ORTEP of complex **4** is shown in Figure 3, and the selected bond lengths and bond angles are listed in Table 2. Complex **4** shows a centrosymmetric dimeric feature containing a Nd_2O_2 core bridging through the oxygen atoms of the aryloxo groups. The overall molecule structure is quite different from that of complex **3**, which revealed that the coordinated solvent molecule has significant influence on the solid-state structure. Each of the neodymium ions is six-coordinate by two oxygen atoms from bis(phenolate) ligand, two oxygen atoms from two aryloxo groups, and two oxygen atoms from two THF molecules to form a distorted octahedron. The Nd(1)–O[bis(phenolate)] bond lengths are 2.169(2) and 2.217(2) Å, respectively, giving the average of 2.193(2) Å, which is comparable with the corresponding bond lengths in complexes **1** and **3** when the difference in ionic radii between neodymium and lanthanum is considered, and the bond length in $[(MBMP)Nd(\mu\text{-}OiPr)(THF)_2]_2$.[22] The *tert*-butylphenoxo group is asymmetrically coordinated to the neodymium ions. The Nd(1)–O(3) bond length of 2.434(2) Å is about 0.076 Å longer than the Nd(1)–O(3A) bond length of 2.358(2) Å. The average Nd(1)–O(Ar) bond length of 2.386(2) Å is comparable with the Nd–O(alkox) bond length in $[(MBMP)Nd(\mu\text{-}OiPr)(THF)_2]_2$,[22] but apparently longer than the La(1)–O(Ar) bond length in complexes **1** and **3**, although the ionic radius of lanthanum ion is larger than that of neodymium ion. This difference can be attributed to the formation of bridging bond in the latter.

Ring-opening Polymerization of ε-Caprolactone

Poly(ε-caprolactone) and related copolymers have received considerable interest in the past ten years, because of their biodegradable property and the wide application in the medical field.[26–29] It has been found that many organolanthanide complexes are efficient initiators for the ring-opening polymeriza-

Table 2. Selected bond lengths /Å and bond angles /° for complexes **1**, **3**, and **4**.

Bond lengths	**1**	**3a**	**3b**	**4**
Ln(1)–O(1)	2.279(2)	2.266(7)	2.260(7)	2.169(2)
Ln(1)–O(2)	2.302(2)	2.220(8)	2.241(8)	2.217(2)
Ln(1)–O(3)	2.259(2)	2.230(8)	2.241(8)	2.434(2)
Ln(1)–O(3A)				2.358(2)
Ln(1)–O(4)	2.604(2)	2.74(2)	2.67(2)	2.510(2)
Ln(1)–O(5)	2.701(4)	2.66(3)	2.66(3)	2.585(2)
Ln(1)–O(6)	2.691(2)	2.76(2)	2.63(2)	
Ln(1)–O(7)	2.678(2)	2.76(2)	2.66(2)	
O(1)–C(1)	1.342(3)	1.36(1)	1.33(1)	1.338(4)
O(2)–C(7)	1.334(4)	1.35(1)	1.35(1)	1.349(4)
O(3)–C(24)	1.340(3)	1.36(1)	1.34(1)	1.361(4)
Bond angles	**1**	**3**		**4**
O(1)–Ln(1)–O(2)	86.40(5)	86.8(3)	87.8(3)	94.22(8)
O(1)–Ln(1)–O(3)	96.08(6)	103.6(3)	101.4(3)	89.67(8)
O(2)–Ln(1)–O(3)	176.69(6)	96.0(3)	97.1(3)	103.49(8)
Ln(1)–O(1)–C(1)	154.2(1)	149.8(7)	149.6(7)	158.2(2)
Ln(1)–O(2)–C(7)	152.4(1)	160.2(7)	160.3(9)	144.7(2)
Ln(1)–O(3)–C(24)	174.1(1)	172.1(8)	170.5(8)	105.2(2)
Ln(1)–O(3A)–C(24)				142.7(2)

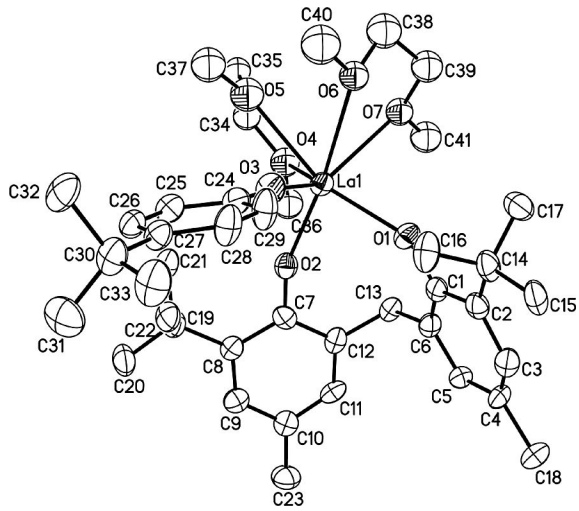


Figure 2. ORTEP diagram of complex **3a** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

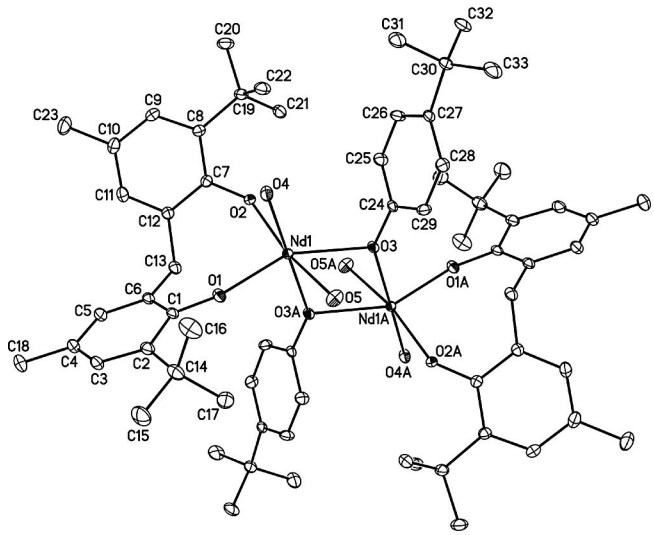
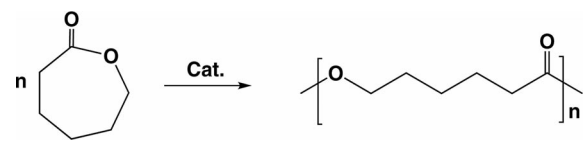


Figure 3. ORTEP diagram of complex **4** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms and carbon atoms on THF molecules are omitted for clarity.

tion (ROP) of ε-caprolactone.[20–22,30–32] To further explore the influence of the initiating group of organolanthanide complexes on the catalytic property, the catalytic behaviors of complexes **1**–**6** for the ROP of ε-caprolactone were tested (Scheme 2), and the results are listed in Table 3.

These lanthanide aryloxo complexes can serve as active initiators to polymerize ε-caprolactone in toluene to give the polymers with high molecular weights and moderate molecule weight distributions. The molecule weights of the resultant polymers range from 2.61×10^{-4} to 8.92×10^{-4} g·mol^{-1} as the increase of molar ratio of monomer to initiator, but there is no linear relationship between the molar ratios of monomer to initiator and the molecular weights. On the other hand, the molecule weight distributions range from 1.40 to 1.64. These results indicated that the polymerization initiated by these lanthanide aryloxo complexes is not well-controlled. This is quite



Scheme 2. Ring-opening polymerization of ε-caprolactone.

different from the cases initiated by lanthanide alkoxo complexes stabilized by the same bis(phenolate) ligand, and the latter can initiate ε-caprolactone polymerization in a controlled manner.[21,22] It has been reported that the silylamide initiating group is inferior to alkoxo group for controlled polymerization of lactide, because the silylamide group is less nucleophilic than alkoxo group, which caused the relatively slow initiating

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Table 3. Polymerization of ε-caprolactone initiated by complexes **1** to **6** [a].

Run	Initiator	$[M]_0/[I]_0$	*t* /h	T_p /°C	Yield /%[b]	M_n (obsd)[c] /× 10^{-4} g·mol^{-1}	PDI
1	1	400	1	50	100	4.35	1.64
2	1	600	1	50	100	6.53	1.60
3	1	800	2	50	96	8.32	1.53
4	1	1000	2	50	79	8.67	1.47
5	2	200	1	50	100	2.51	1.58
6	2	400	1	50	87	4.08	1.49
7	2	600	2	50	93	5.84	1.55
8	2	800	2	50	76	6.34	1.42
9	2	1000	4	50	81	8.92	1.45
10	3	600	1	50	100	6.13	1.46
11	3	800	2	50	98	8.68	1.49
12	3	1000	2	50	82	8.91	1.43
13	4	400	4	50	96	3.74	1.63
14	4	600	4	50	55	2.88	1.45
15	5	400	4	50	100	4.21	1.56
16	5	600	4	50	100	6.29	1.52
17	5	800	4	50	89	7.52	1.47
18	6	400	4	50	93	3.94	1.48
19	6	600	4	50	60	3.55	1.40

a) General polymerization conditions: toluene as solvent, $V_{sol}/V_{[M]}$ = 4:1. b) Yield: weight of polymer obtained/weight of monomer used. c) Measured by GPC in THF calibrated with standard polystyrene samples.

speed.[33] The results in our cases revealed that the aryloxo group is also inferior to alkoxo group in controllability for ε-caprolactone polymerization. It is worthy to note that the cyclopentadienyl precursors showed very low activity under the same polymerization conditions, indicating that the reactivity of Ln–Cp bonds is lower than that of Ln–O(Ar) bond.

The ionic radii of the lanthanide ions have an obvious influence on the catalytic activity for ε-caprolactone polymerization. The catalytic activity decreased apparently with a decrease of the ionic radii. Using the lanthanum complex **1** as the initiator, the yield was 96% when the molar ratio of monomer to initiator is 800 in 2 h (Table 3, entry 3), whereas the yield was 76% using the neodymium complex **2** as the initiator under the same polymerization conditions (Table 3, entry 8). Similar active trend has also been observed in the carbon bridged bis(phenolate) lanthanide systems for ε-caprolactone polymerization,[20–22] and the diketiminato lanthanide bis(allyl) complexes for lactide polymerization.[34] This difference can be attributed to that the lanthanide metal with larger ionic radius has more opening coordination sphere, which is advantageous for the coordination of monomer to the central metal atom. The bulkiness of the aryloxo group seems to have no obvious effect on the catalytic activity for ε-caprolactone polymerization. Complex **1** showed similar activity for this polymerization in comparison with complex **3**. In contrast, the solid-state structure of the initiator has an influence on the catalytic activity. The initiator having monomeric structure showed higher activity than that having dimeric structure. For example, complexes **1** and **3** can polymerize completely in 2 h when the molar ratio of monomer to initiator is 800 (Table 3, entries 3 and 11); whereas the yield is 89% even the polymerization time extends to 4 h under the same polymerization conditions (Table 3, entry 17). The difference in activity among these lanthanide complexes can be attributed to the lower initiating speed, because *Okuda* et al. has suggested that the dimeric structure should be cleaved and produced the monomeric species, which is the really active center, when a dimeric complex was used as the initiator for lactide polymerization.[33]

To gain more information about the initiation mechanism, the oligomer of ε-caprolactone was prepared by the reaction of ε-caprolactone with complex **6** in a 10:1 molar ratio, and then quenched by 2-propanol. The oligomer was characterized by ^{1}H NMR spectroscopy as shown in Figure 4. In the ^{1}H NMR spectrum, the signals at about 2.96 and 3.63 ppm can be assigned to the end of *H*O*C*H_2(CH_2)$_4$CO–. On the other hand, the signals at about 1.21 and 5.02 ppm revealed that another end group of the oligomer is an isopropoxo group, but not the 4-methoxyphenoxo group. We postulated that an exchange reaction occurred between aryloxo group and isopropoxo group during quenching the oligomerization by 2-propanol. Similar phenomenon was also observed by *Shen* et al. in the polymerization of cyclic carbonate initiated by lanthanide aryloxides.[35]

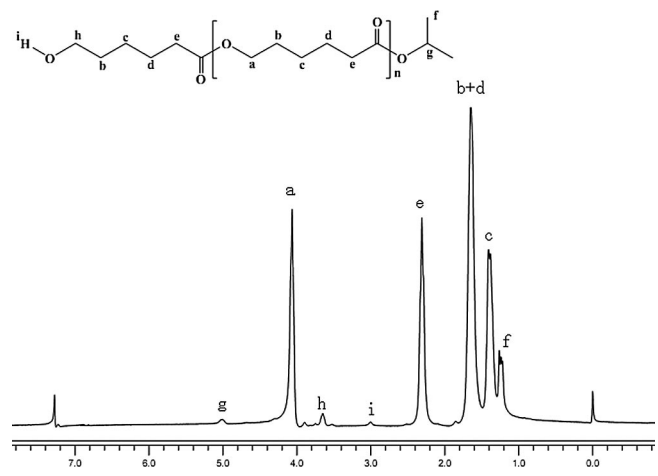

Figure 4. ^{1}H NMR spectrum of the oligomer of ε-caprolactone initiated by complex **6**, and quenched by 2-propanol in $CDCl_3$.

Conclusions

Some new carbon bridged bis(phenolate) lanthanide aryloxo complexes were synthesized, and their structural features were provided by single-crystal X-ray diffraction. It was found that the coordination solvent molecule has a profound influence on the solid-state structure of the bis(phenolate) lanthanide aryloxo complexes. The complexes crystallized from DME-containing solvent have monomeric structures, whereas the complexes crystallized from THF have dimeric structure. These lanthanide aryloxo complexes are efficient initiators for ε-caprolactone polymerization, but the polymerization is not well controlled. These results revealed that the aryloxo group is inferior to alkoxo group in controllability for ε-caprolactone polymerization. Furthermore, the complexes having dimeric structure showed relatively lower activity than the complexes having monomeric structure.

Acknowledgements

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