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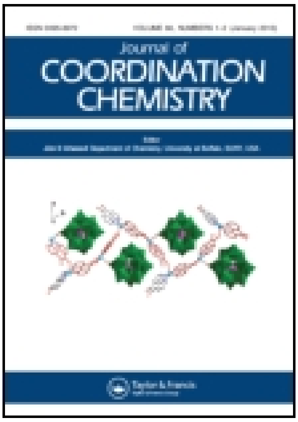

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Synthesis, structure, and catalytic activity of lanthanide Gd(III) and La(III) complexes with N-(cyclohexyl)isopropyl amidate ligand

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Synthesis, structure, and catalytic activity of lanthanide Gd(III) and La(III) complexes with *N*-(cyclohexyl)isopropyl amidate ligand

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Two new lanthanide amidate complexes, $\{Gd_2[Cy(NCO)^iPr]_6\}$ (**1**) and $\{La_2[Cy(NCO)^iPr]_6[Cy(HNCO)^iPr]\}$ (**2**) (^{i}Pr = isopropyl, Cy = cyclohexyl), have been synthesized in good yields by silylamine elimination reaction between $Gd[N(SiMe_3)_2]_3$ or $La[N(SiMe_3)_2]_3$ and *N*-(cyclohexyl)isopropyl amide. Complexes **1** and **2** have been characterized by NMR, elemental analyzes, and X-ray diffraction. The molecular structures of $\{[Cy(NCO)^iPr]Gd[\mu_2\text{-}Cy(NCO)^iPr]_3Gd[Cy(NCO)^iPr]_2\}$ (**1**) and $\{[Cy(NCO)^iPr]La[\mu_2\text{-}Cy(NCO)^iPr]_3La[Cy(NCO)^iPr]_2[Cy(HNCO)^iPr]\}$ (**2**) exhibit a dimer structure with three μ_2-O bridging bonds that look like a windmill. Additionally, **2** formed an intramolecular N–H···O hydrogen bond via a neutral amide. The catalytic properties of **1** and **2** for ring-opening polymerization (ROP) of ε-caprolactone have been studied. The results show that **1** and **2** are efficient catalysts for the ROP of ε-caprolactone.

Keywords: Organolanthanide (Gd or La); *N*-(cyclohexyl)isopropyl amide; Polymerization of ε-caprolactone

1. Introduction

There is interest in the development of efficient catalytic systems for the preparation of biodegradable, biocompatible, and permeable aliphatic polyesters, such as poly(ε-caprolactone) (PCL) [1] and poly(lactide) (PLA) [2]. Numerous catalysts, alkali metals [3], alkaline earth metals [4], transition metals [5], and lanthanides [6] have been explored for the ring-opening polymerization (ROP) of lactones. Among them, organolanthanide catalysts have received much interest due to their high activities and capabilities of preparing polymers with high molecular weights in narrow polydispersity [7–11]. Simple rare-earth-metal complexes such as $Y(N(SiMe_3)_2)_3$, $[CyNC(Me)NCy]_3Nd$, and $Ln[(BH_4)]_3(THF)_x$ (1: Ln = La, $x = 3$; 2: Ln = Pr, $x = 2$; 3: Ln = Nd, $x = 3$; 4: Ln = Sm, $x = 3$; 5: Ln = Y, $x = 2.5$; 6: Ln = Yb, $x = 3$) exhibit high activity for ROP of cyclic esters to give polyesters with controlled molecular weight [12, 13]. Finding new catalytic systems would be important to prepare high molecular weight and narrow polydispersity polyester materials. Lanthanide amidate

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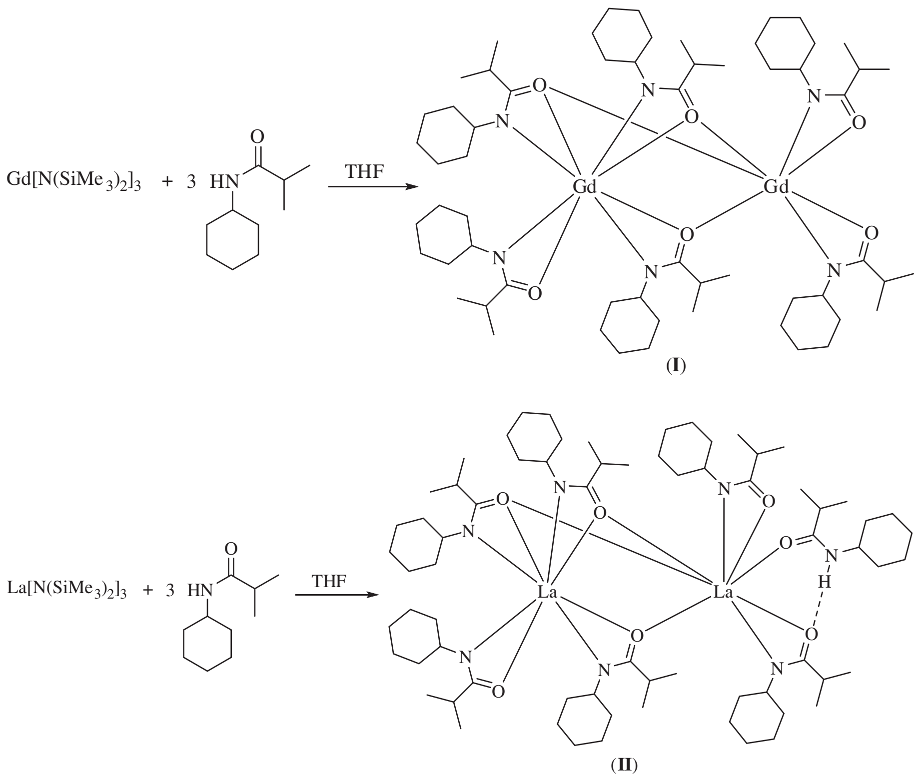
complexes showed high catalytic activities and good controlled polymerization for ROP of ε-caprolactone [14]. Stanlake and co-workers previously reported that yttrium amidate complexes using the simple reaction of naphthyl amides and $Y[N(SiMe_3)_2]_3$ result in high activity in preparation of PCL [12]. Zhang *et al.* also demonstrated that rare-earth metal amidate complexes with chiral binaphthyl-based amidate ligands showed high catalytic activities for the ROP of ε-caprolactone [15]. Preparation of lanthanide amidate complexes and search for their application in the polymerization of ε-caprolactone could be very attractive.

From previous reports, steric environment around the metal centers of the initiators had a significant influence towards polymerization [16, 17]. Selecting medium-sized amide ligands, like *N*-(cyclohexyl)isopropyl amide, may be effective in the next polymerization of ε-caprolactone. Rare-earth metal amidate complexes can be efficiently prepared via silylamine elimination reactions between $Ln[N(SiMe_3)_2]_3$ and protic amidate ligands [12, 15]. Here, we report the syntheses and structures of Gd(III) and La(III) complexes with the *N*-(cyclohexyl)isopropyl amidate following similar silylamine elimination, $\{Gd_2[Cy(NCO)^iPr]_6\}$ (**1**) and $\{La_2[Cy(NCO)^iPr]_6[Cy(HNCO)^iPr]\}$ (**2**) (scheme 1). The catalytic properties of the complexes have also been studied in the polymerization of ε-caprolactone under mild conditions.



Scheme 1. Synthesis of **1** and **2**.

2. Experimental

2.1. *Chemical materials*

The chemicals $HN(TMS)_2$ and *n*-BuLi were commercially available. $HN(TMS)_2$ was dried over CaH_2 for four days and distilled before use. THF, toluene, and *n*-hexane were dried and freed of oxygen by refluxing over sodium/benzophenone ketyl and distilling prior to use. $La[N(SiMe_3)_2]_3$, $Gd[N(SiMe_3)_2]_3$, and *N*-(cyclohexyl)isopropyl amide were synthesized as described in the literature [18–20]. ε-Caprolactone was dried over calcium hydride, vacuum distilled, and degassed prior to use.

2.2. *Physical measurements*

NMR spectra were recorded on a Bruker Avance 400 spectrometer at resonant frequencies of 400 MHz for ^1H and 100 MHz for ^{13}C nuclei using C_6D_6 or $CDCl_3$ as solvent. The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) were determined by GPC on a Water GPC system equipped with four Waters Ultrastyragel columns (300 × 7.5 mm, guarded and packed with 1×10^5, 1×10^4, 1×10^3, and 500 A gels) in series. Tetrahydrofuran (THF, 1 mL min^{-1}) was used as the eluent and the signal was monitored by a differential refractive index detector. Monodispersed polystyrene was used as the molecular weight standard. Elemental analyzes were performed on a Perkin-Elmer 240C elemental analyzer. Single-crystal X-ray structure measurement was performed on a BRUKER SMART Apex CCD single-crystal X-ray diffractometer. The detector was equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 173 K. Melting points were observed in sealed capillaries and were uncorrected.

2.3. *Preparation of $\{Gd_2[Cy(NCO)^iPr]_6\}$ (1)*

All manipulations were performed under nitrogen atmosphere using standard Schlenk-line or glove-box techniques. For synthesis of **1**, $Gd[N(SiMe_3)_2]_3$ (0.6374 g, 0.998 mM) in THF (10 ml) was added to a THF (20 ml) solution of $Cy(HNCO)^iPr$ (0.5070 g, 2.994 mM) at room temperature. The reaction mixture was stirred for 24 h and then evaporated to dryness under vacuum to afford a pale yellow solid. The residue was extracted with a mixture of THF and hexane. **1** was obtained from the filtered extract at –30 °C as colorless crystals. Yield: 0.542 g (82%). M.p.: 148.3–150.1 °C (dec). Anal. Calcd for $C_{60}H_{108}Gd_2N_6O_6$: Gd, 23.75; C, 54.43; H, 8.22; N, 6.35. Found: Gd, 23.57; C, 54.24; H, 8.05; N, 6.21.

2.4. *Preparation of $\{La_2[Cy(NCO)^iPr]_6[Cy(HNCO)^iPr]\}$ (2)*

2 was obtained by protolysis of $La[N(SiMe_3)_2]_3$ (0.6548 g, 1.056 mM) with $Cy(HNCO)^iPr$ (0.5362 g, 3.168 mM) following similar procedure as for **1**. 0.592 g (Yield: 77%) colorless crystals were obtained. M.p.: 176.8–178.0 °C (dec). Anal. Calcd for $C_{70}H_{127}La_2N_7O_7$: La, 19.07; C, 57.72; H, 8.79; N, 6.73. Found: La, 18.95; C, 57.57; H, 8.62; N, 6.56. ^1H NMR (400 MHz, C_6D_6): 9.54 (s, 1 H, N*H*), 3.83–3.91 (m, 1 H, C*H*$(CH_3)_2$), 3.24–3.29 (m, 7 H, Cy-*H*), 2.82–2.97 (m, 6 H, C*H*$(CH_3)_2$), 1.81–1.93 (m, 28 H, Cy-*H*), 1.62–1.71 (m, 14 H, Cy-*H*), 1.31–1.40 (m, 28 H, Cy-*H*), 1.27 (d, *J* = 7.4 Hz, 36 H, $CH(CH_3)_2$), 1.08 (d, *J* = 6.7 Hz, 6 H, $CH(CH_3)_2$)). $^{13}C\{H\}$ NMR (100 MHz, C_6D_6): δ 183.2, 174.9 (C = O), 56.3, 55.7 (Cy-*C*), 36.6, 35.7 (*C*H(CH$_3$)$_2$), 33.4, 32.3 (Cy-*C*), 30.2, 29.8 (Cy-*C*), 26.2, 25.2 (Cy-*C*), 20.5, 20.0 (CH(*C*H$_3$)$_2$).

2.5. *X-ray data collection and refinement of crystal structure*

The crystals of the complexes were mounted on a glass fiber for X-ray measurement. Reflection data were collected at low temperature (173 K) on a BRUKER SMART Apex CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and a ω scan mode. All measured independent reflections ($I > 2\sigma(I)$) were used in the structural analyzes and semi-empirical absorption corrections were applied using SADABS [21].

The structure was solved and refined using SHELXL-97 [22]. All hydrogens bound to carbon were positioned geometrically and refined using a riding model, and hydrogen of nitrogen was located in difference Fourier syntheses. The non-hydrogen atoms were refined with anisotropic thermal parameters. In **1**, the disordered cyclohexyl unit split into C6C7C8C9C10 and C6′C7′C8′C9′C10′ with occupancies of 55.6 (26) and 44.4 (26)%, respectively. In **2**, the disordered cyclohexyl group split into C6C7C8C9C10 and C6aC7aC8aC9aC10a with occupancies of 27.1 (35) and 72.9 (35)%, respectively. The crystallographic data and experimental details of the data collection, as well as the structure refinements are given in table 1. Diagrams were made with SHELXL-97 and all calculations were performed on a Pentium 4 computer.

Table 1. X-ray structural details for {Gd$_2$[Cy(NCO)^{i}Pr]$_6$} (**1**) and {La$_2$[Cy(NCO)^{i}Pr]$_6$[Cy(HNCO)^{i}Pr]} (**2**).

	1	**2**
Formula	$C_{60}H_{108}Gd_2N_6O_6$	$C_{70}H_{127}La_2N_7O_7$
Formula weight	1324.02	1456.61
Space group	$P2_1/n$	$P-1$
Crystal size (mm)	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.20
Crystal system	Monoclinic	Triclinic
Z value	4	2
a (Å)	11.326(2)	12.834(3)
b (Å)	26.866(5)	15.071(3)
c (Å)	21.188(4)	20.318(4)
α (°)	90	90.50(3)
β (°)	90.75(3)	90.77(3)
γ (°)	90	107.72(3)
D_{Calcd} [g/cm^3]	1.364	1.292
Index ranges	$-8 \le h \le 13$	$-12 \le h \le 15$
	$-32 \le k \le 32$	$-17 \le k \le 17$
	$-25 \le l \le 25$	$-20 \le l \le 24$
Crystal shape/color	Prism/colorles	Prism/colorless
F (0 0 0)	2744	1532
μ (Mo Kα) (mm^{-1})	2.09	1.18
λ (Mo Kα) (Å)	0.71073	0.71073
Temperature (K)	173	173
θ Range (°)	2.8–29.2	3.3–29.1
Independent reflections [$(I) > 2\sigma(I)$]	11,728	12,978
R_1 [$I > 2\sigma(\theta)$]	0.032	0.024
wR_2 [$I > 2\sigma(\theta)$]	0.061	0.056
Goodness-of-fit on F^{2c}	1.10	1.05

Notes: (a) $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)]^{1/2}$. (b) $w_{\text{I}} = 1/[\sigma^2(F_o^2) + (0.0188P)^2 + 4.3576P]$, $P = (F_o^2 + 2F_c^2)/3$. $w_{\text{II}} = 1/[\sigma^2(F_o^2) + (0.0263P)^2 + 2.0001P]$, $P = (F_o^2 + 2F_c^2)/3$. (c) $S = [\Sigma w(F_o^2 - F_c^2)^2]/(n-p)^{1/2}$, n = number of reflections, p = parameters used.

2.6. *Experimental for ε-caprolactone ROP*

The polymerizations for ROP of ε-caprolactone were carried out in nitrogen atmosphere in Schlenk tubes. In a typical experiment, 0.0245 g (0.0185 mM) of **1** was dissolved in 5 mL of toluene. ε-Caprolactone 0.5279 g (4.63 mM) was dissolved in 5 mL of toluene and pipetted directly into the vigorously stirred solution of **1**. The reaction was stirred for 10 min within the glove-box and then exposed to air. A couple of drops of 1 M HCl and ethanol solution were added to fully quench the reaction. The polymer was precipitated from cold *n*-hexane, isolated by vacuum filtration, and then dried overnight in vacuum. Yield: 0.5170 g, 98%.

For product analyzes, 0.0400 g of poly(CL) was dissolved in 4 mL THF overnight. After centrifugation, the clear solution was measured by GPC with THF (1 mL min^{-1}) as the eluent. The weights of poly(CL) were calculated with monodispersed polystyrene as the molecular weight standard.

3. Results and discussion

3.1. *Synthesis*

Treating $Gd[N(SiMe_3)_2]_3$ or $La[N(SiMe_3)_2]_3$ with 3 equiv of *N*-(cyclohexyl)isopropyl amide in THF, the organolanthanide amidate complexes $\{Gd_2[Cy(NCO)^iPr]_6\}$ (**1**) and $\{La_2[Cy(NCO)^iPr]_6[Cy(HNCO)^iPr]\}$ (**2**) were obtained in good yields after recrystallization from a THF and *n*-hexane mixed solution (scheme 1). Complexes **1** and **2** were stable in dry nitrogen, but very sensitive to moisture. Complexes **1** and **2** were soluble in THF and toluene, but only slightly soluble in *n*-hexane.

3.2. *Structural description of 1 and 2*

X-ray crystallographic analyzes of **1** and **2** reveal that the two complexes are both dimeric in the solid state. The molecular structures are presented in figures 1 and 2, respectively, and selected bond distances and angles within the two complexes are given in table 2.

1 crystallizes as a non-centrosymmetric binuclear cluster, consisting of two Gd^{3+} and six $[Cy(NCO)^iPr]^-$ anions (figure 1). Four $[Cy(NCO)^iPr]^-$ anions are chelating to Gd2 as bidentate model with O and N forming four-membered chelate rings; the middle three anions are bridging to Gd1 via oxygens. Another two $[Cy(NCO)^iPr]^-$ chelate to Gd1 bidentate. Thus, Gd1 is seven-coordinate to two N and five O, forming a distorted $[GdO_5N_2]$ pentagonal bipyramidal coordination geometry. Gd2 is eight-coordinate to four N and four O, forming a distorted $[GdO_4N_4]$ dodecahedron. Two Gd^{3+} centers occupy two axial positions and three μ_2-O atoms occupy three equatorial positions, forming a distorted trigonal bipyramid with Gd1 and Gd2 1.7424(15) and –1.8690(15) Å out of the equatorial plane, respectively. In **2**, the structure is a non-centrosymmetric binuclear cluster made up of two La^{3+}, six $[Cy(NCO)^iPr]^-$ and one $Cy(HNCO)^iPr$ molecule (figure 2). The structure of **2** is quite similar to **1** except for the $Cy(HNCO)^iPr$ molecule. In **2**, four $[Cy(NCO)^iPr]^-$ anions chelate to La1 as a bidentate model with O and N forming four-membered chelate rings, and the middle three anions bridge to La2 via oxygens. Another two $[Cy(NCO)^iPr]^-$ chelate to La2 as bidentate. The $Cy(HNCO)^iPr$ molecule just coordinates to La2 with its O and forms a N–H···O hydrogen bond with adjacent bidentate $[Cy(NCO)^iPr]^-$. As a result, La1 and La2

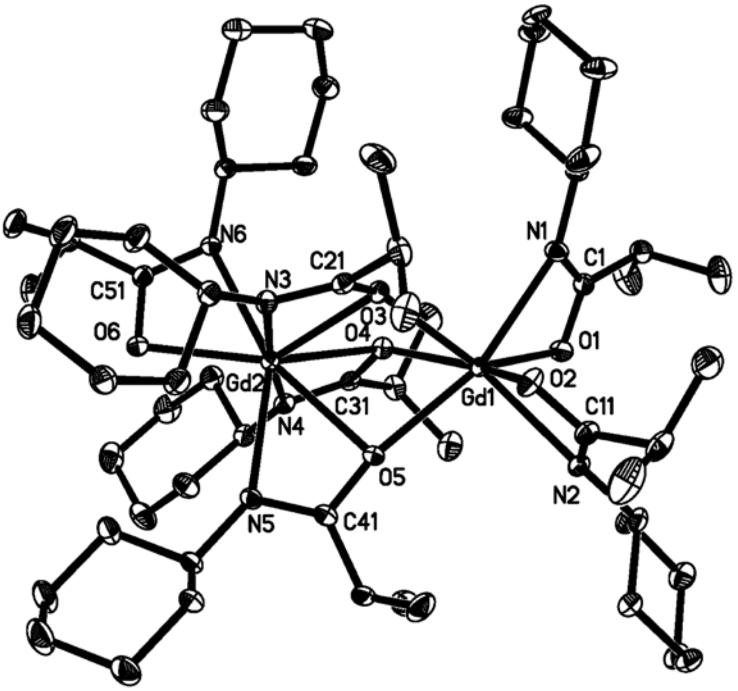


Figure 1. Molecular structure of **1**. Hydrogens are omitted for clarity.

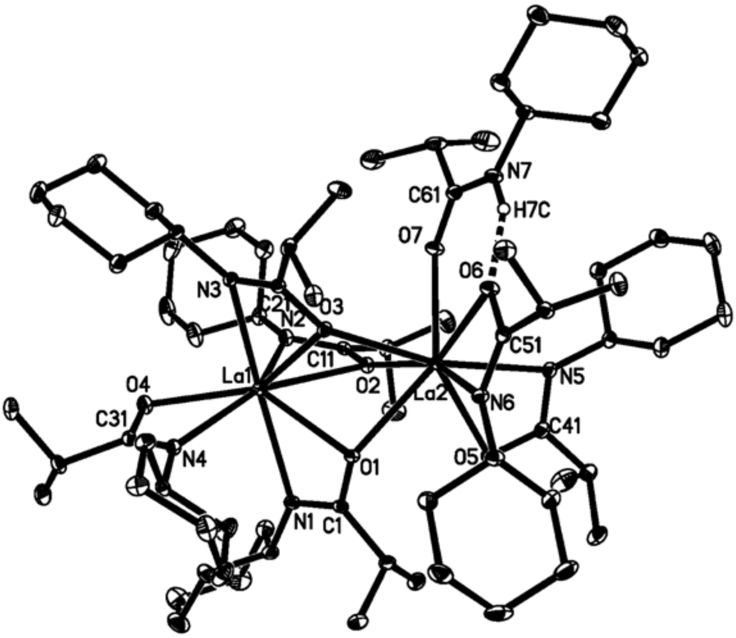


Figure 2. Molecular structure of **2**. Hydrogens are omitted for clarity except for hydrogen bonds.

Table 2. Selected bond lengths (Å) and angles (°) of **1** and **2**.

{$Gd_2[Cy(NCO)^iPr]_6$} (**1**)			
Gd1–O2	2.314(2)	Gd2–N6	2.429(3)
Gd1–O1	2.346(2)	Gd2–O3	2.452(2)
Gd1–O3	2.350(2)	Gd2–O5	2.458(2)
Gd1–O4	2.363(2)	Gd2–O4	2.478(2)
Gd1–O5	2.390(2)	Gd2–N4	2.480(3)
Gd1–N1	2.454(3)	Gd2–N3	2.496(3)
Gd1–N2	2.457(3)	Gd2–N5	2.500(3)
Gd2–O6	2.349(2)	Gd1···Gd2	3.6116(7)
O1–Gd1–N1	55.13(8)	O5–Gd2–N5	53.26(8)
O2–Gd1–N2	55.52(8)	Gd1–O4–Gd2	96.46(8)
O6–Gd2–N6	55.42(8)	Gd1–O3–Gd2	97.54(8)
O4–Gd2–N4	53.16(7)	Gd1–O5–Gd2	96.30(8)
O3–Gd2–N3	53.05(7)		
{$La_2[Cy(NCO)^iPr]_6[Cy(HNCO)^iPr]$} (**2**)			
La2–O5	2.4519(17)	La1–O3	2.5195(17)
La2–O2	2.4775(16)	La1–O1	2.5564(16)
La2–O3	2.5145(16)	La1–N4	2.584(2)
La2–O6	2.5423(17)	La1–N1	2.5914(19)
La2–O7	2.5552(17)	La1–O2	2.5965(16)
La2–O1	2.5871(17)	La1–N2	2.6221(19)
La2–N6	2.617(2)	La1–N3	2.6398(19)
La2–N5	2.6210(19)	La1···La2	3.8338(9)
La1–O4	2.4690(16)		
O6–La2–N6	50.89(6)	O3–La1–N3	51.13(6)
O5–La2–N5	51.92(6)	La1–O1–La2	96.38(5)
O4–La1–N4	52.31(6)	La2–O2–La1	98.13(5)
O1–La1–N1	51.10(6)	La2–O3–La1	99.21(5)
O2–La1–N2	50.51(6)		

are both eight-coordinate with distorted [LaO_4N_4] and [LaO_6N_2] dodecahedra coordination geometries. Similarly, two La^{3+} centers and three μ_2-O form a distorted trigonal bipyramid, and La1 and La2 1.9401(13) and –1.8912(13) Å out of the equatorial plane, respectively.

In **1**, the Gd–O distances average 2.389(2) Å, close to previously reported complexes Gd $(tmhd)_3$(monoglyme) (2.393(2) Å) [23] and [$(C_5Me_5)Gd(CH_2C_6H_5)_2(thf)$] (2.390(4) Å) [24]. The bond distances of the Gd–N bonds in **1** (av Gd–N = 2.469(3) Å) are comparable with those in $Na_5[Gd(C_7H_2NO_5)_2(C_7H_3NO_5)]\cdot16H_2O$ (2.484(6) Å) [25] and [$(AIP)_3Gd$] (2.442(2) Å) [26]. In **2**, the average La–O distances (2.5270(17) Å) are similar to $La(PF_6)_3\cdot5C_7H_{14}N_2O_2$ (2.54(1) Å) [27] and $La(hfa)_3\cdot$monoglyme$\cdot H_2O$ (2.560(6) Å) [28]. The La–N bond lengths in **2** (av La–N = 2.613(2) Å) are comparable with those in $Cp_2Ln[N(SePPh_2)_2]$ (2.615(2) Å) [29] and $(C_2mim)_3[La(dcnm)_6]$ (2.629(2) Å) [30]. The average Gd–N and Gd–O bond lengths in **1** are shorter than those in **2**, La–N and La–O (table 2), since La^{3+} has a larger radius (Gd^{3+}: 0.94 Å; La^{3+}: 1.06 Å) [31].

Viewed along the Ln1···Ln2 axis in **1** and **2**, the $Ln_2(CyNCO^iPr)_3$ unit looks like a three-leaf windmill. The dihedral angles of **1** between the three planes Gd1Gd2O3, Gd1Gd2O4, and Gd1Gd2O5 are 125.14(12)°, 119.82(10)°, and 115.05(8)°, respectively, and the dihedral angles of **2** concerning the three planes La1La2O1, La1La2O2, and La1La2O3 are 112.36(7)°, 111.46(8)°, and 136.18(6)°, respectively. Since the bonding between the lanthanide ions and ligands is electrostatic and non-directional, it depends mainly on steric factors associated with the ligands [32, 33]. In both complexes, the average Ln–O [Gd–O: 2.415(2) Å; La–O: 2.5419(17) Å] and Ln–N [Gd–N: 2.4923(3) Å; La–N: 2.617(2) Å] bond lengths of the middle three bridging amidates, which have larger steric

Table 3. Hydrogen-bond geometry (Å, °) of **2**.

D–H…*A*	*D*–H	H…*A*	*D*…*A*	*D*–H…*A*
N7–H7C…O6	0.909(16)	1.850(18)	2.715(3)	158(2)

factors, are slightly longer than that of the side bidentate amidates [Gd–O: 2.336(2) Å; Gd–N: 2.446(3) Å; La–O: 2.4606(16) Å; La–N: 2.602(2) Å]. The Ln1···Ln2 distances [Gd1···Gd2: 3.6116(7) Å; La1···La2: 3.8338(9) Å] in both complexes are similar to those of previously reported complexes with three μ_2-O bonds [34–36] and shorter than those usually observed in dimers with two μ_2-O bonds [37–40]. In **2**, the N–H···O hydrogen bond links N7 to O6 coordinated to the La center [N7···O6 = 2.715(3) Å]. Hydrogen bond parameters for **2** are listed in table 3. The angle and distance correspond to previous reports [41–44]. The La2–O6 bond length [2.5423(18) Å] is slightly longer than that of the other two bidentate amidates [2.4606(16) Å] and close to the length of bridging La-μ_2-O bonds [2.5419(17) Å].

3.3. *Catalytic activity studies*

Both **1** and **2** as catalysts for ε-caprolactone polymerization have been systematically examined in toluene and THF with different monomer ratio (table 4). The polymerization data show that **1** and **2** can initiate ring opening polymerization (ROP) of ε-caprolactone under mild conditions. When comparing entries 1–4 and 6–9, the molecular weight M_w of the polymer increased as the monomer to initiator ratio ([*M*]/[*I*]) increased, however, giving a minimum PDI value in the [*M*]/[*I*] ratio of 250. Polymerizations with these Gd and La initiators/catalysts proceed much more slowly in THF (table 4, entries 5 and 10), presumably due to competitive coordination between the monomer and this donor solvent [40]. With the same [*M*]/[*I*] ratio, the PDI values are slightly lower in toluene (table 4, entries 3, 5, 8, and 10). Control experiments (table 4, entries 11 and 12) confirmed that no poly(CL) was formed in the absence of *N*-(cyclohexyl)isopropyl amide ligand or without any initiator

Table 4. Summary of ROP of ε-caprolactone.

Entry	I	[*M*]/[*I*][a]	Solvent[b]	Yield[c] (%)	M_w[d] (×10^4) g mol^{-1}	PDI[d]
1	**1**	50	Toluene	95	5.4	2.34
2	**1**	100	Toluene	100	10.3	2.10
3	**1**	250	Toluene	100	15.0	1.85
4	**1**	500	Toluene	98	27.6	2.06
5	**1**	250	THF	93	22.9	2.39
6	**2**	50	Toluene	96	4.6	2.45
7	**2**	100	Toluene	99	7.3	2.38
8	**2**	250	Toluene	100	23.3	2.05
9	**2**	500	Toluene	100	34.6	2.26
10	**2**	250	THF	94	20.8	2.27
11[e]	Amide ligand	250	Toluene	–	–	–
12[f]	–	250	Toluene	–	–	–

Notes: [a] [*M*]/[*I*]: the ratio of monomer to Ln (Gd or La).
[b] In toluene, 10 min of stirring, at room temperature; In THF, 30 min of stirring, at room temperature.
[c] Yield: weight of polymer obtained/weight of monomer used.
[d] Measured by GPC in THF calibrated with polystyrene standard.
[e] Contrast experiment used *N*-(cyclohexyl)isopropyl amide ligand as initiator.
[f] Blank experiment without any initiator.

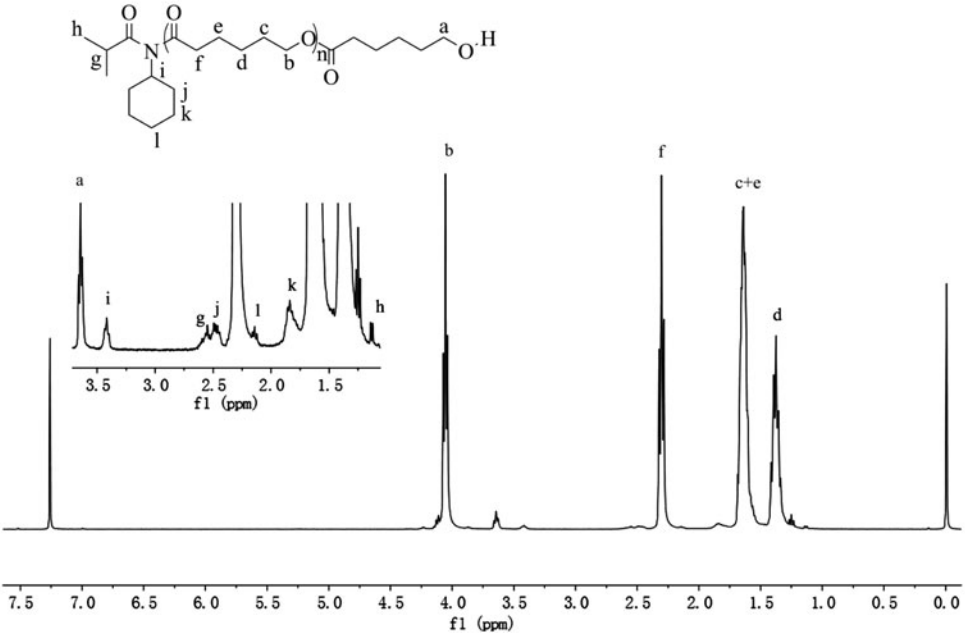


Figure 3. ^{1}H NMR (400 MHz) spectrum (in $CDCl_3$) of poly(ε-caprolactone) using initiator **2**.

under the same conditions. In comparison with yttrium amidate complexes reported by Stanlake and co-workers (time of polymerization 15 min, temperature 25 °C, yield 56–96%, PDI 2.12–2.56) [12], **1** and **2** exhibit lower catalytic activity. The catalytic activity of **1** and **2** is similar to that of homoleptic lanthanide amidinate complexes (time 15 min, temperature –5–40 °C, yield 27.2–100%, PDI 1.71–2.29) [8] and better than the catalytic activity of anionic lanthanide complexes supported by a pyrrole-based tetradentate Schiff base (time 10–48 h, temperature 40–80 °C, yield 22–80%, PDI 1.09–1.39) [45].

The microstructure of the polymers was determined by ^{1}H NMR experiments using initiator **2** and a 15:1 monomer to initiator ratio, as shown in figure 3. The signal at 3.64 ppm can be assigned to the methylene protons in the α-position to the terminal hydroxyl, and the signals at 2.55 and 1.13 ppm can be assigned to the isopropyl group of the *N*-(cyclohexyl) isopropyl amidate. This is consistent with the mechanism of polymerization proceeding through *N*-(cyclohexyl)isopropyl amidate ligand promoted initiation to produce a polymer with –[Cy(NCO)^{i}Pr] as the terminus.

4. Conclusion

Two new lanthanide amidate complexes have been prepared via silylamine elimination reaction between La[N($SiMe_3$)$_2$]$_3$ or Gd[N($SiMe_3$)$_2$]$_3$ and the *N*-(cyclohexyl)isopropyl amide ligand. Both complexes are active catalysts for the polymerization of ε-caprolactone. The mechanism of polymerization proceeds through ε-caprolactone monomer's successive insertion of the Ln–N(amidate) bond to produce a polymer with –[Cy(NCO)^{i}Pr] and –OH as the terminus following protonolysis.

Supplementary material

CCDC 875880 and 920576 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

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References

[1] H. Miao, S. Wang, S. Zhou, Y. Wei, Z. Zhou, H. Zhu, S. Wu, H. Wang. *Inorg. Chim. Acta*, **363**, 1325 (2010).
[2] Q. Wang, F. Zhang, H. Song, G. Zi. *J. Organomet. Chem.*, **696**, 2186 (2011).
[3] L. Chen, L. Jia, F. Cheng, L. Wang, C.-c. Lin, J. Wu, N. Tang. *Inorg. Chem. Commun.*, **14**, 26 (2011).
[4] X. Xu, Y. Chen, G. Zou, Z. Ma, G. Li. *J. Organomet. Chem.*, **695**, 1155 (2010).
[5] A. Arbaoui, C. Redshaw, N.M. Sanchez-Ballester, M.R.J. Elsegood, D.L. Hughes. *Inorg. Chim. Acta*, **365**, 96 (2011).
[6] S. Zhou, C. Yin, H. Wang, X. Zhu, G. Yang, S. Wang. *Inorg. Chem. Commun.*, **14**, 1196 (2011).
[7] H.-T. Sheng, J.-M. Li, Y. Zhang, Y.-M. Yao, Q. Shen. *Polyhedron*, **27**, 1665 (2008).
[8] Y. Luo, Y. Yao, Q. Shen, J. Sun, L. Weng. *J. Organomet. Chem.*, **662**, 144 (2002).
[9] M. Xue, Y. Yao, Q. Shen, Y. Zhang. *J. Organomet. Chem.*, **690**, 4685 (2005).
[10] G. Du, Y. Wei, W. Zhang, Y. Dong, Z. Lin, H. He, S. Zhang, X. Li. *Dalton Trans.*, 1278 (2013).
[11] W. Li, M. Xue, J. Tu, Y. Zhang, Q. Shen. *Dalton Trans.*, 7258 (2012).
[12] L.J.E. Stanlake, J.D. Beard, L.L. Schafer. *Inorg. Chem.*, **47**, 8062 (2008).
[13] Y. Nakayama, K. Sasaki, N. Watanabe, Z. Cai, T. Shiono. *Polymer*, **50**, 4788 (2009).
[14] Y. Wei, Z. Yu, S. Wang, S. Zhou, G. Yang, L. Zhang, G. Chen, H. Qian, J. Fan. *J. Organomet. Chem.*, **693**, 2263 (2008).
[15] F. Zhang, J. Zhang, H. Song, G. Zi. *Inorg. Chem. Commun.*, **14**, 72 (2011).
[16] T.L. Huang, C.T. Chen. *J. Organomet. Chem.*, **725**, 15 (2013).
[17] D. Kong, Y. Peng, D. Li, Y. Li, P. Chen, J. Qu. *Inorg. Chem. Commun.*, **22**, 158 (2012).
[18] D.C. Bradley, J.S. Ghotra, F.A. Hart. *J. Chem. Soc., Dalton Trans.*, 1021 (1973).
[19] G.L. Thomas, C. Böhner, M. Ladlow, D.R. Spring. *Tetrahedron*, **61**, 12153 (2005).
[20] J.J. Ritter, P.P. Minieri. *J. Am. Chem. Soc.*, **70**, 4045 (1948).
[21] G.M. Sheldrick. *SADABS, Program for Empirical Absorption Correction for Area Detector Data*, University of Göttingen, Göttingen, Germany (1996).
[22] G.M. Sheldrick. *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany (1997).
[23] I. Baxter, S.R. Drake, M.B. Hursthouse, K.M. Abdul Malik, J. McAleese, D.J. Otway, J.C. Plakatouras. *Inorg. Chem.*, **34**, 1384 (1995).
[24] A. Mandel, J. Magull. *Z. Anorg. Allg. Chem.*, **622**, 1913 (1996).
[25] A.K. Hall, J.M. Harrowfield, B.W. Skelton, A.H. White. *Acta Crystallogr., Sect. C*, **56**, 407 (2000).
[26] D. Drees, J. Magull. *Z. Anorg. Allg. Chem.*, **620**, 814 (1994).
[27] E.E. Castellano, R.W. Becker. *Acta Crystallogr., Sect. B*, **37**, 1998 (1981).
[28] G. Malandrino, C. Benelli, F. Castelli, I.L. Fragalà. *Chem. Mater.*, **10**, 3434 (1998).
[29] C.G. Pernin, J.A. Ibers. *Inorg. Chem.*, **39**, 1216 (2000).
[30] A.S.R. Chesman, M. Yang, N.D. Spiccia, G.B. Deacon, S.R. Batten, A.-V. Mudring. *Chem. Eur. J.*, **18**, 9580 (2012).
[31] J. Kuang, Y. Liu, B. Lei. *J. Lumin.*, **118**, 33 (2006).
[32] N. Marques, A. Sella, J. Takats. *Chem. Rev.*, **102**, 2137 (2002).
[33] H.C. Aspinall, J.F. Bickley, J.M. Gaskell, A.C. Jones, G. Labat, P.R. Chalker, P.A. Williams. *Inorg. Chem.*, **46**, 5852 (2007).
[34] I.A. Setyawati, S. Liu, S.J. Rettig, C. Orvig. *Inorg. Chem.*, **39**, 496 (2000).
[35] J.M. Harrowfield, M.I. Ogden, A.H. White. *Aust. J. Chem.*, **44**, 1249 (1991).
[36] J.M. Harrowfield, M.I. Ogden, A.H. White. *Aust. J. Chem.*, **44**, 1237 (1991).

[37] A. Panagiotopoulos, T.F. Zafiropoulos, S.P. Perlepes, E. Bakalbassis, I. Masson-Ramade, O. Kahn, A. Terzis, C.P. Raptopoulou. *Inorg. Chem.*, **34**, 4918 (1995).

[38] A. Dei, D. Gatteschi, C.A. Massa, L.A. Pardi, S. Poussereau, L. Sorace. *Chem. Eur. J.*, **6**, 4580 (2000).

[39] B.J. Hellmann, A. Venugopal, A. Mix, B. Neumann, H.-G. Stammler, A. Willner, T. Pape, A. Hepp, N.W. Mitzel. *Chem. Eur. J.*, **15**, 11701 (2009).

[40] H. Bußkamp, G.B. Deacon, M. Hilder, P.C. Junk, U.H. Kynast, W.W. Lee, D.R. Turner. *CrystEngComm*, **9**, 394 (2007).

[41] R. Taylor, O. Kennard. *Acta Crystallogr., Sect. B*, **39**, 133 (1983).

[42] R. Taylor, O. Kennard, W. Versichel. *J. Am. Chem. Soc.*, **105**, 5761 (1983).

[43] R. Taylor, O. Kennard, W. Versichel. *J. Am. Chem. Soc.*, **106**, 244 (1984).

[44] R. Taylor, O. Kennard, W. Versichel. *Acta Crystallogr Sect. B*, **40**, 280 (1984).

[45] X.Q. Zhang, M.S. Lin, B. Hu, W.Q. Chen, L.N. Zheng, J. Wu, Y.M. Chen, F.Y. Zhou, Y.H. Li, W. Li. *Polyhedron*, **33**, 273 (2012).