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Synthesis and characterization of lanthanide amides bearing phenoxy(quinolinyl)amide ligand and their application in the ring-opening polymerization of 1,4-dioxan-2-one

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ABSTRACT

The amine elimination reaction of quinolinyl aminophenol (LH_2) with $Ln[N(SiMe_3)_2]_3(\mu\text{-}Cl)Li(THF)_3$ in THF afforded lanthanide-lithium aminophenoxy complexes $L_2LnLi(THF)_2$ (Ln = Yb (**1**), Sm (**2**)), while the similar reaction with $Ln[N(SiMe_3)_2]_3$ in toluene gave normal monoamido lanthanide complexes $LLnN(SiMe_3)_2(DME)$ (Ln = Sm (**3**), Nd (**4**), La (**5**)). All complexes have been fully characterized. X-ray structural determination revealed that complexes **1** and **2** have a monomeric C_2-symmetric heterobimetallic structure, in which the lanthanide atom is connected to the lithium atom by two oxygen bridges from two phenoxy(quinolinyl)amide ligands. Complexes **4** and **5** have a solvated monomeric structure, and the lanthanide metal centers adopt a distorted octahedral geometry. It was found that complexes **3**–**5** initiated the ring-opening polymerization of 1,4-dioxan-2-one (PDO) with high activity.

Introduction

Poly(1,4-dioxan-2-one) (PPDO), as one of the biodegradable aliphatic polyesters, has attracted much attention as biomaterials for medical purposes because of its biodegradable, biocompatible and bioabsorbable properties [1–3]. Ring-opening polymerization (ROP) of 1,4-dioxan-2-one (PDO) initiated by organometallic complexes is a convenient method for synthesis of this type of aliphatic polyester. Up to date, numerous metal complexes such as Tin(II) bis(2-ethylhexanoate) [4], triethylaluminum [4], aluminum isopropoxide [5], zinc lactate [6], titanium alkoxides [7], and organolanthanide complexes [8–10] have been explored for the ROP of PDO. Among them, most of initiators failed to provide satisfactory results due to the stable hexacyclic structure of PDO monomer, and only lanthanum isopropoxide $La(O^iPr)_3$ and titanium tetraisopropoxide $Ti(O^iPr)_4$ showed high activity. Therefore, development of highly active and efficient organometallic catalysts that are readily available and easy to handle is an important objective.

The phenoxyamide ligands, which are accessible by simple reduction of Schiff base precursors and are easily modifiable by varying the phenoxide and amido units, have attracted attention in main group and transition-metal coordination chemistry [11–19]. Furthermore, most of organometallic complexes bearing such ligands show good activity in homogeneous catalysis. However, this type of ligands has seldom been introduced to the synthesis of lanthanide complexes [20–24]. Recently, we began studying the synthesis and reactivity of lanthanide complexes stabilized by dianionic phenoxyamide ligands. In our earlier work, a series of anionic and neutral lanthanide amides based on the phenoxyamide ligands were synthesized, which showed high activity in the ring-opening polymerization of L-lactide, *rac*-lactide and 2,2-dimethyltrimethylene carbonate [25–27]. It was found that the structure of the lanthanide amides has significant influence on their catalytic activity and neutral lanthanide amides performed better than corresponding anionic ones. To further study the application of these lanthanide amides, we are interested in exploring their potential application as a single component catalyst

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in ring-opening polymerization of PDO. In this contribution, several neutral lanthanide amides and lanthanide-lithium heterobimetallic complexes stabilized by phenoxy(quinolinyl)amide ligand (3,5-Bu^t_2-2-O-$C_6H_2CH_2$N-8-C_9H_6N) were synthesized via silylamine elimination reaction. It was found that these aminophenoxy lanthanide amides initiated the ring-opening polymerization of PDO with high activity. Herein we report these results.

Experiment section

General considerations

All manipulations were performed under purified argon or nitrogen atmosphere using standard Schlenk techniques and a glovebox. Solvents were dried and distilled from sodium/benzophenone ketyl prior to use. The monomer 1,4-dioxan-2-one (PDO) was purchased from Jiaxing Jlight Chemical Co. Ltd., dried over CaH_2 for 48 h at room temperature, and distilled twice under reduced pressure before use. Quinolinyl aminophenol [H_2L = 3,5-Bu^t_2-2-(OH)$C_6H_2CH_2$NH-8-C_9H_6N] [12], Ln[$N(SiMe_3)_2$]$_3$ [28], Ln[$N(SiMe_3)_2$]$_3$(μ-Cl)Li(THF)$_3$ [29,30], {[ON]$^{MeO\text{-}o}$NdN(-$SiMe^3)_2$}$_2$ ([ON]$^{MeO\text{-}o}$ = 3,5-Bu^t_2-2-O-$C_6H_2CH_2NC_6H_4$-*o*-OMe) and {[ON]^{py}NdN$(SiMe_3)_2$(THF)}$_2$ ([ON]^{py} = 3,5-Bu^t_2-2-O-$C_6H_2CH_2$N (C_5H_4N)) [26] were prepared according to the literature procedures. Lanthanide analyses were performed by ethylenediaminetetraacetic acid (EDTA) titration with a xylenol orange indicator and a hexamine buffer. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Unity Varian instrument and processed using MestReNova software. The IR spectra were recorded with a Nicolet-550 FTIR spectrometer as KBr pellets. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges. Molecular weight and molecular weight distribution were determined against a polystyrene standard by gel permeation chromatography (GPC) on a PL 50 apparatus, and $CHCl_3$ was used as an eluent at a flow rate of 1.0 mL/min at 40 °C.

*Synthesis of L_2YbLi(THF)$_2$ (**1**)*

To a THF solution of Yb[$N(SiMe_3)_2$]$_3$(μ-Cl)Li(THF)$_3$ (1.86 g, 2.04 mmol) was added a THF solution of quinolinyl aminophenol (H_2L) (0.74 g, 2.04 mmol). The mixture was stirred at 60 °C for 1 day, and the solvent was removed in vacuum. The residue was extracted with hot toluene to remove LiCl by centrifugation and a dark red solution was obtained. After the solvent was removed, and the residue was washed with hexane, crystallization from a mixture of THF/*n*-hexane at room temperature gave the product **1** as dark red crystals (0.75 g, 70% based on aminophenol). Mp: 174–176 °C. Anal. Calcd for $C_{56}H_{72}LiN_4O_4Yb$: C, 64.35; H, 6.94; N, 5.36; Yb, 16.56. Found: C, 64.43; H, 6.49; N, 5.45; Yb, 16.83. IR (KBr, cm^{-1}): 2967(s), 2896(w), 2865(m), 2341(w), 1620(s), 1550(m), 1511(s), 1471(s), 1438(w), 1389(m), 1360(w), 1301(w), 1274(w), 1200(w), 1165(m), 1012(w), 935(w), 835(s), 732(m).

*Synthesis of L_2SmLi(THF)$_2$ (**2**)*

This compound was prepared following the procedure described above for complex **1** starting from H_2L (0.72 g, 2.00 mmol) in THF (20 mL) and Sm[$N(SiMe_3)_2$]$_3$(μ-Cl)Li(THF)$_3$ (1.78 g, 2.00 mmol) in THF (25 mL). Compound **2** was isolated as red block microcrystals (0.59 g, 58% based on aminophenol). Mp: 171–173 °C. Anal. Calcd for $C_{56}H_{72}LiN_4O_4Sm$: C, 65.78; H, 7.10; N, 5.48; Sm, 14.71. Found: C, 65.90; H, 7.51; N, 5.57; Sm, 14.96. IR (KBr, cm^{-1}): 2957(s), 2896(w), 2868(m), 2341(w), 1627(s), 1541(m), 1510(s), 1479(s), 1431(w), 1377(m), 1351(w), 1309(w), 1274(w), 1200(w), 1164(m), 1017(w), 931(w), 832(s), 736(m).

*Synthesis of LSmN(SiMe$_3$)$_2$(DME)·0.5DME (**3**·0.5DME)*

A solution of H_2L (1.09 g, 3.0 mmol) in toluene was slowly added to a stirred solution of Sm[$N(SiMe_3)_2$]$_3$(THF) (2.16 g, 3.0 mmol) in toluene at room temperature. The reaction mixture was stirred at 90 °C for three days to give a dark red suspension. The dark red solids were obtained by centrifugation, and recrystallized with a mixture of 1,2-dimethoxyethane (DME) and *n*-hexane at room temperature to afford product **3** as dark red crystals (1.55 g, 64%). Mp: 222–224 °C. Anal. Calcd for $C_{36}H_{61}N_3O_4Si_2Sm$: C, 53.62; H, 7.62; N, 5.21; Sm, 18.65. Found: C, 54.24; H, 7.48; N, 5.47; Sm, 18.97. IR (KBr, cm^{-1}): 2957(s), 2896(w), 2861(m), 2345(w), 1620(s), 1548(m), 1509(s), 1476(s), 1436(w), 1378(m), 1358(w), 1304(w), 1271(w), 1198(w), 1164(m), 1015(w), 936(w), 835(s), 740 (m).

*Synthesis of LNdN(SiMe$_3$)$_2$(DME)·0.5DME (**4**·0.5DME)*

The synthesis of complex **4** was carried out in the same way as that described for complex **3** from Nd[$N(SiMe_3)_2$]$_3$ (1.88 g, 3.0 mmol). Red crystals were obtained at room temperature after several days (1.63 g, 68%). Mp: 220–222 °C. Anal. Calcd for $C_{36}H_{61}N_3NdO_4Si_2$: C, 54.03; H, 7.68; N, 5.25; Nd, 18.02. Found: C, 54.10; H, 7.72; N, 5.22; Nd, 17.89. IR(KBr, cm^{-1}): 2959(s), 2904(w), 2870(m), 2340(w), 1601(s), 1548(m), 1519(s), 1480(s), 1432(w), 1388(m), 1362(w), 1320(w), 1250(w), 1200(w), 1160(m), 1086(w), 931(w), 833(s), 790(m).

*Synthesis of LLaN(SiMe$_3$)$_2$(DME)·0.5DME (**5**·0.5DME)*

The synthesis of complex **5** was carried out in the same way as that described for complex **3** from La[$N(SiMe_3)_2$]$_3$ (1.86 g, 3.0 mmol). Red crystals were obtained at room temperature after several days (1.65 g, 69%). Mp: 219–221 °C. Anal. Calcd for $C_{36}H_{61}N_3LaO_4Si_2$: C, 54.39; H, 7.73; N, 5.29; La, 17.47. Found: C, 54.63; H, 7.74; N, 5.32; La, 17.89. IR (KBr, cm^{-1}): 2954(s), 2902(w), 2866(m), 2344(w), 1609(s), 1543(m), 1511(s), 1476(s), 1436(w), 1382(m), 1362(w), 1325(w), 1252(w), 1200(w), 1159(m), 1085(w), 930(w), 833(s), 790(m). ^{1}H NMR (400 MHz, THF-*d8*): δ (ppm) = 8.56 (d, *J* = 4.1 Hz, 1H, C_9H_6N), 8.03 (d, *J* = 8.1 Hz, 1H, C_9H_6N), 7.32 (m, 1H, C_9H_6N), 7.18 (m, 1H, C_9H_6N), 7.10 (s, 1H, C_6H_2), 7.03 (s, 1H, C_6H_2) 6.48 (d, *J* = 8.0 Hz, 1H, C_9H_6N), 6.39 (d, *J* = 7.8 Hz, 1H, C_9H_6N), 4.36 (s, 2H, NCH_2), 3.45 (s, 4H, DME), 3.28 (s, 6H, DME), 1.45 (s, 9H, C(CH_3)$_3$), 1.26 (s, 9H, C(CH_3)$_3$), 0.00 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR (75 MHz, THF-*d8*): δ (ppm) = 163.3, 156.6, 144.4, 144.3, 138.8, 135.6, 134.4, 132.3, 131.4, 130.1, 124.4, 121.9, 120.5, 106.3 (Ar), 72.6, 59.5 (DME), 50.6 (NCH_2), 35.8, 34.5 (*C*(CH_3)$_3$), 32.6, 31.1(C(CH_3)$_3$), 4.9 (Si(CH_3)$_3$).

General procedure for polymerization

The bulk polymerization of PDO was carried out in a pre-dried 20 mL vial, which is equipped with a magnetic stirring bar. The desired amount of purified and dried PDO was introduced into the vial, which was stirred at the desired temperature. A solution of the initiator in THF (0.07 mol/L) was then added. After a predetermined polymerization time, the reaction vial was rapidly immersed in ice water to quench the reaction. The polymerization product was dissolved in $CHCl_3$ and precipitated from cold methanol, which was dried to constant weight under vacuum at 50 °C.