

# Synthesis and structural characterization of a new tetranuclear Zr complex supported by unsymmetric N<sub>2</sub>O<sub>2</sub> ligand and its catalytic behaviors for ring-opening polymerization of rac-lactide



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## ABSTRACT

A Zr complex [Zr<sub>4</sub>L<sub>2</sub>(μ<sub>3</sub>-O)<sub>2</sub>(μ-OMe)<sub>2</sub>(O<sup>i</sup>Pr)<sub>6</sub>] (**1**) containing two heterochiral N atoms was synthesized from an unsymmetric N<sub>2</sub>O<sub>2</sub> ligand 2-(((2-pyridylmethyl)(2-hydroxyphenyl)amino)methyl)-4,6-di(*tert*-butyl)phenol (H<sub>2</sub>L) and characterized by single crystal X-ray diffraction. The complex **1** is an unusual tetranuclear zirconium complex with two oxo-, two methoxy- and two phenoxy-bridges. The four zirconium atoms are unequivalently coordinated. Two Zr atoms are 7-coordinate in a distorted pentagonal bipyramidal geometry, and another two Zr atoms are 6-coordinate in a distorted octahedron geometry. The ring-opening polymerization of *rac*-lactide catalyzed by complex **1**, gave slightly isotactic enriched polylactide with moderate polydispersities.

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## 1. Introduction

In recent years, group 4 metal complexes have attracted more and more attention because of their rich structural chemistry and their potential applications as Lewis acid catalysts. As demonstrated by the large amount of research, the complexes are used widely among the interesting transformations in synthesis and show excellent catalysis properties in many reactions, such as cycloaddition of hydrazones [1,2], hydrogenation of olefin [3], dehydrogenation of cycloalkane [4,5], epoxidation of olefin [6,7], polymerization of olefins [8,9], and ring-opening polymerization of lactide [10–13]. Group 4 complexes can also be widely employed in stereoselective synthesis. Some chiral zirconium complexes were reported as highly active catalysts for asymmetric Mannich type reactions [14,15], asymmetric Diels–Alder reactions [16–18] and enantioselective oxidations [19–23]. It is notable that the catalysis properties of group 4 complexes depends largely on the structure of complexes, so the design of multidentate ligands that can wrap around central metals and lead to complexes of tunable geometry and symmetry and excellent catalysis properties is still a major topic in the fields. Chelating amine-phenolate ligands, such as amine-bis(phenolate) [24,25], amine-tris(phenolate)

[26,27], and diamine-bis(phenolate) [28,29] are versatile in view of the wide range of distinct aryl substituents potentially available for electronic and steric tuning, and the two or three phenolate rings of the ligands can be directly conveniently connected to nitrogen through methylene in the ortho position. Recently, many efforts have been given in exploiting the amine-phenolate ligands and a rich structural variety of amine-phenolato group 4 complexes has evolved. Here, we report a zirconium complex (**1**) containing unsymmetric aminobisphenolates with side-arm pyridyl donors ligand (Scheme 1), and studied its structure and catalytic activity.

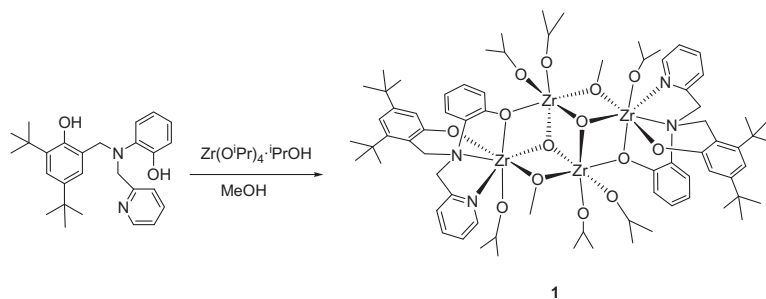
## 2. Experimental

### 2.1. General procedures and instruments

All reactions and manipulations involving air- and moisture-sensitive organometallic compounds were carried out under dinitrogen atmosphere using standard Schlenk techniques. Solvents toluene and *n*-hexane were distilled from sodium/diphenyl ketone prior to use. *rac*-Lactide and Zr(O<sup>i</sup>Pr)<sub>4</sub>·<sup>i</sup>PrOH were purchased from Aldrich. *rac*-Lactide was recrystallized three times from ethyl acetate, which was distilled from calcium hydride. The other reagents were used as received.

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**Scheme 1.** The synthesis of complex **1**.

Elemental analyses were performed with an Elementar Vario EL III elemental analyzer. Molecular weight and molecular weight distribution were determined by gel permeation chromatography (PL-GPC 220). The GPC column was eluted with THF at 40 °C at a rate of 1 mL/min and the data were calibrated with polystyrene standards. The unsymmetric  $N_2O_2$ -ligand ( $H_2L$ ) was prepared according to a literature procedure [30] (Scheme S1).

## 2.2. Preparation of the complexes

To a solution of  $Zr(O^iPr)_4 \cdot iPrOH$  (1.939 g, 5.0 mmol) in toluene (30 mL), a solution of  $H_2L$  (1.045 g, 2.5 mmol) in toluene (20 mL) containing 1 equiv of MeOH (100  $\mu$ L, 2.5 mmol) was added. The solution was stirred for 6 h at room temperature. After removal of solvent, the crude product was recrystallized with toluene/hexane to give complex **1** as an off-white solid. Yield: 0.721 g (35%). *Anal.* Calcd for  $C_{74}H_{112}N_4O_{14}Zr_4$ : C, 53.98; H, 6.86; N, 3.40. Found: C, 53.87; H, 6.90; N, 3.37%. The crystal of **1** suitable for X-ray analysis was obtained from toluene/hexane.

## 2.3. X-ray structural determination

A single crystal of **1** suitable for X-ray crystallographic analysis was selected following examination under a microscope. X-ray diffraction measurements were performed on a Bruker Smart Apex II CCD diffractometer with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) at 298 K using the  $\omega$ - $2\theta$  scan mode. Data processing was accomplished with the SAINT processing program [31]. Intensity data were corrected for absorption by the SADABS program [32]. The structures were solved by direct methods and refined on  $F^2$  against full-matrix least-squares methods using the SHELX-97 program package [33].

## 2.4. Typical procedure for polymerization of *rac*-LA

The toluene solution (10 mL) of the racemic initiator **1** (0.083 g, 0.05 mmol) and *rac*-LA (1.44 g, 10 mmol) was stirred at prescribed temperature for the prescribed time. The reaction was terminated by cooling the tube quickly with an ice-water bath. A sample was taken from the resulting solution for determination of the conversion of *rac*-LA by  $^1H$  NMR spectroscopy. The volatiles were removed in vacuo and the residue was dissolved in a minimum amount of  $CH_2Cl_2$ . The polymer was precipitated with addition of cold methanol. The resulting solid was filtered and washed with ethanol (10 mL) twice and was then dried under high vacuum.

## 3. Results and discussion

### 3.1. Synthesis

The unsymmetric  $N_2O_2$ -ligand ( $H_2L$ ) was prepared by reported methods [30]. The reaction of  $H_2L$  with zirconium(IV) isopropoxide

in the freshly distilled toluene, followed recrystalling gave a novel zirconium complex  $[Zr_4L_2(\mu_3-O)_2(\mu-Ome)_2(O^iPr)_6]$  (**1**) in small yield, which is an oxo-, methoxy- and phenoxy-bridged tetranuclear zirconium complex. It is proposed that the methoxy bridge in the tetranuclear complex **1** comes from the small amount of methanol that remained in the synthesis of the ligand. Because some multinuclear complexes employing multiple active centers successfully catalyze high efficient and selective reaction, as metalloenzymes having multiple metal centers activate a high active and selective reaction in nature, such multinuclear complexes attracted researcher's interesting recent decade [34,35]. However, multinuclear Zr complexes with N,O multidentate ligand is relatively rare. Until now, Only a few structurally characterized multinuclear Zr complexes bearing Schiff base ligands are found in literature [36].

We are interested in the tetranuclear Zr complex and try to improve the yield of **1** by addition of methanol to the reaction solution. The reaction of  $H_2L$  and  $Zr(O^iPr)_4 \cdot iPrOH$  in the presence of 1 equiv of methanol in toluene afforded tetranuclear complex **1** in 35% yield (Scheme 1). The single crystal of **1** suitable for X-ray study was obtained from toluene. Complex **1** was identified by elemental analysis, and X-ray analysis.

### 3.2. X-ray structure

The structure of complex **1** is solved in the monoclinic space group  $P2(1)/c$  and details of the crystal data collection and refinement parameters for **1** are listed in Table S1. Complex **1** is a centrosymmetric tetranuclear structure composed of four Zr atoms and each asymmetric unit has a half molecule (Fig. S1). The Molecular structure of the tetranuclear zirconium complex **1** is shown in Fig. 1. Selected bond lengths and angles are listed in Table S2. The X-ray analysis shows that complex **1** is an unusual tetranuclear zirconium complex with two oxo-, two methoxy- and two phenoxy-bridges. Each of the two bridging  $\mu_3$ -oxo atoms was found coordinating to three metal centers, leading to the formation of tetranuclear species containing two  $\mu_3$ -oxo bridges. The  $\mu_3$ -oxo bridged complex **1** is formed because of hydrolyzes in water that is introduced by workup. Usually  $Zr^{4+}$  ion strongly hydrolyzes in water due to the high charge/radius ratio [37].

There are two molecules in unit cell of **1** (Fig. 2). The N atom of the tertiary amine in  $L^{2-}$  becomes a chiral center because of the restriction on the conformation inversion of the unsymmetric tertiary amine upon coordination. It is notable that each molecule of tetranuclear Zr complex **1** possesses two heterochiral N atoms ( $N1(R)$ ,  $N1A(S)$ ). However, homochiral complexes were formed in our previous work and in preparation of other transition metal complexes containing tertiary amine ligands because of chiral induction upon coordination [30,38].

The four zirconium atoms of **1** are unequivalently coordinated. Two Zr centers (Zr1 and Zr1A) are 7-coordinate in a distorted pentagonal bipyramidal geometry, and each of them is coordinated by an isopropoxy O, a methoxy O and a bridging  $\mu_3$ -oxo atom, as well

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