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Synthesis and structural characterization of a new tetranuclear Zr complex supported by unsymmetric N₂O₂ ligand and its catalytic behaviors for ring-opening polymerization of rac-lactide

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Minggang Hu^{a,*}, Qingbin Cao^a, Qigang Deng^{a,*}, Hailong Yan^b, Wenhui Ma^a, Weiming Song^a, Guohua Dong^a

^a College of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar 161006, China ^b Qiqihar Environmental Protection Bureau Monitoring Center, Qiqihar 161005, China

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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 noteable 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)

* Corresponding authors. Tel.: +86 452 2738251.

E-mail addresses: hmgxs@163.com (M. Hu), dqigang@163.com (Q. Deng).

ABSTRACT

A Zr complex $[Zr_4L_2(\mu_3-O)_2(\mu-OMe)_2 (O^iPr)_6]$ (1) containing two heterochiral N atoms was synthesized from an unsymmetric N₂O₂ ligand 2-(((2-pyridylmethyl)(2-hydroxyphenyl)amino)methyl)-4,6-di(*tert*butyl)phenol (H₂L) 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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[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 moisturesensitive 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(OⁱPr)₄.ⁱPrOH 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 (H₂L) was prepared according to a literature procedure [30] (Scheme S1).

2.2. Preparation of the complexes

To a solution of $Zr(O^iPr)4^{.i}PrOH$ (1.939 g, 5.0 mmol) in toluene (30 mL), a solution of H₂L (1.045 g, 2.5 mmol) in toluene (20 ml) containing 1 equiv of MeOH (100 µL, 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 C₇₄H₁₁₂N₄O₁₄Zr₄: 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 α radiation ($\lambda = 0.71073$ Å) at 298 K using the ω -2 θ 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_2CI_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 $Zr(O^iPr)_{4}$.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 methoxyand two phenoxy-bridges. Each of the two bridging μ_3 -oxo atoms was found coordinating to three metal centers, leading to the formation of tetranuclear species containing two μ_3 -oxo bridges. The μ_3 -oxo bridged complex **1** is formed because of hydrolyzes in water that is introduced by workup. Usually Zr⁴⁺ 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 μ_3 -oxo atom, as well



Fig. 1. Molecular structure of complex 1 (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.



Fig. 2. Molecular structures of the enantiomeric pair in a unit cell of 1, showing 30% probability thermal ellipsoids with hydrogen atoms omitted for clarity.

as two O and two N atoms of unsymmetric ligands. Another two Zr centers (Zr2 and Zr2A) are 6-coordinate in a distorted octahedron geometry, and each of them is coordinated by a methoxy O, two isopropoxy O, and two bridging μ_3 -oxo atoms, as well as an O atom of a bridging phenoxy group in unsymmetric ligands. The rhombus central core is formed by four Zr, two bridging μ_3 -oxo (O1and O1A), two methoxy O (O2 and O2A), and two O (O3 and O3A) atoms of two bridging phenoxy groups in the ligands (Fig. 3).

The distances between two Zr atoms (3.5296(7)-3.4538(9) Å) are longer than those observed in the tetranuclear Zr complexes [39,40]. The bridge μ_3 -oxo (O1) atom attached to three Zr atoms with the Zr–O1–Zr bond angle of 114.62 (13)–107.89 (12)° and the Zr–O1 bond length of 2.070 (3)–2.148 (3) Å, which is close to that reported for the μ_3 -oxo bridged tetranuclear Zr complex (Zr–O1–Zr, 128.71(11)–104.84(9)°; Zr–O, 2.053(2)–2.173(2) Å) [39]. The bridging methoxy O (O2) atom bridges two Zr atoms and the Zr1–O2–Zr2 bond angle of 108.24 (12)° is bigger than that in the trinuclear Zr complex with the bridging O^tBu groups (Zr–O–Zr, 97.1(5)–96.1(4)°) [41]. The Zr–O2 bond lengthes of 2.148 (3)–2.158 (3) Å compare well with that reported for the *tert*-butoxy bridged trinuclear Zr complex (2.131(11)–2.176(9) Å) [41]. The O (O3) atom of bridging phenoxy group is coordinated to two Zr atoms with the Zr1–O3–Zr2A bond angle of 104.21



Fig. 3. Rhombus core of compound 1 (30% probability ellipsoids).

(11)°. The Zr–O3 bond lengthes of 2.203 (3)–2.269 (3) Å are similar to that in the dinuclear Zr complex containing μ -OPh bridges (Zr–O, 2.178(5) Å) [42]. Except for the longer Zr–O bonds in the bridges, the other bond formed by ligand (Zr–O, 2.032 (3) Å;

Zr–N, 2.412 (4)–2.476 (4) Å) are comparable to that reported for the dinuclear Zr complex bearing Schiff base ligand (Zr–O, 2.057 (2)–2.094(2) Å; Zr–N, 2.432(3)–2.448(2) Å) [36]. The distances between Zr and O (O6) of the OⁱPr group (1.929 (3)–1.953 (3) Å) are in good agreement with those observed in the multimetallic alkoxo zirconium complex bearing O^tBu ligand (1.913(3)–1.961 (3) Å) [43].

3.3. Catalytic properties of 1

Lactide polymerizations to produce biodegradable and biocompatible polylactide (pLA) are an intensely active area. In recent years, group 4 metal complexes have been reported to be efficient catalysts for ring-opening polymerization (ROP) of lactide [44-49]. We are interested in utilizing complexes 1 as a polymerization catalyst for this biocompatible material derived from biorenewable feed stocks. Ring-opening polymerizations of rac-lactide by complex 1 were carried out in a 200:1 molecular ratio of rac-lactide to 1 in toluene (from 25 to 130 °C). Representative results are collected in Table 1. The conversion of monomer to PLA was less than 1% in 26 h at 25 °C (Table 1, entry 1). When the reaction temperature increases, the conversion of rac-lactide are up to 91% at 70 °C and 92% at 130 °C (Table 1, entry 4 vs. 5) and the dispersities of molecular weight changed from 1.23 to 1.32 (Table 1, entries 2 and 5), which are similar to those of previously reported ROP catalysts of Zr phenolate complexes [30,49]. The evidence for the

Table 1

Polymerization of rac-LA by complex 1.^a

Entry	T (°C)	Time (h)	Conv ^b	M_n^{c}	$M_{\rm w}/M_n^{\rm c}$	P_m^{d}
1	25	26	<1			
2	70	10	39	4000	1.23	0.57
3	70	26	91	7100	1.27	0.56
4	130	10	43	5200	1.31	0.55
5	130	26	92	7300	1.32	0.55

^a Conditions: [*rac*-LA] = 1 M, [*rac*-LA]/[1] = 200:1, toluene 10 mL.

^b Determined by ¹H NMR.

^c Determined by GPC in THF, calibrated with polystyrene standards. The M_n values have been corrected by a Mark–Houwink factor of 0.58, due to the use of polystyrene standards [50].

 d P_{m} is the probability of isotactic enchainment calculated by analysis of the homonuclear decoupled ¹H NMR spectra [51].



Fig. 4. Homonuclear decoupled ${}^{1}H$ NMR spectrum (400 M Hz, CDCl₃) of the methane region of the PLA.

stereoselective polymerization of *rac*-lactide by the Homonuclear decoupled ¹H NMR spectrum (Fig. 4) and the P_m values are in the range of 0.55–0.57, which are close to those reported for the Zr complexes containing analogous phenolate ligands [30,52].

4. Conclusion

In conclusion, an unusual oxo-, methoxy- and phenoxy-bridged tetanuclear zirconium complex (1) containing two homochiral N atoms was prepared from an unsymmetric N_2O_2 -ligand and structurally characterized. The four zirconium atoms of 1 are unequivalently coordinated. Two heptacoordinated Zr atoms show distorted pentagonal bipyramidal geometry, and another two hexacoordinated atoms show distorted octahedron geometry. Complex 1 is used as a catalyst for ring-opening polymerization of *rac*-lactide. Preliminary studies show that complex 1 possesses moderate catalytic activity and seteroselective. Currently, we are doing our efforts to prepare the zirconium complexes containing analogous ligands, optimize reaction condition, explore more detailed mechanism and improve seteroselectivity of the reaction.

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Appendix A. Supplementary data

CCDC 1047596 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10. 1016/j.poly.2015.09.031. These data include MOL files and InChiKeys of the most important compounds described in this article.

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