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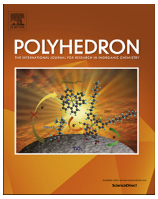

Dinuclear zinc complexes with chiral tetra-azane ligands: Synthesis, structures and catalytic properties for ring-opening polymerization of cyclic esters

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ABSTRACT

Reactions of chiral tetra-azane chelating ligands (1R,2R)-$[(NHAr)C_6H_4CH{=}N]_2C_6H_{10}$ ($\mathbf{L}^1H_2$ (Ar = 2,6-$^iPr_2C_6H_3$); $\mathbf{L}^2H_2$ (Ar = 2,6-$Et_2C_6H_3$); $\mathbf{L}^3H_2$ (Ar = 2,6-$Me_2C_6H_3$) with 2 equivalents of $ZnMe_2$ to afford the dinuclear zinc complexes ($\mathbf{L}^1Zn_2Me_2$(**1**), $\mathbf{L}^2Zn_2Me_2$(**2**), $\mathbf{L}^3Zn_2Me_2$(**3**)), respectively. These complexes were characterized by ^1H and ^{13}C NMR spectroscopies and elemental analyses. Single crystal X-ray diffraction analyses reveal that complex **1** adopts a trigonal planar geometry around the Zn centers. Subsequent investigations showed that all the zinc complexes were efficient catalysts for the ring-opening polymerization of cyclic esters in the presence of benzyl alcohol in a controlled fashion.

1. Introduction

Considerable attention has been paid to the synthesis of polyesters (polylactide and polycaprolactone), owing to their potential applications as delivery medium for the controlled release of drugs, scaffolds, antibodies and genes [1,2]. The most efficient method for the synthesis of polyesters is the ring-opening polymerization (ROP) of esters catalyzed by the metal complexes [3–6]. Numerous metal complexes with various ligands have been developed for the polymerization of esters to polyesters [3–6]. Among them, zinc complexes were mostly studied as catalysts for the ROP of esters, due to their relatively high Lewis acidity, low toxicity and good catalytic abilities [7–31]. Coates's group reported the catalysis of the polymerization of *rac*-LA in high activity and selectivity via a chain-end control mechanism using β-Diiminate zinc complexes [32]. Recently, Lin's and Gao's groups independently, reported NNN-tridentate anilido-aldimine zinc complexes with high productivities for ROP of L-LA in the presence of benzyl alcohol (BnOH) in a controlled fashion [33,34]. Mu's group reported the dinuclear zinc complexes supported by ethylene-bridged anilido-aldimine ligands to be efficient catalysts for controlled polymerization of ε-caprolactone (ε-CL) due to their cooperation [35]. To explore the activity and cooperation of the dinuclear zinc complexes, we sought to develop a dinuclear zinc complexes bearing chiral anilido-aldimine ligands. It was found that the catalytic performance of our new dinuclear zinc catalysts is better than that of the ethylene-bridged dinuclear zinc complexes. There were, to our knowledge, a few zinc catalysts, with chiral ligands that have been reported for esters polymerization [36,37]. In this paper, we wish to report the syntheses and structures of the dinuclear zinc complexes coordinated by the chiral tetradentate anilido-aldimine ligands, as well as their catalytic properties for ROP of cyclic esters.

2. Results and discussion

2.1. Synthesis and characterization

The free chiral tetra-azane chelating ligands (*o*-$(C_6H_4(NHAr)$-$CH{=}N)_2C_6H_{10}$ ((1R,2R)-$\mathbf{L}^1H_2$ (Ar = 2,6-$^iPr_2C_6H_3$); (1R,2R)-$\mathbf{L}^2H_2$ (Ar = 2,6-$Et_2C_6H_3$); (1R,2R)-$\mathbf{L}^3H_2$ (Ar = 2,6-$Me_2C_6H_3$) were synthesized according to the literature procedure [38]. Reaction of the free ligands with 2 equiv of $ZnMe_2$ gave the binuclear zinc complexes $\mathbf{L}^1Zn_2Me_2$ (**1**), $\mathbf{L}^2Zn_2Me_2$ (**2**), $\mathbf{L}^3Zn_2Me_2$ (**3**) respectively (Scheme 1). All the complexes **1**–**3** were obtained in good yields in toluene by alkane elimination reaction.

Complexes **1**–**3** were all characterized by elemental analyses, ^1H and ^{13}C NMR spectroscopies. The analytical results are in accord with their respective formulae. The disappearance of the N—H signal of the free ligands and the appearance of signals for protons

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of ZnMe (δ, −0.29 to −0.56) in high-field regions in ^{1}H NMR spectra demonstrate the formation of the complexes **1**–**3**.

Crystals of complex **1** suitable for X-ray crystal structure determination were grown from hexane at −20 °C. The molecular structure of complex **1** is displayed in Fig. 1 with selected bond lengths and angles. The ligand bonds to the central zinc atom in a bidentate manner. The central zinc atom has a trigonal planar coordination geometry with the metal center chelated by imine and amido nitrogen atoms of the ligand. The six-membered chelating ring is nearly planar, with the zinc atom lying out of the plane by 0.6916 and 0.0155 Å. The N—Zn—N angles (96.36° and 95.82°) in **1** are also close to those in the known anilido-imine Zn complexes [33–35]. The imino C=N bonds within the chelating rings retain their double bond character, being 1.297(4) and 1.292(4) Å. The Zn—N (amido) distances (1.921(2) and 1.929(2) Å) are shorter than the Zn—N (imine) distances (1.991(2) and 1.989(3) Å), which is similar to the case in the reported Zn complexes with anilido-imine ligands [33–35].

2.2. ROP of ε-CL using complexes **1**–**3**

The catalytic capabilities of the complexes **1**–**3** were assessed for ROP of ε-CL. The results of ROP of ε-CL are summarized in Table 1. Preliminary experiments showed that the complexes **1**–**3** exhibited only very low activities for the ROP of ε-CL in the absence of BnOH (Table 1, entries 1–3). However, the complexes **1**–**3** exhibited high activities for the ROP of ε-CL when BnOH was used (Table 1, entries 4–6). The optimal BnOH/Zn molar ratio was equal to 1 for the catalytic systems (Table 1, entries 4–6). Under the same experimental conditions, the catalytic activity of these complexes **1**–**3** (Table 1, entries 5, 7, 8) as initiators for the ROP reaction of CL under the same conditions is in the order of **1** > **2** > **3**, suggesting that increasing the size of the substituents can considerably increase the catalytic activity. Furthermore, in comparison with the ethylene-bridged dinuclear anilido-aldimine zinc complexes **A1** and **A2** (Scheme 2) reported earlier (Turn over frequency (TOF): 3856, 5880 h^{-1}) [35], complexes **1**–**3** (TOF: 23760, 19800, 16971 h^{-1}) showed much higher activity. These results indicate that increasing the steric hindrance of the linker of the two metals can considerably increase the catalytic activity. The linear relationship between the number average molecular weight (M_n) and the monomer-to-BnOH ratio($[CL]_0/[BnOH]_0$) exhibited by complex **1** (Table 1, entries 5, 11–13) implies the “living” character of the polymerization process (Fig. 2). The “immortal” character was examined using four equivalent ratios (on $[BnOH]_0/[Zn]_0$) of BnOH as the chain transfer agent (Table 1, entry 6). The end-group analysis is demonstrated by the ^{1}H NMR spectrum of the polymer produced from ε-CL and complex **1** as shown in Fig. 3. Signals are similar to those produced by ethylene-bridged dinuclear anilido-aldimine zinc complexes [35].

2.3. ROP of *rac*-LA using complexes **1**–**3**

Complexes **1**–**3** were also tested as catalysts for the ROP of *rac*-LA in the presence of 2 equiv of BnOH. The results are listed in Table 2. The reactivity of these complexes (Table 2, entries 1–3) as initiators for the ROP of *rac*-LA under the same conditions is in the order of **1** > **2** > **3**. The same trend was also found in the polymerization of ε-CL. The reactivity of complexes **1**–**3** is quite dependent on the reaction temperature and increases quickly upon elevating the reaction temperature from 30 to 70 °C. The catalytic activities of the dinuclear complexes **1**–**3** were compared with those of the mononuclear anilido-imine zinc complexes **A3**–**A5** (Scheme 3) reported previously [40]. **A3**–**A5** have the same substituents of aniline as complexes **1**–**3**, respectively. Under the same conditions, the activities of complexes **1**–**3** (TOF: 570, 435, 412 h^{-1}) were higher than those of mononuclear anilido-imine zinc complexes **A3**–**A5** (TOF: 146, 118 and 114 h^{-1}), respectively [40]. The higher activity of the dinuclear complexes may be due to a cooperative effect which was also found in other dinuclear aluminum complexes catalytic system [41]. The activity of our dinuclear complexes **1**–**3** (TOF: 570, 435, 412 h^{-1}) is also higher than that of the dinuclear zinc complexes **A1** and **A2** (TOF: 126 and 116 h^{-1}) (Table 2, entries 1–3, 13, 14). The same phenomenon has been observed in the polymerization of ε-CL. Note that, the higher TOF was get (Table 2, entries 1–6, 13–16) when the lower conversion was reached. This is probably owing to that the polymerization system became extremely viscous which made the monomer diffusion difficult when the higher conversion was reached. The complexes **1**–**3** did not have selectivity for ROP of *rac*-LA giving atactic polymer (see ESI, Fig. S1), probably because the dinuclear complex can not provide a special geometry space for the monomer *rac*-LA to enter and react with the active mental center. A similar phenomenon has also been found in the dinuclear chiral salicylaldimine–aluminum catalyst system [42]. The polydispersity index (PDI) of the resultant polymers ranges from 1.07 to 1.21. The narrow molecular weight distribution is a well-known feature of coordination polymerization reactions. The ^{1}H NMR spectrum of polymer of *rac*-LA show that the polymer chain should be capped with one benzyl ester and one hydroxyl chain end (Fig. 4).

To further explore the behavior of this catalytic system, polymerization experiments for different times with a monomer/complex **1**/BnOH = 600:1:2 system were carried out. It was found that the molecular weight M_n of the resultant polymers increases linearly with the increase of the monomer conversion, as shown in Fig. 5. These results further demonstrate the living characterization of the catalytic system.

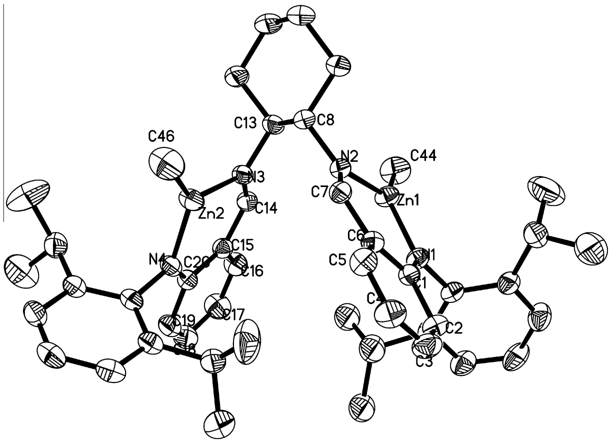
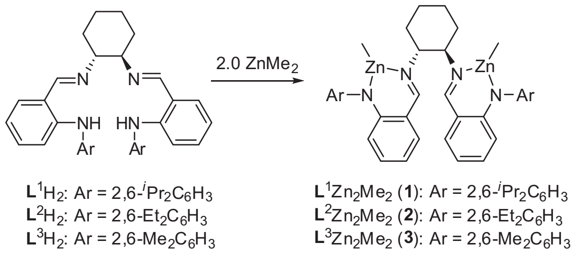


Fig. 1. The molecular structure of complex **1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)—N(1) 1.921(2), Zn(1)—N(2) 1.991(2), Zn(2)—N(3) 1.989(3), Zn2—N4 1.929(2), N(2)—C(7) 1.297(4), N(3)—C(14) 1.292(4), N(1)—Zn(1)—N(2) 96.36(1), N(3)—Zn(2)—N(4) 95.82(1), N(1)—Zn(1)—C(44) 132.90(2), N(2)—Zn(1)—C(44) 130.74(2), N(4)—Zn(2)—C(46) 133.15(2), N(3)—Zn(2)—C(46) 130.99(2).



Scheme 1. Synthetic routes to complexes **1**–**3**.