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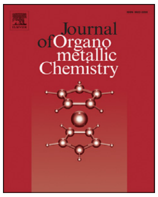

Zinc complexes supported by (benzimidazolyl)pyridine alcohol ligands as highly efficient initiators for ring-opening polymerization of ε-caprolactone

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ABSTRACT

A series of air-stable zinc complexes (**1**–**3**) supported by (benzimidazolyl)pyridine alcohol ligands {tridentate [N,N,O]} has been synthesized and well characterized by FT-IR, ^{1}H and ^{13}C NMR, elemental analysis and single-crystal X-ray diffraction analysis. In combination with methyllithium, these zinc complexes were proved to be highly efficient initiators for the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL). The ROP of ε-CL in the absence or presence of benzyl alcohol, as well as the influences of monomer concentration, reaction temperature and the substituent on the ligand, were investigated in detail.

1. Introduction

Owing to their biocompatibility, biodegradability and renewability, aliphatic biodegradable polyesters, especially poly(ε-caprolactone) (PCL) [1] and polylactide (PLA) [2], have a wide range of applications in biomedical, packing, agricultural areas, and so on. The ring-opening polymerization (ROP) of cyclic esters in the presence of well-defined metal catalysts is a powerful and convenient method for the preparation of polyesters [3,4]. In the recent years, various organometallic complexes, such as alkali metals [5–8], alkaline earth metals [9–13], group IV metals [14–19], rare earth metals [20–24], and aluminum [25–32], have been widely studied and proved to be active to initiate the ROP of cyclic esters. However, the traces of organometallic complexes embedded in polymers are extremely hard to be completely removed, which can make damages to the environment or human bodies and limit the applications of polymers. In recent years, zinc-based metal catalysts for the ROP of cyclic esters are arousing great interest because nontoxic zinc is an essential element for human bodies. Zinc complexes bearing various bidentate [33–37] or tridentate [38–49] organic ligands have been found to actively initiate the ROP of cyclic esters to form biodegradable polyesters with high molecular weight and narrow molecular weight distribution.

Many zinc complexes bearing tridentate ligands for the ROP of cyclic esters contained [N,N,O] tridentate ligands, among which oxygen atom mainly came from phenolate [38–42] or enolate ligands [43–47]. Only few ligands containing oxygen atom from alkyl alcohols [48,49] were used in the zinc complexes for the ROP of cyclic esters. As is well-known, alkyl alcohols, such as benzyl alcohol, could be usually used as initiators to react with metal complexes to form metal alkoxide [50], which were real active species in the ROP of cyclic esters. This inspired us to make zinc complexes bearing (benzimidazolyl)pyridine alcohol ligands, which have been used for cobalt complexes showing high catalytic activity for the polymerization of 1,3-butadiene to yield *cis*-1,4-polybutadiene with high selectivity [51]. In addition, most reported zinc-based catalysts for the ROP of cyclic esters were zinc alkyl complexes that were air-sensitive and unstable. Herein, we reported the synthesis and structural characterization of air-stable zinc complexes containing (benzimidazolyl)pyridine alcohol ligands {tridentate [N,N,O]}. In combination with methyllithium, the ROP of ε-caprolactone catalyzed by these zinc complexes in the absence or presence of benzyl alcohol were also investigated.

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2. Results and discussion

2.1. Synthesis and characterization of zinc complexes

The ligands **L1**–**L3** were prepared according to the reported literature and determined by ^{1}H NMR [51]. The zinc complexes **1**–**3** were readily prepared by combining ligands **L1**–**L3** with anhydrous $ZnCl_2$ in absolute ethanol at room temperature (Scheme 1) and isolated as pale yellow air-stable powders in high yield and purity. All the characterization for these complexes, including FT-IR, ^{1}H and ^{13}C NMR spectra as well as elemental analysis, matched with their structures, which were also established by single-crystal X-ray diffraction analysis.

The X-ray diffraction analysis of complexes **1** and **3** indicates that the coordination geometry around zinc center can be described as a distorted trigonal bipyramidal, in which the nitrogen atom of pyridyl group (N1) and two chlorides (Cl1 and Cl2) compose an equatorial plane. Their crystal structures are shown in Figs. 1 and 2, and their selected bond lengths and angles are listed in Table 1. Because these two zinc complexes have very similar geometries and structural parameters, only complex **1** will be described in detail. In the structure of complex **1** (Fig. 1), the zinc atom deviates by 0.1220 Å from the triangular plane of N1, Cl1 and Cl2 with the equatorial angles: Cl1–Zn–Cl2 (115.51(6)°), N1–Zn–Cl1 (121.16(8)°), and N1–Zn–Cl2 (122.41(8)°), respectively. The axial Zn–N2 and Zn–O1 bonds subtend an angle of 147.12(11)° (O–Zn–N2). The equatorial plane is nearly perpendicular to the pyridyl plane with a dihedral angle of 88.7°. A slight difference in bond length was observed between Zn–N1(pyridyl) (2.177(3) Å) and Zn–N2(imidazolyl) (2.122(3) Å) bonds, and Zn–Cl1 (2.2773(13)) and Zn–Cl2 (2.2147(12)) bonds. The Zn–N and Zn–O bond lengths are longer than those in the corresponding cobalt complex with the same ligand [51]. The C2–O1 bond length is 1.399(5) Å with the typical character of a C–O single bond.

2.2. Ring-opening polymerization of ε-caprolactone

The ring-opening polymerization of ε-caprolactone was performed with complexes **1**–**3** as catalysts in toluene in the presence or absence of benzyl alcohol (BnOH). As was to be expected, zinc dichloride complexes are inactive in the ROP of ε-CL whether BnOH involving or not. Therefore, methyllithium was considered to be added to generate zinc methyl species *in situ*, which were found to be highly active in the ROP of ε-CL in the absence or presence of BnOH as summarized in Tables 2 and 3. This approach was also found in the ROP of *rac*-lactide catalyzed by zinc methyl complexes *in situ* generated by the reaction of methyllithium and bidentate zinc dichloride complexes [52–54].

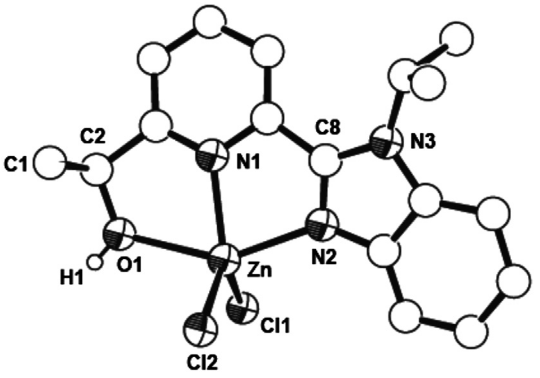


Fig. 1. Molecular structure of complex **1** with thermal ellipsoids at the 50% probability level. Hydrogen atoms (apart from H1) have been omitted for clarity.

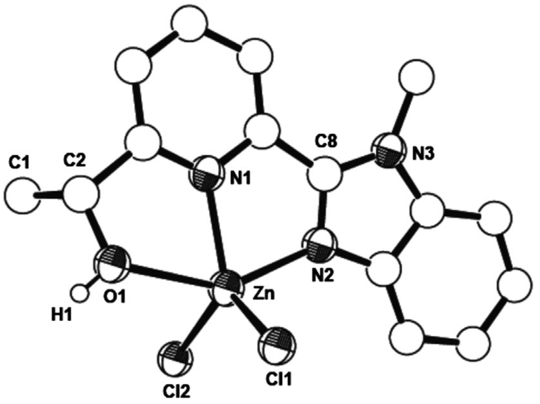


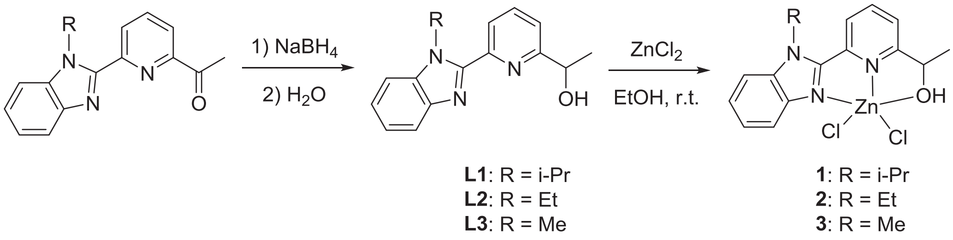
Fig. 2. Molecular structure of complex **3** with thermal ellipsoids at the 50% probability level. Hydrogen atoms (apart from H1) have been omitted for clarity.

Table 1
Selected bond lengths (Å) and bond angles (°) of complexes **1** and **3**.

Bond lengths	1	3	Bond angles	1	3
Zn–N1	2.117(3)	2.113(3)	N1–Zn–N2	76.40(10)	77.06(11)
Zn–N2	2.122(3)	2.109(3)	N1–Zn–O1	71.32(11)	70.39(10)
Zn–O1	2.266(3)	2.350(3)	N1–Zn–Cl1	121.16(8)	118.79(9)
Zn–Cl1	2.2773(13)	2.2683(11)	N1–Zn–Cl2	122.41(8)	122.43(9)
Zn–Cl2	2.2147(12)	2.2216(12)	N2–Zn–O1	147.12(11)	147.22(11)
C8–N2	1.315(4)	1.324(4)	N2–Zn–Cl1	99.19(8)	100.86(8)
C8–N3	1.364(4)	1.354(4)	N2–Zn–Cl2	104.59(8)	107.24(9)
C2–O1	1.399(5)	1.389(5)	O1–Zn–Cl1	92.27(10)	91.54(9)
			O1–Zn–Cl2	97.86(10)	93.66(10)
			Cl1–Zn–Cl2	115.51(6)	116.49(5)

2.2.1. ROP of ε-CL in the absence of BnOH

In the absence of BnOH, all the complexes **1**–**3**/MeLi catalytic systems were highly active for the ROP of ε-CL in toluene and the complete conversions of monomer were achieved in 2 min in all the cases and relatively broad polydispersity indexes (PDIs) were obtained (Table 2). The solution became very sticky quickly as the increase of $[CL]_0/[Zn]_0$ ratio so that the magnetic stir bar was stuck.



Scheme 1. Synthesis of zinc complexes **1**–**3**.