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Synthesis and structural characterisation of zinc complexes bearing furanylmethyl and thiophenylmethyl derivatives of (*R*,*R*)-1,2-diaminocyclohexanes for stereoselective polymerisation of poly(*rac*-lactide)

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ABSTRACT

Novel dichloro zinc complexes based on enantiopure *N*,*N*-diamine ligands bearing furanylmethyl and thiophenylmethyl pendent groups were synthesised, and their crystal structures were determined using X-ray crystallography. The isopropoxide derivatives (generated *in situ*) of these well-characterised complexes efficiently catalysed the ring-opening polymerisation (ROP) of *rac*-lactide (*rac*-LA) at two different temperatures under controlled conditions. Highly heterotactic polylactide (PLA) was obtained with $P_r = 0.80$ at −25 °C in THF.

1. Introduction

PLA has been commonly used as an eco-friendly commodity polymer over the past decade due to its biodegradable and biocompatible nature [1,2], and is an attractive alternative to petrochemical-derived polyolefins due to the fact that lactide feedstocks are derived from renewable resources [3–5]. PLA is typically produced by ring-opening polymerisation (ROP) of LA initiated by metal catalysts. Among the metal-based initiators, complexes based on titanium [6], zirconium [7], calcium [8], magnesium [9–11], zinc [12–14] and aluminium [15] have attracted attention due to the broad applicability of PLA in food packaging [16,17], biomedical and pharmaceutical fields [18,19]. Zinc-based catalysts are common, highly active and stereoselective metal-based catalysts used to control LA polymerisation. For example, zinc complexes with anionic N-donor ligands including β-diketiminates [20,21], phenoxyamines [22], trispyrazolylborates [23], Schiff bases [24], aminophenolate- and pyrazole-based N,N,O-tridentate ligands [25,26] were reported to polymerise *rac*-LA with effective stereoselectivity. Several other zinc complexes bearing neutral ligands such as guanidines [27], carbenes [28], phosphinimines [29], trispyrazolylmethanes [30] and substituted amines [31] were also shown to be active catalysts for ROP of LA. Choosing the appropriate ancillary ligand is important to control the molecular weight distribution and microstructure of PLA, which determine the polymer's mechanical and physical properties. Recently, chiral zinc catalysts for *rac*-LA polymerisation [32], specifically those based on C_2 symmetric chiral ligands bearing (*R*,*R*)-1,2-diaminocyclohexane derivatives, have been used as auxiliaries to serve as powerful stereo-regulating systems for ROP of *rac*-LA [33].

Our previous report described a zinc complex ligated to *N*,*N*′-bis-(2,6-dichloro-benzyl)-(*R*,*R*)-1,2-diaminocyclohexane for stereoselective polymerisation of *rac*-LA [34]. In the current study, we optimised the ligand scaffold by installing furanylmethyl and thiophenylmethyl pendent groups. Herein, we report the synthesis and structural characterisation of dichloro zinc complexes containing furanylmethyl and thiophenylmethyl derivatives of (*R*,*R*)-1,2-diaminocyclohexanes. The isopropoxide derivatives of these complexes, generated *in situ*, were assessed for ROP of *rac*-LA.

2. Experimental

2.1. General considerations and materials

All manipulations involved in the synthesis of enantiopure *N*,*N*′-diamine ligands and their corresponding dichloro zinc complexes were performed using bench-top techniques in the air, unless

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otherwise specified. All ROP reactions were performed using the standard Schlenk techniques, high vacuum, and in a glove box under argon. THF was dried over Na/benzophenone ketyl. EtOH, MeOH, hexane and Et_2O were purchased from high-grade commercial suppliers and used as received. Starting materials, (±)-trans-1,2-diaminocyclohexane, L-(+)-tartaric acid, $NaBH_4$, 5-methyl-2-thiophenecarboxaldehyde, 5-methyl-2-furaldehyde, $ZnCl_2$ and Me_2CHOLi (2.0 M in THF) were purchased from Aldrich. NMR solvents were purchased from Sigma Aldrich and stored over 3-Å molecular sieves. The 3,6-dimethyl-1-dioxane-2,5-dione (*rac*-LA) was purchased from Aldrich and stored in a glove box. L^1 and L^3 were synthesised as described previously [35,36].

2.2. Instrumentation

^{1}H NMR spectra were recorded on a Bruker Advance Digital 400-NMR spectrometer and chemical shifts were recorded in ppm units using $SiMe_4$ as an internal standard. Coupling constants were reported in Hertz (Hz). Infrared (IR) spectra were recorded on Bruker FT/IR-Alpha (neat) and the data were reported in reciprocal centimetres (cm^{-1}). Elemental analysis was performed using an EA 1108-Elemental Analyzer, and gel-permeation chromatography (GPC) was conducted on a Waters Alliance GPCV2000, equipped with differential refractive index detectors at the Chemical Analysis Laboratory of the Center for Scientific Instruments of Kyungpook National University. The GPC columns were eluted using THF at 1 ml/min at 25 °C, and were calibrated with monodisperse polystyrene standards.

2.2.1. Synthesis of L^2

(1*R*,2*R*)-(+)-1,2-diaminocyclohexane L-tartrate salt (3.54 g, 13.00 mmol) was dissolved in 2 *N* NaOH aqueous followed by addition of CH_2Cl_2 (40 mL) solution of 5-methyl-2-furylcarbaldehyde (2.95 g, 26.00 mmol). The organic layer was separated after stirring at RT for 4 days, dried over $MgSO_4$ and concentrated *in vacuo* giving a crude diimine as a waxy solid). MeOH (40 mL) solution of the crude diimine (4.07 g, 15.00 mmol) was treated with $NaBH_4$ (1.26 g, 33.00 mmol) at 0 °C. Solvent was removed *in vacuo* after stirring for 24 h and the resultant residue was treated with water (40 mL) and CH_2Cl_2 (40 mL). Combined organic phase was separated, dried over $MgSO_4$ and concentrated *in vacuo* to yield light yellow oil as final product (3.76 g, 83% yield). *Anal.* Calc. for $C_{18}H_{26}N_2O_2$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.32; H, 8.69; N, 9.29%. ^{1}H NMR (400 MHz, $CDCl_3$): δ5.95 (d, J = 3.03 Hz, 2H, Ar*H*), 5.79–5.77 (m, 2H, Ar*H*), 3.71 (d, J = 14.1 Hz, 2H, CH_AH_B), 3.54 (d, J = 14.4 Hz, 2H, CH_AH_B), 2.17 (s, 6H, (Ar-CH_3)$_2$), 2.20–2.10 (m, 2H, Cy*H*), 2.01–1.92 (m, 2H, Cy*H*), 1.85 (br s, 2H, (N*H*)$_2$), 1.67–1.56 (m, 2H, Cy*H*), 2.20–1.07 (m, 2H, Cy*H*), 1.01–0.90 (m, 2H, Cy*H*). IR (solid neat; cm^{-1}): 3302 (w), 2854 (m), 1567 (m), 1450 (s), 1348 (br, m), 1216 (s), 1112 (m), 1058 (s), 1017 (w), 945 (m), 1851 (w), 770 (s).

2.2.2. Synthesis of L^4

The synthesis of L^4 was carried out with analogous procedure to that of L^2 except that (3.40 g, 26.00 mmol) of 5-methyl-2-thiophenecarboxaldehyde was used. The product was obtained as light yellow oil (4.03 g, 93% yield). *Anal.* Calc. for $C_{18}H_{26}N_2S_2$: C, 64.62; H, 7.83; N, 8.37. Found: C, 64.51; H, 7.79; N, 8.29%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.60 (d, J = 3.28 Hz, 2H, Ar*H*), 6.49–6.47 (m, 2H, Ar*H*), 3.93 (d, J = 14.1 Hz, 2H, CH_AH_B), 3.72 (d, J = 14.1 Hz, 2H, CH_AH_B), 2.36 (s, 6H, (Ar–CH_3)$_2$), 2.22–2.25 (m, 2H, Cy*H*N), 2.07–2.00 (m, 2H, Cy*H*), 1.84 (br s, 2H, (N*H*)$_2$), 1.67–1.58 (m, 2H, Cy*H*), 1.20–1.07 (m, 2H, Cy*H*), 1.00–0.85 (m, 2H, Cy*H*). IR (solid neat; cm^{-1}): 3300 (w), 2922 (s), 2854 (m), 1448 (s), 1352 (br, m), 1216 (w), 1155 (m), 1107 (s), 1038 (w), 963 (w), 855 (w), 702 (s), 677 (w), 601 (w).

2.2.3. Synthesis of L^1ZnCl_2

The EtOH (10 mL) solution of the L^1 (1.04 g, 3.80 mmol) was added dropwise to EtOH (7 mL) solution of $ZnCl_2$ (0.52 g, 3.81 mmol). The precipitated solid resulted after stirring for 12 h was filtered. Subsequent washing of solid with cold EtOH and Et_2O followed by drying *in vacuo* for overnight resulted in white product (1.35 g, 87% yield). *Anal.* Calc. for $C_{16}H_{22}Cl_2N_2O_2Zn$: C, 46.80; H, 5.40; N, 6.82. Found: C, 46.71; H, 5.36; N, 6.79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, J = 2.52 Hz, J = 0.75 Hz, 2H, Ar*H*), 6.50 (d, J = 3.28 Hz, 2H, Ar*H*), 6.28 (dd, J = 3.28 Hz, J = 1.76 Hz, 2H, Ar*H*), 4.05–3.90 (m, 4H, (CH_AH_B)$_2$), 2.50–2.40 (m, 2H, Cy*H*), 2.32–2.19 (m, 2H, Cy*H*), 1.85–1.72 (m, 2H, Cy*H*), 1.69 (br s, 2H, (N*H*)$_2$), 1.31–1.13 (m, 2H, Cy*H*), 1.12–1.00 (m, 2H, Cy*H*). IR (solid neat; cm^{-1}): 3188 (m), 2933 (w), 2865 (w), 1504 (w), 1451 (m), 1350 (w), 1149 (m), 1104 (m), 1065 (m), 1009 (s), 987 (m), 917 (m), 951 (m), 857 (m), 807 (m), 733 (s).

2.2.4. Synthesis of L^2ZnCl_2

The analogues method to that of L^1ZnCl_2 was applied to L^2ZnCl_2 except that L^3 (1.06 g, 3.46 mmol) and $ZnCl_2$ (0.48 g, 3.52 mmol) were used. The product was obtained as white solid (1.36 g, 90% yield). *Anal.* Calc. for $C_{18}H_{26}Cl_2N_2O_2Zn$: C, 49.28; H, 5.97; N, 6.39. Found: C, 49.21; H, 5.89; N, 6.36%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (d, J = 3.03 Hz, 2H, Ar*H*), 5.85 (m, 2H, Ar*H*), 3.98–3.81 (m, 4H, (CH_AH_B)$_2$), 2.50–2.37 (m, 2H, (N*H*)$_2$), 2.30–2.14 (m, 2H, Cy*H*), 2.20 (s, 6H, (Ar-CH_3)$_2$), 1.82–1.71 (m, 2H, Cy*H*), 1.26–1.16 (m, 2H, Cy*H*), 1.26–1.16 (m, 2H, Cy*H*), 1.12–0.98 (m, 2H, Cy*H*). IR (solid neat; cm^{-1}): 3182 (w), 2934 (w), 2863 (w), 1560 (w), 1447 (m), 1365 (w), 1286 (w), 1218 (m), 1100 (w), 1010 (m), 949 (m), 805 (s).

2.2.5. Synthesis of L^3ZnCl_2

The analogues method to that of L^1ZnCl_2 was applied to L^3ZnCl_2 except that L^3 (1.05 g, 3.47 mmol) and $ZnCl_2$ (0.48 g, 3.52 mmol) were used. The product was obtained as white solid (1.30 g, 85% yield). *Anal.* Calc. for $C_{16}H_{22}Cl_2N_2S_2Zn$: C, 43.40; H, 5.01; N, 6.33. Found: C, 43.31; H, 4.97; N, 6.28%. ^{1}H NMR (400 MHz, DMSO): δ 7.48–7.42 (m, 2H, Ar*H*), 7.30–7.20 (m, 2H, Ar*H*), 7.02–6.97 (m, 2H, Ar*H*), 4.18–3.90 (m, 4H, (CH_AH_B)$_2$), 2.40 (br s, 2H, (N*H*)$_2$), 2.27–2.14 (m, 2H, Cy*H*), 1.93–1.83 (m, 2H, Cy*H*), 1.73–1.57 (m, 2H, Cy*H*), 1.40–1.20 (m, 2H, Cy*H*), 1.17–1.02 (m, 2H, Cy*H*). IR (solid neat; cm^{-1}): 3197 (w), 2933 (w), 2863 (w), 1434 (m), 1350 (w), 1219 (w), 1100 (w), 1031 (m), 1004 (m), 843 (m), 715 (s).

2.2.6. Synthesis of L^4ZnCl_2

The analogues method to that of L^1ZnCl_2 was applied to L^4ZnCl_2 except that L^4 (1.02 g, 3.05 mmol) and $ZnCl_2$ (0.42 g, 3.08 mmol) were used. The product was obtained as white solid (1.28 g, 89% yield). *Anal.* Calc. for $C_{18}H_{26}Cl_2N_2S_2Zn$: C, 45.92; H, 5.57; N, 5.95. Found: C, 45.89; H, 5.59; N, 5.90%. ^{1}H NMR (400 MHz, DMSO): δ 7.08–6.97 (m, 2H, Ar*H*), 6.69–6.63 (m, 2H, Ar*H*), 4.03–3.81 (m, 4H, (CH_AH_B)$_2$), 2.40 (s, 6H, (Ar–CH_3)$_2$), 2.40 (br s, 2H, (N*H*)$_2$), 2.25–2.13 (m, 2H, Cy*H*), 1.92–1.84 (m, 2H, Cy*H*), 1.71–1.57 (m, 2H, Cy*H*), 1.37–1.19 (m, 2H, Cy*H*), 1.17–1.02 (m, 2H, Cy*H*). IR (solid neat; cm^{-1}): 3243 (w), 3197 (w), 2933 (w), 2863 (w), 1550 (w), 1434 (m), 1350 (w), 1219 (w), 1100 (m), 1031 (m), 904 (w), 843 (m), 715 (s).

2.3. General procedure for ROP of rac-LA

The active isopropoxide derivative initiators [(L^1–L^4)ClZnOCHMe$_2$] were prepared *in situ* by treating (L^1–L^4)$ZnCl_2$ with 1 equiv. of Me_2CHOLi in THF. The synthesis of $L^1ClZnOCHMe_2$ was carried out as follows. L^1ZnCl_2 (0.205 g, 0.50 mmol) was added to a 100 mL flame dried Schlenk flask and thoroughly vacuumed for 30 min followed by the addition of dried THF (7.75 mL) to make a homogenous solution, under argon. Me_2CHOLi (0.25 mL of

2.0 M solution in THF, 0.50 mmol) was added dropwise *via* gas tight syringe at (78 °C) to the above mentioned solution. After being stirred for 2 h at room temperature, the solvent from ca. 1 ml of the resultant isopropoxide derivative solution was removed *in vacuo* to prepare NMR sample for $L^1ClZnOCHMe_2$. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44–7.31 (m, 2H, Ar*H*), 6.38–6.31 (m, 2H, Ar*H*), 6.31–6.20 (m, 2H, Ar*H*), 4.17–3.73(m, 4H, CH_AH_B), 3.97 (br, 1H, C*H*Me$_2$), 2.53 (br s, 2H, (N*H*)$_2$), 2.40–2.17 (m, 2H, Cy*H*), 2.14–1.96 (m, 2H, Cy*H*), 1.82–1.51 (m, 2H, Cy*H*), 1.33–1.13 (m, 2H, Cy*H*), 1.13–0.95 (m, 2H, Cy*H*), 1.16 (br, 6H, CH*Me*$_2$).

For the polymerisation reaction 100 mL of Schlenk flask was charged with *rac*-LA (0.90 g, 6.25 mmol) in the glove box. Dried THF (5 mL) was transferred to the reaction vessel *via* gas tight syringe and stirred to make a homogenous solution. The reaction was initiated by adding the THF solution of catalyst (2.00 mL, 0.0625 mmol) *via* gas tight syringe under argon at 25 °C. The reaction mixture was stirred at 25 °C or 25 °C for specified time. The polymerisation reaction was quenched after prescribed duration using H_2O (3 mL) and sequentially precipitated by adding hexane (20 mL). The resultant sticky polymeric material was dried completely *in vacuo* for 12 h to get white solid as final polymeric material. ^1H NMR (400 MHz, $CDCl_3$): δ 5.14–5.25 (m, 1H, –OC*H*–Me–C(=O)), 1.54–1.63 (m, 3H, –OCH–*Me*–C(=O)).

2.4. X-ray crystallography

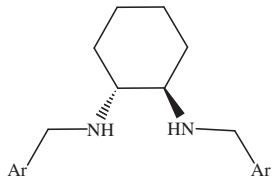
An X-ray quality single crystal was mounted in a thin-walled glass capillary on an Enraf-Noius CAD-4 diffractometer with Mo Kα radiation (λ = 0.71 073 Å). Unit cell parameters were determined by least-squares analysis of 25 reflections ($10° < \theta < 13°$). Intensity data were collected with θ range of 1.59°–25.47° in $\omega/2\theta$ scan mode. Three standard reflections were monitored every 1 h during data collection. The data was corrected for Lorentz-polarization effects and decay. Empirical absorption corrections with χ-scans were applied to the data. The structure was solved by using Patterson method and refined by full-matrix least-squares techniques on *F* using SHELXL-97 and SHELXS-97 program packages [37]. All non hydrogen atoms were refined positioned geometrically using riding model with fixed isotropic thermal factors except the disordered oxygen atoms at furanyl rings of L^1ZnCl_2 which were refined isotropically.

3. Results and discussion

3.1. Synthesis and characterisation

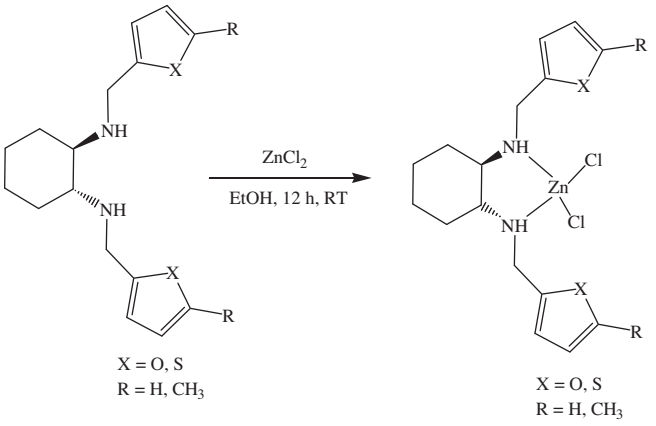
The synthesis of two new C_2 symmetric enantiopure *N,N′*-diamine ligands with furanylmethyl and thiophenylmethyl pendent groups, L^2 and L^4, was performed as described previously [34,38]. These ligands were isolated in high yields (92%). Reactions of enantiopure *N,N′*-bidentate ligands (Chart 1) with $ZnCl_2$ in a 1:1 M ratio in absolute EtOH at ambient temperature yielded L^1ZnCl_2, L^2ZnCl_2, L^3ZnCl_2, and L^4ZnCl_2 as white solids with high yields (88–90%) (Scheme 1). These complexes were characterised using ^1H NMR, IR and CHN elemental analysis. All resonance peaks and the integration ratios of ^1H NMR spectra were completely consistent with the formulation of the complexes, indicating that the compounds seen in the solid state by X-ray diffraction was preserved. The structure of L^3ZnCl_2 was confirmed by the NMR spectrum of the complex compared with that of L^4ZnCl_2 which established by X-ray structure.

A single X-ray quality crystal was obtained from slow evaporation of hot EtOH solutions. The crystal structures of L^1ZnCl_2, L^2ZnCl_2 and L^4ZnCl_2 were determined using single crystal X-ray diffraction. Some details on data collection and refinement are



L^1: Ar = 2-Furaldehyde ($C_5H_4O_2$)
L^2: Ar = 5-Methyl-2-furaldehyde ($C_6H_6O_2$)
L^3: Ar = 2-Thiophenecarbaldehyde (C_5H_4OS)
L^4: Ar = 5-Methyl-2-thiophenecarbaldehyde (C_6H_6OS)

Chart 1. List of *N,N*-diamine ligands used for syntheses of dichloro zinc complexes.



Scheme 1. Synthesis of dichloro zinc complexes bearing furanylmethyl and thiophenylmethyl derivatives of (*R,R*)-1,2-diaminocyclohexanes.

Table 1
Crystal data and structure refinement for L^1ZnCl_2, L^2ZnCl_2, and L^4ZnCl_2.

	L^1ZnCl_2	L^2ZnCl_2	L^4ZnCl_2
Empirical formula	C_{16} H_{22} Cl_2 N_2 O_2 Zn	C_{18} H_{26} Cl_2 N_2 O_2 Zn	C_{18} H_{26} Cl_2 N_2 S_2 Zn
Formula weight	410.65	438.70	470.80
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	*C*2/*c*	$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions			
a (Å)	12.6721(7)	10.0073(11)	10.2683(10)
b (Å)	13.2123(11)	11.1202(6)	11.1405(12)
c (Å)	11.2029(9)	18.4284(11)	18.7145(15)
β (°)	108.795(5)		
V (Å^3)	1775.7(2)	2050.8(3)	2140.8(4)
Z	4	4	4
D_{calc} (Mg/m^3)	1.536	1.421	1.461
F(0 0 0)	848	912	976
Reflections collected	1774	4494	4712
Independent reflections	1650	3797	3984
Reflections obsd (>2δ)	1374	3132	3037
Data Completeness	0.979	1.000	1.000
Data/parameters	1617/104	3797/228	3984/228
Goodness-of-fit on F^2	1.027	1.063	1.030
Final R [$I > 2\delta(I)$]	R_1 = 0.0268 wR_2 = 0.0734	R_1 = 0.0280 wR_2 = 0.0705	R_1 = 0.0338 wR_2 = 0.0892
R (all data)	R_1 = 0.0364 wR_2 = 0.0757	R_1 = 0.0424 wR_2 = 0.0736	R_1 = 0.0586 wR_2 = 0.0950
$\Delta\rho_{max,\ min}$ (e Å^{-3})	0.346 and −0.348	0.371 and −0.384	0.324 and −0.392

given in Table 1. An ORTEP drawings of L^1ZnCl_2, L^2ZnCl_2 and L^4ZnCl_2 with atomic labelling are shown in Figs. 1-3, respectively, along with their selected bond lengths (Å) and angles (°). These complexes were found to be solvent-free and existed in a four-coordinated monomeric form. The central zinc atom of each complex was four-coordinated and adopted a somewhat distorted tetrahedral geometry by coordinating to the two N atoms of the enantiopure *N*,*N*-diamine ligands and two chloro ligands. The difference between the angles (°) N1–Zn1–$N^{\#1}$ and N1–Zn1–N2 [86.3(1) and 84.15(8), 86.7(1)] and Cl1–Zn1–$Cl1^{\#1}$ and Cl1–Zn1–Cl2 [118.49(4) and 122.30(3), 122.98(6)] for L^1ZnCl_2, L^2ZnCl_2 and L^4ZnCl_2, respectively, are indicative of distortion from ideal tetrahedral geometry. A similar distorted tetrahedral coordination sphere with smaller N–Zn–N angles has been reported in compounds containing diamine ligands [30d,39]. Furthermore, the Zn–N and Zn–Cl bond lengths of the complexes L^1ZnCl_2, L^2ZnCl_2, and L^4ZnCl_2 showed only minor variations [2.079(2)–2.103(2) and 2.198(1)–2.2241(7)], and these metric parameters were similar to complexes reported previously [34,38,40]. Distances between Zn and O or S at L^2ZnCl_2, and L^4ZnCl_2 were 3.118(2) & 3.332(2) Å and 3.498(1) & 3.500(1) Å, respectively, which are indicative of weak interactions between Zn with O or S atoms. Moreover, two chiral centres R_C and $R_{C'}$ were confirmed based on the crystal structures of these dichloro-zinc complexes, which are derived from the (*R*,*R*)-1,2-diaminocyclohexane fragment, while the hydrogen atoms of the chiral carbon and nitrogen were found to be in a head-to-tail conformation. Coordination of the enantiopure ligand with a divalent zinc centre resulted in five-membered metallaheterocyclic rings that induced chirality in two nitrogen atoms, i.e. R_N and R_N, of diaminocyclohexane moieties.

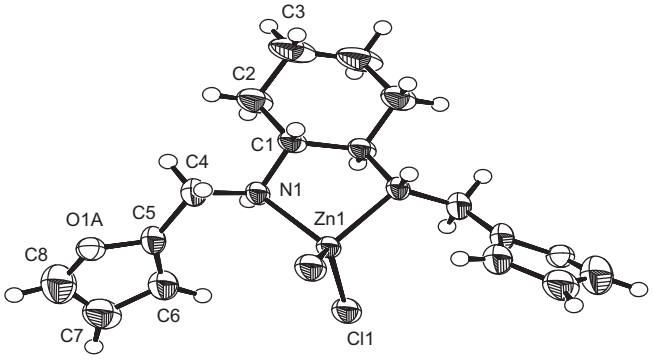


Fig. 1. An ORTEP drawing of L^1ZnCl_2 with the numbering scheme at 40% probability level. Zn–N1, 2.079(2); Zn–Cl1, 2.2218(6). $N1^{\#1}$–Zn–N1, 86.3(1); $N1^{\#1}$–Zn–$Cl1^{\#1}$, 114.74(5); N1–Zn–$Cl1^{\#1}$, 109.13(5); $N1^{\#1}$–Zn–Cl1, 109.13(5); N1–Zn–Cl1, 114.74(5); $Cl1^{\#1}$–Zn–Cl1, 118.49(4). $^{\#1}$ Symmetry transformations used to generate equivalent atoms: $-x, y, -z + 1/2$.

3.2. Ring-opening polymerisation of rac-LA using $Me_2CHOZnCl(L^1–L^4)$ complexes

The catalytic capabilities of isopropoxide derivatives from zinc complexes, generated *in situ* by treating dichloro analogues with one equivalent of Me_2CHOLi in THF, were assessed for ROP of *rac*-LA. The polymerisation was conducted at two different temperatures; i.e. 25 and 25 °C. The isopropoxide complexes acted as highly effective single component living initiators for ROP of *rac*-LA at both temperatures. The ROP for 50 equivalent of *rac*-LA was completed almost within 30 min. The *in situ* formation of active catalytic species was confirmed using ^1H NMR analysis. The M_n values of the PLA were determined based on end-group analysis with NMR spectra and by GPC in THF relative to the polystyrene standard. The polymerisation results are summarised in Table 2. The experimentally determined M_n values of the PLAs obtained from NMR and GPC were similar to the theoretical values. In addition, relatively narrow PDIs of 1.26–1.30 were indicative of well-controlled living polymerisation mechanisms with a single reaction site provided by these isopropoxide zinc complexes (Table 2). However, M_n values determined by GPC were lower than the predicted/theoretical values based on (%) conversion. The ^1H NMR spectra of the resultant PLAs indicated that the polymer chain was capped with an ester [–C(=O)OCHMe_2] group at one end and a hydroxyl group [–CH(Me)–OH] at the other end. These results suggested that polymerisation mediated by these isopropoxide zinc complexes may be initiated by the transfer of an alkoxy (–OCH-Me_2) group to the monomer, with the formation of metal alkoxide species for a propagating step [42,43].

Microstructure analysis of the PLAs at two different temperatures were assigned using the peak area of the methine proton

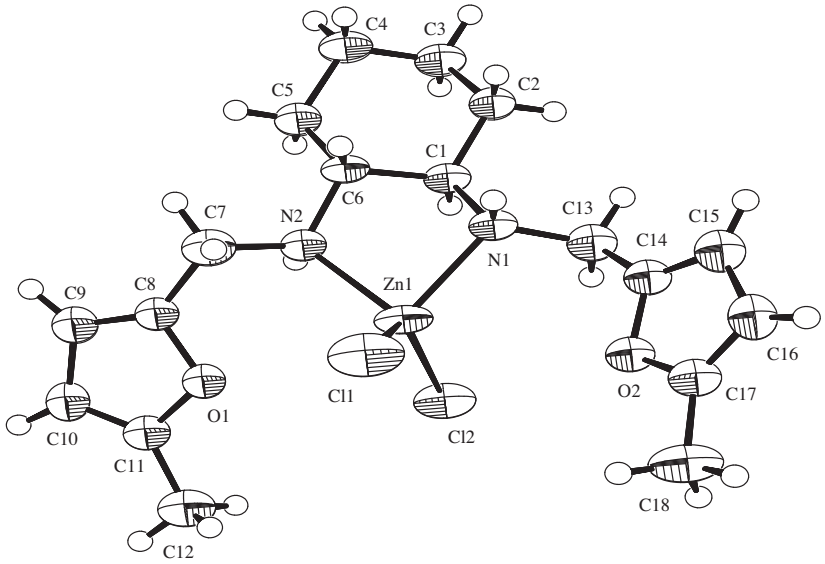


Fig. 2. An ORTEP drawing of L^2ZnCl_2 with the numbering scheme at 40% probability. Selected bond distances (A) and angles (°): Zn–N1, 2.103(2); Zn–N2, 2.110(2); Zn–Cl1, 2.2047(8); Zn–Cl2, 2.2241(7). N1–Zn–N2, 84.15(8); N1–Zn–Cl1, 113.65(6); N1–Zn–Cl2, 108.95(6); N2–Zn–Cl1, 110.61(6); N2–Zn–Cl2, 110.73(6); Cl1–Zn–Cl2, 122.30(3).

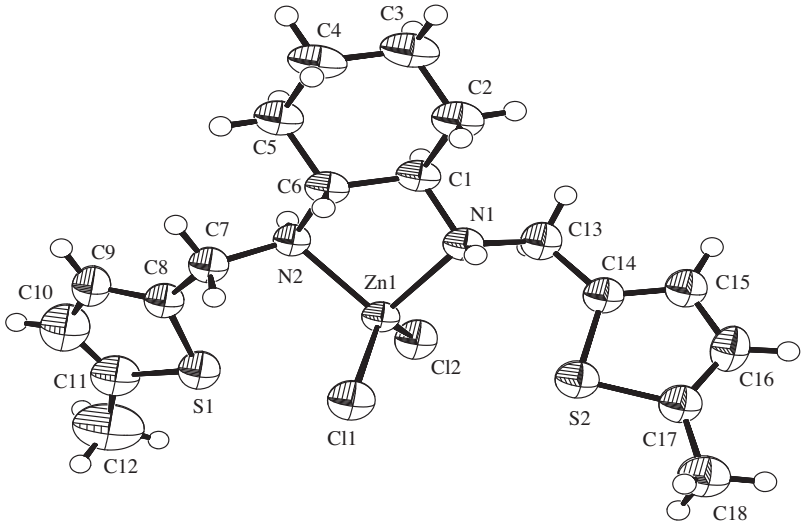
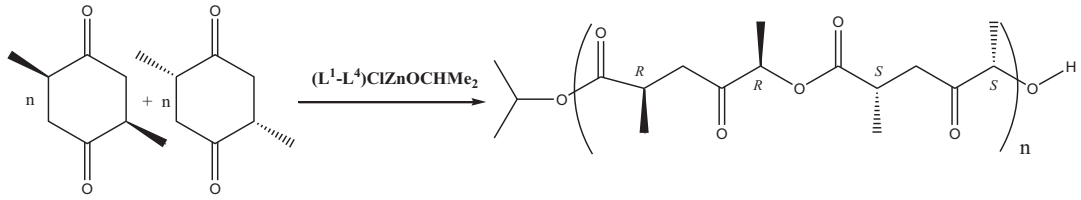


Fig. 3. An ORTEP drawing of L^4ZnCl_2 with the numbering scheme at 40% probability. Selected bond distances (Å) and angles (°): Zn–N1, 2.086(3); Zn–N2, 2.081(3); Zn–Cl1, 2.216(1); Zn–Cl2, 2.198(1). N1–Zn–N2, 86.7(1), N2–Zn–Cl2, 114.84(9); N1–Zn–Cl1, 110.05(9), N1–Zn–Cl2, 109.0(1), N2–Zn–Cl2, 114.84(9); N2–Zn–Cl1, 107.31(9); Cl2–Zn–Cl1, 122.98(6).

Table 2
Polymerisation of *rac*-LA with *in situ* generated $(L^1–L^4)ClZnOCHMe_2$ initiators.



Run[a]	Catalyst	T (°C/min.)	Conv. %[b]	M_n (g/mol)[c] x10^3 (calcd.)	M_n (NMR) (g/mol)[d] $\times 10^3$	M_n (g/mol)[e] $\times 10^3$	PDI[d]	P_r[f]
1	Me_2CHOLi	25/10	>99	7.2	8.51	7.93	1.30	0.50
2	Me_2CHOLi	−25/20	>99	7.2	8.61	8.03	1.30	0.54
3	$(L^1)ClZnOCHMe_2$	25/5	>99	7.2	6.11	5.14	1.30	0.71
4	$(L^1)ClZnOCHMe_2$	−25/10	>99	7.2	6.31	5.23	1.30	0.74
5	$(L^2)ClZnOCHMe_2$	25/5	>99	7.2	6.12	5.12	1.31	0.74
6	$(L^2)ClZnOCHMe_2$	−25/10	>99	7.2	6.35	5.24	1.29	0.74
7	$(L^3)ClZnOCHMe_2$	25/15	>99	7.2	7.15	5.27	1.30	0.71
8	$(L^3)ClZnOCHMe_2$	−25/30	>99	7.2	6.75	5.59	1.25	0.77
9	$(L^4)ClZnOCHMe_2$	25/15	>99	7.2	7.17	5.79	1.30	0.77
10	$(L^4)ClZnOCHMe_2$	−25/30	>99	7.2	7.62	5.54	1.31	0.80

[a] Conditions: [Initiator] = 0.0625 mmol, [*rac*-LA]/[Initiator] = 50, 5 mL of THF, polymerization time = 10 ~ 30 min.
[b] Conversion (%) determined by ^1H NMR spectroscopy.
[c] Calculated from [molecular weight of *rac*-LA] × [*rac*-LA]/[initiator] × conversion%.
[d] Experimental molecular weight determined by ^1H NMR from the relative intensities of the main chain and terminal resonances.
[e] Experimental values (corrected using the Mark-Houwink factor of 0.58) [41] were determined by gel permeation chromatography (GPC) in THF relative to polystyrene standard.
[f] Probability of heterotactic enchainment (P_r) were calculated on the basis of homonuclear decoupled ^1H NMR spectra using equation $Pr = 2I_1/(I_1 + I_2)$, where $I_1 = (sis + sii)$, and $I_2 = (iis + iii + isi)$ [12b,44,46].

region of the homodecoupled ^1H NMR spectra [12b,44–46]. Analysis of the polymer microstructures indicated that all complexes showed a strong preference for alternating insertion of *RR*- and *SS*-enantiomers, leading to heterotactic PLA ($P_r = 0.80$) at 25 °C, where P_r is the probability of *rac*-dyad by insertion [12b,44–48]. However, PLAs obtained using Me_2CHOLi as an initiator were almost atactic. The homodecoupled ^1H NMR spectrum obtained with $(L^4)ClZnOCHMe_2$ (at 25 °C in THF) is shown in Fig. 4, and calculated heterotacticities of obtained PLAs are listed in Table 2.

Polymerisation data shown in Table 2 clearly indicated that temperature significantly influenced microstructures of the obtained PLAs. Decreases in the polymerisation temperature from 25 to 25 °C resulted in a minor increase of heterotactic bias in all cases. Methyl groups of furanylmethyl and thiophenylmethyl moieties of the (*R*,*R*)-1,2-diaminocyclohexane fragment would impart steric hindrance around the metal centre and then improve slightly heterotacticities comparing L^1 to L^2 and L^3 to L^4. As reported by other researchers, more flexible ligands can increase the stereopreference in ROP of *rac*-LA [33b,49]. Unexpectedly, the heterotactic bias was not affected by methyl substituents in pendent groups at both temperatures in our current study. The 99% conversion periods of LA by using L^1 or L^2 were shorter than those by using L^3 or L^4 at 25 and 25 °C. The initiators $(L^1–L^4)ClZnOCHMe_2$ may generate heterotactic-enriched PLA by a chain-end-control mechanism with unclear assist of the stereogenic centers, which has been observed in previous studies [50,51], which is similar to findings at

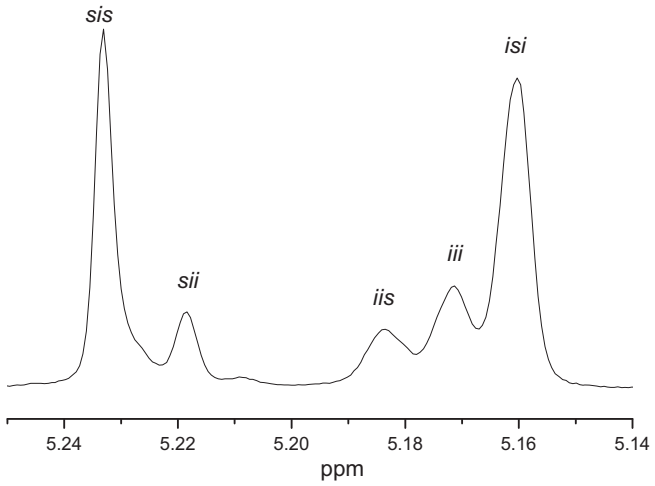


Fig. 4. Homonuclear decoupled ^{1}H NMR spectrum of methine region of heterotactic PLA produced by (L^4)ClZnOCHMe$_2$ at 25 °C in THF.

the report by using zinc complexes containing Schiff base ligands with bulk substituents as initiators [52].

4. Conclusions

Isopropoxy derivative (generated *in situ*) of well-characterised dichloro zinc complexes ligated with furanylmethyl and thiophenylmethyl derivatives of (*R*,*R*)-1,2-diaminocyclohexanes were assessed for ROP of *rac*-LA. These isopropoxy zinc complexes demonstrated very efficient activities and polymerisation of *rac*-LA that proceeded in a living fashion, resulting in relatively narrow PDIs. The M_n of the obtained polymers from NMR or GPC was close to the ratio of the [monomer]/[initiator]. An increased degree of heterotacticity, with P_r values of 0.80 at 25 °C, has been observed for these isopropoxy initiators. Overall, a decrease in polymerisation temperature resulted in an increase in heterotacticity.

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Appendix A. Supplementary data

CCDC 980197, 980198 & 980199 contain the supplementary crystallographic data for L^1ZnCl_2, L^2ZnCl_2, and L^4ZnCl_2. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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