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Synthesis and X-ray crystal structure of derivatives from the *N*,*N*-bis(1H-pyrazolyl-1-methyl)aniline(dichloro)Zn(II) complex: Substituent effects on the phenyl ring versus the pyrazole ring

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ABSTRACT

The reaction of anhydrous $ZnCl_2$ with ancillary ligands, including *N*,*N*-bis(1H-pyrazolyl-1-methyl)aniline (**L_1**), *N*,*N*-bis(1H-pyrazolyl-1-methyl)-*p*-methoxyaniline (**L_2**), *N*,*N*-bis(1H-pyrazolyl-1-methyl)-*p*-fluoroaniline (**L_3**) and *N*,*N*-bis(3,5-dimethyl-1H-pyrazolyl-1-methyl)aniline (**L_4**), in ethanol yields Zn(II) chloride complexes, i.e., **L_1ZnCl_2**, **L_2ZnCl_2**, **L_3ZnCl_2** and **L_4ZnCl_2**. X-ray crystallographic analysis revealed that the Zn atoms of all of the synthesized complexes have a distorted tetrahedral geometry involving a nitrogen atom from each of two pyrazole groups and two chloro ligands. However, the nitrogen atom of the aniline group is not coordinated to the Zn center, resulting in the formation of an eight-membered chelate ring. The catalytic activity of the Zn(II) complexes in the polymerization of methyl methacrylate (MMA) in the presence of modified methylaluminoxane (MMAO) results in a higher molecular weight and a narrow polydispersity index (PDI) range.

1. Introduction

Transition metal complexes with two or three chelate pyridyl ligands have been studied in detail, largely because of their catalytic abilities, biological significance and sensor applications [1–5]. For example, Ni(II), Zn(II) and Cu(II) complexes with N-substituted di(2-picolyl)amine derivatives were prepared and their enzyme activities were investigated, including hydrolysis and CO_2 conversion to oxalate [6,7]. Similarly, chelate pyrazolyl ligands were first reported by Driessen in 1982 [8], after a variety of complexes were synthesized for use as cancer sensors [9–14]. Transition metal complexes with bis-pyrazolyl ligands are of interest due to their stability and applications as catalyst precursors [15,16]. The Zn(II) complex with *N*,*N*-bis(3,5-dimethylpyrazolylmethyl)-L-alanine methyl ester was prepared for use as a catalyst in catecholase. Several additional complexes have also been studied for styrene oxidation and *rac*-lactide polymerization [17–20]. Although there have been few reports regarding transition metal complexes ligated to chelating pyrazolyl ligands, recent studies documented the use of transition metals as catalysts for olefin polymerization and methyl methacrylate polymerization [21–27]. Previously, we reported Co(II) complexes with *N*,*N*-bis(1H-pyrazolyl-1-methyl)aniline and its derivatives for MMA polymerization [28]. Although *N*,*N*-bis(3,5-dimethyl-1H-pyrazolyl-1-methyl)aniline zinc(II) chloride [Zn(bdmpab)Cl_2] has already been synthesized and reported by Driessen in 1985 [29], its X-ray crystal structure was not investigated.

In this study, we describe the synthesis and characterization of Zn(II) complexes with the bidentate ligand *N*,*N*-bis(1H-pyrazolyl-1-methyl)aniline, which contain two pyrazoles as N-donor atoms. We also investigate the Zn(II) complexes and the effects of the introduction of substituents on the benzene moiety (H, OCH_3, F) or pyrazole ring unit (CH_3). We focus on structural variations and catalytic activities by X-ray crystal structure and MMA polymerization in toluene at 60 °C, respectively. These studies clarify the properties and MMA polymerization catalytic activities of the new Zn(II) complexes.

2. Experimental

2.1. Physical measurements

$ZnCl_2$, pyrazole, 3,5-dimethylpyrazole, *para*-formaldehyde, *para*-xaniline (X = H, OCH_3, F) and methacrylate (MMA) were purchased from Aldrich and used without further purification. The solvents CH_3OH, CH_2Cl_2, toluene and C_2H_5OH were refluxed over calcium hydride under argon, and checked for purities by GC just before use. Modified methylaluminoxane (MMAO) was purchased from Tosoh Finechem Corporation as a 6.9% weight aluminum toluene solution and it was used without further

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purification. Elemental analyses (C, H, N) of the prepared complexes were carried out on an elemental analyzer (EA 1108; Carlo-Erba, Milan, Italy). ^{1}H NMR (400 MHz, 600 MHz) and ^{13}C NMR (75.46 MHz, 150.85 MHz operating, respectively) were recorded on Bruker Advance Digital 400 and 600 NMR spectrometers and the chemical shifts were recorded in ppm units using $SiMe_4$ as an internal standard. Electronic absorption spectra were obtained on an Ocean Optics USB4000 spectrophotometer (Ocean Optics, Dunedin, FL). The molecular weight and molecular weight distribution of the obtained PMMA were determined using gel permeation chromatography (GPC) ($CHCl_3$, Alliance e2695; Waters Corp., Milford, MA). The glass transition temperature (T_g) was determined using a thermal analyzer (Q2000; TA Instruments, New Castle, DE).

2.2. Preparation of the ligands and the Zn(II) complexes

2.2.1. 1H-pyrazolyl-1-methanol and 3,5-dimethyl-1H-pyrazolyl-1-methanol

1H-pyrazolyl-1-methanol and 3,5-dimethyl-1H-pyrazolyl-1-methanol, as starting materials, were prepared in processes described elsewhere [8]. A CH_2Cl_2 solution (100 mL) of pyrazole (20.4 g, 0.30 mol) or 3,5-dimethylpyrazole (28.8 g, 0.30 mol) was added to a CH_2Cl_2 solution (100 mL) of *para*-formaldehyde (9.00 g, 0.30 mol). The solution was refluxed for 5 days and the filtrate solvent was removed under reduced pressure to give a white powder (28.5 g, 98.0% for 1H-pyrazolyl-1-methanol and 36.3 g, 96.0% for 3,5-dimethyl-1H-pyrazolyl-1-methanol). ^{1}H NMR ($CDCl_3$, 400 MHz) for 1H-pyrazolyl-1-methanol δ: 7.71 (s, 1H), 7.59 (d, 1H, J = 2.24 Hz), 7.56 (d, 1H, J = 1.48 Hz), 6.29 (t, 1H, J = 1.8 Hz), 5.51 (s, 2H); 3,5-dimethyl-1H-pyrazolyl-1-methanol δ: 7.81(s, 1H), 5.83 (s, 1H), 5.40 (s, 2H), 2.34 (s, 3H), 2.20 (s, 3H).

2.2.2. N,N-bis(1H-pyrazolyl-1-methyl)aniline (*L_1*)

L_1 was prepared by a similar procedure as described in the literature [30–32]. A CH_2Cl_2 solution (10.0 mL) of aniline (1.86 g, 0.020 mol) was added to a CH_2Cl_2 solution (30.0 mL) of 1H-1-pyrazolyl-1-methanol (3.92 g, 0.040 mol). The reaction solution was dried over $MgSO_4$ after stirring the reaction mixture at room temperature for 3 days. The filtrate solvent was removed under reduced pressure to give a bright yellow oil (3.54 g, 70.0%). ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 7.83 (d, 2H, J = 2.4 Hz), 7.50 (t, 2H, J = 1.2 Hz), 7.17 (d, 2H, J = 5.4 Hz), 7.16 (d, 2H, J = 2.4 Hz), 6.77 (t, 2H, J = 7.2 Hz), 6.25 (t, 2H, J = 1.8 Hz), 5.91 (s, 4H). ^{13}C{^{1}H} NMR (DMSO-d_6, 600 MHz) δ: 145.48 (s), 139.50 (d, J = 178 Hz), 130.27(d, J = 114 Hz), 129.16 (d, J = 84 Hz), 119.78 (d, J = 164 Hz), 114.53 (d, J = 160 Hz), 106.09 (d, J = 176 Hz), 66.37 (t, J = 153 Hz). UV–Vis: λ_{max} (nm) and ε_{max} (M^{-1} cm^{-1}) in DMF: 269 and 1052, and 283 and 1232.

2.2.3. N,N-bis(1H-pyrazolyl-1-methyl)-p-methoxyaniline (*L_2*)

L_2 was prepared by an analogous method as described for **L_1**, except utilizing *p*-methoxyaniline. The product was obtained as a dark brown oil (4.30 g, 76.0%). ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 7.79 (d, 2H, J = 1.8 Hz), 7.51 (d, 2H, J = 1.2 Hz), 7.09 (d, 2H, J = 9.6 Hz), 6.79 (d, 2H, J = 9.0 Hz), 6.25 (t, 2H, J = 1.8 Hz), 5.83 (s, 4H), 3.65 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 600 MHz) δ: 153.67 (s), 139.54 (s), 139.45 (d, J = 186 Hz), 130.00 (d, 2C, J = 187 Hz), 116.91 (d, J = 158 Hz), 114.84 (d, J = 158 Hz), 105.95 (d, J = 176 Hz), 67.03 (t, J = 152 Hz), 55.65 (q, J = 144 Hz). UV–Vis: λ_{max} (nm) and ε_{max} (M^{-1} cm^{-1}) in DMF: 268 and 684, and 298 and 1389.

2.2.4. N,N-bis(1H-pyrazolyl-1-methyl)-p-fluoroaniline (*L_3*)

L_3 was prepared by an analogous method as described for **L_1**, except utilizing *p*-fluoroaniline. A bright yellow oil product was obtained (4.34 g, 80.0%). ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 7.84 (d, 2H, J = 1.8 Hz), 7.53 (d, 2H, J = 1.8 Hz), 7.21 (d, 2H, J = 4.8 Hz), 7.03 (d, 2H, J = 8.4 Hz), 6.28 (t, 2H, J = 1.2 Hz), 5.88 (s, 4H). ^{13}C{^{1}H} NMR (DMSO-d_6, 600 MHz) δ: 156.02 {^{13}C(^{19}F)} (d, J = 236 Hz), 142.43 (s), 139.59 (d, J = 184 Hz), 130.13 (d, J = 186 Hz), 116.52 (d, J = 153 Hz), 115.82 (d, J = 174 Hz), 106.08 (d, J = 167 Hz), 66.72 (t, J = 153 Hz). UV–vis: λ_{max} (nm) and ε_{max} (M^{-1} cm^{-1}) in DMF: 260 and 1421, and 293 and 1706.

2.2.5. N,N-bis(3,5-dimethyl-1H-pyrazolyl-1-methyl)aniline (*L_4*)

L_4 was prepared by an analogous method as described for **L_1**, except utilizing 3,5-dimethyl-1H-pyrazolyl-1-methanol. A white solid product was obtained (4.20 g, 68.0%). ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 7.20 (t, 2H, J = 7.2 Hz), 7.12 (d, 2H, J = 7.8 Hz), 6.82 (t, 1H, J = 7.2 Hz), 5.78 (s, 2H), 5.64 (s, 4H), 2.16 (s, 6H), 2.08 (s, 6H). ^{13}C{^{1}H} NMR (DMSO-d_6, 600 MHz) δ: 146.34 (s), 139.30 (s), 129.07 (s), 120.47 (d, J = 161 Hz), 117.34 (d, J = 157 Hz), 113.12 (d, J = 155 Hz), 106.18 (d, J = 175 Hz), 63.49 (t, J = 147 Hz), 13.47 (q, J = 126 Hz), 10.69 (q, J = 129 Hz). UV–vis: λ_{max} (nm) and ε_{max} (M^{-1} cm^{-1}) in DMF: 269 and 1199, and 284 and 1231.

2.2.6. N,N-bis(1H-pyrazolyl-1-methyl)aniline zinc(II) chloride (*L_1ZnCl_2*)

A solution of **L_1** (0.253 g, 1.00 mmol) in dried ethanol (10.0 mL) was added to a solution of anhydrous $ZnCl_2$ (0.136 g, 1.00 mmol) in dried ethanol (10.0 mL) at room temperature. Precipitation of a white material occurred while stirring at room temperature for 12 h. The white powder was filtered and washed with ethanol (50.0 mL), followed by washing with diethyl ether (50.0 mL) (0.28 g, 72%). X-ray quality crystals of **L_1ZnCl_2** were obtained within 5 days from diethyl ether (10.0 mL) diffusion into an acetone solution (10.0 mL) of **L_1ZnCl_2** (0.10 g). *Anal.* Calc. for $C_{14}H_{15}Cl_2N_5Zn$: C, 43.16; H, 3.88; N, 17.98. Found: C, 43.01; H, 3.94; N, 18.16%. ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 7.85 (d, 2H, J = 2.4 Hz), 7.52 (d, 2H, J = 1.4 Hz), 7.20 (d, 2H, J = 9.0 Hz), 7.17 (d, 2H, J = 9.0 Hz), 6.79 (t, 2H, J = 6.6 Hz), 6.27 (t, 2H, J = 2.4 Hz), 5.92 (s, 4H). ^{13}C{^{1}H} NMR (DMSO-d_6, 600 MHz) δ: 145.66 (s), 139.58 (d, J = 184 Hz), 130.17 (d, J = 188 Hz), 129.43 (d, J = 159 Hz), 119.85 (d, J = 161 Hz), 114.58 (d, J = 157 Hz), 106.04 (d, J = 176 Hz), 66.38 (t, J = 157 Hz). UV–Vis: λ_{max} (nm) and ε_{max} (M^{-1} cm^{-1}) in DMF: 269 and 734, and 284 and 817.

2.2.7. N,N-bis(1H-pyrazolyl-1-methyl)-p-methoxyaniline zinc(II) chloride (*L_2ZnCl_2*)

L_2ZnCl_2 was prepared according to a similar procedure as described for **L_1ZnCl_2**. The white powder was filtered and washed with ethanol (50.0 mL), followed by washing with diethyl ether (50.0 mL) (0.32 g, 76%). X-ray quality crystals of **L_2ZnCl_2** were obtained within five days from diethyl ether (10.0 mL) diffusion into an acetone solution (10.0 mL) of **L_2ZnCl_2** (0.10 g). *Anal.* Calc. for $C_{15}H_{17}Cl_2N_5Zn$: C, 42.93; H, 4.08; N, 16.69. Found: C, 42.96; H, 4.08; N, 17.03%. ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 7.77 (d, 2H, J = 1.8 Hz), 7.49 (d, 2H, J = 1.8 Hz), 7.05 (d, 2H, J = 7.2 Hz), 6.78 (d, 2H, J = 6.0 Hz), 6.24 (t, 2H, J = 1.8 Hz), 5.81 (s, 4H), 3.63 (s, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 600 MHz) δ: 153.54 (s), 139.17 (s), 139.26 (d, J = 184 Hz), 129.99 (d, J = 188 Hz), 116.80 (d, J = 159 Hz), 114.65 (d, J = 154 Hz), 105.90 (d, J = 176 Hz), 66.91 (t, J = 153 Hz), 55.47 (q, J = 144 Hz). UV–vis: λ_{max} (nm) and ε_{max} (M^{-1} cm^{-1}) in DMF: 268 and 672, and 303 and 1308.

2.2.8. N,N-bis(1H-pyrazolyl-1-methyl)-p-fluoroaniline zinc(II) chloride (*L_3ZnCl_2*)

L_3ZnCl_2 was prepared according to a similar procedure as described for **L_1ZnCl_2**. The white powder was filtered and washed with ethanol (50.0 mL), followed by washing with diethyl ether (50.0 mL) (0.38 g, 83.0%). X-ray quality crystals of **L_3ZnCl_2** were obtained within five days from diethyl ether (10.0 mL) diffusion into an acetone solution (10.0 mL) of **L_3ZnCl_2** (0.10 g). *Anal.* Calc. for

$C_{15}H_{14}Cl_2FN_5Zn$: C, 41.25; H, 3.46; N, 17.18. Found: C, 41.18; H, 3.51; N, 17.91%. ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 7.64 (d, 2H, J = 2.4 Hz), 7.44 (d, 2H, J = 1.2 Hz), 7.07 (d, 2H, J = 7.8 Hz), 6.95 (d, 2H, J = 7.8 Hz), 6.15 (t, 2H, J = 2.4 Hz), 5.44 (s, 4H). ^{13}C{^{1}H} NMR (DMSO-d_6, 600 MHz) δ: 156.03 {^{13}C(^{19}F)}(d, J = 236 Hz), 142.36 (s), 139.65 (d, J = 185 Hz), 130.25 (d, J = 188 Hz), 116.57 (d, J = 163 Hz), 115.78 (d, J = 165 Hz), 106.09 (d, J = 177 Hz), 66.76 (t, J = 153 Hz). UV–Vis: λ_{max} (nm) and ε_{max} (M^{-1} cm^{-1}) in DMF: 261 and 1382, and 293 and 1523.

2.2.9. N,N-bis(3,5-dimethyl-1H-pyrazolyl-1-methyl)aniline zinc(II) chloride (*L_4ZnCl_2*)

L_4ZnCl_2 was prepared according to a similar procedure as described for **L_1ZnCl_2**. The white powder was filtered and washed with ethanol (50.0 mL), followed by washing with diethyl ether (50.0 mL) (0.33 g, 73.0%). X-ray quality crystals of **L_4ZnCl_2** were obtained within five days from diethyl ether (10.0 mL) diffusion into an acetone solution (10.0 mL) of **L_4ZnCl_2** (0.10 g). *Anal.* Calc. for $C_{18}H_{23}Cl_2N_5Zn$: C, 48.50; H, 5.20; N, 15.71. Found: C, 48.51; H, 5.24; N, 15.96%. ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 7.19 (t, 2H, J = 5.3 Hz), 7.11 (d, 2H, J = 7.2 Hz), 6.83 (t, 1H, J = 7.2 Hz), 5.79 (s, 2H), 5.63 (s, 4H), 2.15 (s, 6H), 2.09 (s, 6H). ^{13}C{^{1}H} NMR (DMSO-d_6, 600 MHz) δ: 146.22 (s), 145.51(s), 139.67 (s), 129.16 (d, J = 159 Hz), 120.82 (d, J = 161 Hz), 117.78 (d, J = 161 Hz), 105.74 (d, J = 164 Hz), 63.35 (t, J = 152 Hz), 13.59 (q, J = 126 Hz), 10.89 (q, J = 125 Hz). UV–vis: λ_{max} (nm) and ε_{max} (M^{-1} cm^{-1}) in DMF: 269 and 919, and 284 and 716.

2.3. X-ray crystallographic studies

A colorless cubic-shaped crystal was picked up with paraton oil and mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation source and a nitrogen cold stream (−100 °C). Data collection and integration were performed with SMART (Bruker, 2000) and SAINT-PLUS (Bruker, 2001) [33]. Semi-empirical absorption corrections based on equivalent reflections were applied by SADABS [34]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL [35]. All the non-hydrogen atoms were refined anisotropically and hydrogen atoms were added in their geometrically ideal positions.

2.4. Catalytic activity

In a Schlenk line, the complex (5.8 mg for **L_1ZnCl_2**, 6.3 mg for **L_2ZnCl_2**, 6.1 mg for **L_3ZnCl_2**, 6.7 mg for **L_4ZnCl_2**) was dissolved in dried toluene (2.3 mL) followed by the addition of modified methylaluminoxane (MMAO) (3.25 mL, 7.50 mmol) as a co-catalyst. The solution was stirred for 20 min at 60 °C. MMA (5.0 mL, 47.1 mmol) was added to the above reaction mixture and stirred for 2 h to obtain a viscous solution. Methanol (50.0 mL) was added to terminate polymerization. The reaction mixture was poured into a large quantity of MeOH (500 mL), and 35% HCl (5.0 mL) was injected to remove the remaining co-catalyst (MMAO). PMMA was obtained by filtration and was dried under vacuum at a mild temperature for 24 h.

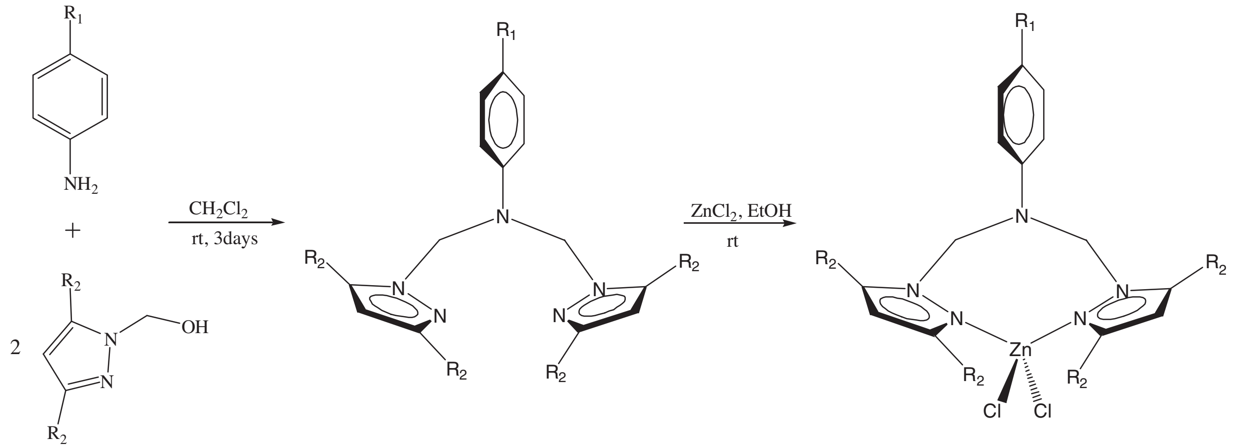
3. Results and discussion

3.1. Synthesis and chemical properties

Scheme 1 shows the synthesis of the ligands and the Zn(II) complexes. The ligands were obtained in yields of approximately 68–85% from the aniline derivate and 1H-pyrazolyl-1-methanol or 3,5-dimethyl-1H-pyrazolyl-1-methanol in methylene chloride. The Zn(II) chloride complexes (approximately 72–83% yields) were obtained from the corresponding ligands with anhydrous zinc(II) chloride in anhydrous ethanol. The results of ^{1}H NMR, ^{13}C NMR and elemental analyses were consistent with the formulation for the ligands and the Zn(II) complexes. The ^{1}H NMR and ^{13}C NMR peaks of the Zn(II) complexes were little shifted compared with the ligands due to resonance effects of the N and C atoms of the pyrazole group. The ligands and their corresponding Zn complexes have the same values of λ_{max} (due to π → π of the phenyl and pyrazolyl groups) in the UV–Vis spectra because the π electrons of the phenyl and pyrazole rings do not participate in bonds between the ligand and the Zn metal directly [36].

3.2. Crystal structures

The structures together with selected bond distances and bond angles of the Zn(II) complexes are shown in Figs. 1–4. Crystal structure data, details of data collection and refinement parameters are listed in Table 1.



R_1, R_2 = H [$\mathbf{L_1}$]
R_1 = OCH_3, R_2 = H [$\mathbf{L_2}$]
R_1 = F, R_2 = H [$\mathbf{L_3}$]
R_1 = H, R_2 = CH_3 [$\mathbf{L_4}$]

[$\mathbf{L_1ZnCl_2}$]
[$\mathbf{L_2ZnCl_2}$]
[$\mathbf{L_3ZnCl_2}$]
[$\mathbf{L_4ZnCl_2}$]

Scheme 1. Synthesis of the ligands and the dichloro L_nZn(II) complexes.

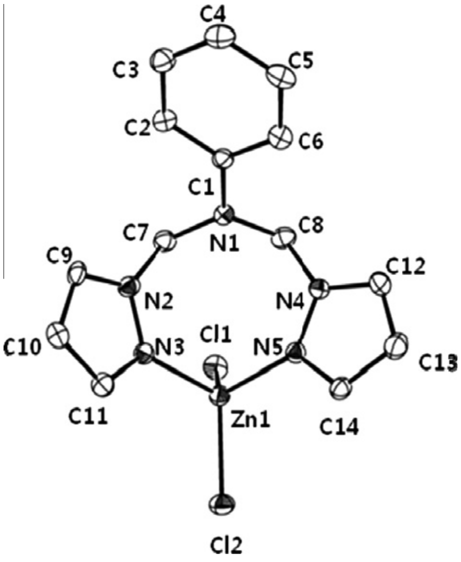


Fig. 1. ORTEP drawing of **L$_1$ZnCl$_2$** with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–N(3) 2.031(4), Zn(1)–N(5) 2.035(4), Zn(1)–Cl(2) 2.2083(15), Zn(1)–Cl(1) 2.2348(16), N(4)–N(5) 1.356(6), N(1)–C(1) 1.418(7), N(1)–C(8) 1.439(7), N(1)–C(7) 1.447(7), C(13)–C(14) 1.400(8), C(12)–C(13) 1.364(8); N(3)–Zn(1)–N(5) 100.64(17), N(3)–Zn(1)–Cl(2) 108.10(13), N(5)–Zn(1)–Cl(2) 106.85(12), N(3)–Zn(1)–Cl(1) 110.59(13), N(5)–Zn(1)–Cl(1) 112.78(13), Cl(2)–Zn(1)–Cl(1) 116.59(6), C(8)–N(1)–C(7) 119.0(4), N(1)–C(7)–N(2) 115.0(4), N(1)–C(8)–N(4) 115.9(4), N(3)–N(2)–C(7) 121.4(4).

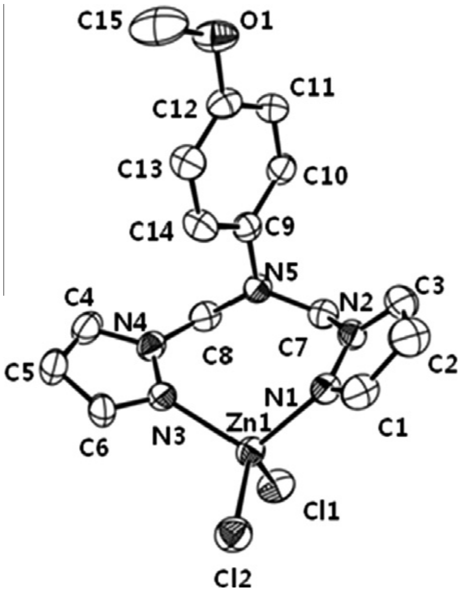


Fig. 2. ORTEP drawing of **L$_2$ZnCl$_2$** with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–N(1) 2.035(3), Zn(1)–N(3) 2.046(3), Zn(1)–Cl(2) 2.2197(13), Zn(1)–Cl(1) 2.2229(11), N(1)–C(1) 1.328(5), N(1)–N(2) 1.355(5), N(2)–C(3) 1.338(5), C(2)–C(3) 1.362(8), C(1)–C(2) 1.376(7); N(1)–Zn(1)–N(3) 108.80(13), N(1)–Zn(1)–Cl(2) 104.34(10), N(3)–Zn(1)–Cl(2) 108.11(10), N(1)–Zn(1)–Cl(1) 111.46(10), N(3)–Zn(1)–Cl(1) 106.48(10), Cl(2)–Zn(1)–Cl(1) 117.42(5), C(8)–N(5)–C(7) 120.0(3), N(5)–C(7)–N(2) 111.3(3), N(5)–C(8)–N(4) 112.9(3), N(3)–N(4)–C(8) 121.7(3).

A single crystal suitable for X-ray crystallography was obtained from diethyl ether (10.0 mL) diffusion into an acetone solution (10.0 mL). The structures of all of the Zn(II) complexes show a very similar distorted tetrahedral coordination of the Zn atom. The zinc is coordinate by two N atoms of the pyrazole groups and two

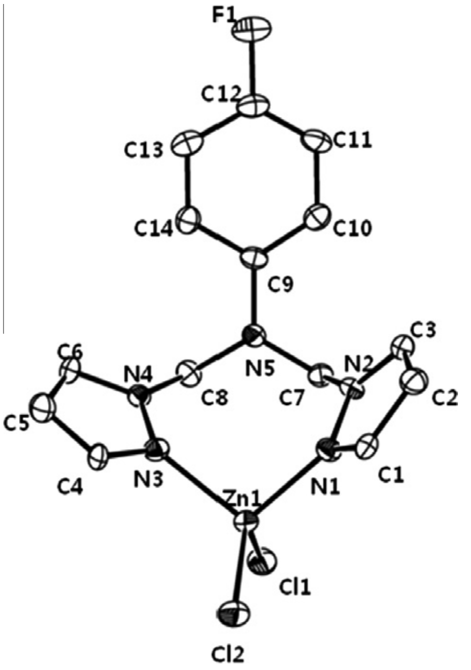


Fig. 3. ORTEP drawing of **L$_3$ZnCl$_2$** with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–N(1) 2.023(4), Zn(1)–N(3) 2.040(4), Zn(1)–Cl(2) 2.2134(13), Zn(1)–Cl(1) 2.2254(13), N(1)–C(1) 1.345(6), N(1)–N(2) 1.365(5), N(2)–C(3) 1.348(6), N(2)–C(7) 1.463(5), C(1)–C(2) 1.378(6) C(2)–C(3) 1.373(6); N(1)–Zn(1)–N(3) 99.53(15), N(1)–Zn(1)–Cl(2) 107.26(11), N(3)–Zn(1)–Cl(2) 108.81(11), N(1)–Zn(1)–Cl(1) 112.71(11), N(3)–Zn(1)–Cl(1) 111.49(11), Cl(2)–Zn(1)–Cl(1) 115.74(5), C(7)–N(5)–C(8) 118.9(4), N(5)–C(7)–N(2) 114.3(3), N(5)–C(8)–N(4) 115.6(4), N(3)–N(4)–C(8) 122.5(4).

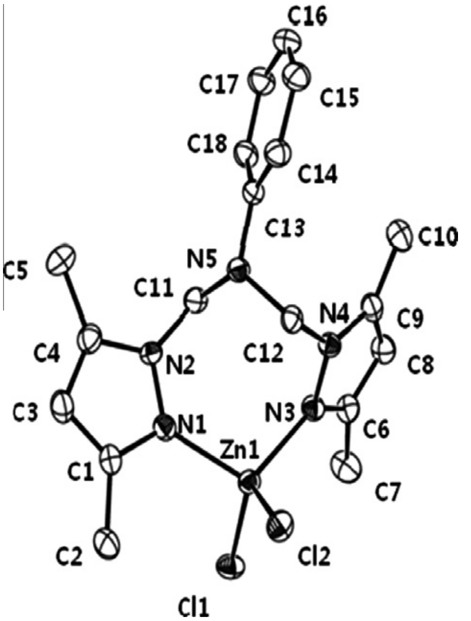


Fig. 4. ORTEP drawing of **L$_4$ZnCl$_2$** with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–N(3) 2.044(3), Zn(1)–N(1) 2.069(4), Zn(1)–Cl(2) 2.2189(12), Zn(1)–Cl(1) 2.2510(12), N(1)–C(1) 1.337(5), N(1)–N(2) 1.373(4), N(2)–C(4) 1.350(5), N(2)–C(11) 1.444(5), C(1)–C(3) 1.374(6), C(3)–C(4) 1.374(7); N(3)–Zn(1)–N(1) 108.61(14), N(3)–Zn(1)–Cl(2) 112.08(10), N(1)–Zn(1)–Cl(2) 108.20(9), N(3)–Zn(1)–Cl(1) 110.06(10), N(1)–Zn(1)–Cl(1) 102.57(10), Cl(2)–Zn(1)–Cl(1) 114.73(5), C(1)–N(1)–N(2) 105.4(3), C(1)–N(1)–Zn(1) 124.3(3), N(2)–C(11)–N(5) 112.0(3), N(5)–C(12)–N(4) 114.6(3).

Table 1
Crystal data and structure refinement of the dichloro $L_nZn(II)$ complexes.

	L_1ZnCl_2	L_2ZnCl_2	L_3ZnCl_2	L_4ZnCl_2
Empirical formula	$C_{14}H_{15}Cl_2N_5Zn$	$C_{15}H_{17}Cl_2N_5OZn$	$C_{14}H_{14}Cl_2FN_5Zn$	$C_{18}H_{23}Cl_2N_5Zn$
Formula weight	389.58	419.61	407.57	445.68
Temperature (K)	200(2)	200(2)	200(2)	200(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	P2(1)/c	P2(1)/c	P2(1)/n	Pbca
Unit cell dimensions				
a (Å)	9.865(3)	8.917(15)	9.7115(18)	8.659(6)
b (Å)	12.536(3)	15.015(3)	13.471(3)	17.243(12)
c (Å)	13.674(4)	13.815(2)	13.234(2)	27.441(18)
α (°)	90	90	90	90
β (°)	110.205(5)	91.089(4)	109.637(4)	90
γ (°)	90	90	90	90
Volume (Å^3)	1587.1(7)	1849.2(5)	1630.6(5)	4097.1(5)
Z	4	4	4	8
Density (calculated) (mg/m^3)	1.630	1.507	1.660	1.445
Absorption coefficient (mm^{-1})	1.886	1.629	1.848	1.471
$F(000)$	792	856	824	1840
Crystal size (mm)	0.38 × 0.31 × 0.30	0.40 × 0.34 × 0.33	0.38 × 0.31 × 0.25	0.38 × 0.27 × 0.26
Theta range for data collection (°)	2.20–28.30	2.00–28.32	2.23–26.04	1.48–28.30
Index ranges	$-13 \leqslant h \leqslant 13$	$-11 \leqslant h \leqslant 11$	$-11 \leqslant h \leqslant 10$	$-11 \leqslant h \leqslant 10$
	$-15 \leqslant k \leqslant 16$	$-15 \leqslant k \leqslant 20$	$-16 \leqslant k \leqslant 16$	$-22 \leqslant k \leqslant 22$
	$-18 \leqslant l \leqslant 13$	$-18 \leqslant l \leqslant 17$	$-13 \leqslant l \leqslant 16$	$-31 \leqslant l \leqslant 36$
Reflections collected	11349	13346	9545	28786
Independent reflections	3912 [R_{int} = 0.0266]	4584 [R_{int} = 0.0539]	3187 [R_{int} = 0.0536]	5098 [R_{int} = 0.1598]
Completeness to theta = 28.30°	99.2%	99.6%	98.9%	99.9%
Absorption correction	none	none	none	none
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	3912/0/200	4584/0/218	3187/0/208	5098/0/240
	1.190	1.047	1.138	1.036
Goodness-of-fit on F^2	R_1 = 0.0484	R_1 = 0.0462	R_1 = 0.0502,	R_1 = 0.0565
Final R indices [$I > 2\sigma(I)$]	wR_2 = 0.1361	wR_2 = 0.1113	wR_2 = 0.1274	wR_2 = 0.1347
	R_1 = 0.0761	R_1 = 0.0878	R_1 = 0.0671	R_1 = 0.1021
R indices (all data)	wR_2 = 0.2221	wR_2 = 0.1571	wR_2 = 0.1765	wR_2 = 0.1927
Largest difference peak and hole (e Å^{-3})	1.126 and −1.505	0.586 and −0.998	1.028 and −0.909	1.118 and −1.316

chloride ions. The N atom of aniline does not take part in a coordinative bond to Zn, as determined from the bond lengths between the N atom of aniline and the Zn metal, which ranged from 3.419 to 3.879 Å. The phenyl ring and the two pyrazole rings of **L_1ZnCl_2** and **L_3ZnCl_2** appear as the back of a chair and elbow rests, respectively. However, the phenyl rings in **L_2ZnCl_2** and **L_4ZnCl_2** are distorted by approximately 90°. The planes of the phenyl and pyrazole rings are virtually parallel in **L_4ZnCl_2**, which has four bulky methyl groups on the two pyrazole rings. This parallel phenomenon is more or less alleviated in **L_2ZnCl_2**, which has a large methoxy substituent on the *para* position of the phenyl ring and no steric hindrance on the pyrazole rings. Although a substituent at the *para* position of the phenyl ring is present in **L_3ZnCl_2**, this is a fairly small size fluorine atom, and consequently the other complexes, **L_1ZnCl_2** and **L_3ZnCl_2**, have the phenyl and pyrazole rings in different planes. The synthesized ligands and Zn metal result in large chelate ring complexes which are comparable to the complexes with the ligands bis(cysteinyl)thiolate [37] and bis(benzimidazolylmethyl)sulfides [38] bonded to Zn metal. The Zn–Cl bond distances for the synthesized complexes are in the range 2.2083–2.2510 Å, and these are only slightly affected by substituents on the phenyl or pyrazole rings. These values are in good agreement with the analogous distances found for related compounds (2.196–2.251 Å) [39–41]. The Zn–N bond distances are in the range 2.023–2.069 Å, which are comparable to those observed in related compounds (*i.e.*, 2.002–2.007 Å for $H_2B(3,5\text{-}MePz)_2$ and 2.014–2.039 Å for $H_2B[3,5\text{-}(CF_3)_2Pz]_2$) [42].

The Cl–Zn–Cl angles for the complexes are in the range 114.73–118.99°. Thus, the angles are unaffected by the substituents (H, OCH_3, F, CH_3) on the phenyl and pyrazole rings. N–Zn–N showed various angles for the **L_1ZnCl_2** (100.64°), **L_2ZnCl_2** (108.80°), **L_3ZnCl_2** (99.53°) and **L_4ZnCl_2** (108.61°) complexes. The **L_2ZnCl_2** and **L_4ZnCl_2** complexes exhibit nearly ideal tetrahedral angles, although those of the **L_1ZnCl_2** and **L_3ZnCl_2** complexes are approximately 10° smaller. These results are best explained by steric repulsion between the substituents of the phenyl ring and those of the pyrazole rings. The N–Zn–Cl bond angles are in the range 104.34–112.71°, indicating a slightly distorted tetrahedral configuration.

3.3. MMA polymerization

All the complexes could be activated with MMAO to polymerize methyl methacrylate (MMA), yielding PMMA with T_g ranging from 120 to 145 °C [43–46]. The polymers were isolated as white solids and characterized by GPC in THF using standard polystyrene as the reference. The triad microstructure of the PMMA was analyzed by ^1H NMR spectroscopy. The results of polymerization, including the tacticity as isotactic (mm), heterotactic (mr) and syndiotactic (rr), and the polydispersity index (PDI) as the average degree of polymerization in terms of the numbers of structural units and molecules, are summarized in Table 2 [47].

To confirm the catalytic activity of MMA polymerization, the blank polymerization of MMA was performed with $ZnCl_2$ and MMAO at a specified temperature, respectively. The tacticity of PMMA was identified in the range around syndiotactic (0.85 ppm), heterotactic (1.02 ppm), isotactic (1.21 ppm) by ^1H NMR [48]. The high molecular weight, narrow PDI and catalytic activity at 60 °C showed good results compared with previous cobalt complexes [28]. The PDI of the Zn(II) complexes were observed

Table 2
Polymerization of MMA by dichloro L$_n$Zn(II) complexes in the presence of MMAO.

Entry	Catalyst[a]	Temperature (°C)	Yield[b] (g)	Activity[c] (g/mol-Cat h) × 10^4	T_g (°C)	Tacticity			M_w[d] (g/mol) × 10^5	M_w/M_n
						%mm	%mr	%rr		
1	ZnCl$_2$[e]	60	0.52	1.73	124.24	9.210	24.24	66.55	4.96	15.3
2	MMAO[f]	60	0.42	1.40	119.61	37.20	10.92	51.88	6.78	2.09
3	**L$_1$ZnCl$_2$**	60	0.61	2.03	130.48	9.240	26.96	65.80	8.00	1.75
5	**L$_2$ZnCl$_2$**	60	0.81	2.70	131.91	7.310	22.76	69.93	8.91	1.89
6	**L$_3$ZnCl$_2$**	60	0.34	1.13	121.80	10.32	24.12	65.56	9.20	1.73
7	**L$_4$ZnCl$_2$**	60	1.45	4.83	145.88	8.510	23.35	68.14	9.39	1.77

[a] [Zn(II) catalyst]$_0$ = 15 μmol, and [MMA]$_0$/[MMAO]$_0$/[Zn(II) catalyst]$_0$ = 3100:500:1.
[b] Yield defined as mass of dried polymer recovered/mass of monomer used.
[c] Activity is g of PMMA/(mol-Zn h).
[d] Determined by GPC eluted with THF at room temperature by filtration with polystyrene calibration.
[e] Blank polymerization done with ZnCl$_2$ activated by MMAO.
[f] Blank polymerization done solely by MMAO.

in the range 1.75–1.89. The PDI range was slightly narrowed when the molecular weight of PMMA was increased. These results are explained by the narrower PDI range of the higher molecular weight polymer [49,50]. **L$_4$ZnCl$_2$** obtained the narrowest PDI and highest molecular weight of PMMA. This can be explained by the fact that the substituent of the pyrazole ring moiety, which is located near the Zn metal, is more effective than a remotely located phenyl ring. The syndiotacticity was not sufficiently high to confer a mechanism of coordination polymerization, but it was similar in all the synthesized Zn(II) complexes. This also indicates that the syndiotacticity is only slightly affected by the substituents of the ligand. The catalytic activity and the effects of substituents increased following the trend F < H < OCH$_3$ < 4(CH$_3$), as determined from the amounts of PMMA product. The electron-rich cloud around the Zn metal in **L$_4$ZnCl$_2$** provides increased activity compared with the electronic effect of the Zn metal alone. However, an electron withdrawing substituent on the ligand decreases the electron density of the complex, making it more difficult to attack the metal center compared to having an electron donating group on the complex. The activity of the **L$_3$ZnCl$_2$** complex is significantly low. Therefore, the MMA polymerization activity of these Zn complexes should be considered in reference to the electron density of the metal center.

4. Conclusion

We investigated the synthesis and X-ray crystallographic structures of novel *N*,*N*-bis(1-pyrazolyl)methyl ligands based on aniline bridge units with ZnCl$_2$. The study of the coordination of these ligands to the Zn metal revealed formation of (*NN*)ZnCl$_2$ complexes. The PDI for MMA polymerization showed little influence of the substituent. However, the molecular weight of PMMA is affected by the substituents of the pyrazole ring to a greater extent than those of the phenyl ring. The substituent catalytic activity was increased by overall electron donating substituents compared with electron withdrawing substituents on the Zn metal.

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Appendix A. Supplementary materials

CCDC 884038-884041 contains the supplementary crystallographic data for **L$_1$ZnCl$_2$**, **L$_2$ZnCl$_2$**, **L$_3$ZnCl$_2$** and **L$_4$ZnCl$_2$**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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