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Synthesis, structural features, and methyl methacrylate polymerisation of binuclear zinc(II) complexes with tetradentate pyrazolyl ligands

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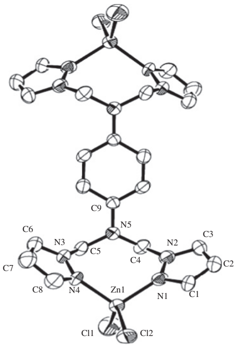
HIGHLIGHTS

- The bispyrazole-containing binuclear and tetrahedral Zn(II) complexes are synthesized.
- The Zn(II) complexes were active toward polymerization of MMA.
- The activity increased by two-fold compared to the monomeric Zn(II) complex.

GRAPHICAL ABSTRACT

The bispyrazole-containing binuclear and tetrahedral zinc (II) complexes, **[$L_1Zn_2Cl_4$]** and **[$L_2Zn_2Cl_4$]** have been structurally characterised. The catalytic activity of Zn(II) complexes toward the polymerisation of MMA in the presence of MMAO increased by two-fold compared to the corresponding monomeric Zn(II) complex, **[$LZnCl_2$]** at 60 °C.



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Binuclear zinc(II) complex
MMA polymerization

ABSTRACT

The reaction of $ZnCl_2$ with ancillary ligands, including 1,4-bis-(N,N-di-(1H-pyrazolyl-1-methyl)amine) benzene (**L_1**) and 4,4′-bis-(N,N-di(1H-pyrazolyl-1-methyl)phenyl)methane (**L_2**), in ethanol yields Zn(II) chloride complexes, i.e., 1,4-bis-(N,N-di-(1H-pyrazolyl-1-methyl)amine)benzene(dichloro)Zn(II) [**$L_1Zn_2Cl_4$**] and 4,4′-bis-(N,N-di-(1H-pyrazolyl-1-methyl)phenyl)methane(dichloro)Zn(II) [**$L_2Zn_2Cl_4$**]. The X-ray crystal structures of Zn(II) complexes revealed that they are binuclear, and each zinc atom has a distorted tetrahedral geometry which involves a nitrogen atom from two pyrazole groups and two chloro ligands. The catalytic activity of [**$L_1Zn_2Cl_4$**] and [**$L_2Zn_2Cl_4$**] for the polymerisation of methyl methacrylate (MMA) in the presence of modified methylaluminoxane (MMAO) increased by twofold compared to the corresponding monomeric Zn(II) complex, N,N-bis(1H-pyrazolyl-1-methyl)aniline(dichloro)Zn(II) [**$LZnCl_2$**], at 60 °C.

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1. Introduction

Bis(1H-pyrazol-1-ly)methylaniline and its various derivatives form a variety of complexes due to the possible binding modes of N,N-bidentate, N,N′,N-tridentate, and N,N′,N′,N-tetradentate with proper linker units of amine derivatives depending on the transition metals. These derivatives were first introduced by Driessen in 1982 [1]. Driessen et al. synthesised and characterised N-bidentate and N-tetradentate pyrazole ligands, which contain a proper amine linker unit, such as 1-(2-ethylaminoethyl]-3,5-dimethylpyrazole (deae), bis-(3,5-dimethylpyrazolylmethyl)ethylamine (bdmae), or bis-(3,5-diemtylpyrazolylethyl)ethylamine (ddae), with several transition metals [2–9]. For example, metal complexes such as monomeric/dimeric Rh(I) [10–12], Co(II) [6,13–16], dimeric Fe(II) [17,18], metals of group 6 (Cr, Mo, W) [19,20], metals of group 10 (Ni, Pd, Pt) [21–25], Cu(II) [26–31], Cd(II) [32,33], and Zn(II) [3,34–37] complexed with N-substituted pyrazole ligands have unique structural properties and catalytic activities. Although a large variety of transition metal complexes with N-substituted pyrazole derivatives have been characterised, further studies are required on the design and synthesis of transition metals ligated with bis N-substituted pyrazole derivatives to manipulate the amine linker unit. In addition, the zinc-containing complexes have drawn a huge interest for the photo-induced optical and nonlinear optics applications [38,39]. Along with this fact, we are interested in the zinc complexes as catalyst for producing the polymethyl methacrylate (PMMA). PMMA is very universal polymers as optical usage. Usually, the higher the glass transition temperature (T_g) represents the higher optical quality and syndiotacticity content of PMMA. The glass transition temperature (T_g) of isotactic PMMA, which is produced by radical process in commercial is around 65 °C. Thus, the research on non-radical mediated polymerization of MMA have been attracted and some transition metal complexes used successfully [37,40–47]. Previously, we reported tetrahedral Co(II) and Zn(II) complexes with N,N-bis(1H-pyrazolyl-1-methyl)aniline and its derivatives, as well as the binding mode of N,N-bidentate for methyl methacrylate (MMA) polymerisation [37,45]. In addition, the Cd(II) complex with ligand N,N-bis(3,5-dimethyl-1H-pyrazolyl-1-methyl)aniline has revealed the binding mode of N,N′,N-tridentate by binding the aniline nitrogen to cadmium [48]. Although the molecular structure of the ligand N,N,N′,N′-tetra-[(3,5-di-substituted-1-pyrazolyl)methyl]-*para*-phenylenediamine was reported by Daoudi et al. in 2003 [49,50], the synthesis, crystal structure, and catalytic activity of this transition metal complex with the bis-N,N-bidentate ligand has not been investigated [51]. Thus, we report the synthesis, X-ray crystal structure, and MMA polymerisation of binuclear Zn(II) complexes with the tetradentate ligands 1,4-bis-(N,N-di(1H-pyrazolyl-1-methyl)amine)benzene and 4,4′-bis-(N,N-di(1H-pyrazolyl-1-methyl)phenyl)methane, which contain four pyrazoles as N-donor atoms. We expect to observe the “effect of double metal existence in one molecule” on MMA polymerisation [42,46] compared to the previously reported corresponding monomeric Zn(II) complex.

2. Experimental

2.1. Materials and instrumentation

$ZnCl_2$, pyrazole, *para*-formaldehyde, *para*-phenylenediamine, 4,4′-diaminophenylmethane were purchased from Aldrich and anhydrous solvents such as ethanol, dimethylformamide (DMF), diethyl ether, acetone, dichloromethane were purchased from Merck and used without further purification. Modified methylaluminoxane (MMAO) was purchased from Tosoh Finechem Corporation as 6.9% weight aluminum of a toluene solution and used without further purification. Elemental analyses (C, H, N) of the prepared complexes were carried out on an elemental analyzer (EA 1108; Carlo-Erba, Milan, Italy). ^1H NMR (400 MHz) and ^{13}C NMR (75.46 MHz operating) 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. Electronic absorption spectra were obtained on an Ocean Optics USB4000 spectrophotometer (Ocean Optics, Dunedin, FL). Absorption spectra were obtained on Jasco V-530 UV/VIS spectrophotometer. The molecular weight and molecular weight distribution of the obtained PMMA were carried out using gel permeation chromatography (GPC) ($CHCl_3$, Alliance e2695; Waters Corp., Milford, MA). Glass transition temperature (T_g) was determined using a thermal analyzer (Q2000; TA Instruments, New Castle, DE).

2.2. Synthesis of ligands and complexes

2.2.1. Preparation of organic compounds

The 1H-pyrazolyl-1-methanol as starting material were prepared in processes described in literature [1]. The CH_2Cl_2 solution (100 mL) of pyrazole (20.4 g, 0.30 mol) was added a CH_2Cl_2 solution (100 mL) of *para*-formaldehyde (9.00 g, 0.30 mol). The solution was reflux for 5 days and the filtrate solvent was removed under reduced pressure to give white powder (28.5 g, 98.0%). ^1H 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).

2.2.2. 1,4-Bis-(N,N-di(1H-pyrazolyl-1-methyl)amine)benzene (***L*₁**)

L_1 was prepared by a similar procedure as described in the literature [6,49,52–54]. The CH_2Cl_2 solution (10.0 mL) of *para*-phenylenediamine (1.08 g, 0.010 mol) was added a CH_2Cl_2 solution (50.0 mL) of 1H-1-pyrazolyl-1-methanol (3.92 g, 0.040 mol). The reaction solution was dried over the $MgSO_4$ after stirring the reaction mixture at room temperature for 3 days. The white solid product was obtained (4.07 g, 95.0%). Analysis calculated for $C_{22}H_{24}N_{10}$: C, 61.67%; H, 5.65%; N, 32.69%. Found: C, 61.69%; H, 5.65%; N, 31.81%. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, 4H, J = 1.6 Hz, $\mathrm{-N{=}C\mathbf{H}-CH{=}CH-N-}$), 7.42 (d, 4H, J = 2.0 Hz, $\mathrm{-N{=}CH-CH{=}C\mathbf{H}-N-}$), 7.02 (s, 4H, *o*-,*m*-$\mathrm{NC_6\mathbf{H}_5N-}$), 6.25 (dd, 4H, J = 1.6 Hz, J = 2.0 Hz, $\mathrm{-N{=}CH-C\mathbf{H}{=}CH-N-}$), 5.62 (s, 8H, $-CH_2-$). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 140.67 (2C, ipso-$\mathrm{N\mathbf{C}_6H_5N-}$), 139.89 (4C, $\mathrm{-N{=}\mathbf{C}H-CH{=}CH-N-}$), 129.03 (4C, $\mathrm{-N{=}CH-CH{=}\mathbf{C}H-N-}$), 118.48 (4C, *o*-,*m*-$\mathrm{N\mathbf{C}_6H_5N-}$), 106.17 (4C, $\mathrm{-N{=}CH-\mathbf{C}H{=}CH-N-}$), 66.82 (4C, $\mathrm{-CH_2-}$). IR (solid neat; cm^{-1}): 3102(w), 2361(s), 1697(s), 1522(w), 1470(s), 1370(s), 1265(s), 1206(s), 1156(s), 1089(s), 1046(s), 947(s), 880(s), 750(s), 650(s), 610(s).

2.2.3. 4,4′-Bis-(N,N-di(1H-pyrazolyl-1-methyl))phenyl)methane (**L_2**)

L_2 was prepared by analogous method as described for **L_1** except utilizing 4,4′-diaminophenylmethane. The white solid product was obtained (4.77 g, 92%). Analysis calculated for $C_{29}H_{30}N_{10}$: C, 66.49%; H, 5.73%; N, 26.25%. Found: C, 67.16%; H, 5.73%; N, 26.25%. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, 4H, J = 1.6 Hz, $\mathrm{-N{=}C\mathbf{H}-CH{=}CH-N-}$), 7.43 (d, 4H, J = 2.0 Hz, $\mathrm{-N{=}CH-CH{=}C\mathbf{H}-N-}$), 7.02 (d, 4H, J = 8.8 Hz, *m*-$\mathrm{NC_6\mathbf{H}_4-CH_2-C_6\mathbf{H}_4N-}$), 7.00 (d, 4H, J = 8.8 Hz, *o*-$\mathrm{NC_6\mathbf{H}_4-CH_2-C_6\mathbf{H}_4N-}$), 6.25 (dd, 4H, J = 1.6 Hz, J = 2.0 Hz, $\mathrm{-N{=}CH-C\mathbf{H}{=}CH-N-}$), 5.69 (s, 8H, $-CH_2-$), 3.80 (s, 2H, $\mathrm{-NC_6H_4-C\mathbf{H}_2-C_6H_4N-}$). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 144.44 (2C, -ipso$\mathrm{-N\mathbf{C}_6H_4-CH_2-\mathbf{C}_6H_4N-}$), 140.35 (4C, $\mathrm{-N{=}\mathbf{C}H-CH{=}CH-N-}$), 134.52 (4C, *m*-$\mathrm{N\mathbf{C}_6H_4-CH_2-\mathbf{C}_6H_4N-}$), 130.32 (4C, $\mathrm{-N{=}CH-CH{=}\mathbf{C}H-N-}$), 129.26 (2C, *p*-$\mathrm{N\mathbf{C}_6H_4-CH_2-\mathbf{C}_6H_4N-}$), 116.37 (4C, *o*-$\mathrm{N\mathbf{C}_6H_4-CH_2-\mathbf{C}_6H_4N-}$), 106.65 (4C, $\mathrm{-N{=}CH-\mathbf{C}H{=}CH-N-}$), 66.90 (4C, $-CH_2-$), 40.42 (1C, $\mathrm{-NC_6H_4-\mathbf{C}H_2-C_6H_4N-}$). IR (solid neat; cm^{-1}): 3110(w), 2969(w), 2903(w), 1611(w), 1512(s), 1461(s), 1342(w), 1260(s), 1217(s), 1172(s), 1082(s), 1049(s), 956(s), 903(s), 844(s), 791(s), 745(s), 648(s), 604(s).

2.3. Synthesis of Zn(II) complexes

2.3.1. 1,4-Bis-(N,N-di(1H-pyrazolyl-1-methyl)aminebenzene (dichloro)zinc(II)) ([$L_1Zn_2Cl_4$])

A solution of **L**$_1$ (0.214 g, 0.50 mmol) in dried ethanol (10.0 mL) was added to a solution of $ZnCl_2$ (0.136 g, 1.00 mmol) in dried ethanol (10.0 mL) at room temperature. Precipitation of 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) (0.29 g, 83%). The X-ray crystals of **[$L_1Zn_2Cl_4$]** were obtained within five days from diethyl ether (10.0 mL) diffusion into a DMF solution (10.0 mL) of **[$L_1Zn_2Cl_4$]** (0.10 g). Analysis calculated for $C_{22}H_{24}Cl_4N_{10}Zn_2$: C, 37.69%; H, 3.45%; N, 19.98%. Found: C, 37.69%; H, 3.54%; N, 20.01%. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 7.80 (d, 4H, *J* = 2.0 Hz, —N=C**H**—CH=CH—N—), 7.49 (d, 4H, *J* = 1.2 Hz, —N=CH—CH=C**H**—N—), 7.00 (s, 4H, *o*-,*m*-NC$_6$**H**$_5$N—), 6.24 (dd, 4H, *J* = 2.0 Hz, *J* = 1.6 Hz, —N=CH—C**H**=CH—N—), 5.81 (s, 8H, —C*H*$_2$—). ^{13}C NMR (DMSO-d$_6$, 400 MHz) δ 139.36 (4C, —N=**C**H—CH=CH—N—), 138.87 (2C, ipso-N**C**$_6$H$_5$—), 129.95 (4C, —N=CH—CH=**C**H—N—), 115.84 (4C, *o*-,*m*-NC$_6$H$_5$N—), 105.87 (4C, —N=CH—**C**H=CH—N—), 66.68 (4C, —CH$_2$—). IR (solid neat; cm^{-1}): 3123(w), 2364(s), 1694(s), 1648(w), 1522(s), 1469(s), 1409(s), 1316(s), 1251(s), 1194(s), 1163(s), 1069(s), 992(s), 949(s), 867(s), 784(s), 736(s), 643(s), 611(s), 566(s).

2.3.2. 4,4′-Bis-(N,N-di(1H-pyrazolyl-1-methyl))phenylmethane (dichloro)zinc(II)) ([$L_2Zn_2Cl_4$])

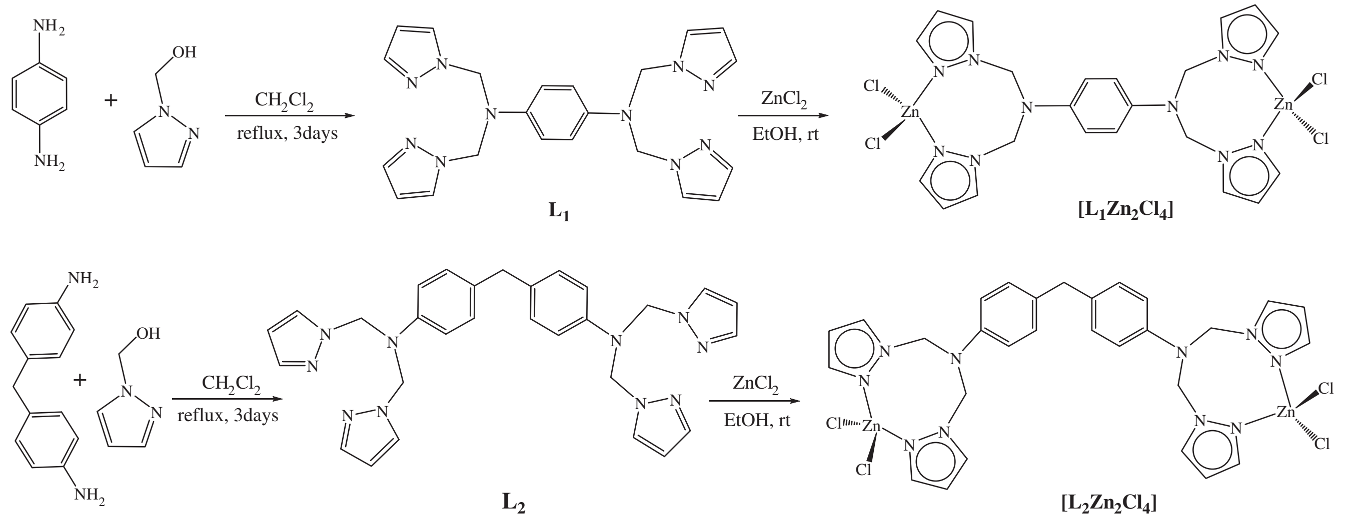
The **[$L_2Zn_2Cl_4$]** was prepared according to the similar procedure described for **[$L_1Zn_2Cl_4$]**. The white powder was filtered and washed with ethanol (50.0 mL), followed by washing with diethyl ether (50.0 mL) (0.34 g, 87%). The X-ray crystals of **$L_2Zn_2Cl_4$** were obtained within five days from diethyl ether (10.0 mL) diffusion into an acetone solution (10.0 mL) of **[$L_2Zn_2Cl_4$]** (0.10 g). Analysis calculated for $C_{29}H_{30}Cl_4N_{10}Zn_2$: C, 44.02%; H, 3.82%; N, 17.70%. Found: C, 43.92%; H, 3.76%; N, 17.75%. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 8.14 (d, 4H, *J* = 1.6 Hz, —N=C**H**—CH=CH—N—), 7.49 (d, 4H, *J* = 1.6 Hz, —N=CH—CH=C**H**—N—), 7.03 (d, 4H, *J* = 8.8 Hz, *m*-NC$_6$H$_4$—**CH**$_2$—C$_6$H$_4$N—), 6.97 (d, 4H, *J* = 8.8 Hz, *o*-NC$_6$H$_4$—**CH**$_2$—C$_6$H$_4$N—), 6.24 (dd, 4H, *J* = 1.6 Hz, *J* = 2.0 Hz, —N=CH—C**H**=CH—N—), 5.69 (s, 8H, —C*H*$_2$—), 3.65(s, 2H, —NC$_6$H$_4$—C**H**$_2$—C$_6$H$_4$N—). ^{13}C NMR (DMSO-d$_6$, 400 MHz): δ 143.54 (2C, -ipso-N**C**$_6$H$_4$—CH$_2$—**C**$_6$H$_4$N—), 139.41 (4C, —N=**C**H—CH=CH—N—), 133.02 (4C, *m*-N**C**$_6$H$_4$—CH$_2$—**C**$_6$H$_4$N—), 129.97 (4C, —N=CH—CH=**C**H—N—), 129.41 (2C, *p*-N**C**$_6$H$_4$—CH$_2$—**C**$_6$H$_4$N—), 114.45 (4C, *o*-N**C**$_6$H$_4$—CH$_2$—**C**$_6$H$_4$N—), 105.91 (4C, —N=CH—**C**H=CH—N—), 66.30 (4C, —CH$_2$—), 39.84 (1C, —NC$_6$H$_4$—**C**H$_2$—C$_6$H$_4$N—). IR (solid neat; cm^{-1}): 3110(w), 2968(w), 2888(w), 1746(w), 1696(s), 1618(s), 1518(w), 1469(s), 1411(s), 1317(s), 1257(s), 1170(s), 1072(s), 953(s), 764(s), 647(s), 612(s).

2.4. Representative polymerization procedure of MMA

Methyl methacrylate (MMA) was extracted with 10% sodium hydroxide, washed with water, dried over magnesium sulfate, and distilled over calcium hydride under reduced pressure before use. To a 100-mL Schlenk flask containing the complex (11 mg, 15 μmol for **[$L_1Zn_2Cl_4$]** and 12 mg, 15 μmol for **$L_2Zn_2Cl_2$**) in toluene (1 mL) was added MMAO (modified methylaluminoxane, 6.9 wt% in toluene, 3.25 mL, $[MMAO]_0/[Zn(II)\ catalyst]_0 = 500$) under a dry argon atmosphere. After the mixture had been stirred at room temperature for 10 min, it was transferred into MMA (5.0 mL, 47.0 mmol, $[MMA]_0/[Zn(II)\ catalyst]_0 = 3100$). Then, the reaction flask was immersed in an oil bath at 60 °C and stirred for 2 h. The resulting polymer was precipitated in methanol (400 mL) and HCl (3 mL) was added with stirring for 10 min. The polymer was filtered and washed with methanol (400 mL × 3) to give PMMA, which was vacuum-dried at 60 °C.

2.5. X-ray crystallographic analysis

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) [55]. Semiempirical absorption corrections based on equivalent reflections were applied by SADABS [56]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL [57]. All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions.



Scheme 1. Synthetic scheme for the preparation of **[$L_1Zn_2Cl_4$]** and **[$L_2Zn_2Cl_4$]**.

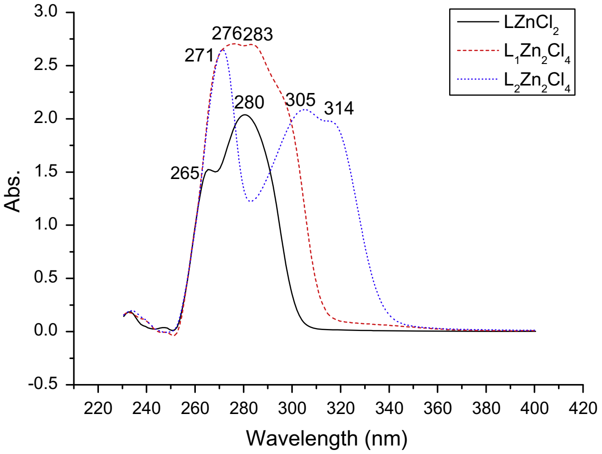


Fig. 1. UV absorption spectra of Zn(II) complexes.

3. Results and discussion

The zinc(II) complexes 1,4-bis-N,N-di(1H-pyrazolyl-1-methyl)aminebenzene(dichloro)zinc(II) **[L$_1$Zn$_2$Cl$_4$]** and 4,4′-bis-N,N-di(1H-pyrazolyl-1-methyl))phenylmethane(dichloro)zinc(II) **[L$_2$Zn$_2$Cl$_4$]** were synthesised using the method illustrated in Scheme 1.

Ligands were obtained at yields of 95% (**L$_1$**) and 92% (**L$_2$**) from the reaction of 1H-pyrazolyl-1-methanol with *p*-phenylenediamine and 4,4′-diaminophenylmethane in methylene chloride, respectively. The Zn(II) chloride complexes (83% for **[L$_1$Zn$_2$Cl$_4$]** and 87% for **[L$_2$Zn$_2$Cl$_4$]**) were obtained from the reaction between the corresponding ligands and anhydrous zinc(II) chloride in anhydrous ethanol. The results of ^{1}H NMR, ^{13}C NMR, and elemental analyses were consistent with ligand and Zn(II) complex formulation. ^{1}H NMR and ^{13}C NMR peaks of the Zn(II) complexes were shifted slightly down-field compared to the ligands due to resonance effects of the N and C atoms of the pyrazole group.

The electronic absorption spectra of ligands and Zn complexes in dimethylformamide (DMF) appeared similar and mainly consisted of intra-ligand characteristics (Fig. 1). For example, ligands **L** and **LZnCl$_2$** showed the same two absorption bands at $\lambda_1 = 265$ nm and $\lambda_2 = 279$ nm with molar absorption coefficients of 1650 cm^{-1} M^{-1} and 2250 cm^{-1} M^{-1}, respectively, which were attributed to π–π* interactions of the aniline and pyrazolyl moiety. The absorption spectra of ligands **L$_1$** and **[L$_1$Zn$_2$Cl$_4$]** showed two bands at approximately $\lambda_1 = 274$ nm and $\lambda_2 = 283$ nm with molar absorption coefficients of 2670 cm^{-1} M^{-1} and 2740 cm^{-1} M^{-1}, respectively. The absorption spectra of ligands **L$_2$** and **L$_2$Zn$_2$Cl$_4$** showed three bands, due to the presence of diphenylmethylene units between bis-didentate pyrazole, near $\lambda_1 = 265$ nm, $\lambda_2 = 305$ nm, and $\lambda_3 = 318$ nm with molar absorption coefficients of 2647 cm^{-1} M^{-1}, 2150 cm^{-1} M^{-1}, and 2070 cm^{-1} M^{-1}, respectively. The absorption band of ligands and complexes showed very slight red shifts, increasing from **[LZnCl$_2$]** to **[L$_1$Zn$_2$Cl$_4$]** and then **[L$_2$Zn$_2$Cl$_4$]**. These Zn(II) complexes are substantially disturbed by the electron-vibration broadening and particularly anharmonic ones.

A single crystal suitable for X-ray analysis was obtained from diethyl ether diffusion in DMF for **[L$_1$Zn$_2$Cl$_4$]** and acetone for **[L$_2$Zn$_2$Cl$_4$]** solution. Crystal data and structure refinement of **[L$_1$Zn$_2$Cl$_4$]** and **[L$_2$Zn$_2$Cl$_4$]** are listed in Table 1. The structures of the Zn(II) complexes and the selected bond distances and bond angles of Zn(II) complexes are shown in Figs. 2 and 3, respectively. Both **[L$_1$Zn$_2$Cl$_4$]** and **[L$_2$Zn$_2$Cl$_4$]** crystallised in the triclinic P_1 space group, and the unit cell included a DMF for **[L$_1$Zn$_2$Cl$_4$]** and an acetone for **[L$_2$Zn$_2$Cl$_4$]** solvent. The coordination geometry around the Zn(II) atom bound by the two nitrogen atoms from pyrazole and two chlorine atoms showed slightly distorted tetrahedral coordination. The N atom of aniline did not take part in the coordinative bond to the zinc atom, thus achieving the N,N-bidentate binding mode, as determined based on the bond lengths between the N of aniline and the Zn metal.

The average bond lengths of Zn—N$_{\text{pyrazole}}$ and Zn—Cl were 2.039 and 2.2115 Å for **[L$_1$Zn$_2$Cl$_4$]** and 2.0205 and 2.228 Å for **[L$_2$Zn$_2$Cl$_4$]**, respectively. The bond lengths were slightly affected by the

Table 1
Crystal data and structural refinement of **[L$_1$Zn$_2$Cl$_4$]** and **[L$_2$Zn$_2$Cl$_4$]**.

	[L$_1$Zn$_2$Cl$_4$]	**[L$_2$Zn$_2$Cl$_4$]**
Empirical formula	$C_{22}H_{24}Cl_4N_{10}Zn_2$	$C_{29}H_{30}Cl_4N_{10}Zn_2$
Formula weight	774.15	849.25
Temperature	200(2) K	200(2) K
Crystal system	Triclinic	Triclinic
Space group	P_1	P_1
Unit cell dimensions	$a = 8.8611(7)$ Å, $\alpha = 72.191(2)$°	$a = 11.9336(13)$ Å, $\alpha = 102.497(3)$°
	$b = 12.7048(9)$ Å, $\beta = 79.461(2)$°	$b = 12.1475(14)$ Å, $\beta = 110.424(4)$°
	$c = 15.6390(13)$ Å, $\gamma = 89.157(2)$°	$c = 15.664(3)$ Å, $\gamma = 105.428(2)$°
Volume	1646.2(2) Å^3	1927.4(4) Å^3
Z	2	2
Calculated density	1.562 Mg m^{-3}	1.463 Mg m^{-3}
Absorption coefficient	1.821 mm^{-1}	1.562 mm^{-1}
F(000)	788	868
F(000′)		
Crystal size	0.29 × 0.18 × 0.11 mm	0.34 × 0.18 × 0.17 mm
Theta range for data collection	1.39° to 28.29°	1.48° to 28.34°
Index range	$-11 \leqslant h \leqslant 11$, $-16 \leqslant k \leqslant 16$, $-17 \leqslant l \leqslant 20$	$-15 \leqslant h \leqslant 15$, $-8 \leqslant k \leqslant 16$, $-20 \leqslant l \leqslant 17$
Reflections collected	12353	14391
Independent reflections	8069[Rint = 0.0377]	9471[Rint = 0.0663]
Data completeness	0.987	0.985
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8069/0/390	9471/6/444
Goodness-of-fit on F^2	1.130	0.933
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0652$, $wR_2 = 0.1407$	$R_1 = 0.0802$, $wR_2 = 0.1943$
R indices (all data)	$R_1 = 0.1439$, $wR_2 = 0.2281$	$R_1 = 0.1808$, $wR_2 = 0.2892$
Largest diff. peak and hole	1.511 and −2.387 e Å^{-3}	1.131 and −1.294 e Å^{-3}

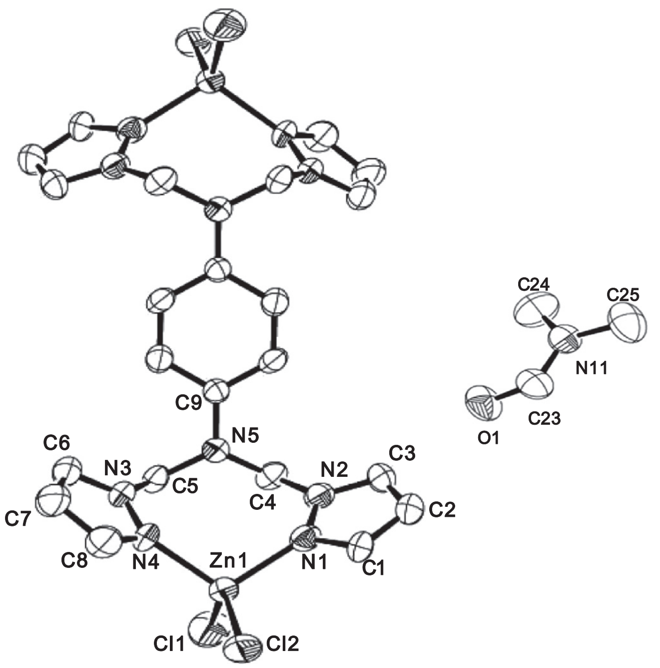


Fig. 2. ORTEP drawing of **[$L_1Zn_2Cl_4$]** with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)—N(1) 2.036(6), Zn(1)—N(4) 2.042(7), Zn(1)—Cl(2) 2.222(2), Zn(1)—Cl(1) 2.201(3), N(1)—C(1) 1.330(9), N(1)—N(2) 1.345(8), N(2)—C(3) 1.355(10), C(1)—C(2) 1.385(12), C(2)—C(3) 1.359(12), N(1)—Zn(1)—N(4) 107.0(3), Cl(1)—Zn(1)—Cl(2) 119.62(11), N(1)—Zn(1)—Cl(1) 110.3(2), N(1)—Zn(1)—Cl(2) 101.93(18), N(4)—Zn(1)—Cl(1) 111.5(2), N(4)—Zn(1)—Cl(2) 105.4(2), C(4)—N(5)—C(5) 118.5(6).

environment around the zinc metal. These values were in good agreement with the distances for related zinc complexes with pyrazole ligands, specifically **[$LZnCl_2$]**. The Cl—Zn—Cl and N$_{pyrazole}$—Zn—N$_{pyrazole}$ angles for the complexes were 119.62(11)° and 107.0(3)° for **[$L_1Zn_2Cl_4$]** and 117.27(10)° and 109.5(2)° for **[$L_2Zn_2Cl_4$]**, respectively. The angle of C(12)—C(15)—C(16) in **[$L_2Zn_2Cl_4$]** was 112.0(7)°, which was greater than the tetrahedral angle (109.5°) due to slight steric repulsion by the phenyl rings. The N$_{pyrazole}$—Zn—N$_{pyrazole}$ angle showed nearly ideal tetrahedral angles, but those of the Cl—Zn—Cl angle were approximately 10° larger. The geometry at each zinc centre was best described as a distorted tetrahedral with two equivalent half-molecules showing overall C$_2$ symmetry. The two zinc atoms for complex **[$L_1Zn_2Cl_4$]** were located across the phenyl plane due to the lack of steric hindrance. The bond angles of N—Zn—Cl were in the range of 101.93°~111.5°, indicative of a slightly distorted tetrahedral configuration.

[$L_1Zn_2Cl_4$] and **[$L_2Zn_2Cl_4$]** were activated by modified methylaluminoxane (MMAO) to polymerise MMA, yielding poly(methyl methacrylate) (PMMA) with a T_g ranging from 120 to 130 °C [40,41,43]. The polymers were isolated as white solids and characterised by GPC in tetrahydrofuran (THF) using standard polystyrene as a reference. The triad microstructure of the PMMA was analysed using ^{1}H NMR spectroscopy. The results of polymerisation, including tacticity (isotactic (mm), heterotactic (mr), or syndiotactic (rr)), as well as the polydispersity index (PDI) as the average degree of polymerisation in terms of the number of structural units and molecules, are summarised in Table 2.

For comparison, catalytic activity of the corresponding mononuclear complex, **[$LZnCl_2$]** [N,N-bis(1H-pyrazolyl-1-methyl)aniline (dichloro)zinc(II)] for MMA polymerisation, blank polymerisation of MMA with MMAO itself, and ZnCl$_2$/MMAO were cited [37]. The tacticity of PMMA was identified around syndiotactic (0.85 ppm), heterotactic (1.02 ppm), and isotactic (1.21 ppm) by ^{1}H NMR [58]. **[$L_1Zn_2Cl_4$]** exhibited a wider PDI and similar molecular weights as PMMA, but twofold higher activity compared to mononuclear **[$LZnCl_2$]** [59]. In addition, syndiotacticity designated by **[$L_1Zn_2Cl_4$]** was much higher than any other comparable bispyrazoyl-containing Zn complexes. However, **[$L_2Zn_2Cl_4$]** showed

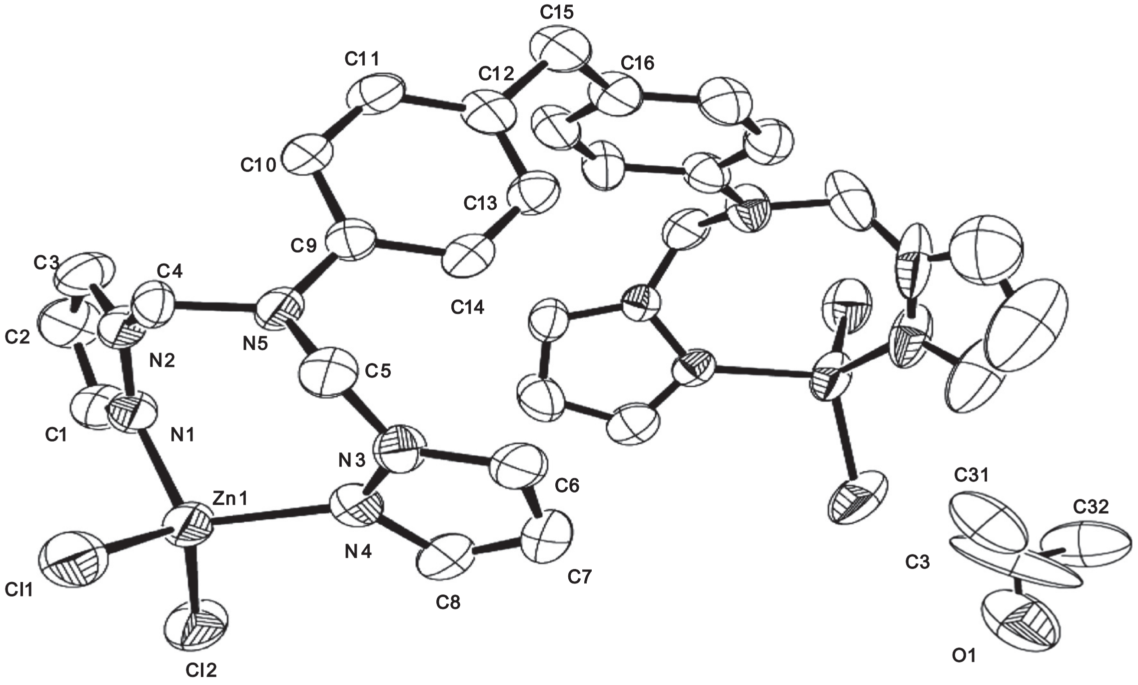


Fig. 3. ORTEP drawing of **[$L_1Zn_2Cl_4$]** with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)—N(1) 2.009(6), Zn(1)—N(4) 2.032(6), Zn(1)—Cl(2) 2.210(2), Zn(1)—Cl(1) 2.246(2), N(1)—C(1) 1.352(9), N(1)—N(2) 1.349(8), N(2)—C(3) 1.329(9), C(1)—C(2) 1.401(11), C(2)—C(3) 1.372(11), N(1)—Zn(1)—N(4) 109.5(2), Cl(1)—Zn(1)—Cl(2) 117.27(10), N(1)—Zn(1)—Cl(1) 109.49(19), N(1)—Zn(1)—Cl(2) 106.84(18), N(4)—Zn(1)—Cl(1) 107.92(19), N(4)—Zn(1)—Cl(2) 105.64(19), C(12)—C(15)—C(16) 112.0(7).

Table 2
Polymerisation of MMA by **[$L_1Zn_2Cl_4$]** and **[$L_2Zn_2Cl_4$]** in the presence of MMAO.

Entry	Catalyst[a]	Temp. (time)	Yield[b]	Activity[c]	T_g	Tacticity			M_w[d]	M_w/M_n
		(°C)	(g)	(g/mol Cat h) × 10^4	(°C)	%mm	%mr	%rr	(g mol^{-1}) × 10^5	
1	Zn_2Cl_2[e],[37]	60 (2 h)	0.52	1.73	124.24	9.2	24.2	66.6	4.96	15.3
2	MMAO[f],[37]	60 (2 h)	0.42	1.40	119.61	37.2	10.9	51.9	6.78	2.09
3	**[$LZnCl_2$]**[g],[37]	60 (2 h)	0.61	2.03	130.48	9.2	26.0	64.8	8.00	1.75
4	**[$L_1Zn_2Cl_4$]**	60 (2 h)	1.24	4.13	128.76	8.8	24.1	67.1	7.26	2.34
5	**[$L_2Zn_2Cl_4$]**	60 (2 h)	0.96	3.20	129.89	9.2	30.1	60.7	4.41	6.36

[a] $[Zn(II)\ catalyst]_0 = 15$ μmol, and $[MMA]_0/[MMAO]_0/[Zn(II)\ catalyst]_0 = 3100:500:1$.
[b] Yield defined as the 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 polymerisation in which $ZnCl_2$ was activated by MMAO.
[f] Blank polymerisation performed by MMAO alone.
[g] **[$LZnCl_2$]** refers to the N,N-bis(1H-pyrazolyl-1-methyl)aniline(dichloro)zinc(II) complex.

increased activity compared to monomeric **[$LZnCl_2$]** with mediocre syndiotacticity, which has been shown for other bispyrazoyl-containing Zn complexes. Presumably, syndiotacticity was slightly affected by the rigid phenylene bridge in **[$L_1Zn_2Cl_4$]** compared to the rotatable and distant diphenylmethylene bridge unit in **[$L_2Zn_2Cl_4$]**. Thus, there is a steric effect on the Zn centre. This is supported by the fact that catalytic activity of binuclear **[$L_1Zn_2Cl_4$]** and **[$L_2Zn_2Cl_4$]** was exactly double that of the mononuclear **$LZnCl_2$**.

4. Conclusion

The bispyrazole-containing binuclear zinc(II) complexes **[$L_1Zn_2Cl_4$]** and **[$L_2Zn_2Cl_4$]** have been prepared and structurally characterised. The coordination geometry around the Zn(II) atom bound by the two nitrogen atoms from pyrazole and two chlorine atoms showed slightly distorted tetrahedral coordination. In addition, the N atom of aniline did not take part in the coordinative bond to the zinc atom, thus achieving the N,N-bidentate binding mode. The catalytic activity of **[$L_1Zn_2Cl_4$]** and **[$L_2Zn_2Cl_4$]** toward the polymerisation of methyl methacrylate (MMA) in the presence of modified methylaluminoxane (MMAO) resulted in a twofold increase in activity compared to the corresponding monomeric N,N-bis(1H-pyrazolyl-1-methyl)aniline(dichloro)zinc(II) complex **[$LZnCl_2$]** at 60 °C with syndiotacticity of *ca*. 67%.

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Appendix A. Supplementary material

CCDC 973734 and CCDC 973735 contain the supplementary crystallographic data for **[$L_1Zn_2Cl_4$]** and **[$L_2Zn_2Cl_4$]**, respectively. 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.molstruc.2014.01.038.

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