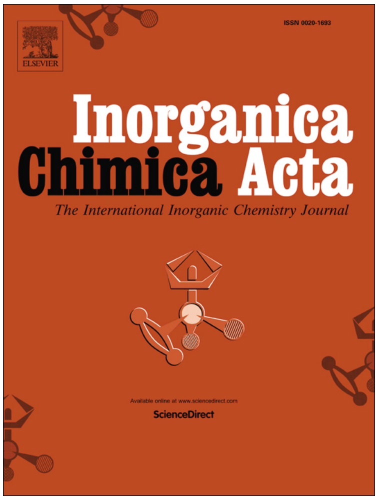

Cobalt(II) Complexes Containing *N* ’-Substituted *N,N′,N*-bis((1H-pyrazol-1-yl)methyl)amine Ligands: The Formation of Four-Coordinate or Five-Coordinate Complexes as a Function of the *N* ’-Substitution group in *N,N′,N*-bis((1H-pyrazol-1-yl)methyl)amine

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Cobalt(II) Complexes Containing *N'*-Substituted *N,N',N*-bis((1H-pyrazol-1-yl)methyl)amine Ligands: The Formation of Four-Coordinate or Five-Coordinate Complexes as a Function of the *N'*-Substitution group in *N,N',N*-bis((1H-pyrazol-1-yl)methyl)amine

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Abstract

N,N-bis((1H-pyrazol-1-yl)methyl)(cyclohexyl)methanamine (**L_A**), *N,N*-bis((1H-pyrazol-1-yl)methyl)-2,6-diethylbenzenamine (**L_B**), *N,N*-bis((1H-pyrazol-1-yl)methyl)-4-bromobenzenamine (**L_C**), *N,N*-bis((1H-pyrazol-1-yl)methyl)cyclohexanamine (**L_D**), *N,N*-bis((1H-pyrazol-1-yl)methyl)(furan-2-yl)methanamine (**L_E**), *N,N*-bis((1H-pyrazol-1-yl)methyl)-2-methoxyethanamine (**L_F**), and *N,N*-bis((1H-pyrazol-1-yl)methyl)-3-(methylthio)propan-1-amine (**L_G**) with **$[CoCl_2 \cdot 6H_2O]$** in ethanol yield a novel series of Co(II) chloride complexes; i.e. **$[L_nCoCl_2]$** ($L_n = L_A - L_G$), respectively. The molecular structures of **$[L_nCoCl_2]$** ($L_n = L_A - L_C$) and **$[L_nCoCl_2]$** ($L_n = L_D - L_G$) exist as monomeric four-coordinated and five-coordinated complexes, respectively. **$[L_nCoCl_2]$** ($L_n = L_A - L_C$) showed a distorted tetrahedral geometry involving non-coordination of the nitrogen atom of the *N′*-substitution amine moiety and the Co(II) centre, resulting in the formation of an eight-membered chelate ring. The geometry at each Co(II) centre in **$[L_nCoCl_2]$** ($L_n = L_D - L_G$) were best described as a distorted trigonal bipyramid involving coordination of the nitrogen atom of the *N′*-substitution amine group and the Co(II) centre. Specifically, a distorted trigonal bipyramid was achieved in **$[L_DCoCl_2]$** through a coordinative interaction of the nitrogen atom of the cyclohexylamine unit and the Co(II) atom with an σ plane of symmetry based on the bond length of Co-$N_{cyclcohexylamine}$ [2.466(4) Å]. Moreover, **$[L_DCoCl_2]$** showed the highest activity for methyl methacrylate (MMA) polymerization in the presence of modified methylaluminoxane (MMAO) at 60°C and yielded poly(methylmethacrylate) (PMMA) with a high molecular weight (M_w) and narrower polydispersity index (PDI) compared to the other Co(II) complexes. However, all Co(II) complexes produced syndiotactic (PMMA), characterised using ^{1}H-NMR spectroscopy, with *ca.* 0.70.

Keywords: *N′*-substituted *N,N′,N*-bis((1H-pyrazol-1-yl)methyl)amine, Co(II) complexes, Molecular structures, Methyl methacrylate Polymerization, Syndiotacticity

Introduction

The coordination chemistry of pyrazole-based ligands has been extensively studied [1-4]. Specifically, the bonding properties of pyrazole derivatives of simple amines have been well-documented and show furnished metal complexes of varying coordination geometries and nuclearity [1,4,5]. The versatility of the *N*-alkylaminopyrazole ligands is found not only regarding the ability to prepare both bi- and tri-dentate ligands but also in the variability of substituents of the amine and pyrazolyl rings [6-9]. Since the pioneering work of Driessen in 1982 [10,11], pyrazolyl-based chelating ligands and their transition metal complexes, due to their structural stability and catalytic ability, have been synthesised and applied as supra-molecules for metal-organic frames (MOF) [12,13], as catalysts for organic transformation [14-17], as biological agents [18-20], as cancer sensors, and as hydrolysis and oxidation agents [21-24].

More recently, *N*-alkylaminopyrazole ligands [25] ligated to transition metals including Rh(I), Ru(II), Pd(II), Pt(II), Zn(II), and Co(II) have exhibited a variety of potentially useful chemical properties [26-30], and are used as catalysts for olefin polymerisation [31-33] and methyl methacrylate (MMA) polymerisation [34-40]. Particularly, cobalt complexes in which we are interested as precatalyst for MMA polymerisation, extensively were used for catalysts for ethylene polymerisation [41,42]. Previous work from our group applied Co(II), Zn(II), and Pd(II) complexes with *N*,*N*-bis(1H-pyrazolyl-1-methyl)aniline and their derivatives for MMA polymerisations [43-45]. These results and potential merit of pyrazole-amine based ligands, that show fine tuning of the reactivity of the metal centre to which they are bound, prompted us to explore the complexing properties of *N,N',N*-bis((1H-pyrazol-1-yl)methyl)amine ligands to the Co(II) centre and its catalytic capabilities.

The current study describes the synthesis and structural characterisation of four-coordinated and five-coordinated monomeric Co(II) complexes supported with *N′*-substituted *N,N′,N*-bis((1H-pyrazol-1-yl)methyl)amine ligand and its derivative serving as bi- and tridentate ancillary ligands. The structural aspects of the synthesised Co(II) complexes and the effects of various substituents attached to the *N′*-substituted amine moiety on catalytic activity of MMA polymerisation in the presence of MMAO were further investigated.

2. Experimental Section

2.1. Chemicals and Physical Measurement

98% [$CoCl_2 \cdot 6H_2O$], pyrazole, cyclohexylmethanamine, 2,6-diethylbenzenamine, 4-bromobenzenamine and 2-methoxyethanamine, 95% *para*-formaldehyde, 99% cyclohexylamine and (furan-2-yl)methanamine, 97% 3-(methylthio)propan-1-amine, 99.5% $MgSO_4$, and 99% MMA were purchased from Aldrich. Anhydrous solvents, such as methanol (MeOH), ethanol (EtOH), acetone, dimethylformamine (DMF), diethyl ether (Et_2O), and dichloromethane (CH_2Cl_2) of HPLC grade were purchased from Merck and used without further purification. Modified methylaluminoxane (MMAO) was purchased from Tosoh Finechem Corporation as 6.9% weight aluminium in a toluene solution and used without further purification. The 1H-pyrazolyl-1-methanol as starting material was prepared according to reported method [10,11].

2.2. Instrumentation

^{1}H-NMR (400.01 MHz) and ^{13}C NMR (100.61 MHz) spectra were recorded on a Bruker Advance Digital 400 NMR spectrometer and chemical shifts were recorded in parts-per-million (ppm) using $SiMe_4$ as an internal standard. Elemental analysis (C, H, N) of the prepared complexes were carried out on an elemental analyser (EA 1108; Carlo-Erba, Milan, Italy). The molecular weight and molecular weight distribution of the obtained PMMA were determined by gel permeation chromatography (GPC) ($CHCl_3$, Alliance e2695; Waters Corp., Milford, MA). Glass transition temperatures (T_g) were determined using a thermal analyser (Q2000; TA Instruments, New Castle, DE). X-ray crystallography was carried by Western Seoul Center of Korea Basic Science Institute.

2.3. Preparation of ligands and corresponding Co(II) complexes

*2.3.1. N-((1H-pyrazol-1-yl)methyl)-N-(cyclohexylmethyl)(1H-pyrazol-1-yl)methanamine (**L$_A$**)*

L$_A$ was prepared by a similar procedure as described in the literature [46]. The CH_2Cl_2 solution (10.0 mL) of cyclohexylmethanamine (2.26 g, 0.0200 mol) was added to CH_2Cl_2 solution (30.0 mL) of 1H-1-pyrazolyl-1-methanol (3.92 g, 0.0400 mol). The reaction solution was dried over $MgSO_4$ after stirring at room temperature for 3 days. The filtrate solvent under reduced pressure to give a colorless and transparent oil product was obtained (4.38 g, 80.2%). Analysis calculated for $C_{15}H_{23}N_5$: C, 65.9, H, 8.48, N, 25.6. Found: C, 65.8, H, 8.62, N, 25.0%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.51 (d, 2H, J = 1.2 Hz, -N=C**H**-CH=CH-N-), 7.50 (d, 2H, J = 2.4 Hz, -N=CH-CH=C**H**-N-), 6.26 (dd, 2H, J = 1.2 Hz, J = 2.0 Hz, -N=CH-C**H**=CH-N-), 4.97 (s, 4H, -N-C**H**$_2$-N-), 2.45 (d, 2H, J = 2.8 Hz, -C_6H_{11}-C**H**$_2$-N-), 1.72-1.65 (m, 5H, -C$_6$**H**$_{11}$-), 1.53-1.50 (m, 1H, *ipso*-C$_6$**H**$_{11}$-), 1.24-1.07 (m, 3H, -C$_6$**H**$_{11}$-), 0.81-0.73 (m, 2H, -C$_6$**H**$_{11}$-). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 140.69 (d, 2C, J = 176 Hz, -N=**C**H-CH=CH-N-), 130.92 (d, 2C, J = 177 Hz, -N=CH-CH=**C**H-N-), 107.13 (d, 2C, J = 185 Hz, -N=CH-**C**H=CH-N-), 68.62 (t, 2C, J = 150 Hz, -N-**C**H$_2$-N-), 56.97 (t, 1C, J = 132 Hz, -C_6H_{11}-**C**H$_2$-N-), 36.64 (d, 1C, J = 123 Hz, *ipso*-**C**$_6$H$_{11}$-), 31.60 (t, 2C, J = 123 Hz, *o*-**C**$_6$H$_{11}$-), 27.06 (t, 1C, J = 124 Hz, *p*-**C**$_6$H$_{11}$-), 26.32 (t, 2C, J = 125 Hz, *m*-**C**$_6$H$_{11}$-). IR (liquid neat; cm$^-$

^{1}): 3110 (w), 2922 (s), 2850 (m), 1512 (m), 1387 (m), 1251 (m), 1124 (w), 1084 (m), 1044 (s), 962 (m), 859 (w), 746 (s), 614 (m).

*2.3.2. N,N-bis((1H-pyrazol-1-yl)methyl)-2,6-diethylbenzenamine (**L_B**)*

Analogous method is applied for synthesis of L_B as described for L_A. The CH_2Cl_2 solution (10.0 mL) of 2,6-diethylbenzenamine (3.29 mL, 0.0200 mol) was added a CH_2Cl_2 solution (30.0 mL) of 1H-1-pyrazolyl-1-methanol (3.92 g, 0.0400 mol). The reaction solution was dried over the $MgSO_4$ after stirring the reaction mixture at room temperature for 3 days. The filtrate solvent was removed under reduced pressure to give bright yellow oil (5.54 g, 89.5%). Analysis calculated for $C_{18}H_{23}N_5$: C, 69.8; H, 7.49; N, 22.6. Found: C, 68.1; H, 7.41; N, 21.6%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, 2H, J = 2.0 Hz, -N=C**H**-CH=CH-N-), 7.28 (d, 2H, J = 2.0 Hz, -N=CH-CH=C**H**-N-), 7.19 (t, 1H, J = 7.2 Hz, *p*-$NC_6\mathbf{H}_3(CH_2CH_3)_2$-), 7.09 (d, 2H, J = 7.6 Hz, *m*-$NC_6\mathbf{H}_3(CH_2CH_3)_2$-), 6.24 (t, 2H, J = 2.0 Hz, -N=CH-C**H**=CH-N-), 5.40 (s, 4H, -N-C$\mathbf{H}_2$-N-), 2.10 (q, 4H, J = 7.6 Hz, -$NC_6H_3(C\mathbf{H}_2CH_3)_2$-), 1.05 (t, 6H, J = 7.6 Hz, -$NC_6H_3(CH_2C\mathbf{H}_3)_2$-). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 142.94 (s, 1C, *ipso*-$N\mathbf{C}_6H_3(CH_2CH_3)_2$), 142.41 (s, 2C, *o*-$N\mathbf{C}_6H_3(CH_2CH_3)_2$-), 139.90 (d, 2C, J = 183 Hz, -N=**C**H-CH=CH-N-), 129.27 (d, 2C, J = 184 Hz, -N=CH-CH=**C**H-N-), 127.25 (d, 2C, J = 158 Hz, *m*-$N\mathbf{C}_6H_3(CH_2CH_3)_2$-), 126.42 (d, 1C, J = 156 Hz, *p*-$N\mathbf{C}_6H_3(CH_2CH_3)_2$-), 105.95 (d, 2C, J = 176 Hz, -N=CH-**C**H=CH-N-), 68.85 (t, 2C, J = 149 Hz, -N-**C**H_2-N-), 23.00 (t, 2C, J = 125 Hz, -$NC_6H_3(\mathbf{C}H_2CH_3)_2$-), 14.75 (q, 2C, J = 125 Hz, -$NC_6H_3(CH_2\mathbf{C}H_3)_2$-). IR (liquid neat; cm^{-1}): 3845 (w), 3743 (w), 3617 (w), 3110 (w), 2967 (m), 1702 (w), 1151 (m), 1457 (m), 1392 (m), 1264 (s), 1159 (s), 1083 (s), 1042 (s), 962 (m), 873 (w), 812 (w), 744 (s), 653 (w), 616 (m), 581 (w).

*2.3.3. N,N-bis((1H-pyrazol-1-yl)methyl)-4-bromobenzenamine (**L_C**)*

L_C was prepared by analogous method as described for **L_A** except utilizing 4-bromobenzenamine (3.44 g, 0.0200 mol). A bright green solid product was obtained (4.47 g, 88.7%). Analysis calculated for $C_{14}H_{14}N_5$: C, 50.6; H, 4.25; N, 21.1. Found: C, 50.7; H, 4.23; N, 21.9%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, 2H, *J* = 1.6 Hz, -N=C**H**-CH=CH-N-), 7.44 (d, 2H, *J* = 2.4 Hz, -N=CH-CH=C**H**-N-), 7.38 (d, 2H, *J* = 9.2 Hz, *m*-$NC_6\mathbf{H}_4Br$-), 7.05 (d, 2H, *J* = 9.2 Hz, *o*-$NC_6\mathbf{H}_4Br$-), 6.28 (dd, 2H, *J* = 1.6 Hz, *J* = 2.0 Hz, -N=CH-C**H**=CH-N-), 5.69 (s, 4H, -N-C$\mathbf{H}_2$-N-). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 144.84 (s, 1C, *ipso*-N$\mathbf{C}_6H_4Br$-), 140.11 (d, 2C, *J* = 176 Hz, -N=**C**H-CH=CH-N-), 132.32 (d, 2C, *J* = 165 Hz, *m*-NC_6H_4Br-), 128.89 (d, 2C, *J* = 175 Hz, -N=CH-CH=**C**H-N-), 117.51 (d, 2C, *J* = 164 Hz, *o*-N$\mathbf{C}_6H_4Br$-), 113.64 (s, 1C, *p*-N$\mathbf{C}_6H_4Br$-), 106.43 (d, 2C, *J* = 176 Hz, -N=CH-**C**H=CH-N-), 66.24 (t, 2C, *J* = 151 Hz, -N-**C**H_2-N-). IR (liquid neat; cm^{-1}): 3108 (m), 1594 (m), 1495 (s), 1364 (s), 1296 (s), 1263 (s), 1188 (s), 1082 (s), 1044 (s), 951 (m), 971 (s), 881 (m), 822 (s), 741 (s), 632 (s), 589 (m).

*2.3.4. N,N-bis((1H-pyrazol-1-yl)methyl)cyclohexanamine (**L_D**)*

L_D was prepared by analogous method as described for **L_A** except utilizing cyclohexanamine (2.28 mL, 0.0200 mol). A colorless oil product was obtained (4.44 g, 85.7%) Analysis calculated for $C_{14}H_{21}N_5$: C, 64.8, H, 8.16, N, 27.0. Found: C, 66.2, H, 8.27, N, 27.5%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, 2H, *J* = 1.6 Hz, -N=C**H**-CH=CH-N-), 7.51 (d, 2H, *J* = 2.4 Hz, -N=CH-CH=C**H**-N-), 6.27 (dd, 2H, *J* = 2.0 Hz, *J* = 2.4 Hz, -N=CH-C**H**=CH-N-), 5.13 (s, 4H, -N-C$\mathbf{H}_2$-N-), 2.86-2.79 (m, 1H, *ipso*-$C_6\mathbf{H}_{11}$-), 1.73-1.71 (m, 2H, -$C_6\mathbf{H}_{11}$-), 1.63-1.56 (m, 3H, -$C_6\mathbf{H}_{11}$-), 1.24-1.16 (m, 4H, -$C_6\mathbf{H}_{11}$-), 1.08-0.98 (m, 1H, -$C_6\mathbf{H}_{11}$-). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 139.35 (d, 2C, *J* = 175 Hz, -N=**C**H-CH=CH-N-), 129.02 (d, 2C, *J* = 185 Hz, -N=CH-CH=**C**H-N-), 105.94 (d, 2C, *J* = 175 Hz, -N=CH-**C**H=CH-N-), 65.92 (t, 2C, J = 144 Hz, -N-**C**H$_2$-N-), 59.82 (d, 1C, J = 130 Hz, *ipso*-**C**$_6$H$_{11}$-), 30.98 (t, 2C, J = 125 Hz, *o*-**C**$_6$H$_{11}$-), 25.93 (t, 1C, J = 128 Hz, *p*-**C**$_6$H$_{11}$-), 25.71 (t, 2C, J = 127 Hz, *m*-**C**$_6$H$_{11}$-). IR (liquid neat; cm^{-1}): 3111 (w), 2928 (m), 2855 (w), 1510 (w), 1449 (w), 1387 (m), 1258 (m), 1130 (m), 1084 (m), 1042 (s), 966 (m), 882 (w), 745 (s), 653 (w), 614 (m).

*2.3.5. N,N-bis((1H-pyrazol-1-yl)methyl)(furan-2-yl)methanamine (**L$_E$**)*

L$_E$ was prepared by analogous method as described for **L$_A$** except utilizing (furan-2-yl)methanamine (1.76 mL, 0.0200 mol). A colorless oil product was obtained (4.28 g, 83.2%). Analysis calculated for $C_{13}H_{15}N_5$: C, 60.6, H, 5.88, N, 27.2. Found: C, 60.1, H, 5.87, N, 26.2%. ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.55 (d, 2H, J = 2.0 Hz, -N=C**H**-CH=CH-N-),7.54 (d, 2H, J = 2.0 Hz, -N=CH-CH=C**H**-N-), 7.40 (d, 1H, J = 2.0 Hz, -O-C**H**=CH-CH=C-), 6.34 (dd, 1H, J = 2.0 Hz, J = 1.6 Hz, -O-CH=C**H**-CH=C-), 6.29 (t, 2H, J = 1.6 Hz, -N=CH-C**H**=CH-N-), 6.27 (d, 1H, J = 1.6 Hz, -O-CH=CH-C**H**=C-), 5.02 (s, 4H, -N-C**H**$_2$-N-), 3.83 (s, 2H, -O-CH=CH-CH=C-C**H**$_2$-N-). ^{13}C-NMR (CDCl$_3$, 100 MHz): δ 150.96 (s, 1C, *ipso*-O-CH=CH-CH=**C**-), 142.52 (d, 1C, J = 201 Hz, -O-**C**H=CH-CH=C-), 139.71 (d, 2C, J = 198 Hz, -N=**C**H-CH=CH-N-), 129.97 (d, 2C, J = 199 Hz, -N=CH-CH=**C**H-N-), 110.35 (d, 1C, J = 178 Hz, -O-CH=**C**H-CH=C-), 109.23 (d, 1C, J = 173 Hz, -O-CH=CH-**C**H=C-), 105.95 (d, 2C, J = 177 Hz, -N=CH-**C**H=CH-N-), 66.83 (t, 1C, J = 149 Hz, -N-**C**H$_2$-N-), 46.72 (t, 1C, J = 136 Hz, -O-CH=CH-CH=C-**C**H$_2$-N-). IR (liquid neat; cm^{-1}): 3116 (w), 2949 (w), 1693 (w), 1510 (w), 1443 (w), 1384 (w), 1285 (w), 1139 (s), 1082 (w), 1046 (w), 1007 (w), 962 (w), 743 (s), 609 (s).

*2.3.6. N,N-bis((1H-pyrazol-1-yl)methyl)-2-methoxyethanamine (**L$_F$**)*

L$_F$ was prepared by analogous method as described for **L$_A$** except utilizing 2-

methoxyethanamine (1.74 mL, 0.0200 mol). A colorless oily product was obtained (4.10 g, 87.1%). Analysis calculated for $C_{11}H_{17}N_5$: C, 56.1, H, 7.28, N, 29.7. Found: C, 55.0, H, 7.22, N, 29.4%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, 2H, *J* = 2.4 Hz, -N=C**H**-CH=CH-N-), 7.43 (d, 2H, *J* = 2.0 Hz, -N=CH-CH=C**H**-N-), 6.17 (t, 2H, *J* = 2.4 Hz, -N=CH-C**H**=CH-N-), 5.00 (s, 4H, -N-C**H**$_2$-N-), 3.34 (t, 2H, *J* = 5.6 Hz, CH_3-O-CH_2-C**H**$_2$-N-), 3.20 (s, 3H, C**H**$_3$-O-CH_2-CH_2-N-), 2.79 (t, 2H, CH_3-O-C**H**$_2$-CH_2-N-). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 138.53 (d, 2C, *J* = 181 Hz, -N=**C**H-CH=CH-N-), 128.91 (d, 2C, *J* = 185 Hz, -N=CH-CH=**C**H-N-), 104.80 (d, 2C, *J* = 186 Hz, -N=CH-**C**H=CH-N-), 70.75 (t, 2C, *J* = 139 Hz, -N-**C**H$_2$-N-), 67.31 (t, 1C, *J* = 149 Hz, CH_3-O-CH_2-**C**H$_2$-N-), 57.71 (q, 1C, *J* = 140 Hz, **C**H$_3$-O-CH_2-CH_2-N-), 48.44 (t, 1C, *J* = 133 Hz, CH_3-O-**C**H$_2$-CH_2-N-). IR (liquid neat; cm^{-1}): 3113 (w), 2926 (w), 2885 (w), 1489 (w), 1457 (w), 1394 (m), 1280 (m), 1252 (m), 1113 (s), 1084 (s), 1046 (s), 962 (m), 750 (s), 653 (m), 616 (s).

*2.3.6. N,N-bis((1H-pyrazol-1-yl)methyl)-3-(methylthio)propan-1-amine (**L_G**)*

L_G was prepared by analogous method as described for **L_A** except utilizing 3-(methylthio)propan-1-amine (2.24 mL, 0.0200 mol). A colorless oil product was obtained (4.98 g, 93.8%). Analysis calculated for $C_{12}H_{19}N_5$: C, 54.3, H, 7.22, N, 26.4. Found: C, 54.0, H, 7.32, N, 26.9%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, 4H, *J* = 2.4 Hz, -N=C**H**-CH=C**H**-N-), 6.29 (t, 2H, *J* = 2.4 Hz, -N=CH-C**H**=CH-N-), 5.02 (s, 4H, -N-C**H**$_2$-N-), 2.77 (t, 2H, *J* = 7.2 Hz, CH_3-S-CH_2-CH_2-C**H**$_2$-N-), 2.45 (t, 2H, *J* = 7.2 Hz, CH_3-S-C**H**$_2$-CH_2-CH_2-N-), 2.05 (s, 3H, C**H**$_3$-S-CH_2-CH_2-CH_2-N-), 1.76 (m, 2H, CH_3-S-CH_2-C**H**$_2$-CH_2-N-). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 138.65 (d, 2C, *J* = 184 Hz, -N=**C**H-CH=CH-N-), 128.75 (d, 2C, *J* = 184 Hz, -N=CH-CH=**C**H-N-), 104.96 (d, 2C, *J* = 176 Hz, -N=CH-**C**H=CH-N-), 66.73 (t, 2C, *J* = 149 Hz, -N-**C**H$_2$-N-), 47.67 (t, 1C, *J* = 137 Hz, -CH_3-S-CH_2-CH_2-**C**H$_2$-N-), 30.43 (t, 1C, *J* = 137

Hz, CH_3-S-**C**H_2-CH_2-CH_2-N-), 25.73 (t, 1C, *J* = 127 Hz, CH_3-S-CH_2-**C**H_2-CH_2-N-), 14.43 (q, 1C, *J* = 137 Hz, **C**H_3-S-CH_2-CH_2-CH_2-N-). IR (liquid neat; cm^{-1}): 3110 (w), 2915 (w), 2859 (w), 1512 (m), 1439 (m), 1393 (s), 1349 (m), 1277 (m), 1247 (s), 1128 (s), 1084 (s), 1044 (s), 961 (s), 917 (m), 878 (w), 749 (s), 652 (m), 616 (s).

2.3.7.N-((1H-pyrazol-1-yl)methyl)-N-(cyclohexylmethyl)(1H-pyrazol-1-yl)methanamine Co(II) chloride ***[L_ACoCl$_2$]***

A solution of **L_A** (0.273 g, 1.00 mmol) in dried EtOH (10.0 mL) was added to EtOH (10.0 mL) solution of $CoCl_2\cdot 6H_2O$ (0.237 g, 1.00 mmol) at room temperature. The blue powder obtained after stirring at 12 h was filtered and washed with ethanol (50.0 mL × 2), followed by washing with Et_2O (50.0 mL × 2) to yield final product (0.360 g, 89.3%). Crystals suitable for the X-ray study of **[L_ACoCl$_2$]** were obtained within five days from mixture of n-hexane (10.0 mL) and CH_2Cl_2 (10.0 mL) of **[L_ACoCl$_2$]** (0.100 g). Analysis calculated for $C_{15}H_{23}Cl_2CoN_5$: C, 44.6, H, 5.75, N, 17.3. Found: C, 44.9, H, 5.81, N, 17.1%. IR (solid neat; cm^{-1}): 3743 (w), 3104 (w), 2926 (w), 2850 (w), 1698 (w), 1649 (w), 1514 (w), 1453 (m), 1408 (m), 1317 (w), 1248 (m), 1165 (s), 1068 (s), 986 (m), 913 (w), 776 (s), 722 (s), 645 (w), 611 (m).

2.3.8. N,N-bis((1H-pyrazol-1-yl)methyl)-2,6-diethylbenzenamine Co(II) chloride ***[L_BCoCl$_2$]***

The **[L_BCoCl$_2$]** was prepared according to the similar procedure described for **[L_ACoCl$_2$]** except utilizing **L_B** (0.309 g, 1.00 mmol). The blue powder was filtered and washed with EtOH (50.0 mL × 2), followed by washing with Et_2O (50.0 mL × 2) (0.380 g, 86.8%). Crystals suitable for the X-ray study of **[L_BCoCl$_2$]** were obtained within five days from Et_2O (10.0 mL) diffusion into DMF solution (10.0 mL) of **[L_BCoCl$_2$]** (0.100 g).

Analysis calculated for $C_{18}H_{23}Cl_2CoN_5$: C, 49.2, H, 5.28, N, 15.9. Found: C, 48.8, H, 5.45, N, 15.1%. IR (solid neat; cm^{-1}): 3854 (s), 3743 (s), 3616 (m), 3120 (w), 2969 (w), 1835 (w), 1745 (m), 1695 (s), 1649 (s), 1517 (s), 1460 (s), 1409 (s), 1303 (m), 1254 (m), 1173 (s), 1067 (s), 982 (m), 773 (s), 643 (w).

2.3.9.N,N-bis((1H-pyrazol-1-yl)methyl)-4-bromobenzenamine Co(II) chloride ***[L_CCoCl$_2$]***

The **[L_CCoCl$_2$]** was prepared according to the similar procedure described for **[L_ACoCl$_2$]** except utilizing **L_C** (0.332 g, 33.2 mg, 1.00 mmol). The blue powder was filtered and washed with EtOH (50.0 mL × 2), followed by washing with Et_2O (50.0 mL × 2) (0.370 g, 80.0%). Crystals suitable for the X-ray study of **[L_CCoCl$_2$]** were obtained within five days from Et_2O (10.0 mL) diffusion into DMF solution (10.0 mL) of **[L_CCoCl$_2$]** (0.100 g). Analysis calculated for $C_{14}H_{14}BrCl_2CoN_5$: C, 36.3, H, 3.05, N, 15.1. Found: C, 35.7, H, 2.97, N, 14.9%. IR (solid neat; cm^{-1}): 3845 (w), 3743 (m), 3616 (w), 3107 (w), 1835 (w), 1694 (m), 1648 (m), 1496 (m), 1406 (m), 1309 (m), 1247 (m), 1165 (s), 1101 (s), 992 (m), 767 (s), 613 (m), 575 (w).

2.3.10. N,N-bis((1H-pyrazol-1-yl)methyl)cyclohexanamine Co(II) chloride ***[L_DCoCl$_2$]***

The **[L_DCoCl$_2$]** was prepared according to the similar procedure described for **[L_ACoCl$_2$]** except utilizing **L_D** (0.259 g, 1.00 mmol). The blue powder was filtered and washed with EtOH (50.0 mL × 2), followed by washing with Et_2O (50.0 mL × 2) (0.310 g, 80.0%). Crystals suitable for the X-ray study of **[L_DCoCl$_2$]** were obtained within five days from Et_2O (10.0 mL) diffusion into DMF solution (10.0 mL) of **[L_DCoCl$_2$]** (0.100 g). Analysis calculated for $C_{14}H_{21}Cl_2CoN_5$: C, 43.2, H, 5.44, N, 18.0. Found: C, 43.1, H, 5.46, N, 18.1%. IR (solid neat; cm^{-1}): 3127 (w), 3111 (w), 2934 (w), 2859 (w), 1750 (w), 1518 (w), 1454 (m), 1402 (s), 1279 (s), 1196 (m), 1167 (m), 1117 (s), 1098 (m), 924 (w), 843 (w), 777 (s), 759 (s), 611 (s).

2.3.11. N,N-bis((1H-pyrazol-1-yl)methyl)(furan-2-yl)methanamine Co(II) chloride ***[L$_E$CoCl$_2$]***

The **[L$_E$CoCl$_2$]** was prepared according to the similar procedure described for **[L$_A$CoCl$_2$]** except utilizing **L$_E$** (0.257 g, 1.00 mmol). The blue powder was filtered and washed with EtOH (50.0 mL × 2), followed by washing with Et_2O (50.0 mL × 2) (0.310 g, 75.6%). Crystals suitable for the X-ray study of **[L$_E$CoCl$_2$]** were obtained within five days from Et_2O (10.0 mL) diffusion into DMF solution (10.0 mL) of **[L$_E$CoCl$_2$]** (0.100 g). Analysis calculated for $C_{15}H_{15}Cl_2CoN_5O$: C, 40.3, H, 3.91, N, 18.1. Found: C, 40.2, H, 3.89, N, 17.9%. IR (solid neat; cm^{-1}): 3824 (w), 3746 (w), 3126 (w), 1649 (w), 1511 (w), 1458 (w), 1396 (m), 1340 (w), 1277 (m), 1195 (w), 1107 (m), 1067 (m), 1016 (m), 988 (w), 845 (w), 764 (s), 645 (w), 605 (m).

2.3.12. N,N-bis((1H-pyrazol-1-yl)methyl)-2-methoxyethanamine Co(II) chloride ***[L$_F$CoCl$_2$]***

The **[L$_F$CoCl$_2$]** was prepared according to the similar procedure described for **[L$_A$CoCl$_2$]** except utilizing **L$_F$** (0.235 g, 1.00 mmol). The blue powder was filtered and washed with EtOH (50.0 mL × 2), followed by washing with Et_2O (50.0 mL × 2) (0.209 g, 57.4%). Crystals suitable for the X-ray study of **[L$_F$CoCl$_2$]** were obtained within five days from Et_2O (10.0 mL) diffusion into MeOH solution (10.0 mL) of **[L$_F$CoCl$_2$]** (0.100 g). Analysis calculated for $C_{11}H_{17}Cl_2CoN_5O$: C, 36.2, H, 4.69, N, 19.1. Found: C, 36.7, H, 4.85, N, 19.1%. IR (solid neat; cm^{-1}): 3123 (w), 2397 (w), 2872 (w), 2819 (w), 1684 (w), 1541 (m), 1438 (s), 1405 (s), 1351 (w), 1317 (m), 1283 (m), 1245 (m), 1140 (s), 992 (w), 923 (w), 781 (s), 766 (s), 647 (m), 609 (s), 570 (w).

2.3.13. N,N-bis((1H-pyrazol-1-yl)methyl)-3-(methylthio)propan-1-amine Co(II) chloride [L_GCoCl$_2$]

The **[L_GCoCl$_2$]** was prepared according to the similar procedure described for **[L_ACoCl$_2$]** except utilizing **L_G** (0.265 g, 1.00 mmol). The blue powder was filtered and washed with EtOH (50.0 mL × 2), followed by washing with Et_2O (50.0 mL × 2) (0.320 g, 81.0%). Crystals suitable for the X-ray study of **[L_GCoCl$_2$]** were obtained within five days from Et_2O (10.0 mL) diffusion into DMF solution (10.0 mL) of **[L_GCoCl$_2$]** (0.100 g). Analysis calculated for $C_{12}H_{19}Cl_2CoN_5S$: C, 36.4, H, 4.85, N, 17.7. Found: C, 36.2, H, 4.85, N, 16.6%. IR (solid neat; cm^{-1}): 3134 (w), 1510 (w), 1468 (m), 1453 (m), 1403 (s), 1388 (m), 1280 (s), 1235 (m), 1138 (m), 1096 (w), 1063 (s), 1019 (m), 962 (m), 795 (s), 773 (s), 648 (w), 610 (s), 566 (w).

2.4. X-ray crystallographic studies

A blue 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 under nitrogen cold stream (200 K). Data collection and integration were performed with SMART and SAINT-Plus software packages [47]. Semi-empirical absorption corrections based on equivalent reflections were applied by SADABS [48]. Structures were solved by direct methods and refined using a full-matrix least-squares method on F^2 using SHELXTL [49]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added to their geometrically ideal positions. Crystallographic data and refinement parameters are listed in Table 1.

2.5. General Polymerization procedure of methyl methacrylate

In a Schlenk line, 15.0 μmol of initiators, (5.77 mg for **[L_ACoCl$_2$]**, 6.59 mg for **[L_BCoCl$_2$]**, 6.93 mg for **[L_CCoCl$_2$]**, 5.84 mg for **[L_DCoCl$_2$]**, 5.81 mg for **[L_ECoCl$_2$],** 5.48 mg for **[L_FCoCl$_2$]** or 5.93 mg for **[L_GCoCl$_2$]**) was dissolved in dried toluene (10.0 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. The MMA (5.00 mL, 47.10 mmol) was added to the above reaction mixture and stirred for 2 h at 60 °C to obtain a viscous solution. Polymerization was terminated by adding MeOH (2.00 mL). The reaction mixture was poured into a large quantity of MeOH (500 mL), and 35% HCl (5.00 mL) was injected to remove the remaining co-catalyst (MMAO). White PMMA was obtained by filtration, washed by MeOH (250 mL × 2), and dried under vacuum at a mild temperature for 24 h.

3. Results and Discussion

3.1. Synthesis and chemical properties

The synthesis of ligands used in the current study was accomplished by treating various substituted amines with 1H-pyrazolyl-1-methanol in CH_2Cl_2, showing high yields of 80% to 94%. The corresponding Co(II) complexes **[L_nCoCl$_2$]** ($L_n = L_A – L_G$) were obtained by treating [$CoCl_2.6H_2O$] with ligands in anhydrous EtOH (approximately 80% to 89% yields) (Scheme 1). The synthesised ligands and resultant complexes were structurally characterised using various spectroscopic techniques and their results are consistent with the ligands and molecular formulae of the Co(II) complexes. All synthesised Co(II) are stable to both heat and moisture and are paramagnetic, preventing NMR analysis. In addition, these ligands show bidentate coordination (*N,N′*) and tridentate coordination (*N,N′,N*) depending on the orientation of the various *N′*-substituents of the amine moiety to the plane of the pyrazole and metal centre.

3.2. Description of X-ray structures

Structural determination by X-ray diffraction revealed monomeric structures for **[L_nCoCl$_2$]** ($L_n = L_A – L_G$) (Fig. 1 – 7). The selected bond distances and angles are presented in Table 2. It is worth noting that the metal centre in **[L_nCoCl$_2$]** ($L_n = L_A – L_C$) is bonded to their corresponding ligands through the nitrogen atoms of the pyrazolyl moiety in a bidentate manner, forming an eight-membered chelate ring. The resultant geometry around the Co(II) centre exhibited slightly distorted tetrahedral configuration. Geometric distortion from ideal angles can be explained by the need to accommodate the bulky eight-membered chelate ring. Such bulky chelate rings are rare due to the destabilisation caused by non-bonding interactions within the eight-membered rings due to unfavourable torsion angles imposed by the ring size. The presence of sterically demanding substituents and hetero-atoms may contribute to the stability of the eight-membered chelate ring. The geometry around the Co(II) centre in **[L_nCoCl$_2$]** ($L_n = L_D – L_G$) complexes can be best described as distorted trigonal bipyramid with an σ plane of symmetry. These complexes adopted a five-coordinated geometry through coordination of $N_{pyrazole}$ and N_{amine} atoms to the metallic centre. The orientation of *N′*-substituents attached to amine with respect to the plane of the pyrazole ring depends on the nature of the attached moiety.

The average Co–$N_{pyrazole}$ bond lengths for **[L_nCoCl$_2$]** ($L_n = L_A – L_C$) and **[L_nCoCl$_2$]** ($L_n = L_D – L_G$) are 2.017Å and 2.028 Å, respectively, and are comparable to Co(II) complexes [41]. Similarly, the average Co–$Cl_{terminal}$ bond lengths range from 2.239(1) Å to 2.243(1) Å for **[L_nCoCl$_2$]** ($L_n = L_A – L_C$), while for **[L_nCoCl$_2$]** ($L_n = L_D – L_G$) it ranges from

2.257(1) Å to 2.309(1) Å. Monomeric **[L_nCoCl_2]** ($L_n = L_A - L_C$) complexes exhibit a four-coordinated geometry due to the steric effect of the ligand; the bond length of Co–N_{amine} are 3.575(3) Å, 3.437(6) Å, and 3.292(5) Å, which indicates a non-coordinative interaction between the *N* atom of the *N'*-substituted amine moiety and Co(II) atom [50,51]. On the other hand, **[L_nCoCl_2]** ($L_n = L_D - L_G$) adopted a five-coordinated geometry due to weak interactions between the *N* of the cyclohexyl/furan/3-(methylthio)propan-1-amine and the cobalt metal atom based on the Co-N_{amine} bond length of 2.466(4) Å to 2.522 (6) Å.

The bite angles $N_{pyrazole}$-Co-$N_{pyrazole}$ were 108.1(1)°, 115.3(2)°, and 114.9(2)°, while $Cl_{terminal}$-Co-$Cl_{terminal}$ angles were 117.28(5)°, 119.48(5)°, and 116.15(5)° for **[L_ACoCl_2]**, **[L_BCoCl_2],** and **[L_CCoCl_2]**, respectively. Similarly, the $N_{pyrazole}$-Co-$N_{pyrazole}$ angles were 108.3(2)°, 109.1(2)°, 115.0(1)°, and 113.1(1)°, and the $Cl_{terminal}$-Co-$Cl_{terminal}$ angles were 103.18(5)°, 103.13(5)°, 106.76(4)°, and 108.12(5)° for **[L_DCoCl_2]**, **[L_ECoCl_2], [L_FCoCl_2]** and **[L_GCoCl_2]**, respectively [43]. Although, we have not done the calculation on the electronic stability of two different coordinated Co(II) complexes, we carefully suggest by judging from the molecular structures of Co(II) complexes that the substituent R_1 is oriented toward coordination sphere around Co(II) metal, hampers geometrically the coordination of nitrogen in R_1 substituted amine moiety to cobalt metal center. For example, the substituent R_1 in ligands **L_A** – **L_C** occupy the inside coordination space thus producing tetrahedral **[L_nCoCl_2]** ($L_n = L_A - L_c$). However, in case of ligands **L_D** – **L_G**, the substituent R_1 is located in out of coordination sphere around metal and allowing the coordination of nitrogen in R_1 substituted amine unit to cobalt metal center, thus giving distorted trigonal bipyramidal **[L_nCoCl_2]** ($L_n = L_D - L_G$). It seems that the occupation of coordination sphere around Co(II) metal by substituent R_1 in ligands was not obviously irrelevant to the functionality of substituent R_1.

3.3. Discussion of MMA polymerisation

Methyl methacrylate (MMA) polymerisation was investigated with the synthesised Co(II) complexes. The representative results are shown in Table 3. All Co(II) complexes could be activated with modified methylaluminoxane (MMAO) to polymerise MMA, yielding poly(methylmethacrylate) (PMMA) with glass transition temperatures (T_g) ranging from 123°C to 132°C [52-54]. The polymers were isolated as white solids and characterised using gel permeation chromatography (GPC) in THF using standard polystyrene as a reference.

To confirm the catalytic activity of Co(II) complexes for MMA polymerisation, blank tests were performed with anhydrous metal starting material **[$CoCl_2$]** (4.03×10^4 g PMMA/mol·Co·h) or MMAO (1.40×10^4 g PMMA/mol·Al·h) alone at a specific temperature. It has been found that amongst the four-coordinated complexes, i.e. **[L_ACoCl_2]** ($L_n = L_A – L_C$), **[L_ACoCl_2]** (5.77×10^4 g PMMA/mol·Co·h) with a cyclohexyl pendent group exhibited higher activity at 60°C and resulted in PMMA with a greater yield, which may be due to better solubility of the resultant catalytic species compared to the counterparts. Among the five-coordinated Co(II) complexes, i.e. **[L_nCoCl_2]** (L_n= L_D – L_G), the MMA polymerisation activity of complex **[L_DCoCl_2]** (8.33×10^4 g PMMA/mol Co.h) at 60°C, which contains a cyclohexyl pendent group at the *N* atom of the amine moiety that tilted towards the pyrazole ring and located near the cobalt metal (Fig. 4), was significantly higher than the counterparts (Table 3, entries 6 – 9). To explore the effect of temperature on the activity of MMA polymerisation, MMA polymerisation was performed at various temperatures; i.e. 30, 60, 90°C, and the maximum yield and activity were observed at 60°C. Thus, this optimised temperature was used for further polymerisation reactions. In addition, **[L_DCoCl_2]** yielded the narrowest PDI and the highest molecular weight of PMMA compared to the other five-coordinated Co(II) complexes in the current study. This high activity may have resulted from the increased solubility of **[L_DCoCl$_2$]** in toluene compared to other Co(II) complexes. Specifically, **[L_GCoCl$_2$]** showed the lowest activity (2.53×10^4 g PMMA/mol Co.h) due to its poor solubility in reaction media. Since Co(II) complexes themselves have poor solubility in toluene, the co-catalyst MMAO was applied to the Co(II) complex to form a soluble cationic catalyst species. The amount of MMAO was decreased to 250 volumes of MMAO for MMA polymerisation, but the yield of PMMA also decreased. Moreover, PDI and tacticity were not affected by the amount of MMAO. Thus, additional MMAO may function as a scavenger from 500 volumes of MMAO used during MMA polymerisation.

Relative to previously reported cobalt complexes with *N,N*-bis(1H-pyrazolyl-1-methyl)aniline [43], the Co(II) complexes exhibited higher molecular weights (12.6×10^5 g/mol for **[L_DCoCl$_2$]**) of syndiotactic PMMA, narrower PDIs, and higher catalytic activities (8.33×10^4 g PMMA/mol·Co·h) at 60°C. The PDIs of the Co(II) complexes ranged from 1.33 to 1.97. In general, the PDI range narrowed with increasing molecular weight of PMMA (Table 3, entries 6 – 9) [55,56].

The triad microstructure of PMMA was analysed using ^{1}H-NMR spectroscopy [57,58]. The tacticity of PMMA ranged around syndiotactic (*rr*, δ 0.85), atactic (*mr*, δ 1.02), and isotactic (*mm*, δ 1.21). The syndiotacticity ranged from 0.68 to 0.70 in almost all cases, irrespective of their coordination mode and catalytic activities, but was higher than the starting materials (Table 3, entries 1 and 2). This also indicated that syndiotacticity was only slightly affected by substituents on the ligand architecture. A higher T_g typically represents higher optical quality and syndiotacticity content of PMMA. The T_g of isotactic PMMA, which is produced by radical commercial processes, is around 65ºC. Thus, the non-radical-mediated polymerisation of MMA using complex catalysts achieves a high T_g for high content of syndiotactic PMMA [59-62]. However, catalytic activity was affected to a greater extent by steric influences of the substituents at the amine moiety, as determined by the relative amounts of PMMA product yielded. The MMA polymerisation activity of Co(II) complexes should be considered a function of the electron density around the metal centre. However, the molecular weight of PMMA was affected by the steric influences of *N′*-substitution at the amine moiety, where the direction was with respect to the plane of the two pyrazole rings. In addition, when MMA polymerization was done using five equivalents of radical inhibitor TEMPO (2,2,6,6-tetramethylpiperidinyloxy), the yield of PMMA did not much reduce (ca. 2–5% yield). It was an indirect evidence that the mechanism of coordination polymerization is not a radical mechanism, although the moderate syndiotacticity of Co(II) complexes around ca. 70% was not sufficient to confer a mechanism of coordination polymerization [63].

4. Conclusion

Novel Co(II) complexes **[L_nCoCl$_2$]** (L_n = L_A – L_G) were prepared by reaction of [$CoCl_2 \cdot 6H_2O$] with *N′*-substituted *N*,*N*-bis(1-pyrazolyl)methylamine and its derivatives. The coordination of these ligands to the Co(II) metal revealed that **[L_nCoCl$_2$]** (L_n = L_A – L_C) exists in four-coordinated and **[L_nCoCl$_2$]** (L_n = L_D – L_G) exists in five-coordinated geometries, respectively, depending on the interactions between the nitrogen atom of the *N′*-substitution in the amine moiety and the metal centre. The formation of four-coordinate or five-coordinate monomers was determined based on steric effects of *N′*-substituents on the amine residue around the cobalt centre. The catalytic activity of **[L_nCoCl$_2$]** (L_n = L_A – L_G) for MMA polymerisation in the presence of MMAO were investigated: the five-coordinated **[L_DCoCl$_2$]** (8.33×10^4 g PMMA/mol Co·h) showed higher catalytic activity than the other Co(II) complexes in this study. The PDIs of the resultant PMMA did not strongly depend on the substituent effects of the catalyst. However, the molecular weight of the obtained PMMA and the catalytic activities of Co(II) complexes were influenced by the steric encumbrance of the *N′*-substitution amine moiety depending on the orientation of substituents with respect to the plane of the two pyrazole rings.

Supplementary materials

CCDC 1055572–1055578 contains the supplementary crystallographic data for **[L_ACoBr$_2$]**, **[L_BCoBr$_2$]**, **[L_CCoBr$_2$]**, **[L_DCoBr$_2$]**, **[L_ECoBr$_2$]**, **[L_FCoBr$_2$]** and **[L_GCoBr$_2$]**, 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.

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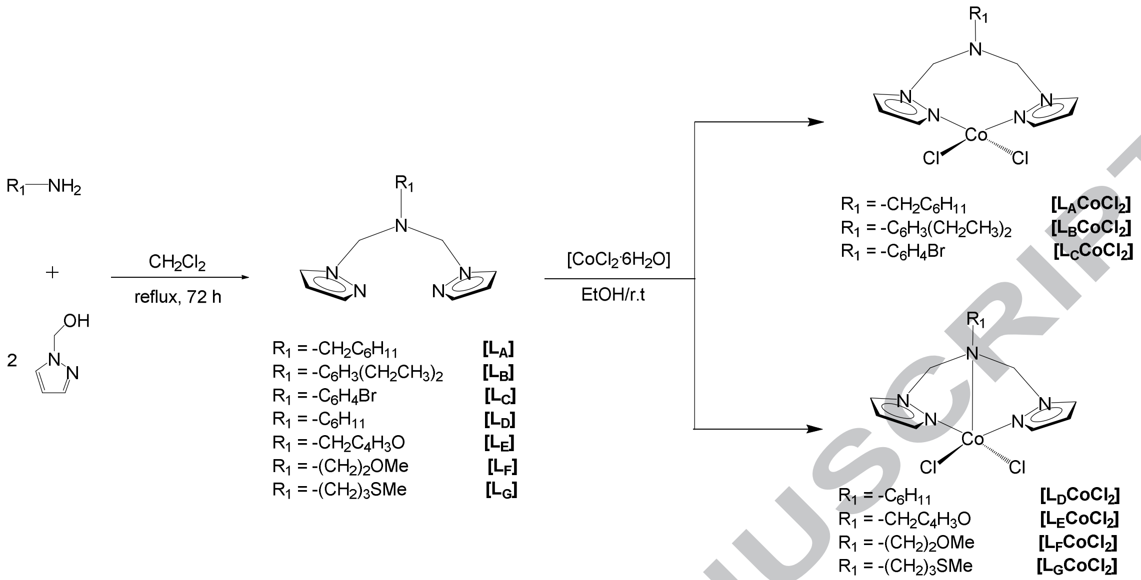


Scheme 1. Synthesis of ligands ($L_n = L_A - L_G$) and their corresponding Co(II) complexes.

Table 1. Crystal data and Structure refinement for **[L_nCoCl$_2$]** ($L_n = L_A – L_G$).

	[L_ACoCl$_2$]	**[L_BCoCl$_2$]**	**[L_CCoCl$_2$]**	**[L_DCoCl$_2$]**	**[L_ECoCl$_2$]**	**[L_FCoCl$_2$]**	**[L_GCoCl$_2$]**
Empirical formula	$C_{15}H_{23}Cl_2CoN_5$	$2(C_{18}H_{23}Cl_2CoN_5),O$	$C_{14}H_{14}Cl_2BrCoN_5$	$C_{14}H_{21}Cl_2CoN_5$	$C_{15}H_{15}Cl_2CoN_5O$	$C_{11}H_{17}Cl_2CoN_5O$	$C_{12}H_{19}Cl_2CoN_5S$
Formula weight	403.21	894.49	462.04	389.19	387.13	365.13	395.21
Crystal system	Monoclinic	Rhombohedral	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	R_{-3}	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P_{na2(1)}$	$P2_1/c$
Unit cell dimensions	a = 8.148(1) Å	a = 17.932(1) Å	a = 8.6341(4) Å	a = 8.468(2) Å	a = 8.4122(9) Å	a = 17.1336(7) Å	a = 8.9428(6) Å
	b = 13.626(2) Å	b = 17.932(1) Å	b = 14.9323(7) Å	b = 13.194(3) Å	b = 12.517(1) Å	b = 7.7035(3) Å	b = 8.2289(5) Å
	c = 16.539(2) Å	c = 17.932(1) Å	c = 13.8870(6) Å	c = 15.270(3) Å	c = 14.636(2) Å	c = 23.576(1) Å	c = 23.365(2) Å
	α = 90°	α = 114.05°	α = 90°	α = 90°	α = 90°	α = 90°	α = 90°
	β = 95.353(3)°	β = 114.05°	β = 98.664(1) °	β = 90.542(4)°	β = 93.411(2)°	β = 90°	β = 92.681(1)°
	γ = 90°	γ = 114.05°	γ = 90°	γ = 90°	γ = 90°	γ = 90°	γ = 90°
Volume (Å^3)	1828.1(4)	3490.9(4)	1770.0(1)	1706.0(6)	1538.3(3)	3111.7(2)	1717.5(2)
Z	4	3	4	4	4	8	4
Density (calculated) (g/cm^3)	1.465	1.276	1.734	1.515	1.762	1.559	1.528
Absorption coefficient mm^{-1}	1.236	0.980	3.533	1.322	1.471	1.448	1.431
F(000)	836	1386	916	804	788	1496	812
Crystal size (mm^3)	0.19 × 0.18 × 0.14	0.28 × 0.28 × 0.19	0.27 × 0.14 × 0.07	0.30 × 0.23 × 0.18	0.19 × 0.17 × 0.14	0.18 × 0.16 × 0.08	0.23 × 0.20 × 0.12
Theta range for data collection	1.94 to 28.29°	1.35 to 28.30°	2.02 to 28.29°	2.04 to 28.33°	2.14 to 28.32°	2.38 to 28.45°	2.28 to 28.29°
Reflections collected	13479	26254	12675	12428	11255	88656	11814
Independent reflections	4535 [R_{int} = 0.0787]	5774 [R_{int} = 0.0886]	4372 [R_{int} = 0.0249]	4234 [R_{int} = 0.0517]	3820 [R_{int} = 0.0441]	7803 [R_{int} = 0.0896]	4190 [R_{int} = 0.0221]
No. parameters	208	246	208	199	199	363	191
Goodness-of-fit on F^2	0.807	0.843	1.136	1.137	1.131	1.068	1.201
Final *R* and *wR*$_2$ indices [$I>2\sigma(I)$]	R_1 = 0.0428, wR_2 = 0.0699	R_1 = 0.0552, wR_2 = 0.1478	R_1 = 0.0353, wR_2 = 0.0671	R_1 = 0.0491, wR_2 = 0.0880	R_1 = 0.0409, wR_2 = 0.0819	R_1 = 0.0350, wR_2 = 0.0670	R_1 = 0.0369, wR_2 = 0.0818
R indices (all data)	R_1 = 0.1246, wR_2 = 0.1016	R_1 = 0.1381, wR_2 = 0.1923	R_1 = 0.0637, wR_2 = 0.1152	R_1 = 0.1020, wR_2 = 0.1413	R_1 = 0.0952, wR_2 = 0.1457	R_1 = 0.0604, wR_2 = 0.0768	R_1 = 0.0576, wR_2 = 0.1458
Largest diff. peak and hole (e.Å^{-3})	0.642 and -0.793	0.953 and -0.585	0.816 and -0.913	0.915 and -1.167	1.054 and -1.313	0.454 and -0.293	0.840 and -0.987

Table 2. The selected bond lengths (Å) and angles (°) of **[L_nCoCl_2]** ($L_n = L_A – L_G$).

[L_ACoCl_2]		**[L_BCoCl_2]**		**[L_CCoCl_2]**	
Co(1)-N(4)	2.008(3)	Co(1)-N(1)	2.018(4)	Co(1)-N(1)	2.009(4)
Co(1)-N(1)	2.019(3)	Co(1)-N(4)	2.024(4)	Co(1)-N(5)	2.021(4)
Co(1)-N(5)	3.575(3)	Co(1)-N(5)	3.437(6)	Co(1)-N(3)	3.292(5)
Co(1)-Cl(2)	2.241 (1)	Co(1)-Cl(1)	2.239 (1)	Co(1)-Cl(1)	2.242 (1)
Co(1)-Cl(1)	2.243 (1)	Co(1)-Cl(2)	2.243 (1)	Co(1)-Cl(2)	2.243 (1)
N(1)-C(1)	1.333(4)	N(1)-C(1)	1.344(6)	N(1)-C(1)	1.329(6)
N(1)-N(2)	1.348(4)	N(1)-N(2)	1.368(5)	N(1)-N(2)	1.359(5)
N(2)-C(3)	1.335(4)	N(2)-C(3)	1.329(6)	N(2)-C(3)	1.350(6)
N(2)-C(4)	1.476(4)	N(2)-C(4)	1.471(5)	N(2)-C(4)	1.457(5)
C(1)-C(2)	1.378(5)	C(1)-C(2)	1.383(7)	C(1)-C(2)	1.381(7)
N(4)-Co(1)-N(1)	108.1(1)	N(1)-Co(1)-N(4)	115.4 (2)	N(1)-Co(1)-N(5)	114.9(2)
N(4)-Co(1)-Cl(2)	104.8 (1)	N(1)-Co(1)-Cl(1)	107.1(1)	N(1)-Co(1)-Cl(1)	109.2 (1)
N(1)-Co(1)-Cl(2)	104.71(9)	N(4)-Co(1)-Cl(1)	107.9 (1)	N(5)-Co(1)-Cl(1)	106.4(1)
N(4)-Co(1)-Cl(1)	110.47(9)	N(1)-Co(1)-Cl(2)	103.8 (1)	N(1)-Co(1)-Cl(2)	103.2 (1)
N(1)-Co(1)-Cl(1)	110.93(9)	N(4)-Co(1)-Cl(2)	103.7(1)	N(5)-Co(1)-Cl(2)	107.3 (1)
Cl(2)-Co(1)-Cl(1)	117.28(5)	Cl(1)-Co(1)-Cl(2)	119.48(5)	Cl(1)-Co(1)-Cl(2)	116.15(5)
C(1)-N(1)-N(2)	105.8(3)	C(1)-N(1)-N(2)	105.1(4)	C(1)-N(1)-N(2)	105.4(4)
C(1)-N(1)-Co(1)	125.7(3)	C(1)-N(1)-Co(1)	126.7(3)	C(1)-N(1)-Co(1)	130.2(3)
N(2)-N(1)-Co(1)	128.1(2)	N(2)-N(1)-Co(1)	128.1(3)	N(2)-N(1)-Co(1)	124.3(3)
C(3)-N(2)-N(1)	111.0(3)	C(3)-N(2)-N(1)	111.0(4)	C(3)-N(2)-N(1)	111.0(4)

[L_DCoCl_2]		**[L_ECoCl_2]**		**[L_FCoCl_2]**		**[L_GCoCl_2]**	
Co(1)-N(1)	2.021(4)	Co(1)-N(4)	2.030(4)	Co(1)-N(1)	2.017(2)	Co(1)-N(5)	2.032(5)
Co(1)-N(3)	2.035(4)	Co(1)-N(1)	2.031(4)	Co(1)-N(5)	2.024(3)	Co(1)-N(1)	2.035(5)
Co(1)-N(5)	2.466(4)	Co(1)-N(5)	2.507(4)	Co(1)-N(3)	2.514(4)	Co(1)-N(4)	2.522(6)
Co(1)-Cl(1)	2.286 (1)	Co(1)-Cl(1)	2.257(1)	Co(1)-Cl(2)	2.268(1)	Co(1)-Cl(2)	2.281(2)
Co(1)-Cl(2)	2.295(1)	Co(1)-Cl(2)	2.305(1)	Co(1)-Cl(1)	2.306(1)	Co(1)-Cl(1)	2.286(2)
N(1)-C(1)	1.328(6)	N(1)-C(1)	1.337(6)	N(1)-C(1)	1.331(4)	N(1)-C(1)	1.337(7)
N(1)-N(2)	1.353(5)	N(1)-N(2)	1.358(5)	N(1)-N(2)	1.344(4)	N(1)-N(2)	1.361(6)
N(2)-C(3)	1.343(6)	N(2)-C(3)	1.345(6)	N(2)-C(3)	1.337(4)	N(2)-C(3)	1.359(7)
N(2)-C(4)	1.452(6)	N(2)-C(4)	1.459(6)	N(2)-C(4)	1.466(4)	N(2)-C(4)	1.453(7)
C(1)-C(2)	1.377(7)	C(1)-C(2)	1.395(7)	N(3)-C(4)	1.450(4)	C(1)-C(2)	1.400(9)
N(1)-Co(1)-N(3)	108.3(2)	N(4)-Co(1)-N(1)	109.1(2)	N(1)-Co(1)-N(5)	115.0(1)	N(4)-Co(1)-N(1)	115.7(2)
N(1)-Co(1)-Cl(1)	108.1(1)	N(4)-Co(1)-Cl(1)	121.2(1)	N(1)-Co(1)-Cl(2)	109.89(8)	N(4)-Co(1)-Cl(2)	99.7(2)
N(3)-Co(1)-Cl(1)	133.6(1)	N(1)-Co(1)-Cl(1)	119.3(1)	N(5)-Co(1)-Cl(2)	124.68(8)	N(1)-Co(1)-Cl(2)	98.6(1)
N(1)-Co(1)-Cl(2)	101.2(1)	N(4)-Co(1)-Cl(2)	98.5(1)	N(1)-Co(1)-Cl(1)	100.11(8)	N(4)-Co(1)-Cl(1)	119.8(2)
N(3)-Co(1)-Cl(2)	97.0(1)	N(1)-Co(1)-Cl(2)	100.7(1)	N(5)-Co(1)-Cl(1)	95.67(8)	N(1)-Co(1)-Cl(1)	111.1(1)
Cl(1)-Co(1)-Cl(2)	103.18(5)	Cl(1)-Co(1)-Cl(2)	103.13(5)	Cl(2)-Co(1)-Cl(1)	106.76(4)	Cl(2)-Co(1)-Cl(1)	108.63(7)
C(1)-N(1)-N(2)	105.8(4)	C(1)-N(1)-N(2)	105.4(4)	C(1)-N(1)-N(2)	105.5(2)	C(1)-N(1)-N(2)	106.5(5)
C(1)-N(1)-Co(1)	135.1(4)	C(1)-N(1)-Co(1)	133.3(3)	C(1)-N(1)-Co(1)	132.6(2)	C(1)-N(1)-Co(1)	132.3(4)
N(2)-N(1)-Co(1)	119.0(3)	N(2)-N(1)-Co(1)	120.3(3)	N(2)-N(1)-Co(1)	121.5(2)	N(2)-N(1)-Co(1)	121.2(3)
C(3)-N(2)-N(1)	110.6(4)	C(3)-N(2)-N(1)	110.7(4)	C(3)-N(2)-N(1)	111.3(3)	C(3)-N(2)-N(1)	110.3(5)

Table 3. Polymerization of MMA by **[L_nCoCl_2]** ($L_n = L_A – L_G$) in the presence of MMAO.

Entry	Catalyst[a]	Temp.	Yield[b]	Activity[c]	T_g[d]	Tacticity			M_w[e]	M_w/M_n[f]
		(℃)	(%)	×10^4 (g/molCat·h)	(℃)	%mm	%mr	%rr	×10^5 (g/mol)	
1	**[$CoCl_2$]**[g]	60	25.9	4.03	125	7.70	24.6	51.9	8.15	1.97
2	MMAO[h]	60	8.97	1.40	120	37.2	10.9	51.9	0.61	2.20
3	**[L_ACoCl_2]**	60	37.0	5.77	131	7.69	23.8	68.5	10.6	1.74
4	**[L_BCoCl_2]**	60	23.9	3.73	123	6.49	22.7	70.8	9.03	1.90
5	**[L_CCoCl_2]**	60	20.5	3.20	129	7.29	21.8	70.8	11.8	1.68
6	**[L_DCoCl_2]**	60	53.4	8.33	128	6.80	23.1	70.0	12.6	1.33
7	**[L_ECoCl_2]**	60	32.7	5.10	131	6.67	24.0	69.3	10.4	1.75
8	**[L_FCoCl_2]**	60	26.7	4.17	132	7.19	23.0	69.8	10.6	1.86
9	**[L_GCoCl_2]**	60	16.2	2.53	129	9.00	23.4	67.6	9.70	1.97

[a] [Co(II) catalyst]$_0$ = 15 µmol, [MMA]$_0$/[MMAO]$_0$/[Co(II) catalyst]$_0$ = 3100:500:1.

[b] Yield defined as mass of dried polymer recovered/mass of monomer used.

[c] Activity is (gPMMA)·(molCo·h)$^{-1}$.

[d] T_g is the glass transition temperature determined using a thermal analyzer.

[e] Determined using gel permeation chromatography (GPC) eluted with THF at room temperature by filtration with polystyrene calibration.

[f] M_n refers to the number average of molecular weights of PMMA.

[g] Blank polymerisation in which anhydrous **[$CoCl_2$]** was also activated by MMAO.

[h] Blank polymerisation with MMAO alone.

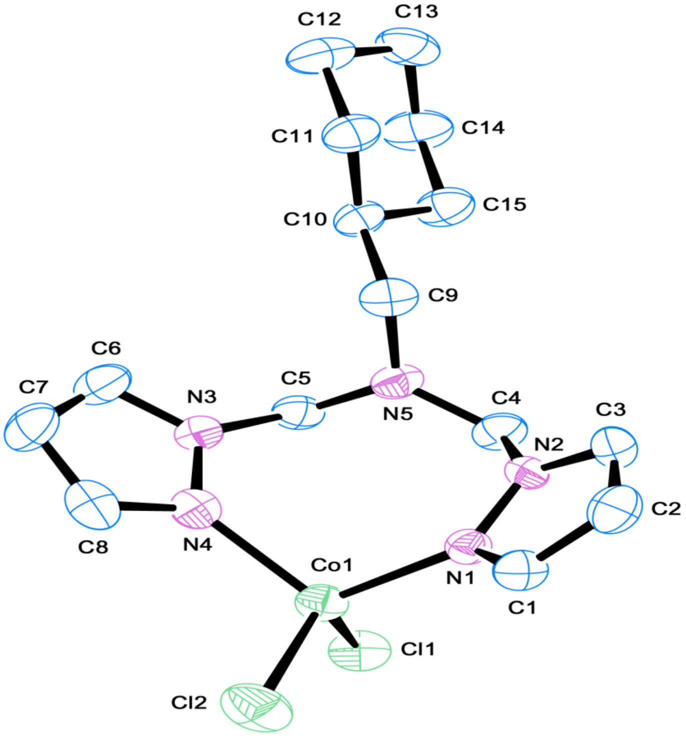


Fig. 1. ORTEP drawing of **[L_ACoCl$_2$]** with displacement at 30% probability. All hydrogen atoms are omitted for clarity. Symmetry codes are #1 -x+1,-y+1,-z+2; #2 -x+1,-y,-z; #3 -x+1,-y+1,-z; #4 x,-y+1/2, z.

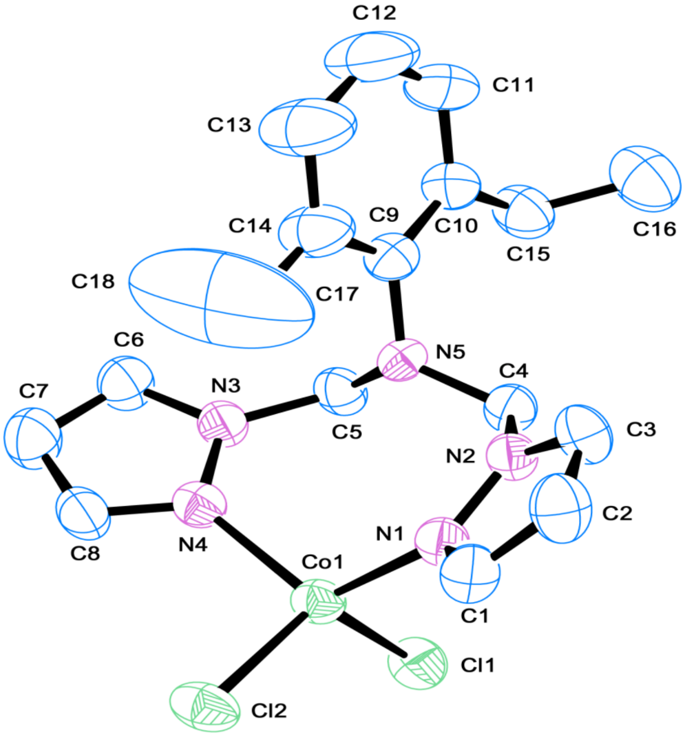


Fig. 2. ORTEP drawing of **[L_BCoCl$_2$]** with displacement at 30% probability. All hydrogen atoms are omitted for clarity. Symmetry codes are #1 -x+1,-y+1,-z+2; #2 -x+1,-y,-z; #3 -x+1,-y+1,-z; #4 x,-y+1/2, z.

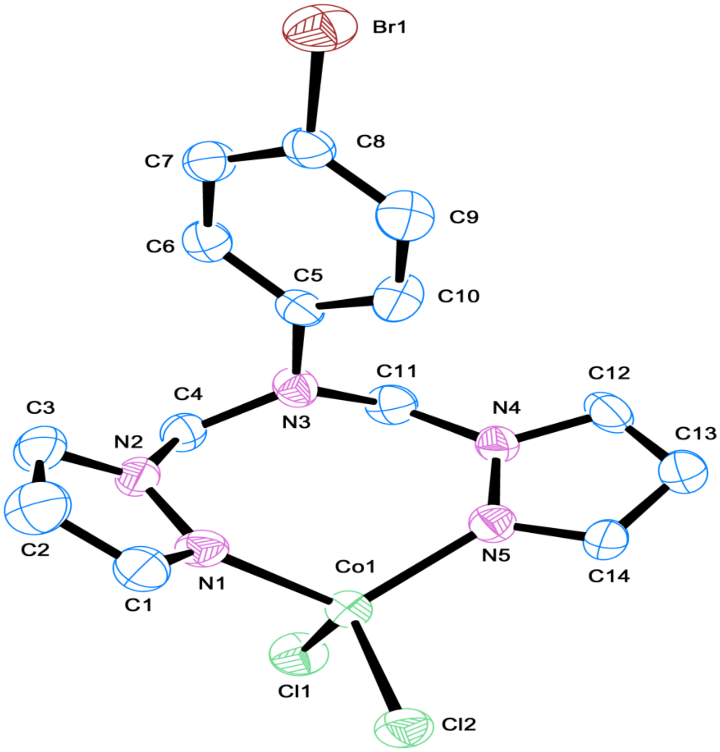


Fig. 3. ORTEP drawing of **[L_CCoCl$_2$]** with displacement at 30% probability. All hydrogen atoms are omitted for clarity. Symmetry codes are #1 -x+1,-y+1,-z+2; #2 -x+1,-y,-z; #3 -x+1,-y+1,-z; #4 x,-y+1/2, z.

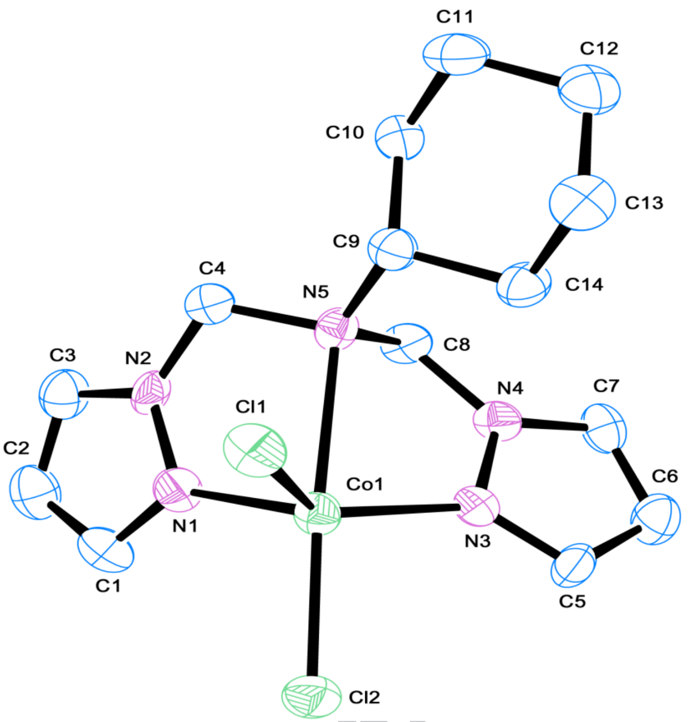


Fig. 4. ORTEP drawing of **[L_DCoCl$_2$]** with displacement at 30% probability. All hydrogen atoms are omitted for clarity. Symmetry codes are #1 -x+1,-y+1,-z+2; #2 -x+1,-y,-z; #3 -x+1,-y+1,-z; #4 x,-y+1/2, z.

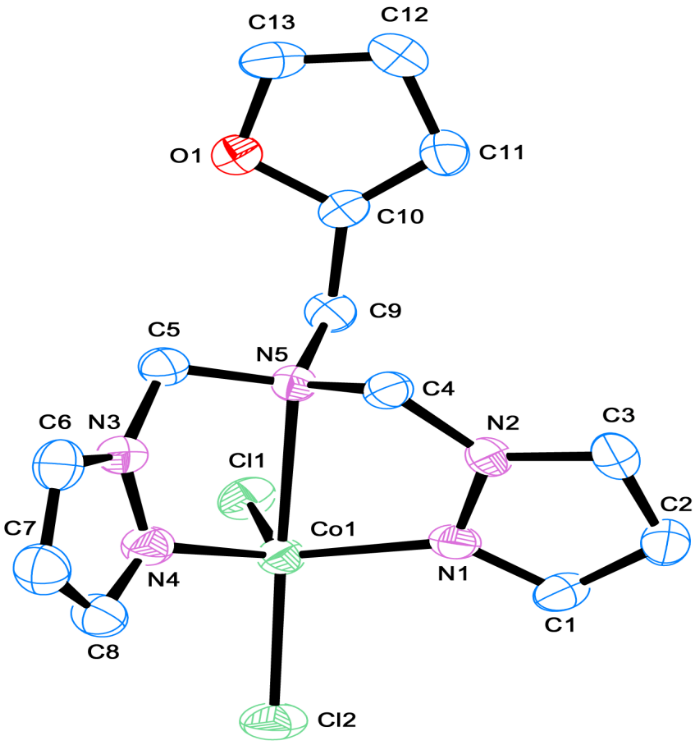


Fig. 5. ORTEP drawing of **[L_ECoCl$_2$]** with displacement at 30% probability. All hydrogen atoms are omitted for clarity. Symmetry codes are #1 -x+1,-y+1,-z+2; #2 -x+1,-y,-z; #3 -x+1,-y+1,-z; #4 x,-y+1/2, z.

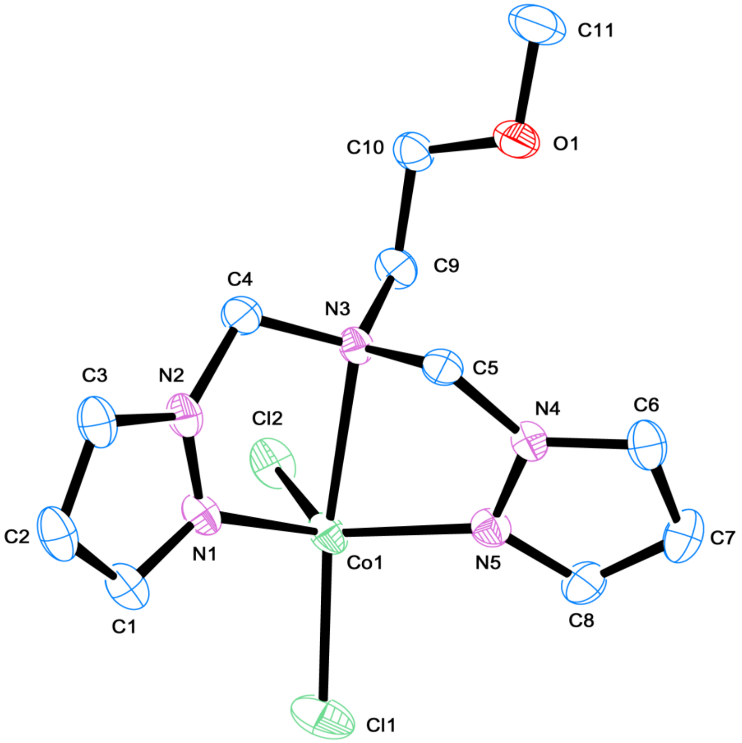


Fig. 6. ORTEP drawing of **[L$_F$CoCl$_2$]** with displacement at 30% probability. All hydrogen atoms are omitted for clarity. Symmetry codes are #1 -x+1,-y+1,-z+2; #2 -x+1,-y,-z; #3 -x+1,-y+1,-z; #4 x,-y+1/2, z.

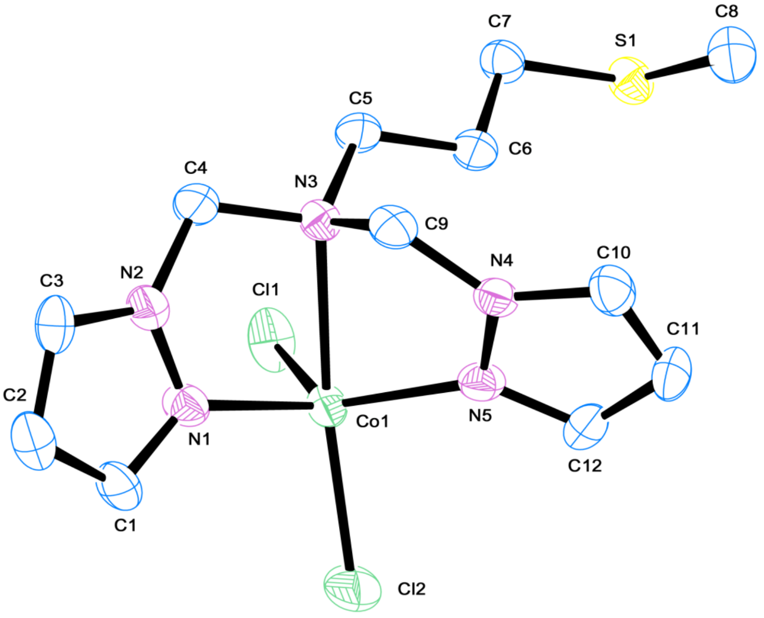


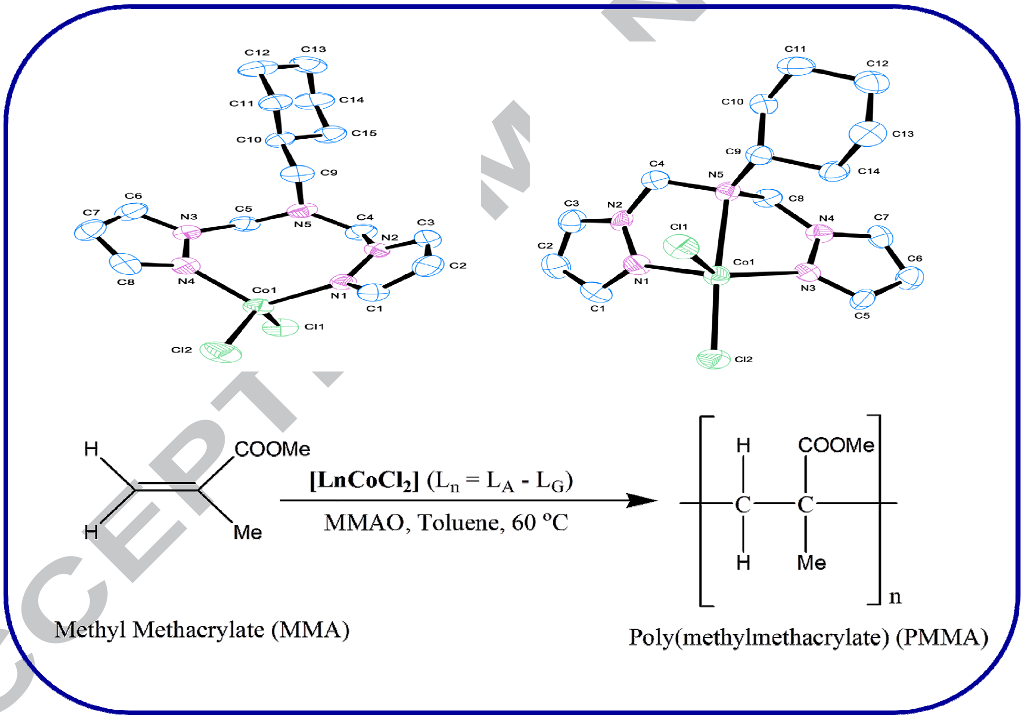
Fig. 7. ORTEP drawing of **[L$_G$CoCl$_2$]** with displacement at 30% probability. All hydrogen atoms are omitted for clarity. Symmetry codes are #1 -x+1,-y+1,-z+2; #2 -x+1,-y,-z; #3 -x+1,-y+1,-z; #4 x,-y+1/2, z.

Graphical Abstract (Synopsis)

Cobalt(II) Complexes Containing *N'*-Substituted *N,N',N*-bis((1H-pyrazol-1-yl)methyl)amine Ligands: The Formation of Four-Coordinate or Five-Coordinate Complexes as a Function of the *N'*-Substitution group in *N,N',N*-bis((1H-pyrazol-1-yl)methyl)amine

Sunghye Choi[a], Saira Nayab[b], Jongho Jeon[c], Sang Hyun Park[c,*], Hyosun Lee[a,*]

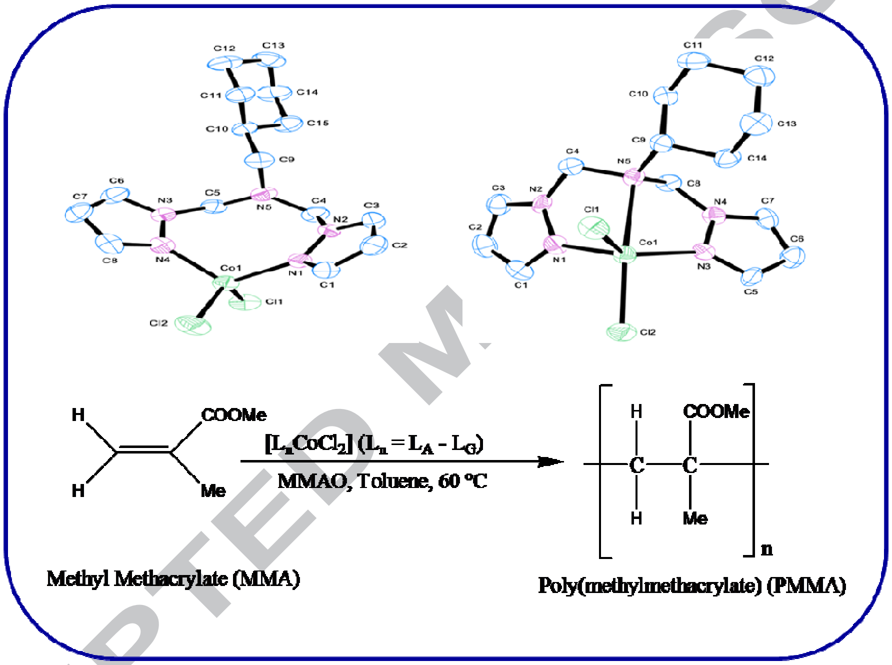
A new series of *N,N',N*-bis((1H-pyrazol-1-yl)methyl)amine supported Co(II) complexes have been synthesized and structurally characterized by X-ray diffraction studies. These Co(II) complexes exhibited diverse coordination geometries around the metal centre i.e. monomeric 4- or 5-coordinated structures determined by the steric encumbrance of the *N'*-substitution amine moiety. The catalytic activities of Co(II) complexes for methyl methacrylate polymerisation are investigated.



Graphical Abstract (Pictorial)

Cobalt(II) Complexes Containing *N'*-Substituted *N,N',N*-bis((1H-pyrazol-1-yl)methyl)amine Ligands: The Formation of Four-Coordinate or Five-Coordinate Complexes as a Function of the *N'*-Substitution group in *N,N',N*-bis((1H-pyrazol-1-yl)methyl)amine

Sunghye Choi[a], Saira Nayab[b], Jongho Jeon[c], Sang Hyun Park[c,*], Hyosun Lee[a,*]



Research Highlights

- Co(II) complexes with *N′*-substituted *N,N′,N*-bis((1H-pyrazol-1-yl)methyl)amine ligands are synthesized.
- The Co(II) complexes showed 4- or 5-coordinated geometries around cobalt centre.
- The Co(II) complexes proved to be active in MMA polymerization.