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Novel Cobalt(II) complexes containing *N*,*N*-di(2-picolyl)amine based ligands; Synthesis, characterization and application towards methyl methacrylate polymerisation

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ABSTRACT

The reaction of **[$CoCl_2 \cdot 6H_2O$]** with *N*′-substituted *N*,*N*-di(2-picolyl)amine ligands such as 1-cyclohexyl-*N*,*N*-bis(pyridin-2-ylmethyl)methanamine (**L_A**), 2-methoxy-*N*,*N*-bis(pyridin-2-ylmethyl)ethan-1-amine (**L_B**), and 3-methoxy-*N*,*N*-bis(pyridin-2-ylmethyl)propan-1-amine (**L_C**), yielded **[L_nCoCl_2]** ($L_n = L_A$, L_B and L_C), respectively. The Co(II) centre in **[L_nCoCl_2]** ($L_n = L_A$, and L_C) adopted distorted bipyramidal geometries through coordination of nitrogen atoms of di(2-picolyl)amine moiety to the Co(II) centre along with two chloro ligands. The 6-coordinated **[L_BCoCl_2]** showed a distorted octahedral geometry, achieved through coordination of the two pyridyl units, two chloro units, and bidentate coordination of nitrogen and oxygen in the *N*′-methoxyethylamine to the Co(II) centre. **[L_CCoCl_2]** (6.70×10^4 gPMMA/molCo h) exhibited higher catalytic activity for the polymerisation of methyl methacrylate (MMA) in the presence of modified methylaluminoxane (MMAO) compared to rest of Co(II) complexes. The catalytic activity was considered as a function of steric properties of ligand architecture and increased steric bulk around the metal centre resulted in the decrease catalytic activity. All Co(II) initiators yielded syndiotactic poly(methylmethacrylate) (PMMA).

1. Introduction

Metal-catalysed coordination polymerisation of methyl methacrylate (MMA) have gained much attention recently due to the ability (of coordination–addition polymerisation) to rapidly produce high molecular weight (M_W) poly(methylmethacrylate) (PMMA) with controlled stereoregularity [1]. The optical properties of PMMA are far improved with high glass transition temperature (T_g) which in turn depend on tacticity of PMMA (T_g of isotactic PMMA is about 65 °C, whereas syndiotactic PMMA exhibits T_g around 140 °C). That is why many attempts aiming to increase the syndiotacticity of PMMA were planned [2,3]. Transition metal complexes with appropriate ancillary ligand are crucial for achieving high degree of control over polymerisation as these metal complexes influence all steps of polymerisation such as initiation, propagation and termination [4–8]. Late transition metal complexes, due to their less oxophilic nature makes them likely targets for the development of catalysts for the polymerisation of polar monomers such as methyl methacrylate (MMA) [9–14]. Syndiotactic PMMA ($rr = 0.72$) produced *via* late transition metal catalysts was first described with Cp_2Ni–MAO [15]. Since then, important research has been conducted with late transition metal complexes such as (α-diimine)nickel, (pyridyl bisimine)iron(II), and (pyridyl bisimine)cobalt(II) complexes activated with MAO that resulted in PMMA with moderate syndiotacticity [16].

Recently reported by our group are Pd(II), Zn(II), Cu(II) and Pt(II) based catalytic systems with *N*′-substituted *N*,*N*-di(2-picolyl)amine ligands that yielded PMMA with moderate syndiotacticity [17–19]. Ligand architecture having *N*,*N*-di(2-picolyl)amine moiety and its various *N*′-substituted derivatives are known to form diverse coordination geometries from mononuclear to poly-nuclear with transition metals [20–34]. Furthermore the stereo-electronic properties of these ligands can be easily tuned by appropriate choice of substituents on pyridine ring or amine residue or on both moieties [35–42]. Thus keeping in view the importance and

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versatility of these architectures we explored several structural variations of *N*′-substituted *N*,*N*-di(2-picolyl)amine based complexes and their effect on MMA polymerisation [43].

In a continuation of our research work which has been synthesis and structure determination of transition metal complexes as a pre-catalyst towards MMA polymerisation, the current work has been focused on synthesis of Co(II) complexes bearing tridentate *N*′-substituted *N*,*N*-di(2-picolyl)amine with various steric and electronic properties and their X-ray structure analysis. Additionally **[L_nCoCl$_2$]** ($L_n = L_A$, L_B, and L_C) complexes as a catalysts are evaluated for their catalytic activities in MMA polymerisation as a function of steric bulk around the metal centre.

2. Experimental

2.1. Physical measurements

$CoCl_2 \cdot 6H_2O$, 2-picolylchloride hydrochloride, cyclohexylmethylamine, 2-methoxyethanamine, 3-methoxypropan-1-amine, KOH, and methylmethacrylate (MMA) were purchased from Sigma–Aldrich (St. Louis, MO) and anhydrous solvents such as C_2H_5OH, DMF, Et_2O, and CH_2Cl_2 were purchased from Merck (Darmstadt, Germany) and used without further purification. The deionized water was prepared using a Millipore Milli-Q water system (Bedford, MA). Modified methylaluminoxane (MMAO) was purchased from Tosoh Finechem Corporation (Tokyo, Japan) as 6.9% aluminium (by weight) in a toluene solution and used without further purification. Synthesis of *N*,*N*-di(2-picolyl)cyclohexylmethylamine (L_A) [44], 2-methoxy-*N*,*N*-bis(pyridin-2-ylmethyl)ethanamine (L_B) and 3-methoxy-*N*,*N*-bis(pyridin-2-ylmethyl)propan-1-amine (L_C) [45], was carried out utilizing previously reported procedures. Elemental analyses (C, H, N) of the prepared complexes were performed on an elemental analyzer (EA 1108; Carlo-Erba, Milan, Italy). ^{1}H NMR (operating at 400 MHz) and ^{13}C NMR (operating at 100 MHz) spectra of ligands were recorded on an Advance Digital 400 NMR spectrometer (Bruker, Billerica, MA); chemical shifts were recorded in ppm units (δ) relative to $SiMe_4$ as the internal standard. Infrared (IR) spectra were recorded on a Bruker FT/IR-Alpha (neat) and the absorbance frequencies are reported in reciprocal centimetres (cm^{-1}). The molecular weights and molecular weight distribution of the obtained poly(methylmethacrylate) (PMMA) were determined 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 Co(II) complexes

*2.2.1. [N,N-di(2-picolyl)cyclohexylmethylamine]cobalt(II) chloride **([L_ACoCl$_2$])***

Ethanolic solution of L_A (0.148 g, 0.500 mmol) was treated with ethanolic solution of $CoCl_2 \cdot 6H_2O$ (0.119 g, 0.500 mol) and stirred for 12 h at ambient temperature. The purple precipitate was filtered and washed with EtOH (25.0 mL × 2), followed by washing with Et_2O (25.0 mL × 2) to get final product (0.185 g, 85.0%). X-ray quality crystals were obtained by diffusion of diethyl ether into acetone solution of **[L_ACoCl$_2$]**. Analysis calculated for $C_{19}H_{25}Cl_2CoN_3$: C, 53.66; H, 5.93; N, 9.88. Found: C, 53.74; H, 5.96; N, 9.77%. IR (Solid neat; cm^{-1}): 2916 (w), 2850 (w), 1606 (m), 1560 (s), 1481 (w), 1441 (m), 1303 (m), 1099 (m), 1025 (m), 981 (m), 772 (s).

*2.2.2. [2-Methoxy-N,N-bis(pyridin-2-ylmethyl)ethanamine] cobalt(II) chloride **([L_BCoCl$_2$])***

Synthesis of **[L_BCoCl$_2$]** was carried out using same manner as described for **[L_ACoCl$_2$]**, except utilizing L_B (0.129 g, 0.500 mmol) and $CoCl_2 \cdot 6H_2O$ (0.119 g, 0.500 mmol). The purple solid was obtained as final product (0.174 g, 89.7%). X-ray quality crystals were obtained by diffusion of methylene chloride into hexane solution of **[L_BCoCl$_2$]**. Analysis calculated for $C_{15}H_{19}Cl_2CoN_3O$: C, 46.53; H, 4.95; N, 10.85. Found: C, 45.80; H, 4.98; N, 10.80%. IR (Solid neat; cm^{-1}): 3016 (w), 2994 (w), 2971 (w), 1602 (s), 1558 (w), 1473 (m), 1435 (s), 1289 (m), 1147 (m), 1118 (s), 1086 (m), 1019 (s), 850 (m), 835 (m), 766 (s).

*2.2.3. [3-Methoxy-N,N-bis(pyridin-2-ylmethyl)propan-1amine] cobalt(II) chloride **([L_CCoCl$_2$])***

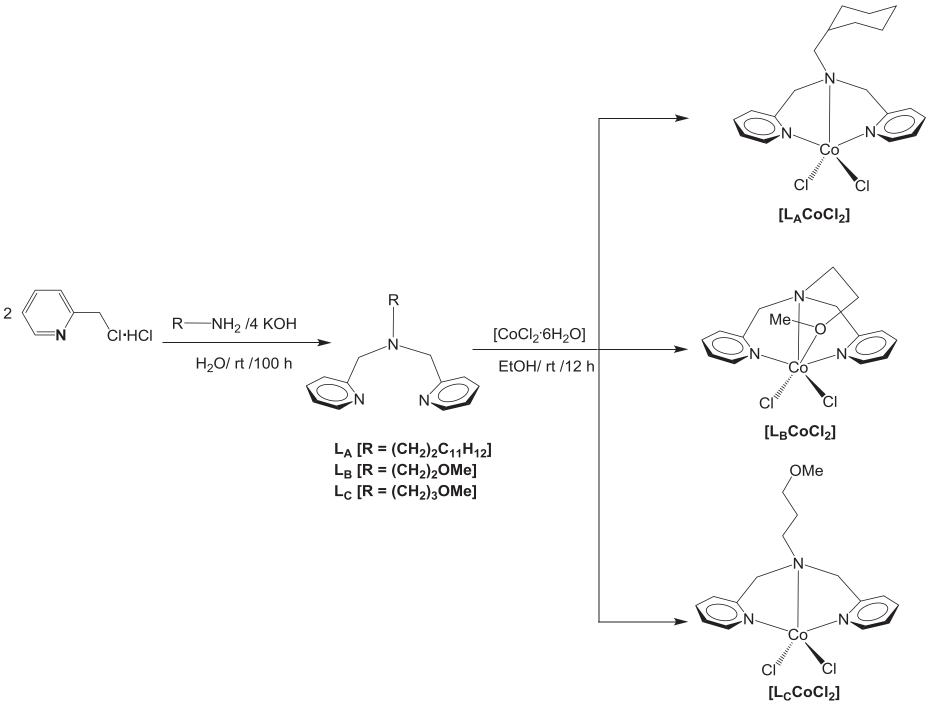
Synthesis of **[L_CCoCl$_2$]** was carried out using same manner as described for **[L_ACoCl$_2$]**, except utilizing L_C (0.135 g, 0.500 mmol) and $CoCl_2 \cdot 6H_2O$ (0.119 g, 0.500 mmol). The purple solid was filtered and washed with EtOH (25.0 mL × 2), followed by washing with Et_2O (25.0 mL × 2) (0.177 g, 88.8%). X-ray quality crystals were obtained by diffusion of diethyl ether into dimethylformamide solution of **[L_CCoCl$_2$]**. Analysis calculated for $C_{16}H_{21}Cl_2CoN_3O$: C, 47.90; H, 5.28; N, 10.47. Found: C, 48.16; H, 5.37; N, 10.48%. IR (Solid neat; cm^{-1}): 3029 (w), 2936 (w), 2927 (w), 2913 (w), 1605 (m), 1570 (w), 1479 (m), 1445 (m), 1393 (m), 1310 (w), 1114 (s), 1053 (m), 1024 (m), 963 (m), 864 (m), 777 (s).

2.3. X-ray crystallographic studies

An X-ray-quality single crystal was coated with paratone-*N* oil and the diffraction data measured at 100(2) K with synchrotron radiation ($\lambda = 0.71073$ Å) for **[L_ACoCl$_2$]** and ($\lambda = 0.63000$ Å) for **[L_BCoCl$_2$]** and **[L_CCoCl$_2$]**, respectively on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, South Korea. The ADSC Q210 ADX program [46] was used for data collection (detector distance is 63 mm, omega scan; $\Delta\omega = 1°$, exposure time is 1 s per frame) and HKL3000sm (Ver. 703r) [47] was used for cell refinement, reduction and absorption correction ($T_{min} = 0.868$, $T_{max} = 0.962$). Structures were solved by direct methods, and refined by full-matrix least-squares refinement using the SHELXL-2014 [48] computer program. The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. All hydrogen atoms were placed using a riding model, and their positions were constrained relative to their parent atoms using the appropriate HFIX command in SHELXL-2014.

2.4. MMA polymerisation studies

The methyl methacrylate (MMA) was extracted with 10% NaOH, washed with water, dried over $MgSO_4$ and distilled over CaH_2 under reduced pressure before use. In a Schlenk line, complex (15.0 μmol, 8.20 mg for **[L_ACoCl$_2$]**; 7.90 mg for **[L_BCoCl$_2$]**; 8.20 mg for **[L_CCoCl$_2$]** was dissolved in dried toluene (10.0 mL) followed by the addition of modified MMAO (6.90 wt% in toluene, 3.25 mL, 7.50 mmol, and $[MMAO]_0/[Co(II)\ catalyst]_0 = 500$) as a co-catalyst. The solution was stirred at 60 °C for 20 min. The MMA (5.00 mL, 47.1 mmol, $[MMA]_0/[Co(II)\ catalyst]_0 = 3100$) was added to the above reaction mixture and stirred at 60 °C for 2 h to obtain a viscous solution. MeOH (2.00 mL) was added to terminate the polymerisation. 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). The resulting polymer was filtered and washed with MeOH (250 mL × 2) to yield poly(methyl methacrylate) (PMMA), which was vacuum-dried at 60 °C.



Scheme 1. Synthetic route for Co(II) complexes.

3. Results and discussion

3.1. Synthetic and spectral aspects

The design of new ligands with diverse coordination modes with transition metals is a current challenge in the field of controlled polymerisation. In this regards *N*,*N*-di(2-picolyl)amine based precursors with various *N*′-substituents are promising ligands in organometallic catalysis. These ligands were easily obtained *via* the condensation of 2-picoline amine and primary amine with various *R* groups in single straightforward step in facile yield [44,45]. The complexation reactions are performed in EtOH at room

Table 1
Crystal data and structural refinement for synthesized Co(II) complexes.

	$[L_ACoCl_2]$	$[L_BCoCl_2]$	$[L_CCoCl_2]$
Empirical formula	$C_{19}H_{25}Cl_2CoN_3$	$C_{15}H_{19}Cl_2CoN_3O$	$C_{16}H_{21}Cl_2CoN_3O$
Formula weight	425.25	387.16	401.19
Temperature K	200(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.630	0.630
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$Pna2_1$	$P2_1/c$
Unit cell dimensions			
a (Å)	9.0133(8)	14.034(3)	8.101(2)
b (Å)	40.854(5)	8.452(2)	13.832(3)
c (Å)	16.289(2)	13.979(3)	15.960(3)
α°	90	90	90
β°	95.435(2)	90	95.67(3)
γ°	90	90	90
Volume ($Å^3$), Z	5971.1(9), 12	1658.1(6), 4	1779.6(6), 4
Density (calculated) (g/cm^3)	1.419	1.551	1.497
Absorption coefficient (mm^{-1})	1.137	0.971	0.907
F(000)	2652	796	828
Crystal size (mm^3)	0.21 × 0.10 × 0.05	0.15 × 0.10 × 0.04	0.50 × 0.15 × 0.10
θ range for data collection	1.00 to 28.32	2.808 to 33.486	1.731 to 29.486
Index ranges	$-11 \le h \le 12, -24 \le k \le 54$ $-21 \le l \le 21$	$-22 \le h \le 22, -13 \le k \le 13,$ $-24 \le l \le 24$	$-12 \le h \le 12, -21 \le k \le 21$ $-24 \le l \le 24$
Reflections collected	42850	25871	25381
Independent reflections	14818 [R(int) = 0.0593]	8137 [R(int) = 0.0299]	7028 [R(int) = 0.0426]
Completeness to θ	99.7%	98.5%	99.5%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	14818/0/676	8137/1/200	7028/0/209
Goodness-of-fit on F^2	1.069	1.091	1.077
Final R indices [I > 2sigma(I)]	$R_1 = 0.0547$; $wR_2 = 0.0976$	$R_1 = 0.0200$; $wR_2 = 0.0593$	$R_1 = 0.0283$; $wR_2 = 0.0762$
R indices (all data)	$R_1 = 0.1121$; $wR_2 = 0.1344$	$R_1 = 0.0204$; $wR_2 = 0.0595$	$R_1 = 0.0310$; $wR_2 = 0.0775$
Largest diff. peak and hole ($e.Å^{-3}$)	0.846 and −0.847	0.491 and −0.871	0.457 and −1.195

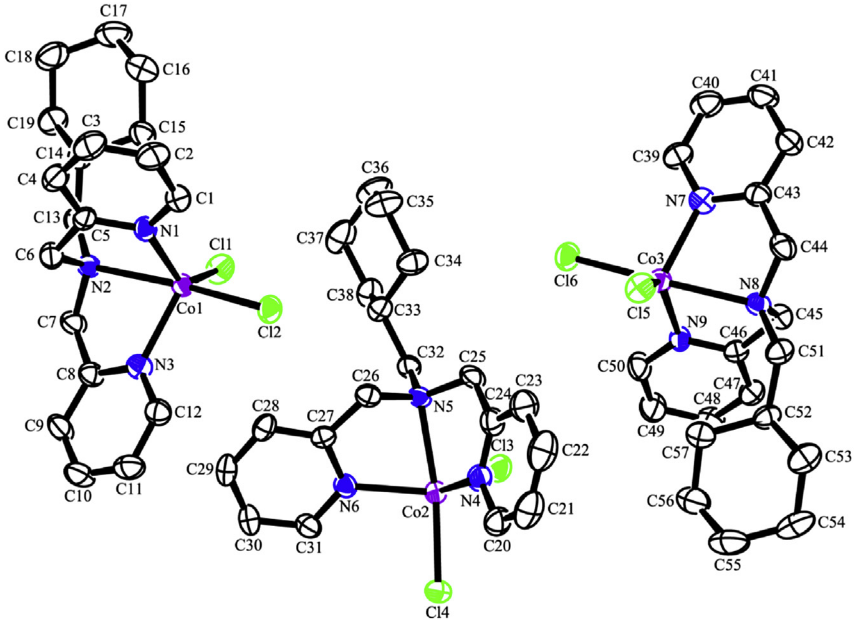


Fig. 1. ORTEP drawing of [L_ACoCl_2] with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity.

temperature by treating $\mathbf{CoCl_2 \cdot 6H_2O}$ with ligands ($L_n = L_A$, L_B, and L_C) in 1:1 ratio and yielded corresponding complexes in quantitative yields (85–90%) as illustrated in (Scheme 1). Complexes are stable toward oxygen and moisture, and readily soluble in DMF and DMSO but insoluble in MeOH, EtOH, and MeCN.

The elemental analysis is consistent with the chemical formula. In the IR spectrum of complexes, the bands in range of 2944–3029 and 1699–1567 cm^{-1} are assigned to C–H and C=C stretching frequencies, respectively, characteristics of aromatic groups.

3.2. Molecular structures

Single crystals suitable for X-ray crystallographic studies are obtained from Et_2O or acetone diffusion into DMF or DMSO. Crystal data and structural refinements for the synthesized Co(II) complexes are summarized in Table 1. The ORTEP drawings and of **[L_ACoCl_2]**, **[L_BCoCl_2]**, and **[L_CCoCl_2]** are shown in Figs. 1–3, respectively. The selected bond lengths and angles are listed in Table 2. The 5-coordinate monomeric **[L_ACoCl_2]** and **[L_CCoCl_2]** had a trigonal bipyramidal geometries obtained *via* coordination of the two pyridyl units and nitrogen in the *N′*-substituted amine moiety to the Co(II) centre. Specifically, Tau (τ) values of [L_ACoCl_2] and [L_CCoCl_2] were 0.59 and 0.60, respectively, indicating trigonal bipyramidal (tbp) geometry [49]. However, **[L_BCoCl_2]** exhibited a distorted octahedral geometry around the metal centre, achieved through coordination of the two pyridyl units, two chlorides and the *N′*,*O*-bidentate of nitrogen and oxygen in the *N′*-methoxyethyl moiety to the Co(II) centre. Such variable coordination modes of 2-methoxy-*N*,*N*-bis(pyridin-2-ylmethyl)etanamine (L_B) and 3-methoxy-*N*,*N*-bis(pyridin-2-ylmethyl)propan-1-amine (L_C) to the metal centre are consistent with the previous reports [45,50–53].

The bond lengths of Co–N_{amine} and Co–$N_{pyridine}$ for Co(II) complexes ranged from 2.193(3) – 2.307(3) Å and 2.072(3) – 2.247(1) Å, respectively. There exist a difference of 0.08–0.235 Å in lengths of Co–N_{amine} and Co–$N_{pyridine}$ in complexes **[L_nCoCl_2]** ($L_n = L_A$, L_B, and L_C) and this might be due to difference in hybridization and basicity of nitrogen atoms. The more basic N_{amine} atom has sp^3 hybridization while $N_{pyridine}$ has sp^2 hybridization with weak basic character. Moreover, the N_{amine} atom was coordinated to Co(II) centre solely through a σ-bond, but the $N_{pyridine}$ atoms were coordinated by both a σ-bond and a weak π-

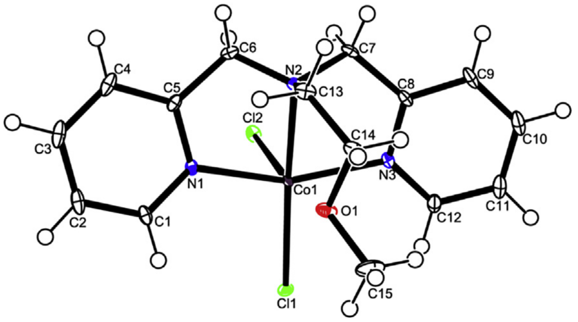


Fig. 2. ORTEP drawing of [L_BCoCl_2] with thermal ellipsoids at 50% probability.

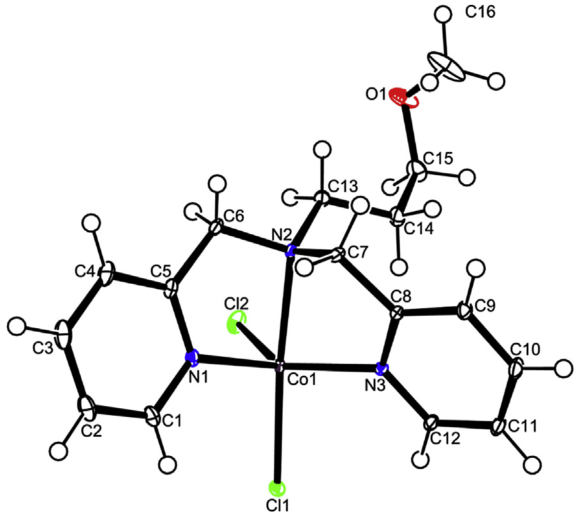


Fig. 3. ORTEP drawing of [L_CCoCl_2] with thermal ellipsoids at 50% probability.

Table 2
Selected bond lengths (Å) and angles (°) of Co(II) complexes.

[L$_A$CoCl$_2$]		[L$_B$CoCl$_2$]		[L$_C$CoCl$_2$]	
Bond lengths (Å)					
Co(1)-N(1)	2.072(3)	Co(1)-N(3)	2.111(1)	Co(1)-N(1)	2.0725(8)
Co(1)-N(3)	2.078(3)	Co(1)-N(1)	2.113(1)	Co(1)-N(3)	2.0906(8)
Co(1)-Cl(1)	2.288(1)	Co(1)-N(2)	2.193(1)	Co(1)-N(2)	2.2476(8)
Co(1)-N(2)	2.307(3)	Co(1)-Cl(1)	2.3263(5)	Co(1)-Cl(2)	2.3124(7)
Co(1)-Cl(2)	2.309(1)	Co(1)-O(1)	2.350(1)	Co(1)-Cl(1)	2.3202(5)
N(1)-C(1)	1.337(5)	Co(1)-Cl(2)	2.3991(4)	N(1)-C(5)	1.348(1)
N(1)-C(5)	1.354(5)	N(1)-C(1)	1.341(2)	N(1)-C(1)	1.348(1)
N(2)-C(6)	1.475(5)	N(1)-C(5)	1.345(2)	N(2)-C(6)	1.473(1)
N(2)-C(7)	1.477(5)	N(2)-C(7)	1.471(2)	N(2)-C(7)	1.479(1)
N(2)-C(13)	1.490(5)	N(2)-C(6)	1.473(2)	N(2)-C(13)	1.486(1)
Bond Angles (°)					
N(1)-Co(1)-N(3)	106.7(1)	N(3)-Co(1)-N(1)	155.17(4)	N(1)-Co(1)-N(3)	112.07(3)
N(1)-Co(1)-Cl(1)	133.5(1)	N(3)-Co(1)-N(2)	79.41(4)	N(1)-Co(1)-N(2)	77.73(3)
N(3)-Co(1)-Cl(1)	113.1(1)	N(1)-Co(1)-N(2)	76.26(4)	N(3)-Co(1)-N(2)	77.15(3)
N(1)-Co(1)-N(2)	77.0(1)	N(3)-Co(1)-Cl(1)	100.58(3)	N(1)-Co(1)-Cl(2)	104.75(3)
N(3)-Co(1)-N(2)	76.7(1)	N(1)-Co(1)-Cl(1)	102.12(3)	N(3)-Co(1)-Cl(2)	136.41(2)
Cl(1)-Co(1)-N(2)	89.64(9)	N(2)-Co(1)-Cl(1)	167.60(3)	N(2)-Co(1)-Cl(2)	89.03(3)
N(1)-Co(1)-Cl(2)	97.2(1)	N(3)-Co(1)-O(1)	81.04(4)	N(1)-Co(1)-Cl(1)	100.18(3)
N(3)-Co(1)-Cl(2)	98.1(1)	N(1)-Co(1)-O(1)	88.55(4)	N(3)-Co(1)-Cl(1)	94.97(3)
Cl(1)-Co(1)-Cl(2)	99.81(5)	N(2)-Co(1)-O(1)	76.60(4)	N(2)-Co(1)-Cl(1)	170.13(2)
N(2)-Co(1)-Cl(2)	170.45(9)	Cl(1)-Co(1)-O(1)	91.11(3)	Cl(2)-Co(1)-Cl(1)	100.82(2)

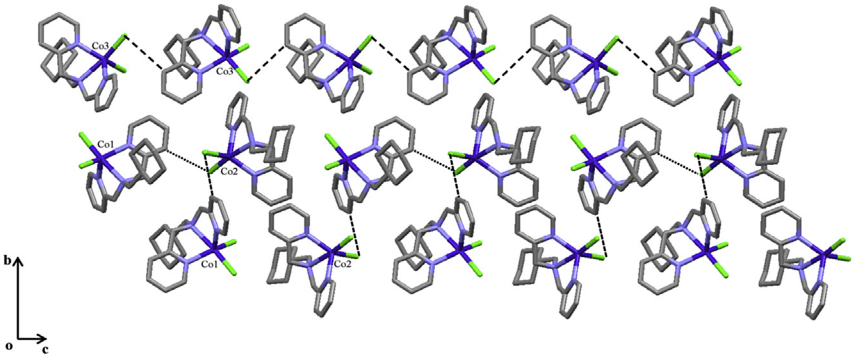


Fig. 4. Perspective view for non-covalent hydrogen bonding interaction of [L$_A$CoCl$_2$] (dot line; C(4)-H(4)-Cl(4), short dash line; C(9)-H(9)Cl(3), and long dash line; C(47)-H(47)-Cl(6)).

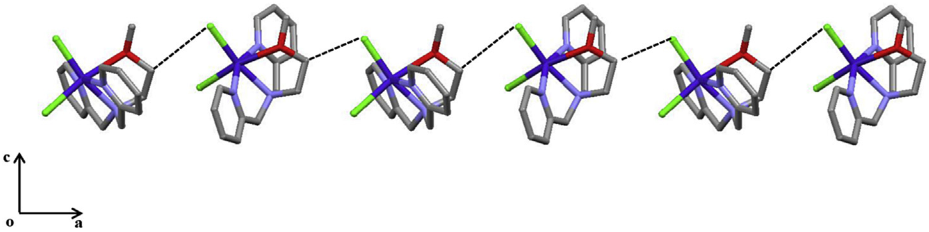


Fig. 5. Perspective view for non-covalent hydrogen bonding interaction of [L$_B$CoCl$_2$].

back bond to Co(II) centre. In addition, the difference in Co–N$_{\text{amine}}$ and Co–N$_{\text{pyridine}}$ for Co(II) complexes might also be attributed to the variable steric environment around the metal centre provided by the different *N*′-substituted moieties at amine unit.

The average N$_{\text{pyridine}}$–Co–N$_{\text{pyridine}}$ bond angles for 5-coordinate complexes i.e. **[L$_A$CoCl$_2$]** and **[L$_C$CoCl$_2$]**, are 106.7(1)° and 112.07(3)°, respectively. Similarly two N$_{\text{amine}}$–Co–N$_{\text{pyridine}}$ angles in **[L$_A$CoCl$_2$]** are [77.0(1)° and 76.7(1)]; **[L$_C$CoCl$_2$]** [77.73(3)° and 77.15(3)°] indicative of 5-memebered fused ring. Additionally, the bond angles of N$_{\text{amine}}$–Co–Cl(1) are [89.64(9)° and 89.03(3)], while N$_{\text{amine}}$–Co–Cl(2) angles are [170.45(9)° and 170.13(2)] in **[L$_A$CoCl$_2$]** and **[L$_C$CoCl$_2$]**, indicated that the geometry around the Co center is a distorted 5-coordinated trigonal bipyramidal involving coordination of the nitrogen of pyridyl units, amine moiety and the metal center, thus forming two 5-membered chelate rings. The bond angles Cl(1)–Co–Cl(2) in 5-coordinated **[L$_A$CoCl$_2$]** and **[L$_C$CoCl$_2$]** are 99.81(5)° and 100.82(2)°, respectively. In a 6-coordinate **[L$_B$CoCl$_2$]**, N$_{\text{pyridine}}$–Co–N$_{\text{pyridine}}$ and two N$_{\text{amine}}$–Co–N$_{\text{pyridine}}$

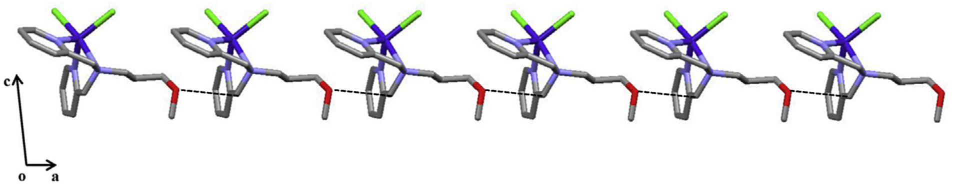


Fig. 6. Perspective view for non-covalent hydrogen bonding interaction of [L$_C$CoCl$_2$].

angles are 155.17(4)°, 79.41(4)° and 76.26(4)°, respectively. There exists a difference of 3.15° in two 5-membered fused rings in **[L$_B$CoCl$_2$]** which might be due to the steric encumbrance provided by coordination of oxygen atom of 2-methoxyethyl moiety to the Co centre. Similarly N(1)–Co–O(1) and N(3)–Co–O(1) angles in **[L$_B$CoCl$_2$]** are 81.04(4)° and 88.55(4)°, respectively and this difference might be representative of the steric adjustment between pyridine moieties and 2-methoxyethyl unit.

Perspective view for non-covalent hydrogen bonding interaction of **[L$_n$CoCl$_2$]** (L$_n$ = L$_A$, L$_B$ and L$_C$) was shown in Figs. 4–5, respectively. Interestingly, **[L$_A$CoCl$_2$]** forms three dimensional (3D) channel by extending 1D channel of Co1 and Co2 along axis *a* to arises *b* and *c* (2D channel, Fig. 4) with combination of Co3. Non-covalent interaction, such as bond distances of C–H ·······X (X = Cl, O) and CHX angles in the complexes was calculated and presented as Table 3. Non-covalent interaction bond lengths of C–H ·······X in **[L$_A$CoCl$_2$]** and **[L$_B$CoCl$_2$]** ranged from 3.517(1) Å to 3.655(5) Å [54–58]. Specifically, hydrogen bond length of C–H ·······O in **[L$_C$CoCl$_2$]** was calculated as 3.26l(1) Å because –OCH$_3$ group is known to be good proton acceptor (Fig. 6).

Table 3
Selected C–H ·······X (X = Cl, O) bond distances (Å) and CHX angles (°).

	C–H·······X	d(C–H)	d(H·······X)	d(C·······X)	<(CHX)
[L$_A$CoCl$_2$][a]	C(4)-H(4) ······· Cl(4)	0.95	2.70	3.583(5)	154.7
	C(9)-H(9) ······· Cl(3)	0.95	2.78	3.655(5)	153.4
	C(10)-H(10) ······· Cl(4)	0.95	2.62	3.517(1)	157.3
	C(47)-H(47) ······· Cl(6)	0.95	2.72	3.637(5)	162.5
[L$_B$CoCl$_2$][b]	C(14)–H(14B) ······· Cl(1)	0.99	2.65	3.618(1)	165.1
[L$_C$CoCl$_2$][c]	C(7)–H(7A) ······· O(1)	0.99	2.58	3.261(1)	126

[a] Symmetry transformations used to generate equivalent atoms: 1-x,-y,1-z x,y,1 + z 2-x,-y,1-z x,1/2-y,-1/2 + z.

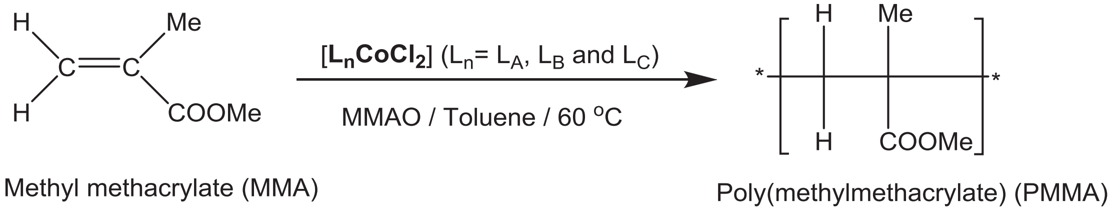
[b] Symmetry transformations used to generate equivalent atoms: x-1/2,-y-1/2,z.

[c] Symmetry transformations used to generate equivalent atoms: 1-x,y,z.

3.3. *Methyl methacrylate (MMA) polymerisation*

The synthesized complexes were assessed towards MMA polymerisation at 60 °C. It has been observed that these complexes act as effective initiators in presence of MMAO and polymerise methyl methacrylate (MMA) to yield poly(methylmethacrylate) (PMMA) with T$_g$ ranging from 129 °C to 131 °C. As mentioned earlier that non-radical mediated polymerisation of MMA is used to achieve syndiotacticity and hence high T$_g$ of PMMA with improved optical properties. The resultant PMMA were isolated as white solids and characterized by gel permeation chromatography (GPC) in THF using standard polystyrene as a reference. No catalytic activities have been observed for these complexes in the absence of MMAO. The molecular weight M$_w$ ranged from 9.71 × 10^5 g/mol to 14.2 × 10^5 g/mol, with a polydispersity index (PDI) value in range of 1.43–1.99. The results of polymerisation are summarized in Table 4.

Table 4
MMA Polymerisation by Co(II) complexes in the presence of MMAO.[a]



Entry	Catalyst	Yield[b]	Activity[c]	T$_g$[d]	Tacticity			M$_w$[e]	M$_w$/M$_n$[f]
		(%)	(g/molcat·h) × 10^4	(°C)	%mm	%mr	%rr	(g/mol) × 10^5	
1	[CoCl$_2$·6H$_2$O][g]	30.3	4.73	133	6.30	23.9	69.8	10.7	1.49
2	MMAO[h]	8.97	1.40	120	37.2	10.9	51.9	0.61	2.20
3	[L$_A$CoCl$_2$]	46.0	7.17	131	5.90	24.1	70.0	9.71	1.99
4	[L$_B$CoCl$_2$]	47.9	7.47	129	6.30	23.4	70.3	10.6	1.92
5	[L$_C$CoCl$_2$]	49.34	9.34	129	5.70	22.0	72.3	14.2	1.43

[a] [Cd(II) catalyst]$_0$ = 15 μmol, [MMA]$_0$/[MMAO]$_0$/[Cd(II) catalyst]$_0$ = 3100:500:1, Temp = 60 °C, and time = 2 h.

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

[c] Activity is gPMMA/(molCo h).

[d] T$_g$ is 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] Mn refers to the number average of molecular weights of PMMA.

[g] It is a blank polymerisation in which [CoCl$_2$.6H$_2$O] was also activated by MMAO.

[h] It is a blank polymerisation which was done solely by MMAO.

It has been found that monomeric **[L$_C$CoCl$_2$]** (9.34×10^4 gPMMA/molCo h) exhibited highest activity and provided PMMA with the PDI value of 1.43 and molecular weight of 14.2×10^5 g/mol at 60 °C. It is clear from polymerisation results that PDIs decreased with increasing molecular weights of the resultant PMMA [59,60]. However, the molecular weights of the polymers isolated did not increase as the yield increased, which might be due to the fact that the chain growth would completed at the beginning of the polymerisation.

The decrease catalytic activity of Co(II) centre in 5-coordinated **[L$_A$CoCl$_2$]** and 6-coordinated **[L$_B$CoCl$_2$]** might be due to the steric encumbrance provided by *N*′-substituted cyclohexyl and 2-methoxyethyl substituents at amine moiety (Figs. 1 and 2). However in case of **[L$_C$CoCl$_2$]** the pendent 3-methoxypropyl group lies away from metal centre and thus resulted in open reactive site for monomer approach. Experiments were carried out using starting materials **$CoCl_2 \cdot 6H_2O$**, or MMAO alone at a specific temperature towards MMA polymerisation. It has been found that PDI and tacticity is almost unchanged particularly in case of **$CoCl_2 \cdot 6H_2O$**.

The tacticity of PMMA, was identified in the range around syndiotactic (*rr*, δ 0.85), heterotactic (*mr*, δ 1.02) and isotactic (*mm*, δ 1.21) based on ^{1}H NMR spectroscopy [61,62]. The syndiotacticity of PMMA by monomeric **[L$_C$CoCl$_2$]** was found to be 0.72, which was slightly higher compared to rest of complexes **[L$_A$CoCl$_2$]**, and **[L$_B$CoCl$_2$]** and even the reference material i.e. **$CoCl_2 \cdot 6H_2O$**. However, there was a significant difference of the syndiotacticity of PMMA compared to the co-catalyst, MMAO. Despite of lower activities observed for **[L$_A$CoCl$_2$]**, and **[L$_B$CoCl$_2$]** the syndiotacticity was not affected much. Furthermore, it has been observed that the current system resulted PMMA with higher molecular weights, higher T_g, and better syndiotacticity compared to our previous reported Co(II) complexes [63].

It has been observed that catalytic activity of complexes was affected by steric encumbrance provided by *N*′-substitution at the amine moiety, as determined by the amount of resultant PMMA. The polymerization activity and resultant molecular weights of PMMA should be considered as a function of steric bulk around the metal centre. MMA polymerisation achieved *via* coordination complexes resulted in syndiotacticity enchainment, which resulted in T_g up to 140 °C. The syndiotacticity of resultant PMMA was around 70%, which was similar to all the synthesized complexes and was not much affected by the steric encumbrance provided by ligand architecture. Thus, the observed moderate syndiotacticity of PMMA was not sufficient to confer a coordination polymerisation mechanism for these complexes.

4. Conclusion

In the work presented here, we demonstrated the synthesis and X-ray crystallographic studies of mononuclear **[L$_n$CoCl$_2$]** ($L_n = L_A$, L_B, L_C) complexes. These novel Co(II) complexes exhibited diverse structural variations on amine moiety of *N*,*N*-di(2-picolyl)amine architecture. The Co(II) centre in **[L$_n$CoCl$_2$]** ($L_n = L_A$, and L_C) is 5-coordinated and adopted a distorted trigonal bipyramidal geometry while **[L$_B$CoCl$_2$]** exhibited 6-coordinated distorted octahedral geometry. The complex **[L$_C$CoCl$_2$]** showed better catalytic activity for MMA polymerisation at 60 °C compared to its counter parts containing L_A and L_B. The catalytic activity in the current study can be explain as a function of steric encumbrance that hinder the monomer approach to the active centre. It is anticipated that new *N*,*N*-di(2-picolyl)amine based architecture may be applied to afford other pyridyl-amine based Co(II) complexes with better catalytic activities. Studies in these respects are under way in our laboratory.

Supplementary materials

CCDC 1412224–1412226 contains the supplementary crystallographic data for complexes **[L$_A$CoCl$_2$]**, **[L$_B$CoCl$_2$]**, and **[L$_C$CoCl$_2$]**, 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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