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FULL PAPER

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Five-coordinate dinuclar cobalt (II), copper (II), zinc (II) and cadmium (II) complexes with 4-bromo-*N*-(2-pyridinylmethylene)benzenamine: Synthesis, characterisation and methyl methacrylate polymerization

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A series of late transition metal complexes, **[(bpma)Co(μ–Cl)Cl]$_2$**, **[(bpma)Cu(μ–Cl)Cl]$_2$**, **[(bpma)Zn(μ–Cl)Cl]$_2$** and **[(bpma)Cd(μ–Br)Br]$_2$** (where **bpma** is 4-bromo-*N*-((pyridin-2-yl)methylene)benzenamine) have been synthesized and structurally characterized. The X-ray structures of dimeric complexes **[(bpma)M(μ–X)X]$_2$** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br) showed a distorted 5-coordinate trigonal bipyramidal geometry involving two nitrogen atoms of *N*,*N*-bidentate ligand, two bridged and one terminal halogen atoms. The complex **[(bpma)Cu(μ–Cl)Cl]$_2$** revealed the highest catalytic activity for the polymerisation of methyl methacrylate in the presence of modified methylaluminoxane with an activity of 9.14×10^4 g PMMA/mol·Cu·h at 60 °C and afforded syndiotactic poly (methylmethacrylate) (*rr* = 0.69).

KEYWORDS
4-bromo-*N*-(2-pyridinylmethylene) benzenamine, dinuclear transition metal complex, MMA polymerization, syndio-enriched PMMA

1 | INTRODUCTION

Schiff bases, such as pyridine-3-ylmethanimine gained attention owing to their easy synthetic approach and resultant stable coordination entities with a variety of transition metals.[1–3] These complexes showed various coordination modes up to the tetradentate.[4–6] Their structural stability and catalytic efficiency made them useful mainly in the area of structural studies,[7] photoluminescence,[8–10] spectroscopy,[11] transfer hydrogenation reactions,[12] biological applications,[13] oxidation catalyst,[14] catalysts for alkene polymerization,[15] epoxidation,[16] olefin[17,18] and MMA polymerizations.[19]

Poly (methylmethacrylate) (PMMA), an acrylic polymer, is commonly used as a thermoplastic with enhanced optical properties and wide range of industrial applications.[20,21] Obviously, the tacticity of the polymer is inherently important to its applications. Pure isotactic PMMA have T_g about 51 °C, whereas for syndiotactic PMMA T_g is near 130 °C.[22] Thus, syndiotactic PMMA *via* metal mediated polymerization is highly desirable for improved optical applications. A great deal of attention has been directed recently toward the development of late-transition-metal-based complexes due to their reduced oxophilicity and presumed better functional group tolerance towards polar monomers. Yasuda and coworkers[23,24] reported that Cp_2^*LnR (Ln = Sm or Yb) catalyzed highly syndiotactic PMMA, and Marks and coworkers[25] showed that chiral *ansa*-bridged lanthanocenes give isotactic or syndiotactic PMMA based on the ligand assembly. Alternatively, Ni $(acac)_2$ catalyst was found to be an effective catalyst for the nonspecific polymerization of MMA in the presence of methylaluminoxane (MAO).[26,27] Schiff base derived late transition metal complexes, such as (*α*-diimine)-based nickel complexes, pyridylbisimine-based Fe (II) and Co (II), iminopyridine- or aminopyridine-based Fe (II) complexes polymerized MMA to give syndio-enriched PMMA.[28] Similarly, bis(*β*-ketiminato) nickel complexes were reported which polymerized MMA and yielded syndiotactic-rich PMMA with relatively wide PDIs.[29]

We have recently used several late transition metals with pyridineimine based ligands for PMMA precatalysts.[30–32] Thus, the current study demonstrate the synthesis and structural studies of 4-bromo-*N*-(2-pyridinylmethylene) benzenamine (**bpma**) based metal complexes **[(bpma)M(μ–X)X]₂** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br). Further, we sought to investigate the catalytic activity of synthesized metal complexes for MMA polymerization in terms of metal centre variation and ligand effect.

2 | EXPERIMENTAL

2.1 | General consideration

$CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$, $CdBr_2 \cdot 4H_2O$, 2-pyridinecarboxaldehyde, 4-bromoaniline, magnesium sulfate, and methyl methacrylate (MMA) were purchased from Aldrich. Anhydrous solvents such as acetonitrile (CH_3CN), ethanol (EtOH), dimethylformamide (DMF), diethyl ether (Et_2O) and dichloromethane (CH_2Cl_2) were purchased from Merck and used without further purification. Modified methylaluminoxane (MMAO) was purchased from Tosoh Finechem Corporation as 5.90% weight aluminum of a toluene solution and used without further purification. 4-bromo-*N*-((pyridin-2-yl)methylene) benzenamine (bpma) was prepared by previously reported procedure.[32–36]

2.2 | Instrumentation

^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker Avance Digital 500 NMR spectrometer; chemical shifts were reported in ppm units (*δ*) relative to $SiMe_4$ as the internal standard. Infrared (IR) spectra were recorded on Bruker FT/IR-Alpha (neat) and the data are reported in reciprocal centimetres (cm^{-1}). Elemental analysis (C, H, N) of the prepared complexes were carried out on an elemental analyser (EA 1108; Carlo-Erba, Milan, Italy). The molecular weights (M_n) and molecular weight distribution (MWD) of the obtained poly (methylmethacrylate) (PMMA) were carried out using gel permeation chromatography (GPC) (in THF, Alliance e2695; Waters Corp., Milford, MA, USA). Glass transition temperature (T_g) was determined using a thermal analyser (DSC 4000; PerkinElmer).

2.3 | Synthetic procedures

2.3.1 | [4-bromo-N-((pyridin-2-yl)methylene)benzenamine] cobalt (II) chloride ([(bpma)co(μ–cl)cl]₂)

A solution of (bpma) (0.601 g, 2.30 mmol) in anhydrous EtOH (40.0 ml) was added to a solution of $CoCl_2 \cdot 6H_2O$ (0.547 g, 2.30 mmol) in anhydrous EtOH (40.0 ml) and stirred at room temperature for 12 hr to give a dark green precipitate. The solid was filtered and washed with cold EtOH (30.0 ml × 2), followed by washing with Et_2O (30.0 ml × 3). The product was dried under vacuum to yield a final product (1.63 g, 90.6%). Analysis calculated for $C_{24}H_{18}Br_2Cl_4Co_2N_4$ (%): C, 36.87; H, 2.32; N, 7.17. Found: C, 37.24; H, 2.33; N, 7.10. IR (solid neat; cm^{-1}): 3067 (C-H stretching), 1565 (N=C stretching), 1485 (-C=C aromatic) 1444 (-C-H bending) 690 (-C-Br).

2.3.2 | [4-bromo-N-((pyridin-2-yl)methylene)benzenamine] copper (II) chloride ([(bpma)cu(μ–cl)cl]₂)

[(bpma)Cu(μ-Cl)Cl]₂ was prepared by analogous method as described for **[(bpma)Co(μ-Cl)Cl]₂** except utilizing (bpma) (0.601 g, 2.30 mmol) and $CuCl_2 \cdot 2H_2O$ (0.392 g, 2.30 mmol) to give a light green solid (1.70 g, 93.4%). Analysis calculated for $C_{24}H_{18}Br_2Cl_4Cu_2N_4$ (%): C, 36.44; H, 2.29; N, 7.08. Found: C, 36.58; H, 2.32; N, 7.23. IR (solid neat; cm^{-1}): 3079 (C-H stretching), 1591 (-N=C stretching), 1482 (-C-H bending), 1359 (-C=C aromatic), 646 (-C-Br).

2.3.3 | [4-bromo-N-((pyridin-2-yl)methylene)benzenamine] zinc (II) chloride ([(bpma)Zn(μ–cl)cl]$_2$)

[(bpma)Zn(μ–Cl)Cl]$_2$ was prepared by analogous method as described for **[(bpma)Co(μ-Cl)Cl]$_2$** except utilizing (bpma) (0.700 g, 2.68 mmol) and $ZnCl_2$ (0.365 g, 2.68 mmol) to give a white solid (2.03 g, 95.3%). Analysis calculated for $C_{24}H_{18}Br_2Cl_4N_4Zn_2$ (%): C, 36.27; H, 2.28; N, 7.05. Found: C, 36.61; H, 2.28; N, 7.20. ^{1}H NMR (DMSO-d$_6$, 500 MHz): δ 8.84 (d, 1H, J = 4.12 Hz, –N=C–CH=CH–CH=C**H**–), 8.68 (s, 1H, –N=C**H**–NC$_5$H$_4$–), 8.13–8.08 (m, 2H, –N=C–C**H**=C**H**–CH=CH–), 7.68 (br s, 1H, –N=C–CH=CH–C**H**=CH–), 7.61 (d, 2H, J = 8.54 Hz, –BrC$_6$**H**$_4$–), 7.33 (d, 2H, J = 7.93 Hz, –BrC$_6$**H**$_4$–). ^{13}C NMR (DMSO-d$_6$, 125 MHz): δ 160.50 (d, 1C, J = 171.66 Hz, –N=**C**H–NC$_5$H$_4$–), 150.13 (s, 1C, *ipso*-N=**C**–CH=CH–CH=CH–), 149.81 (d, 1C, J = 182.56 Hz, –N=C–CH=CH–CH=**C**H–), 147.67 (s, 1C, *ipso*-Br**C**$_6$H$_4$–), 139.36 (d, 1C, J = 168.03 Hz, –N=C–CH=**C**H–CH=CH–), 132.02 (d, 2C, J = 167.12 Hz, *m*-BrC$_6$H$_4$–), 127.48 (d, 1C, J = 168.94 Hz, –N=C–**C**H=CH–CH=CH–), 125.33 (d, 1C, J = 170.75 Hz, –N=C–CH=CH–**C**H=CH–), 123.76 (d, 2C, J = 163.49 Hz, *o*-Br**C**$_6$H$_4$–), 120.09 (s, 1C, *ipso*-Br**C**$_6$H$_4$–). IR (solid neat; cm^{-1}): 3134 (C-H stretching), 1590 (N=C stretching), 1561 (-C-H bending), 1488–1446 (-C=C aromatic), 648 (-C-Br).

2.3.4 | [4-bromo-N-((pyridin-2-yl)methylene)benzenamine] cadmium (II) bromide ([(bpma)cd(μ–Br)Br]$_2$)

[(bpma)Cd(μ–Br)Br]$_2$ was prepared by analogous method as described for **[(bpma)Co(μ-Cl)Cl]$_2$** except utilizing (bpma) (0.601 g, 2.30 mmol) and $CdBr\cdot 4H_2O$ (0.791 g, 2.30 mmol) to give a beige solid (2.28 g, 92.9%). Analysis calculated for $C_{24}H_{18}Br_6Cd_2N_4$ (%): C, 27.02; H, 1.70; N, 5.25. Found: C, 27.48; H, 1.71; N, 5.32. ^{1}H NMR (DMSO-d$_6$, 500 MHz): δ 8.90 (d, 1H, J = 4.58 Hz, –N=C–CH=CH–CH=C**H**–), 8.79 (s, 1H, –N=C**H**–NC$_5$H$_4$–), 8.17 (t, 1H, J = 7.63 Hz, –N=C–CH=C**H**–CH=CH–), 8.11 (d, 1H, J = 7.63 Hz, –N=C–C**H**=CH–CH=CH–), 7.77 (t, 1H, J = 6.26 Hz, –N=C–CH=CH–C**H**=CH–), 7.64 (d, 2H, J = 8.54 Hz, –BrC$_6$**H**$_4$–), 7.44 (d, 2H, J = 8.54 Hz, –BrC$_6$**H**$_4$–). ^{13}C NMR (DMSO-d$_6$, 125 MHz): δ 160.03 (d, 1C, J = 172.57 Hz, –N=**C**H–NC$_5$H$_4$–), 149.97 (d, 1C, J = 184.38 Hz, –N=C–CH=CH–CH=**C**H–), 148.17 (s, 1C, *ipso*-N=**C**–CH=CH–CH=CH–), 147.08 (s, 1C, *ipso*-Br**C**$_6$H$_4$–), 140.01 (d, 1C, J = 168.94 Hz, –N=C–CH=**C**H–CH=CH–), 131.88 (d, 2C, J = 169.84 Hz, *m*-Br**C**$_6$H$_4$–), 128.15 (d, 1C, J = 168.03 Hz, –N=C–CH=CH–**C**H=CH–), 128.05 (d, 1C, J = 169.84 Hz, –N=C–**C**H=CH–CH=CH–), 124.21 (d, 2C, J = 164.40 Hz, *o*-Br**C**$_6$H$_4$–), 120.49 (s, 1C, *ipso*-Br**C**$_6$H$_4$–). IR (solid neat; cm^{-1}): 3086 (C-H stretching), 3058 (w), 1592 (N=C stretching) (w), 1484 (-C-H bending) (s), 1438 (-C=C aromatic), 600 (-C-Br).

2.4 | Catalytic activity for MMA polymerization

In a Schlenk flask, the complex (15.0 μmol, 11.7 mg for **[(bpma)Co(μ–Cl)Cl]$_2$**, 11.9 mg for **[(bpma)Cu(μ–Cl)Cl]$_2$**, 11.9 mg for **[(bpma)Zn(μ–Cl)Cl]$_2$**, 16.0 mg for **[(bpma)Cd(μ–Br)Br]$_2$** was dissolved in dried toluene (10.0 ml) followed by the addition of modified methyl aluminoxane (MMAO) (3.80 ml, 7.50 mmol) as a co-catalyst. The solution was stirred for 20 min at 60 °C. The MMA (5.00 ml, 47.1 mmol) was added to the above reaction mixture and stirred for 2 hr to get a viscous solution. MeOH (4.00 ml) was added to terminate polymerization. The reaction mixture was poured into a large quantity of MeOH (500 ml), and 35.0% HCl (5.00 ml) was injected to remove the remaining co-catalyst (MMAO). The product was obtained by filtration and washed with MeOH (250 ml × 2) to yield PMMA, and dried under vacuum at 60 °C for 12 hr.

2.5 | X-ray crystallographic studies

An X-ray quality crystals of **[(bpma)Co(μ–Cl)Cl]$_2$** and **[(bpma)Cu(μ–Cl)Cl]$_2$** were grown from a Et_2O (10.0 ml) diffusion into an MeOH solution (5.00 ml) of complexes. Similarly, the X-ray quality single crystals of **[(bpma)Zn(μ–Cl)Cl]$_2$** and **[(bpma)Cd(μ–Br)Br]$_2$** were grown from an IPA solution (10.0 ml) diffusion into DMF solution (5.0 ml). An X-ray-quality single crystal was mounted in a thin-walled glass capillary 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) software packages.[36] Semi-empirical absorption corrections based on equivalent reflections were applied by SADABS.[37] Structures were solved by direct methods and refined using a full-matrix least-squares method on F^2 using SHELXTL.[38] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added to their geometrically ideal positions. Crystal and structure refinement data for all structures are summarized in Table 1.

3 | RESULT AND DISCUSSION

3.1 | Synthesis and properties

Ligand (bpma) used in current study was obtained by the condensation reaction between the 4-bromoaniline and 2-pyridinecarboxaldehyde in MeOH as reported.[33–36] The complexation reaction progressed smoothly by treating metal staring salts/precursors with ligand in anhydrous EtOH and afforded **[(bpma)Co(μ–Cl)Cl]$_2$** (90.6%), **[(bpma)Cu(μ–Cl)Cl]$_2$** (93.4%), **[(bpma)Zn(μ–Cl)Cl]$_2$** (95.3%) and **[(bpma)Cd(μ–Br)Br]$_2$** (92.9%) at

TABLE 1 Crystal data and structure refinement for **[(bpma)M(μ–X)X]$_2$** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br)

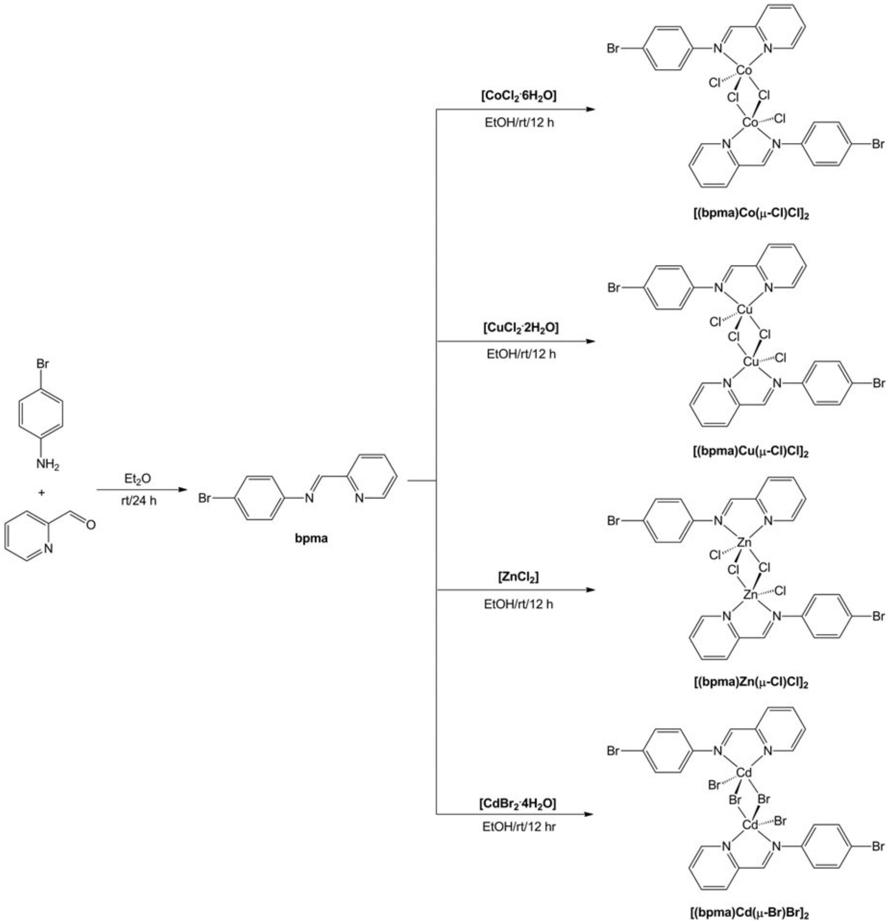
	[(bpma)Co(μ–Cl)Cl]$_2$	[(bpma)Cu(μ–Cl)Cl]$_2$	[(bpma)Zn(μ–Cl)Cl]$_2$	[(bpma)Cd(μ–Br)Br]$_2$
Empirical formula	$C_{24}H_{18}Br_2Cl_4Co_2N_4$	$C_{24}H_{18}Br_2Cl_4Cu_2N_4$	$C_{24}H_{18}Br_2Cl_4N_4Zn_2.CHCl_3$	$C_{24}H_{18}Br_6Cd_2N_4$
Formula weight	781.90	791.12	794.78	1066.68
Temperature/K	100(2)	200(2)	100(2)	100(2)
Wavelength/Å	0.610	0.71073	0.700	0.620
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n	P2(1)/n	P2(1)/n
a/Å	7.5180(2)	7.5294(1)	7.5420(2)	7.7090(2)
b/Å	13.994(3)	13.6544(2)	14.260(3)	15.273(3)
c/Å	12.991(3)	13.2348(2)	12.702(3)	12.474(3)
α/ °	90	90	90	90
β/ °	98.13(3)	98.001(3)	98.45(3)	96.09(3)
γ/ °	90	90	90	90
Volume/Å^3, Z	1353.0(5), 2	1347.4(3), 2	1351.2(5), 2	1460.4(5), 2
Density (calculated) /Mg m^{-3}	1.919	1.950	1.953	2.426
Absorption coefficient/mm^{-1}	3.038	4.963	4.941	6.770
F(000)	764	772	776	992
Crystal size/mm^3	0.10 × 0.06 × 0.03	0.23 × 0.21 × 0.13	0.08 × 0.06 × 0.03	0.20 × 0.15 × 0.10
Theta range for data collection/deg	1.846 to 27.996	2.15 to 28.37	2.128 to 33.319	2.327 to 25.993
Index ranges	$-11 \leq h \leq 11$ $-21 \leq k \leq 21$ $-19 \leq l \leq 19$	$-10 \leq h \leq 8$ $-18 \leq k \leq 16$ $-17 \leq l \leq 17$	$-11 \leq h \leq 11$ $-20 \leq k \leq 20$ $-19 \leq l \leq 19$	$-10 \leq h \leq 10$ $-21 \leq k \leq 21$ $-17 \leq l \leq 17$
Reflections collected/unique	18164	9695	13401	15523
Independent reflections	5163 [R (int) = 0.0537]	3334 [R (int) = 0.0384]	4494 [R (int) = 0.0356]	4325 [R (int) = 0.0302]
Completeness to theta = 28.30°	100.0% (21.469°)	99.1% (28.37°)	97.3% (24.835°)	99.9% (21.839°)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5163/0/163	3334/0/163	4494/0/164	4325/0/164
Goodness-of-fit on F^2	0.950	1.098	1.063	1.065
Final R indices [$I > 2$sigma(I)]	$R_1 = 0.0320$ $wR_2 = 0.0728$	$R_1 = 0.0381$ $wR_2 = 0.0721$	$R_1 = 0.0335$ $wR_2 = 0.0899$	$R_1 = 0.0243$ $wR_2 = 0.0658$
R indices (all data)	$R_1 = 0.0520$ $wR_2 = 0.0774$	$R_1 = 0.0803$ $wR_2 = 0.1168$	$R_1 = 0.0392$ $wR_2 = 0.0931$	$R_1 = 0.0269$ $wR_2 = 0.0670$
Largest diff. Peak and hole/e.Å^{-3}	0.610 and − 1.518	1.090 and − 1.169	0.750 and − 1.290	1.343 and − 1.238

ambient temperature. ^{1}H NMR and ^{13}C NMR along with elemental analyses were consistent with the bpma and corresponding Zn (II) and Cd (II) formulation. ^{1}H NMR spectra of the Zn (II) and Cd (II) complexes were only slightly shifted (δ 0.03–0.24) relative to those in the associated ligands due to resonance effects of the nitrogen and carbon atoms of the 4-bromoaniline and pyridine. Owing to the paramagnetic nature of Cu (II) and Co (II), we were unable to characterized **[(bpma)Co(μ–Cl)Cl]$_2$** and **[(bpma)Cu(μ–Cl)Cl]$_2$** by ^{1}H NMR and ^{13}C NMR spectroscopy. However, the characteristic absorption band around 1590–1592 cm^{-1} for the >C=N moiety was identified for synthesized complexes. Characteristic C–H peaks in the IR spectra were also observed at 3067, 3100, 3134 and 3086 cm^{-1} for **[(bpma)Co(μ–Cl)Cl]$_2$**, **[(bpma)Cu(μ–Cl)Cl]$_2$**, **[(bpma)Zn(μ–Cl)Cl]$_2$** and **[(bpma)Cd(μ–Br)Br]$_2$**, respectively. Elemental analysis of the synthesized complexes was consistent with the proposed structures in Scheme 1 and confirmed the purity of isolated complexes **[(bpma)MX$_2$]** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br). All the synthesized complexes were stable towards oxygen and moisture and could be stored for months at room temperature.

3.2 | Crystal structure description

Dark green needle like crystals of **[(bpma)Co(μ–Cl)Cl]$_2$** and orange cubic crystals of **[(bpma)Cu(μ–Cl)Cl]$_2$** were obtained from a Et$_2$O solution (10.0 ml) diffusion into an MeOH (5.00 ml). The X-ray quality single crystals of **[(bpma)Zn(μ–Cl)Cl]$_2$** and **[(bpma)Cd(μ–Br)Br]$_2$** were grown from an IPA solution (10.0 ml) diffusion into DMF solution (5.0 ml). The ORTEP drawings of complexes are shown in Figure 1 (**[(bpma)Co(μ–Cl)Cl]$_2$**), Figure 2 (**[(bpma)Cu(μ–Cl)Cl]$_2$**), Figure 3 (**[(bpma) Zn(μ–Cl)Cl]$_2$**) and Figure 4 (**[(bpma)Cd(μ–Br)Br]$_2$**). All the synthesized complexes crystallized in monoclinic system with *P*2(1)/n space groups. The selected bond lengths and angles are recorded in Table 2.

X-ray structures revealed chloro-bridged dimeric species with crystallographic inversion symmetry for **[(bpma)M(μ–Cl)Cl]$_2$** (M = Co, Cu and Zn, X = Cl) complexes, whereas a dimeric bromo-bridged species for (**[(bpma)Cd(μ–Br)Br]$_2$**) complex. The coordination geometry around the M (II) centre in **[(bpma)M(μ–X) X]$_2$** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br) can be best described as distorted trigonal bipyramidal



SCHEME 1 Synthesis of the **bpma** and corresponding complexes, **[(bpma)M(μ–X)X]$_2$** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br)

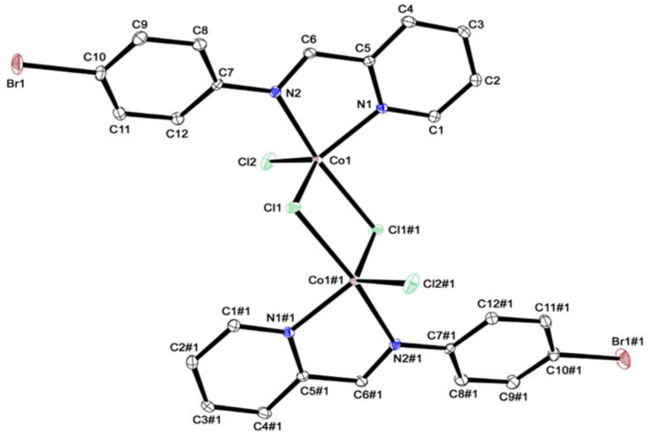


FIGURE 1 ORTEP drawing of **[(bpma)Co(μ–Cl)Cl]$_2$** with thermal ellipsoids at 90% probability. All hydrogen atoms are omitted for clarity

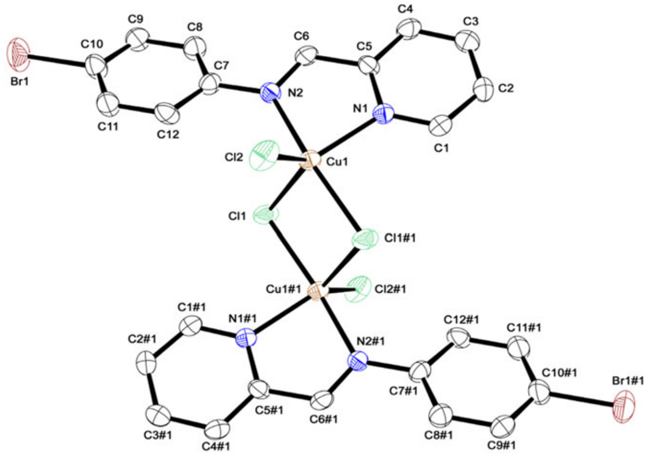


FIGURE 2 ORTEP drawing of **[(bpma)Cu(μ–Cl)Cl]$_2$** with thermal ellipsoids at 60% probability. All hydrogen atoms are omitted for clarity

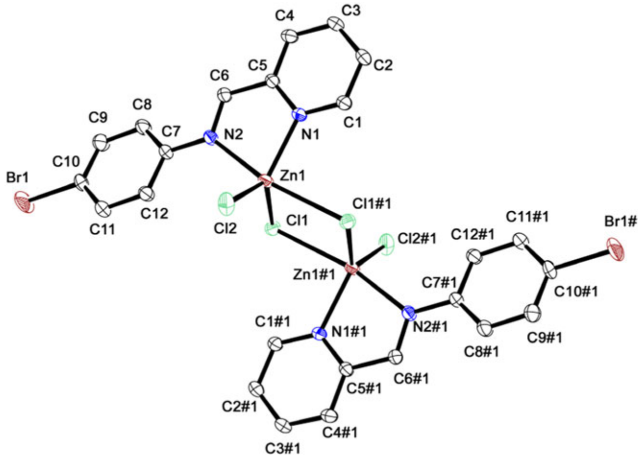


FIGURE 3 ORTEP drawing of **[(bpma)Zn(μ–Cl)Cl]$_2$** with thermal ellipsoids at 50% probability. All hydrogen atoms are omitted for clarity

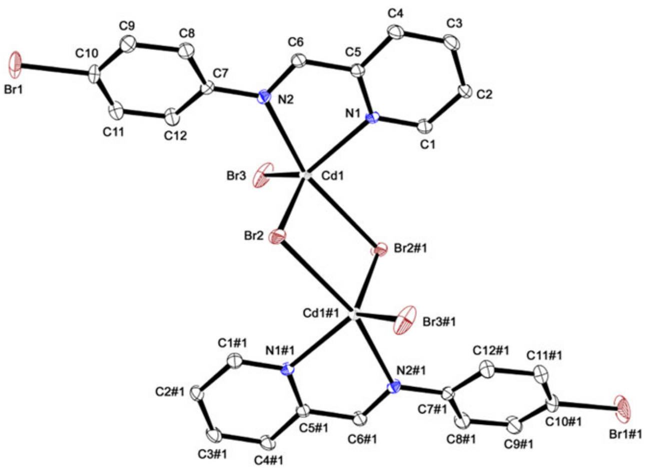


FIGURE 4 ORTEP drawing of **[(bpma)Cd(μ–Br)Br]$_2$** with thermal ellipsoids at 90% probability. All hydrogen atoms are omitted for clarity

consisting of two nitrogen atoms of 4-bromoaniline and pyridine moieties and two bridged halogen atoms along with one terminal halogen atom.

The bond lengths of M–N$_{pyridine}$ (M = Co, Cu, Zn, and Cd) and M–N$_{imine}$ in **[(bpma)M(μ–X)X]$_2$** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br) lie in 2.064(4) – 2.2886(2) Å and 2.038(4) – 2.4160(2) Å range, similar to the M–N bond lengths of trigonal bipyramidal imine M (II) complexes.[39–41] The bond length of M–N$_{imine}$ increased by approximately 0.015–0.200 Å, ranging in size from ([**(bpma)Cu(μ–Cl)Cl]$_2$**) < ([**(bpma)Co(μ–Cl)Cl]$_2$**) < ([**(bpma)Zn(μ–Cl)Cl]$_2$**) < (**[(bpma)Cd(μ–Br)Br]$_2$**). The M–Cl bond lengths ranged from 2.2333(7) – 2.6460(6) Å[42] while those of M–Br ranged from 2.5298(5) – 2.8244(5) Å. The double imine N(2)–C(6) distances of 1.289(2) Å (**[(bpma)Co(μ–Cl)Cl]$_2$**), 1.279(6) Å (**[(bpma)Cu(μ–Cl)Cl]$_2$**), 1.282(2) Å (**[(bpma)Zn(μ–Cl)Cl]$_2$**) and 1.283(3) Å (**[(bpma)Cd(μ–Br)Br]$_2$**) were in accepted range of carbon-nitrogen double bonds. The C(5)–C(6) bond distances of the complexes ranged from 1.458(3) – 1.467(3) Å, reflecting delocalised π-electrons. The bond lengths were slightly affected by the central metal variation.

The average N$_{imine}$–M–N$_{pyridine}$ bond angles for **[(bpma)M(μ–Cl)Cl]$_2$** (M = Co, Cu, Zn and Cd) ranged from 70.07(6) – 80.92(2)°, whereas X–M–X angles ranged from 118.59(6)- 125.42(2)° and were slightly affected by metal center. The N$_{pyridine}$–M(1)–Cl(1), N$_{pyridine}$–M(1)–Cl(2) and Cl(1)–M(1)–Cl(2) angles for the complexes **[(bpma)M(μ–Cl)Cl]$_2$** (M = Co, Cu and Zn) were nearly 120° in the range of 116.63(5)° – 122.98(3)°. Similarly, the N(1)–Cd(1)–Br(3) and Br(2)–Cd(1)–Br(3) angles for the complex **[(bpma)Cd(μ–Br)Br]$_2$** were nearly 120° in the range of 124.85(5)° – 125.42(2)°, excluding the bond angles of N(1)–M(1)–Br(2) which was 109.63(5)°. N$_{imine}$–

TABLE 2 The selected bond lengths (Å) and angles (°) of **[(bpma)M(μ–X)X]$_2$** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br)

[(bpma)Co(μ–Cl)Cl]$_2$		**[(bpma)Cu(μ–Cl)Cl]$_2$**		**[(bpma)Zn(μ–Cl)Cl]$_2$**		**[(bpma)Cd(μ–Br)Br]$_2$**	
Bond lengths							
Co(1)–N(1)	2.0671(2)	Cu(1)–N(1)	2.064(4)	Zn(1)–N(1)	2.0752(2)	Cd(1)–N(1)	2.2886(2)
Co(1)–N(2)	2.1824(2)	Cu(1)–N(2)	2.038(4)	Zn(1)–N(2)	2.2026(2)	Cd(1)–N(2)	2.4160(2)
Co(1)–Cl(1)	2.3258(7)	Cu(1)–Cl(1)	2.4137(2)	Zn(1)–Cl(1)	2.2880(7)	Cd(1)–Br(3)	2.5298(5)
Co(1)–Cl(2)	2.2629(7)	Cu(1)–Cl(2)	2.2878(2)	Zn(1)–Cl(2)	2.2333(7)	Cd(1)–Br(2)	2.6166(6)
Co(1)–Cl(1)$^{\#1}$	2.4721(6)	Cu(1)–Cl(1)$^{\#1}$	2.3085(1)	Zn(1)–Cl(1)$^{\#1}$	2.6460(6)	Cd(1)–Br(2)$^{\#1}$	2.8244(5)
N(1)–C(5)	1.352(2)	N(1)–C(5)	1.346(6)	N(1)–C(5)	1.354(2)	N(1)–C(5)	1.359(3)
N(2)–C(6)	1.289(2)	N(2)–C(6)	1.279(6)	N(2)–C(6)	1.282(2)	N(2)–C(6)	1.283(3)
N(2)–C(7)	1.428(2)	N(2)–C(7)	1.444(6)	N(2)–C(7)	1.426(2)	N(2)–C(7)	1.422(3)
C(5)–C(6)	1.458(3)	C(5)–C(6)	1.462(7)	C(5)–C(6)	1.463(2)	C(5)–C(6)	1.467(3)
Bond angles							
N(1)–Co(1)–N(2)	78.39(6)	N(1)–Cu(1)–N(2)	80.92(2)	N(1)–Zn(1)–N(2)	78.39(6)	N(1)–Cd(1)–N(2)	70.07(6)
N(1)–Co(1)–Cl(2)	117.82(5)	N(1)–Cu(1)–Cl(2)	119.81(1)	N(1)–Zn(1)–Cl(2)	120.44(5)	N(1)–Cd(1)–Br(3)	124.85(5)
N(2)–Co(1)–Cl(2)	95.99(5)	N(2)–Cu(1)–Cl(2)	96.38(1)	N(2)–Zn(1)–Cl(2)	100.77(5)	N(2)–Cd(1)–Br(3)	102.39(5)
N(1)–Co(1)–Cl(1)	118.85(5)	N(1)–Cu(1)–Cl(1)	121.52(1)	N(1)–Zn(1)–Cl(1)	116.63(5)	N(1)–Cd(1)–Br(2)	109.63(5)
N(2)–Co(1)–Cl(1)	89.36(5)	N(2)–Cu(1)–Cl(1)	90.19(1)	N(2)–Zn(1)–Cl(1)	92.03(5)	N(2)–Cd(1)–Br(2)	90.19(5)
N(1)–Co(1)–Cl(1)$^{\#1}$	94.47(5)	N(1)–Cu(1)–Cl(1)$^{\#1}$	93.22(1)	N(1)–Zn(1)–Cl(1)$^{\#1}$	90.78(5)	N(1)–Cd(1)–Br(2)$^{\#1}$	90.82(5)
N(2)–Co(1)–Cl(1)$^{\#1}$	169.55(4)	N(2)–Cu(1)–Cl(1)$^{\#1}$	169.89(1)	N(2)–Zn(1)–Cl(1)$^{\#1}$	166.77(4)	N(2)–Cd(1)–Br(2)$^{\#1}$	161.79(4)
Cl(1)–Co(1)–Cl(2)	122.98(3)	Cl(1)–Cu(1)–Cl(2)	118.59(6)	Cl(1)–Zn(1)–Cl(2)	122.89(3)	Br(3)–Cd(1)–Br(2)	125.42(2)
C(6)–N(2)–C(7)	118.58(2)	C(6)–N(2)–C(7)	118.4(4)	C(6)–N(2)–C(7)	119.95(2)	C(6)–N(2)–C(7)	119.47(2)
C(6)–N(2)–Co(1)	111.54(1)	C(6)–N(2)–Cu(1)	112.7(3)	C(6)–N(2)–Zn(1)	111.23(1)	C(6)–N(2)–Cd(1)	112.85(1)
C(8)–C(7)–N(2)	122.11(2)	C(8)–C(7)–N(2)	120.9(5)	C(8)–C(7)–N(2)	122.34(1)	C(8)–C(7)–N(2)	122.7(2)
C(12)–C(7)–N(2)	118.02(2)	C(12)–C(7)–N(2)	119.2(5)	C(12)–C(7)–N(2)	117.68(2)	C(12)–C(7)–N(2)	117.48(2)

M(1)–Cl(1) and N$_{imine}$–M(1)–X(2) angles for Co (II) and Cu (II) complexes were nearly 90 degrees in the range of 89.36(5)° – 96.38(1)°, excluding N$_{imine}$–Zn(1)–Cl(2) and N$_{imine}$–Cd(1)–Br(3) which were 100.77(5)° and 102.39(5)°, respectively. The N(2)–M(1)–X(1)$^{\#1}$ angles for the complexes **[(bpma)M(μ–X)X]$_2$** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br) were 169.55(4)°, 169.89(1)°, 166.77(4)° and 161.79(4)°, respectively.

The comparison of bond angles and geometric parameter (τ) values it is evident that **[(bpma)M(μ–X)X]$_2$**, showed a distorted trigonal bipyramidal geometry with *N,N′*-bidentate iminopyridine, two bridged and one terminal halogen ligand, achieving a 5-coordinated complexes (Table 3). τ_5 are presented in Table 3 as improved simple metrics for quantitatively evaluating the geometry of the five coordinate complexes.[43,44] The τ_5 value of **[(bpma)M(μ–X)X]$_2$** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br) showed either square-pyramidal or trigonal bipyramidal distorted by 0.606–0.806 while an ideal trigonal bipyramidal arrangement has the value of $\tau_5 = 1$. The τ_5 values of the 4-bromo-*N*-((pyridin-2-yl)methylene) benzenamine (**bpma**)-based complexes showed in the order of **[(bpma)Cu(μ–Cl)Cl]$_2$** (0.806) > **[(bpma)Co(μ–Cl)Cl]$_2$** (0.776) > **[(bpma)Zn(μ–Cl)Cl]$_2$** (0.731) > **[(bpma)Cd(μ–Br)Br]$_2$** (0.606), depending on the bond angles around the metal centre. Among **[(bpma)M(μ–X)X]$_2$** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br), the geometry at copper centre is more

TABLE 3 Five-coordinate geometry indices for **[(bpma)M(μ–X)X]$_2$** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br) and representative examples from the literature

Complexes	**Geometry**	τ_5	**Reference**
trigonal bipyramidal	trigonal bipyramidal	1.00	[43,44]
[(bpma)Co(μ–Cl)Cl]$_2$	trigonal bipyramidal	0.776	This work
[(bpma)Cu(μ–Cl)Cl]$_2$	trigonal bipyramidal	0.806	This work
[(bpma)Zn(μ–Cl)Cl]$_2$	trigonal bipyramidal	0.731	This work
[(bpma)Cd(μ–Br)Br]$_2$	trigonal bipyramidal	0.606	This work
Square-pyramidal	square-pyramidal	0.00	[43,44]

(Table 2). Interestingly, the plane of the 4-bromophenyl moiety and the plane of metal and pyridine were 20.95° for **[(bpma)Co(μ–Cl)Cl]$_2$**, 20.65° for **[(bpma)Cu(μ–Cl)Cl]$_2$**, 18.02° for **[(bpma)Zn(μ–Cl)Cl]$_2$** and 21.31° for **[(bpma)Cd(μ–Br)Br]$_2$**.

3.3 | Catalytic studies

The synthesized metal complexes could be activated with MMAO to polymerise MMA, producing PMMA. The obtained PMMA has the T_g in range of 122–129 °C, characterized by DSC. The polymers were isolated as white solids and characterised by GPC in THF using standard polystyrene as the reference. (Table 4)

To confirm the catalytic activity of MMA polymerisation, metal salts/precursors such as $CoCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $ZnCl_2$, $CdBr_2{\cdot}4H_2O$ and MMAO were tested towards MMA under identical experimental conditions, respectively. The synthesized metal complexes, **[(bpma)Cu(μ–Cl)Cl]$_2$** and **[(bpma)Zn(μ–Cl)Cl]$_2$** exhibited improved catalytic activities with better polymerization control yielding high molecular weight PMMA with narrower PDIs, whereas the Co and Cd complexes exhibited lower activities compared to their corresponding starting materials.

The catalytic activity of **[(bpma)Cu(μ–Cl)Cl]$_2$** was much higher compared to rest of complexes used in current study with identical ligand architecture. Presumably, the electron-rich cloud around the Cu metal in **[(bpma)Cu(μ–Cl)Cl]$_2$** provided increased activity compared to the electronic effect of **[(bpma)M(μ–X)X]$_2$** (M = Co and Zn, X = Cl; M = Cd, X = Br).

To evaluate the total steric hindrance by bulky ligands toward metal centre, it can be predicted and quantitatively calculated by comparison through a topographic steric map of M (II) complexes by use of program ″SambVca″ (see supplementary materials).[45] Figure 1 in the supplementary material shows ball and stick model, space-filling model, and topographic steric map of **[(bpma)M(μ–X)X]$_2$** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br) for presenting steric bulk ligands. Only considering total steric factor by topographic steric maps it is evident that more sterically hindered complex displayed better catalytic performance. For instance, Cu (II) complex despite of having more sterically hindered with buried volume % is 36.2 showed higher activity 9.14 × 10^4 g/molCu.h compared to rest of its analogous under same conditions. These results are in contrast to our previous results where more sterically hindered environment negatively affect the catalytic activity. Similarly the order of activity for **[(bpma)M(μ–X)X]$_2$** (M = Co and Zn, X = Cl; M = Cd, X = Br) was found to be **[(bpma)Zn(μ–Cl)Cl]$_2$** (buried volume % 34.7, activity 3.24 × 10^4 g/molZn.h) > **[(bpma)Co(μ–Cl)Cl]$_2$** (buried volume % 34.7,

TABLE 4 Polymerization of MMA by M (II) complexes in the presence of MMAO

Entry	Catalyst[a]	Yield[b]	Activity[c]	T_g[d]	Tacticity			*Mn*[e]	M_w/M_n[f]
		(g)	(g/mol-Cat·h) × 10^4	(°C)	%mm	%mr	%rr	(g/mol) × 10^5	
1	**[$CoCl_2{\cdot}6H_2O$]**[g]	30.3	4.73	133	6.30	23.9	69.8	10.7	1.49
2	**[$CuCl_2{\cdot}2H_2O$]**[g]	11.1	1.74	136	8.80	23.7	67.5	13.4	1.93
3	**[$ZnCl_2$]**[g]	11.1	1.73	129	9.20	24.2	66.6	1.33	1.58
4	**[$CdBr_2{\cdot}4H_2O$]**[g]	18.2	2.85	131	6.20	29.0	64.8	9.42	1.84
5	MMAO[h]	8.97	1.40	120	37.2	10.9	51.9	6.78	2.09
6	**[(bpma)Co(μ–Cl)Cl]$_2$**	19.8	3.08	125	10.5	20.5	69.0	8.53	2.61
7	**[(bpma)Cu(μ–Cl)Cl]$_2$**	58.6	9.14	128	11.4	20.3	68.3	9.12	1.97
8	**[(bpma)Zn(μ–Cl)Cl]$_2$**	20.8	3.24	129	10.3	21.2	68.5	8.32	2.58
9	**[(bpma)Cd(μ–Br)Br]$_2$**	15.5	2.48	122	11.0	19.9	69.1	9.05	2.56

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

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

[c] Activity is (g PMMA)/(mol-cat·h).

[d] T_g is glass transition temperature which is determined by 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] It is a blank polymerization which was done solely by MMAO. It is a blank polymerization in which $CoCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $ZnCl_2$ and $CdBr_2.4H_2O$ were also activated by MMAO.

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

activity 3.08×10^4 g/molCo.h) > **[(bpma)Cd(μ–Br)Br]$_2$** (buried volume % 30.8, activity 2.48×10^4 g/molCd.h). Thus, it is revealed that the least sterically crowd around the metal centre has detrimental effect on catalytic activity in the current system. Thus, the electronic effects of catalysts are more pronounced compared to steric effect in controlling the polymerization activity. The influence of metal centre variation is also studied. It has been observed that despite of having same buried volume % (supplementary material, Figure S1) for Zn (II) and Co (II) complexes, Zn (II) complex showed higher activity compared to its Co (II) analogous. Thus, the activity of these M (II) complexes with same ligand (bpma) toward MMA polymerisation is influenced by both steric and metal electronics. In addition, it is worth to note that the solubility of complexes in polymerization media showed an impact on polymerization activity in previous research. Thus, the lower activity of **[(bpma)Cd(μ–Br)Br]$_2$** and **[(bpma)Co(μ–Cl)Cl]$_2$** compared to metal precursors $CdBr_2 \cdot 4H_2O$ and $CoCl_2 \cdot 6H_2O$, respectively can be attributed to its lower solubility in reaction media.

Moreover, the catalytic activity of **[(bpma)Cu(μ–Cl)Cl]$_2$** was much higher than **[(bpma)Co(μ–Cl)Cl]$_2$**, **[(bpma)Zn(μ–Cl)Cl]$_2$** and **[(bpma)Cd(μ–Br)Br]$_2$**. Presumably, the electron-rich cloud around the Cu metal in **[(bpma)Cu(μ–Cl)Cl]$_2$** provided increased activity compared to the electronic effect of **[(bpma)M(μ–X)X]$_2$** (M = Co and Zn, X = Cl; M = Cd, X = Br). Thus, the activity of these **[(bpma)M(μ–X)X]$_2$** (M = Co and Zn, X = Cl; M = Cd, X = Br) complexes toward MMA polymerisation is influenced by metal electronics. No regular trend for molecular weight and resultant PDIs can be seen from polymerization in current data.

The tacticity of PMMA was determined in the range around syndiotactic (δ 0.85), heterotactic (δ 1.02), and isotactic (δ 1.21) based on ^{1}H NMR.[46–48] The syndiotacticity of PMMA was around 69%, which was similar to all **[(bpma)M(μ–X)X]$_2$** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br) regardless of the polymerization catalyst. However, the syndiotacticity was higher compared to co-catalyst, MMAO. Although syndiotacticity was not sufficiently high to discuss a coordination polymerization mechanism but was found to be in identical range for all the synthesised complexes (*rr* = 0.69).

Previously studied *N*,*N*-di(2-picolyl) cyclohexylamine[49] based Pd, Cu, Zn, and Cd complexes were found to be active catalysts for the MMA polymerisation to yield syndiotactic PMMA (*rr* = 0.73). Similarly, Cu (II) complexes with ligand *N*-(2-furanylmethyl)-*N*-(1–3,5-dimethyl-1H-pyrazolylmethyl)-*N*-(phenylmethyl) amines[50] yielded syndiotactic PMMA (*rr* = 0.78) with only 30% conversion. Copper (II) complex of 2-(pyrazol-3-yl)-6-(pyrazolate) pyridine and related ligand[51] reported catalyzed MMA polymerization with moderate activity and syndiotacticity. Compared with our previous Co complexes with *N*, *N*-bis(1-pyrazolyl)methyl[52] the current Co complex exhibited better activity and stereoselectivity and yielded PMMA with high molecular weight. The MMA polymerisation activity of complexes in the current study should be considered as a function of the electron density around the metal centre.

4 | CONCLUSIONS

In summary, we investigated the synthesis and X-ray crystallographic structures of **[(bpma)Co(μ–Cl)Cl]$_2$**, **[(bpma)Cu(μ–Cl)Cl]$_2$**, **[(bpma)Zn(μ–Cl)Cl]$_2$** and **[(bpma)Cd(μ–Cl)Cl]$_2$** complexes bearing 4-bromo-*N*-(2-pyridinylmethylene) benzenamine ligand. The coordination geometry around the metal centres in **[(bpma)M(μ–X)X]$_2$** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br) complexes can be best described as distorted triangular bipyramidal. The synthesized complexes **[(bpma)M(μ–X)X]$_2$** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br) were investigated for their catalytic efficacy in MMA polymerization. The catalytic activity of **[(bpma)Cu(μ–Cl)Cl]$_2$** toward the polymerisation of methyl methacrylate (MMA) in the presence of MMAO resulted in an activity of 9.14×10^4 g PMMA/mol·Cu·h at 60 °C. All the complexes in the current investigation afforded syndio-enriched PMMA. The catalytic activity in the present study can be considered as the function of electronic density around the metal centre.

SUPPLEMENTARY MATERIAL

CCDC 1872375~1872378 contains the supplementary crystallographic data for **[(bpma)Cu(μ–Cl)Cl]$_2$**, **[(bpma)Zn(μ–Cl)Cl]$_2$**, **[(bpma)Co(μ–Cl)Cl]$_2$** and **[(bpma)Cd(μ–Cl)Cl]$_2$**, 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. Additionally, steric maps of all **[(bpma)M(μ–X)X]$_2$** (M = Co, Cu and Zn, X = Cl; M = Cd, X = Br) which is calculated by the program ″SambVca″ was also presented in the supplementary material.

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