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Article

Coordination polymers derived from pyridyl carboxylate ligands having amide backbone: An attempt towards selective separation of Cu^{II} cation following *in situ* crystallization under competitive conditions

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Abstract:

A series of coordination polymers (CPs) derived from pyridyl carboxylate ligands equipped with hydrogen bonding backbone (amide) namely L1[Sodium 4-(nicotinamido) benzoate] and L2[Sodium 3-(nicotinamido) benzoate] has been synthesized and characterized by single crystal X-ray diffraction.Effect of ligating topology of these two positional isomers (L1 and L2) on the resultant supramolecular architecture of the corresponding CPswasinvestigated.The results indicate that most of the CPs display 1D looped chain topology. Following *in situ* crystallization technique, attempts were made to separateenvironmentallytoxicmetalcationCu^{II} in the form of the correspondingCu^{II} CPs from a complex mixture of cations (Cu^{II}, Zn^{II} and Co^{II}) using both the ligands; while L1 was unsuccessful, L2 indeed could separate Cu^{II}cation. The coordinating ability of the pyridyl and carboxylate moieties on the selective separation of cation was investigated; the results indicated that selective separation of Cu^{II} followed Irving-Williams series. Atomic absorption spectroscopy revealed that ~97% of Cu^{II} could be separated by this technique.

Introduction:

Spontaneous self-assembly[1] of organic linkers (ligand) and suitable metal centres result in highly crystalline materials known as coordination polymers (CPs).[2] The field of CPs has rapidly grown since the early report by Robson et al.[3] on the synthesis of Cu^{II}-diamondoid network derived from three dimensionally linked rod-like segment namely 4,4′,4′′,4′′′-tetracyanotetraphenyl methane. Because of the remarkable advancement of single crystal X-ray diffraction techniques and highly crystalline nature of CPs, it has been possible to study the structures of CPs in molecular level that enables researchers to design *a priori* CPs with desired structures and functions. Thus, CPs are a special class of supramolecular materials offering various potential applications such as gas storage,[4] catalysis,[5] anion separation,[6] magnetic property,[7] drug delivery,[8] sensors,[9] opto-electronics[10] etc.

As a part of our ongoing research program, we have been interested in developing intriguing CPs derived from various ditopic and tritopic ligands having *non-innocent* (hydrogen bond equipped) backbone.[11] Thus, various bis-pyridyl ligands having amide or urea functionality were exploited in generating intriguing structures like all-helical 3D network,[12a]diamondoid network,[12b]Borromean entangled network,[12c] metalla-cryptand[12d]etc. We have also developed CPs capable of displaying anion separation and metallogelation properties.[6e]

Separation of toxic metal pollutants is important in the context of environmental remediation. Aqueous phase metal cation separation has been achieved by various techniques that include precipitation,[13] adsorption[14] and solvent extraction.[15]While chelating agents like hydroxyoximes, β-diketones etc. have been used in solvent extraction,[16] solid sorbent mediated cation separation[17] includes ligand grafted organic polymers, surface modified silica gels, mesoporous and ion exchange materials.[18] Although solvent extraction offers advantages like flexible operation, ability to handle wide ranges of concentration and selectivity, it, however, suffers from disadvantages like toxicity and flammability of the solvents, time consuming phase separation due to emulsion formation etc. Solvent extraction method also depends on the pH of the medium, which can be considered as an additional disadvantage. Copper plays a crucial role in biology;[19] various copper containing enzymes carry out important biological functions. However, beyond a critical concentration, it is immensely toxic; for example, drinking water containing copper concentration more than 2 mg/L is toxic. Since copper is an indispensible element present in various industrial materials such as stainless steels, nonferrous alloy, metal plating, refractory materials and thermal and electric conductors, it is no wonder that one of the major environmental pollutants[20] (industrial waste) is copper. In a recent report, we showed that Cu^{II} was separated selectively from a complex mixture of divalent cations (Zn^{II}, Co^{II}, Cu^{II}) by exploiting *in situ* crystallization of coordination polymers.[21] In this technique, a suitable ligand was allowed to react with a competitive mixture of metal cations to crystallize out coordination polymer containing the desired metal centre as a part of the coordination network. In this particular study, we exploited bis-pyridyl-bis-amide based chiral ligands derived from L-amino acids to achieve selective separation of Cu^{II} in the form the corresponding coordination polymers. The reasons for obtaining selective formation of

Cu^{II}coordination polymer in this competitive conditions were: a) the stability constant of Cu^{II} compounds were expected to be more than that of the Co^{II} and Zn^{II} as per Irving-Williams series,[22] b) pyridyl N atoms being soft base as per HSAB principle did not react to significant extent with the relatively harder acids such as Co^{II} and Zn^{II} as compared to the borderline Cu^{II} metal centre under competitive conditions.

In the present study, we considered theditopic ligands**L1**and **L2** wherein both soft (pyridyl N) and hard (carboxylate) coordinating sites were available.[23]The reason for choosing such ligands having both hard and soft coordinating sites was to study the driving force behind cation separation – was it mainly governed by hard-soft-acid-base (HSAB) principle or was it controlled by Irving-Willams series?

Herein, we report the syntheses and single crystal structures of two new lignads**L1H** and **L2H**, and their corresponding coordination polymers derived from **L1** and **L2** (corresponding sodium carboxylates) with various transition metal centres (Cu^{II}, Zn^{II}, Co^{II}, Cd^{II} and Fe^{II}). Competitive reactions of **L2** in the presence of a mixture of metal cations (Cu^{II}, Zn^{II}, Co^{II}) from aqueous solution provided exclusive crystallization of Cu^{II} coordination polymers thereby enabling selective separation ofCu^{II} from a complex mixture of cations.

Results and discussion.

The pyridyl-carboxy-amide lignads**L1H** and **L2H** were synthesized by reacting nicotinoyl chloride with the corresponding amino benzoic acid in dichloromethane (DCM)/THF mixture under refluxing condition. The corresponding precipitates, thus formed, were isolated and washed with DCM/THF to yield the pure ligands in good yield (see experimental). Attempts to react these ligands with various metal salts (Cu^{II}, Zn^{II}, Co^{II}, Cd^{II} and Fe^{II}) in DMF/EtOH/water resulted in crystallization and precipitation of **L1H** and **L2H**, respectively. In order to synthesize coordination polymers with these ligands, we then converted the ligands into the corresponding Na salt by reacting the ligands with NaOH solution. Reaction of the Na salts of these ligands with various metal salts resulted in 12 crystalline coordination polymers (Scheme 1). Single crystals of **L1H** and the coordination polymers (**CP1a**-**CP1f** and **CP2a**-**CP2f**) were subjected to single crystal X-ray diffraction (SXRD). It may be mentioned that in the case of **L1**, Cd^{II}CPs namely**CP1e** and **CP1d**were crystallized concomitantly. The same was true for **CP2a** and **CP2b** wherein **L2** was used. Table 1 enlisted the crystal data. Certain crystallographic and structural parameters were given in Table 2.

Single crystal structure of the free ligand L1H.

Colorless blocked shaped crystals of **L1H** belonged to the centrosymmetric orthorhombic space group Pbcn. The asymmetric unit contained a fully occupied ligand molecule. The ligand molecules propagated into 1D hydrogen bonded polymeric chain involving the carboxy-pyridine synthon sustained by N-H…O interactions. Such 1D chains were packed in perpendicular fashion sustained by N-H…O interactions involving the amide -NH and carboxylic O of the neighbouring chains resulting in an overall 3D hydrogen bonded network (Figure 1).

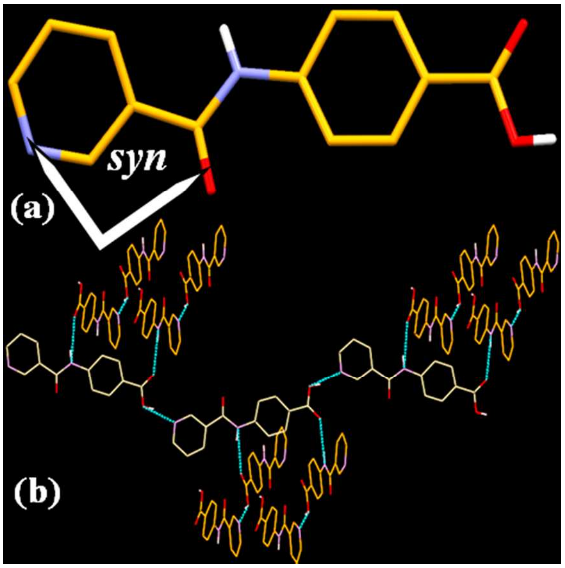


Figure 1. Crystal structure illustration of **L1H**; (a) molecular structure of the free ligand **L1H** displaying *syn*conformation in its singlecrystal structure; (b) perpendicularly packed 1D chains via H-bond (N-H···O).

Single crystal structures of the coordination polymers.

Crystal structures of[{Cu(μ-**L1**)$_2$ (H_2O)$_2$}$\cdot$$H_2O$]∝**CP1a**,[{Co(μ-**L1**)$_2$(H_2O)$_2$}$\cdot$$H_2O$]∝**CP1b**, [{Cd(μ-**L1**)$_2$(H_2O)$_2$}$\cdot$$H_2O$]∝**CP1e**, [{Fe(μ-**L1**)$_2$(H_2O)$_2$}$\cdot$$H_2O$]∝**CP1f**,[{Cu(μ-**L2**)$_2$ (H_2O)$_2$}$\cdot$2H_2O]∝**CP2a** and [{Cd(μ-**L2**)$_2$(H_2O)}$\cdot$(H_2O)(CH_3OH)]∝**CP2e**.SXRD analyses of the coordination polymers revealed that **CP1a**,**CP1b**, **CP1e** and **CP1f**were isomorphous displaying identical space group P2$_1$/n with near identical cell dimensions. It was observed that **CP2a** and **CP2e** crystallizing in different space group (P21/c and C2/c, respectively) were isostructural with the crystals of **CP1a**, **CP1b**, **CP1e** and **CP1f**. Thus, we described below the crystal structure of **CP1a** only.

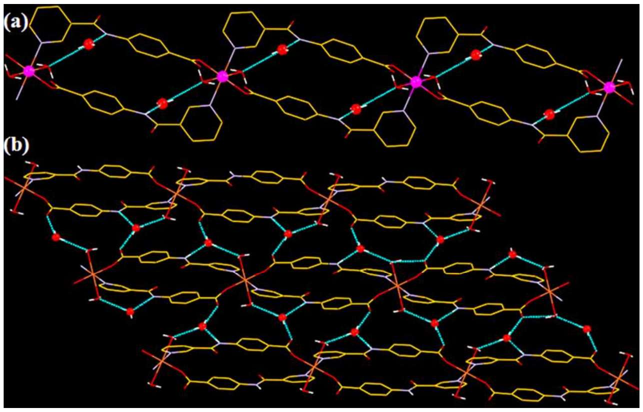
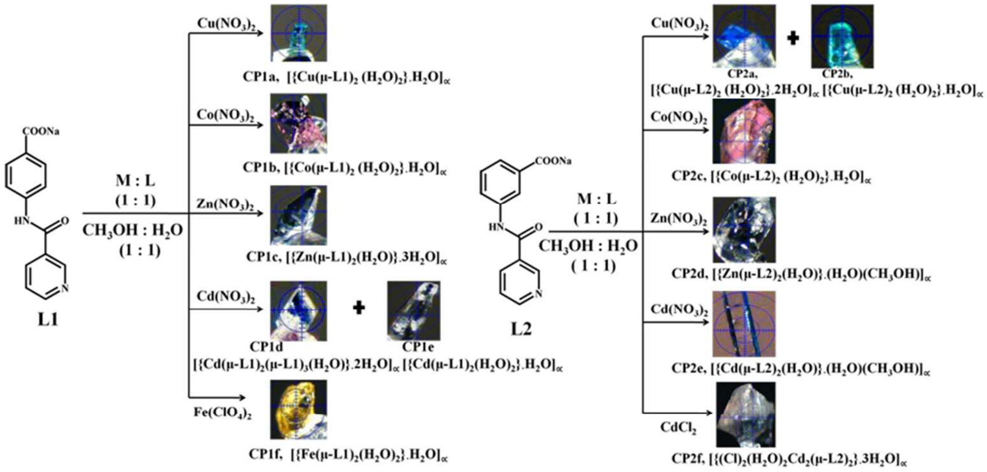


Figure 2. Crystal structure illustration of **CP1a**; (a) 1D looped chain coordination polymerformed via metal (Cu, magenta ball)– ligand (**L1**, *anti*) coordination displaying occluded water (red ball) molecules; (b) parallel packing of the looped chains sustained by various H-bonding interactions.

The asymmetric unit of **CP1a** was comprised of a fully occupied ligand **L1** coordinated to a half occupied Cu^{II} metal center(lies on an inversion centre)via pyridyl N atom, one fully occupied water molecule coordinated to the metal center and a fully occupied lattice occluded water molecule. In the crystal structure, the ligand molecule coordinated the metal center by both the ligating sites (pyridyl N and carboxylate O) to generate 1D looped chain topology. The Cu^{II} metal center displayed almost perfect octahedral geometry wherein the equatorial sites were occupied by O atoms of two water molecules and the carboxylate moiety, and the axial sites were coordinated by pyridyl N atoms. The 1D looped chains were packed in parallel fashion to generate an overall 3D hydrogen bonding network wherein the amide moiety of the ligand participated in hydrogen bonding interactions with the lattice occlude water as well as the metal bound water molecules sustained by both N-H…O and O-H…O interactions (Figure 2).



Scheme I

Crystal structures of $[\{Cu(\mu\text{-}L2)_2(H_2O)_2\}.H_2O]_\propto$CP2b and $[\{Co(\mu\text{-}L2)_2(H_2O)_2\}.H_2O]_\propto$CP2c.

SXRD data revealed that **CP2b** and **CP2c** were isomorphous displaying identical space group $P2_1/n$ having near identical cell dimension. Thus, we described below the crystal structure of **CP2b**.

The asymmetric unit of **CP2b** was comprised of one fully occupied ligand coordinated to the half occupied Cu^{II} metal center(lies on an inversion centre) via pyridyl N atom, one fully occupied water molecule coordinated to the metal center and a fully occupied lattice occluded water molecule. The Cu^{II} metal center displayed slightly distorted octahedral geometry wherein the equatorial sites were occupied by the O atoms of the carboxylate moiety and the pyridyl N atoms and the axial sites were coordinated by the O atoms of the solvate water molecules. The bidentatepyridyl-carboxylate ligands coordinated to the adjacent metal centers in such a way that a highly nonplanar 2D network was formed. Such 2D sheets were packed in parallel fashion. The amide functionality was found to be involved in hydrogen bonding with the carboxylate O of the ligand molecule within the 2D network whereas the lattice occluded water molecules bridged the adjacent 2D networks via hydrogen bonding interactions involving the amide carbonyl and carboxylate of the interacting networks (Figure 3).

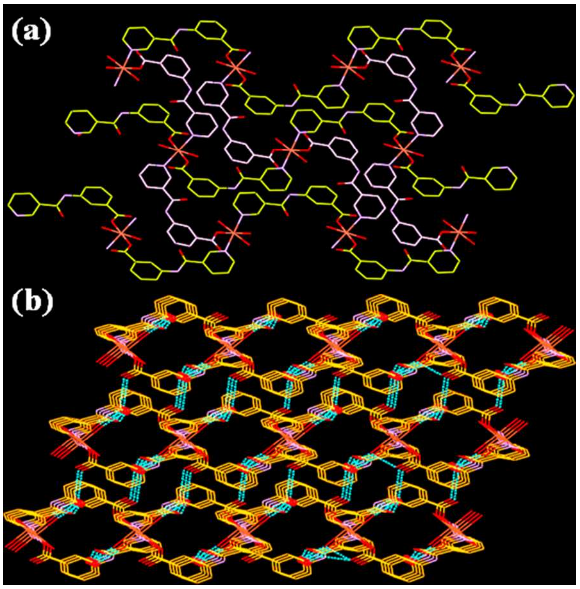


Figure 3. Crystal structure illustration of **CP2b**; (a) nonplanar 2D sheet network; (b) overall 3D network sustained by various H-bonding interactions.

Crystal structure of $[\{Zn(\mu\text{-}L1)_2(H_2O)\}.3H_2O]_\propto$CP1c. The coordination polymer **CP1c** crystallized in the centrosymmetric triclinic space group P-1. In the asymmetric unit, two ligand molecules, one Zn^{II} metal center, one metal bound water and three solvate water molecules were located on general positions. One of the ligands coordinated to the metal center via both the carboxylate and 3-pyridyl N whereas the other ligand coordinated to the metal center via carboxylate keeping the 3-pyridyl N free from coordination resulting in 1D polymeric chain resembling comb-like structure. The coordination environment of Zn^{II} may be considered as highly distorted octahedron wherein the equatorial positions were coordinated by the O atoms ofthetwo carboxylates and one water molecule whereas the axial positions were occupied by the pyridyl N and carboxylate O atoms. The 1D comb-like polymeric chains were packed in inter-digited fashion resulting in bilayer structures which were further packed in parallel fashion though out the crystal structure. The amide functionality of the crystallographically independent ligand molecules displayed hydrogen bonding interactions with the lattice occluded water and carboxylate moiety of the neighbouring chain via N-H…O and O-H…O interactions (Figure 4).

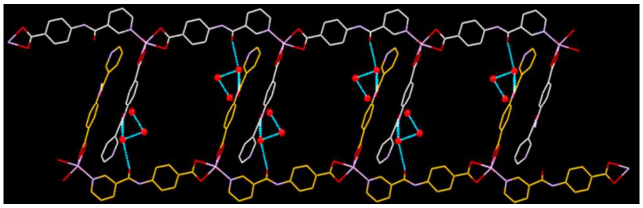


Figure 4. Crystal structure illustration of **CP1c**; 1D comb-like polymeric chainspacked in inter-digited fashion displaying occluded solvent water molecules (red ball) sustained by various hydrogen bonding.

Crystal structure of [{Cd(μ-L1)$_2$(μ-L1)$_3$ (H$_2$O)}.2H$_2$O]∝CP1d.

Single crystals of **CP1d** were found to be crystallized in the centrosymmetric triclinic space group P-1. Two ligand molecules, one Cd^{II} metal center, one metal bound water and two solvate water molecules [of which one molecule was found to be disordered over three positions having site occupancy factors (SOF) of 0.26, 0.24 and 0.50] were located in the asymmetric unit. The topology of the coordination network in the crystal structure may be best described as 2D corrugated sheet network weaved with looped structure generated due to head-to-tail centrosymmetric arrangement of the ligands coordinating the adjacent metal centers via both the carboxylate and pyridyl N. The coordination geometry of the Cd^{II} metal center was found to be distorted octahedral wherein the axial positions were occupied by pyridyl N atoms and the equatorial positions were coordinated by three carboxylate and one water O atoms. The amide functionality of the two ligand molecules present in the asymmetric unit were found to be involved in hydrogen bonding with the lattice occluded water molecules resulting in an overall 3D hydrogen bonded network (Figure 5).

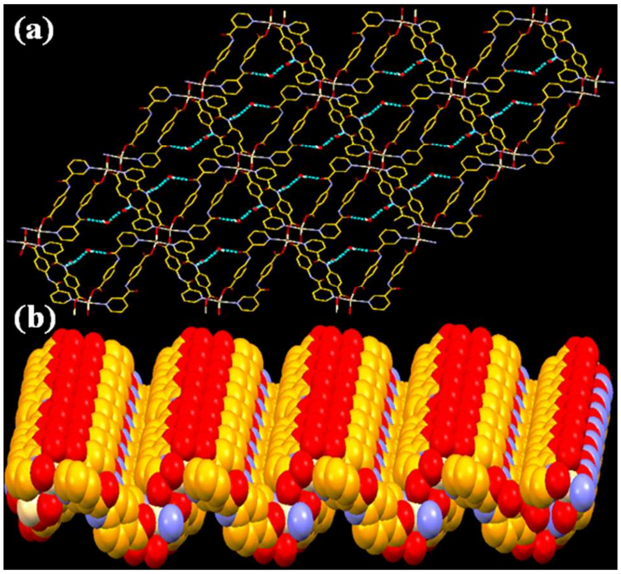


Figure 5. Crystal structure illustration of **CP1d**; (a) a nonplanar 2D network weavedwith looped structure formed via metal–ligandcoordination;(b) the 2D network represents a corrugated sheet.

Crystal structure of [{Zn(μ-L2)$_2$(H$_2$O)}.(H$_2$O)(CH$_3$OH)]∝CP2d.

Coordination polymer **CP2d** crystallized in the centrosymmetric triclinic space group P-1. The asymmetric unit was comprised of two ligand molecules, one Zn^{II} metal center, one metal bound water, two lattice occluded guest molecules namely water and MeOH. Both the crystallographically independent ligand molecules coordinated to the metal centers in such a fashion that it generated a 1D polymeric tape formed via two parallel 1D polymeric chains cross-linked by metallamacrocycles. The coordination environment of Zn^{II} may be considered as highly distorted octahedron wherein the equatorial positions were coordinated by the O atoms coming two carboxylate and one pyridyl N atoms whereas the axial positions were occupied by the pyridyl N and water O atoms. One of the amide carbonyl O of one of the crystallographically independent ligands was found to be free from any hydrogen bonding interactions whereas the rest of the atoms of the amide functionality were involved in hydrogen bonding interactions with the lattice occluded water and MeOH. The 1D coordination polymeric tapes were further packed in parallel fashion and the interstitial space was occupied by the lattice occluded MeOH and water sustained by hydrogen bonding interactions as described above (Figure 6).

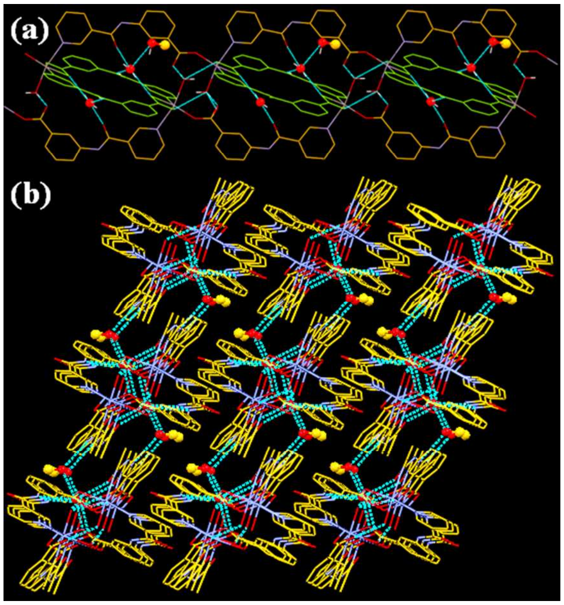


Figure 6. Crystal structure illustration of **CP2d**; (a) 1D polymeric tape formed fromtwoparallelly running 1D chains cross-linked by metallamacrocycle (green);(b) the overall 3D network sustained by H-bonding interactions displaying latticeoccluded water and methanol molecules.

Crystal structure of [{(Cl)$_2$(H$_2$O)$_2$Cd$_2$(μ-L2)$_2$}.3H$_2$O]∝ CP2f.

The coordination polymer **CP2f** crystallized in the centrosymmtric monoclinic space group C2/c. The asymmetric unit contained two ligand molecules, two Cd^{II} metal centers, two coordinated chloride, two metal-bound water (of which one was found to be disordered over two positions whose SOFs were refined to 0.48 and 0.52 using the second variable of FVAR in SHELXL software) and three lattice occluded water molecules (of which one was found be disordered over two positions with the refined SOFs 0.60 and 0.40 obtained using the second variable of FVAR in SHELXL software). Both the ligands coordinated to the metal centers via pyridyl N and carboxylate to generate M_2L_2 type macrocycle. The macrocycles were further propagated in 1D via $Cd^{II}(\mu\text{-}Cl)_2\text{-}Cd^{II}$ bridge. Both the metal centers displayed distorted octahedral geometry. The amide moiety of one of the ligand molecules was involved in hydrogen bonding with the metal-bound water of the neighbouring 1D network keeping the amide NH free from any interactions whereas the amide functionality in the other ligand molecule displayed hydrogen bonding interactions with the lattice occluded water molecules. The 1D coordination networks were packed in parallel fashion and the interstitial space thus created was occupied by the lattice occluded water molecules (Figure 7).

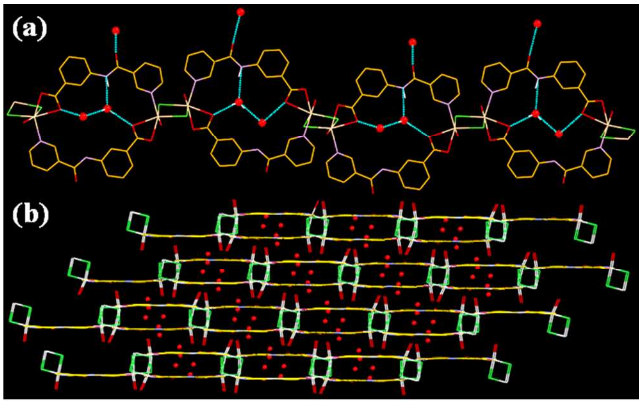
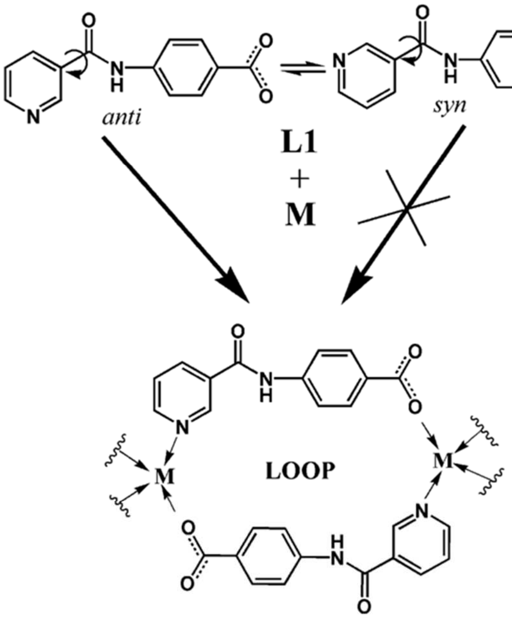


Figure 7. Crystal structure illustration of **CP2f**; (a) 1D looped chain coordination polymer propagated via$Cd^{II}(\mu\text{-}Cl)_2\text{-}Cd^{II}$ bridge; (b) the overall 3D network sustained by H-bonding interactions displaying lattice occluded water molecules (red balls).

The crystalline phase purity of the coordination polymers **CP1b**, **CP1c**, **CP1f**, **CP2a**, **CP2b**, **CP2c**, **CP2e**, **CP2f**were established by PXRD analyses (Supporting Information);in the case of CP1e, there appeared to be an extra phase as a few peaks within the region of 10-17° 2θ did not match with the simulated peaks. PXRD patterns of the bulk crystalline materials of the coordination polymers (**CP1a** and **CP1d**) did not match with the corresponding simulated PXRD patterns obtained from SXRD data which may be attributed to either solvent loss during the experiment or presence of new crystalline phase in the bulk materials.The PXRD pattern in CP2d appeared to be completely different than that of the simulated pattern indicating the formation of a completely new phase presumably due to solvent loss.

The structural features enlisted in Table 2 revealed the following. In the case of **L1**, because of the symmetric position of the carboxylate, the ligating topology mainly depended on the relative orientation of the pyridyl N with respect to the amide >C=O (here after Npy/>C=O) as a result of free rotation around Cpyridyl-Ccarbonyl bond. The free ligand **L1H** displayed *syn*conformation for Npy/>C=O whereas the coordination polymers displaying looped architecture (**CP1a**, **CP1b**, **CP1e** and **CP1f**) showed *anti* conformation understandably required to attain the looped coordination mode resulting in similar ligating angles (~101-109°) in these CPs. Interestingly, **CP1d** displayed both *syn*and *anti*Npy/>C=O conformation in the two crystallographically independent ligand molecules. Detail examination of the structure of **CP1d**revealed that the ligand having *anti*Npy/>C=O conformation was responsible for making the loop whereas the other ligand displaying *syn* conformation connected the looped structure resulting in an overall 2D corrugated sheet. The effect of Npy/>C=O conformation on the resulting coordination architecture was clear in the case of **CP1c** wherein the ligands displaying *syn* conformation was unable to form looped structure(Scheme II); instead it generated comb-like 1D polymeric chain.



Scheme II

In the case of**L2** derived coordination polymers, the coordinating sites i.e. pyridyl N and carboxylate were in 3-position in the aromatic rings making the ligating topology dependent on both the $N_{amide}\text{-}C_{phenyl}$ and $C_{pyridyl}\text{-}C_{carbonyl}$ bond rotation; as a result N_{py}/>C=O conformation become irrelevant and thus, both *syn* and *anti*N_{py}/>C=O conformation were observed in the coordination polymers having looped structure (**CP2a**, **CP2e** and **CP2f**). All the coordination polymers incorporated water or MeOH as guest molecules presumably because of the hydrogen bond capable amide backbone that participated in hydrogen bonding interactions with the guest molecules.

Cation separation.

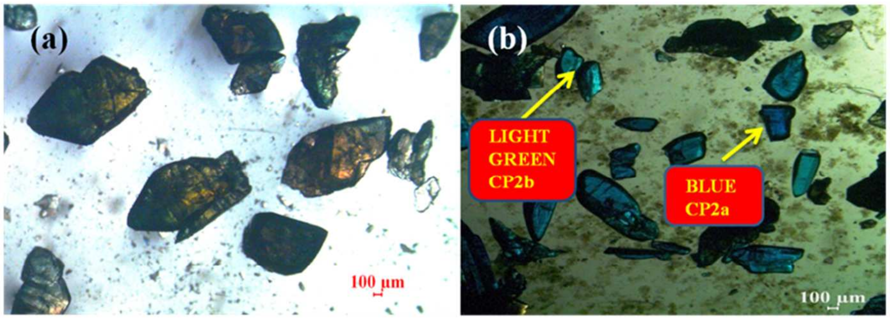
For the reasons stated above (*vide supra*), we next explored the possibility of separating Cu^{II} from a complex mixture of Cu^{II}, Co^{II} and Zn^{II} by competitive reactions of **L1** and **L2** with the corresponding metal-nitrates under three different conditions namely I, II and III. In all the cases, *in situ* crystallization of the coordination polymers were carried out in 1:1 MeOH:water by slow evaporation at room temperature keeping the molar ratio of the reactants i.e. ligand : Cu-salt : other metal salts as 2:1:2, 4:1:4

and 8:1:8 for the conditions I, II and III, respectively. It was observed that in the case of **L1**, the mixture of coordination polymers were obtained as crystalline aggregates revealed by their characteristic colors (blue for Cu^{II}, pink for Co^{II} and colorless for Zn^{II}(Fig. 8a). The PXRD of these crystalline aggregates turned out to be weekly diffracting. However, the major peaks of the diffraction patterns matched well with that of the simulated patterns of **CP1a** (Cu^{II}), **CP1b** (Co^{II}), **CP1c** (Zn^{II}) but failed to display one to one correspondence with any of the individual simulated patterns thereby proving it unsuccessful in selective separation of Cu^{II}(Supporting Information).Whereas the same experiments using **L2** resulted in light green and deep blue colored crystals indicating the concomitant formation of Cu^{II} coordination polymers namely **CP2a** and **CP2b**, respectively (Fig. 8b).The FT-IR of the crystals displayed excellent correspondence with that of the physical mixture of **CP2a** and **CP2b** as obtained concomitantly during their synthesisunder various conditions(condition I, II and III) thereby suggesting the selective separation of Cu^{II} in the form of the coordination polymers **CP2a** and **CP2b**(Fig. 8c). Further support in favour of selective separation of Cu^{II} using **L2** came from the PXRD patterns. It was clear from Fig. 8d that the PXRD patterns of the crystals under various conditions(I, II and III)were reasonably crystalline and the major peaks matched well with that of simulated patterns of **CP2a** and **CP2b** indicating the separation of Cu^{II} as the crystalline coordination polymers **CP2a** and **CP2b**.

To quantify the amount of Cu^{II} being separated during the experiment we run atomic absorption spectroscopy on the supernatant liquid after removing the crystals of **CP2a** and **CP2b**. Interestingly, up to 97% of Cu^{II} could be separated selectively (see Supporting information). Thus, in the case of **L1**, Irving-Williams series did not seem to be operative whereas in the case of **L2**, isolation of the Cu^{II} coordination polymers(**CP2a** and **CP2b**) under competitive conditions indicated that the stability of Cu^{II} coordination networks seemed to be influencing the selective separation of Cu^{II}.

Conclusions

Thus, we have synthesized a series of transition metal (Cu^{II}, Co^{II}, Cd^{II}, Zn^{II} and Fe^{II}) coordination polymers derived from hydrogen bond equipped pyridyl carboxylate ligands and characterized by single crystal X-ray diffraction. The primary objective of the present work was to study the effect of both hard and soft coordinating sites (pyridyl and carboxylate, respectively) on the selective separation of Cu^{II} from a complex mixture of cations following *in situ* crystallization of coordination polymers under various competitive conditions. The results confirmed that it was indeed possible to separate Cu^{II} from a complex mixture of cations (Cu^{II}, Co^{II} and Zn^{II}) in the form of concomitantly produced coordination polymers **CP2a** and **CP2b** when **L2** was used. The fact that such selective separation was unsuccessful in the case of **L1** clearly indicated that subtle change in the position of the coordinating sites (considering the positional isomeric relationship of **L1** and **L2**) greatly influenced the reactivity towards metal centers. Overall, the results presented herein



(c) FT-IR Comparison Plot (d) PXRD Comparison Plot

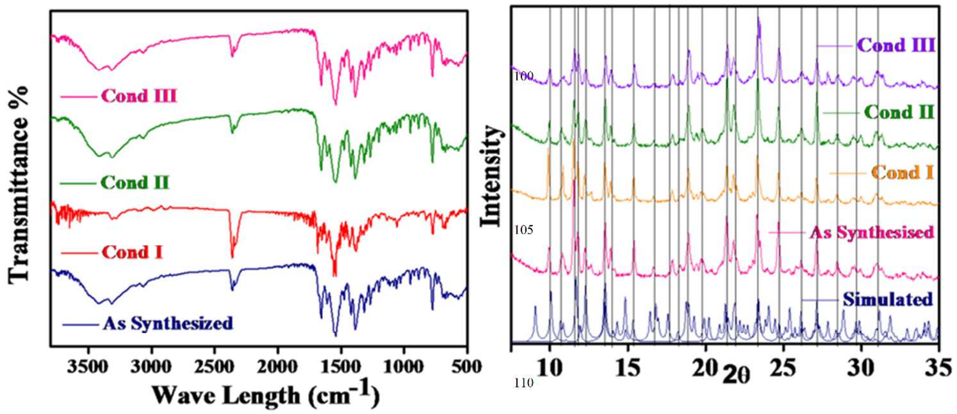


Figure 8. (a) Crystalline aggregates obtained under condition I using **L1**; (b) crystals of **CP2a** and **CP2b** obtained under condition I using **L2**; (c)FT-IR spectra and (d) PXRD patterns of the crystals of **CP2a** and **CP2b** mixture obtained under various conditions (condition I, II and III)using **L2**.

represent one of the rare attempts to separate toxic metal cation such as Cu^{II} by exploiting *in situ* crystallization of coordination polymers.[21]

Experimental

Materials and method.

All the chemicals were commercially available and used without further purification. Ligand 4-(nicotinamido) benzoicacid(**L1H**) and 3-(nicotinamido) benzoicacid(**L2H**) were synthesized by coupling nicotinoyl chloride with the corresponding amino benzoic acids. Elemental analyses ware carried out using a Perkin-Elmer 2400 Series-II CHN analyzer. FT-IR spectra were recorded using Perkin-Elmer Spectrum GX, and TGA analyses were performed on a SDT Q Series 600 Universal VA.2E TA instrument. Powder X-ray diffraction patterns were recorded on a Bruker AXS D8 Advance Powder (Cu $K\alpha_1$ radiation, $\lambda = 1.5406$ Å) Diffractometer. The TEM were recorded in Jeol instrument using carbon coated 300 mesh Au grid at 200 KV. The mass spectrum was recorded on QTOF Micro YA263. NMR spectra (^1H and ^{13}C) were recorded using 300 MHz BrukerAvance DPX300 spectrometer. The copper content in a sample was estimated by using a Shimadzu AA-6300 atomic absorption spectrometer (AAS) fitted with a double beam monochromator.

Synthetic procedure for Ligand L1H and L2H.

In 250 ml 2-neck round bottom flask 100 ml DCM, 5 mmol triethylamine (700μl) and 5 mmol (890 mg) acid chloride (nicotinoyl or isonicotinoyl) were taken. The reaction mixture was then stirred at room temperature under nitrogen atmosphere. A THF solution of 5 mmol amino benzoic acid (755.5 mg) was then added slowly. Then the mixture was allowed to react at room temperature followed by reflux at 60°C. The ppt. was then filtered and washed properly with THF and DCM and used it with further purification.

Characterization data of L1H.

yield:- 1 g, ~57%; m.p: >300°C after crystallization from DMF/EtOH/H_2O (1: 2: 2 v/v).Anal.data calc. for $C_{15}H_{18}O_6$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.01; H, 4.24; N, 11.60.^1H NMR (400 MHz, DMSO-d6): δ = 7.57 (dd, J = 4.6, 1*H*); 7.91 (d, J = 8.8,2*H*); 7.94 (d, J = 8.8,2*H*); 8.30 (s, 1*H*); 8.78 (s, 1*H*); 9.13 (s, 1*H*); 10.70 (s, 1*H*); 12.78 (s, 1*H*). ^{13}C NMR (500 MHz, DMSO-d6): 119.51, 123.22, 130.24, 135.57, 142.88, 148.70, 164.46, 166.85 ppm. ESI-MS: calcd. For $C_{13}H_{10}N_2O_3$242.23 $[M]^+$; found: $[M + Na]^+$273.28. FT-IR (KBr, cm^{-1}): 3309, 3112, 3047, 2883, 2422, 1687s, 1598s, 1531s, 1311s, 1282m, 1242m, 1174s, 1130m, 1101m, 1047s, 892s, 858m, 784s, 705, 644, 548 cm^{-1}.

Characterization data of L2H.

yield:- 1.2 g, ~68%; m.p: 259°C. Anal.data calc. for $C_{15}H_{18}O_6$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.41; H, 4.02; N, 11.34.^1H NMR (400 MHz, DMSO-d6): δ = 7.50 (t, J = 8, 1*H*); 7.70 (d, J = 7.6,1*H*); 8.06 (d, J = 7.6,1*H*); 8.44 (s, 1*H*); 8.00 (t, J = 5.6, 1*H*); 8.86 (s, 1*H*); 8.98 (d, J = 2, 1*H*); 9.39 (d, J = 8.8, 1*H*); 11.11 (s, 1*H*). ^{13}C NMR (400 MHz, DMSO-d6): 121.19, 124.49, 125.04, 128.99, 131.33, 138.75, 167.00 ppm. ESI-MS: calcd. For $C_{13}H_{10}N_2O_3$242.23 $[M]^+$; found: $[M]^+$242.93. FT-IR (KBr, cm^{-1}): 3244, 3072, 2638, 2069, 1699s, 1679s, 1595s, 1548s, 1450s, 1296s, 1267s, 1112m, 906m, 821s, 759s, 678s, 629m, 580 cm^{-1}.

$[\{Cu(\mu\text{-}\mathbf{L1})_2\ (H_2O)_2\}\cdot H_2O]_\infty$**CP1a**was synthesized by adding carefully an aqueous solution of **L1**(40mg, 0.15 mmol) to a methanolic solution of $Cu(NO_3)_2.3H_2O$ (36.57 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks good looking block shaped green crystals were obtained. The crystals were washed in distilled water and finally with methanol and characterized by elemental analysis, X-ray powder diffraction (PXRD) and FT-IR. Yield:~ 36% (35 mg, 0.055mmol). Elemental analysis calcd for **CP1a**, $C_{26}H_{26}CuN_4O_{10}$ (%): C 50.53, H 4.24, N 9.07; found: C 50.22, H 3.93, N 8.86. FT-I.R (KBr pellet): 3310, 1657s, 1609s, 1565, 1525s, 1406, 1382s, 1310m, 1268m, 1177m, 1117, 1207, 909m, 856m, 814m, 780s, 705, 743m, 701m, 513m, 462m cm^{-1}.

Thermogravimetric data analyses (Figure S1, supporting information) revealed a weight loss of 12.12 % that occurred within a temperature range of 29-125 °C; this was attributed to the weight loss of 1 coordinated and 1 lattice occluded water molecules (calculated weight loss 11.56 %); this observation was in good agreement with the single crystal structure of **CP1a**.

$[\{Co(\mu\text{-}\mathbf{L1})_2\ (H_2O)_2\}\cdot H_2O]_\infty$**CP1b**was synthesized by adding carefully an aqueous solution of **L1** (40mg, 0.15 mmol) to a methanolic solution of $Co(NO_3)_2.6H_2O$ (44 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two week good looking block shaped pink crystals were obtained. The crystals were washed in distilled water and finally with methanol and characterized by elemental analysis, X-ray powder diffraction (PXRD) and FT-IR. Yield:~ 34.5 % (32 mg, 0.052mmol). Elemental analysis calcd for **CP1b**, $C_{26}H_{26}CoN_4O_{10}$ (%): C 50.91, H 4.27, N 9.13; found: C 50.76, H 4.24, N 8.86. FT-I.R (KBr pellet): 3487, 3047, 1643, 1622s, 1606s, 1527s, 1388s, 1344m, 1195, 1172m, 896, 831, 788m, 698, 644, 533, 507 cm^{-1}.

Thermogravimetric data analyses (Figure S2, supporting information) revealed a weight loss of 13.77 % that occurred within a temperature range of 60-155°C; this was attributed to the weight loss of 1 coordinated and 1 lattice occluded water molecules (calculated weight loss 11.73 %); this observation was in good agreement with the single crystal structure of **CP1b**.

$[\{Zn(\mu\text{-}\mathbf{L1})_2(H_2O)\}\cdot 3H_2O]_\infty$**CP1c**was synthesized by adding carefully an aqueous solution of **L1**(40mg, 0.15 mmol) to a methanolic solution of $Zn(NO_3)_2.6H_2O$ (45 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks good looking block shaped colorless crystals were obtained. The crystals were washed in distilled water and finally with methanol and characterized by elemental analysis, X-ray powder diffraction (PXRD) and FT-IR. Yield:~ 34.5 % (36 mg, 0.058mmol). Elemental analysis calcd for **CP1c**, $C_{26}H_{26}ZnN_4O_{10}$ (%): C 50.38, H 4.23, N 9.04; found: C 50.57, H 4.02, N 8.71. FT-I.R (KBr pellet): 3444, 3249, 3076, 1658s, 1604s, 1558, 1519, 1477s, 1415s, 1326s, 1276m, 1201m, 1178s, 1122, 1056, 1029m, 904m, 871, 860, 833, 786s, 725m, 694m, 648, 516, 432 cm^{-1}.

Thermogravimetric data analyses (Figure S3, supporting information) revealed a weight loss of 13.98 % that occurred within a temperature range of 48-85°C; this was attributed to the weight loss of 1 coordinated and 3 solvated water molecules (calculated weight loss 11.61 %); this observation was in good agreement with the single crystal structure of **CP1c**.

[{Cd(μ-**L1**)$_2$(μ-**L1**)$_3$(H$_2$O)}.2H$_2$O]$_{\propto}$**CP1d** and [{Cd(μ-**L1**)$_2$(H$_2$O)$_2$}.H$_2$O]$_{\propto}$**CP1e**were synthesized by adding carefully a aqueous solution of**L1**(40mg, 0.15 mmol) to an to a methanolic solution of Cd(NO$_3$)$_2$.4H$_2$O (46.7 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks two types of block shaped crystals were obtained. The crystals were washed in distilled water and finally with methanol and separately characterized by elemental analysis, X-ray powder diffraction (PXRD) and FT-IR. Yield:~36 mg (including both the polymorph). Elemental analysis calcd for **CP1d**, $C_{26}H_{22}CdN_4O_9.2H_2O$ (%): C 46.82, H 3.93, N 8.40; found: C 46.33, H 3.29, N 8.34 and for **CP1e**.H$_2$O, $C_{26}H_{26}CdN_4O_{10}.H_2O$ (%): C 45.59, H 4.12, N 8.18; found: C 45.73, H 3.85, N 8.03. FT-I.R (KBr pellet): 3380, 3272, 3072, 1658s, 1602s, 1521, 1506, 1398s, 1326s, 1276m, 1245m, 1178s, 1126, 1056, 1029m, 902m, 858, 833, 783s, 714m, 700m, 642, 505, 428 cm^{-1}.

Thermogravimetric data analyses (Figure S4, supporting information) of **CP1d** revealed a weight loss of 7.66 % that occurred within a temperature range of 34-85 °C; this was attributed to the weight loss of 1 coordinated and 2 lattice occluded water molecules (calculated weight loss 8.32 %); this observation was in good agreement with the single crystal structure of **CP1d** and the analysis data (Figure S5, supporting information) of **CP1e** revealed a weight loss of 12.42 % that occurred within a temperature range of 48-100 °C; this was attributed to the weight loss of 1 coordinated and 1 lattice occluded water molecules (calculated weight loss 10.79 %); this observation was in good agreement with the single crystal structure of CP1e.

[{Fe(μ-**L1**)$_2$(H$_2$O)$_2$}.H$_2$O]$_{\propto}$**CP1f**was synthesized by adding carefully an aqueous solution of **L1**(40mg, 0.15 mmol) to a methanolic solution of Fe(ClO$_4$)$_2$.xH$_2$O (36.3 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks good looking block shaped yellow crystals were obtained. The crystals were washed in distilled water and finally with methanol and characterized by elemental analysis, X-ray powder diffraction (PXRD) and FT-IR. Yield:~ 30.5 % (28 mg, 0.045 mmol). Elemental analysis calcd for **CP1f**, $C_{26}H_{26}FeN_4O_{10}$ (%): C 51.16, H 4.29, N 9.18; found: C 50.87, H 4.02, N 8.71. FT-I.R (KBr pellet): 3487, 3058, 1602, 1558, 1527s, 1334m, 1245, 788s cm^{-1}.

Thermogravimetric data analyses (Figure S6, supporting information) revealed a weight loss of 11.93 % that occurred within a temperature range of 30-142°C; this was attributed to the weight loss of 2 water molecules (calculated weight loss 11.79 %); this observation was in good agreement with the single crystal structure of **CP1f**.

[{Cu(μ-**L2**)$_2$ (H$_2$O)$_2$}.2H$_2$O]$_{\propto}$**CP2a**and[{Cu(μ-**L2**)$_2$ (H$_2$O)$_2$}.H$_2$O]$_{\propto}$**CP2b**were synthesized by adding carefully an aqueous solution of **L2**(40mg, 0.15 mmol) to a methanolic solution of Cu(NO$_3$)$_2$.3H$_2$O (36.57 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks good two types of crystals (green **CP2a** and deep blue **CP2b**) were obtained. The crystals were washed in distilled water and finally with methanol and characterized by elemental analysis, X-ray powder diffraction (PXRD) and FT-IR. Yield: 38.5 mg (including both the polymorph). Elemental analysis calcd for **CP2a**, $C_{26}H_{30}CuN_4O_{12}$ (%): C 47.74, H 4.62, N 8.57; found: C 48.32, H 4.42, N 8.66 and **CP2b**, $C_{26}H_{26}CuN_4O_{10}$ (%): C 50.53, H 4.24, N 9.07; found: C 50.74, H 4.22, N 9.07. FT-I.R (KBr pellet) for both the polymorphs: 3414, 3314, 3065, 1655s, 1610, 1550s, 1476, 1421, 1387s, 1311, 1269m, 1200, 775s, 689, 675, 669 cm^{-1}.

Thermogravimetric data analyses (Figure S7, supporting information) of **CP2a** revealed a weight loss of 17.51 % that occurred within a temperature range of 28-91 °C; this was attributed to the weight loss of 1 coordinated and 2 lattice occluded water molecules (calculated weight loss 16.51 %); this observation was in good agreement with the single crystal structure of **CP2a** and the analysis data (Figure S8, supporting information) of **CP2b** revealeda weight loss of 10.94 % that occurred within a temperature range of 24-99 °C; this was attributed to the weight loss of 1 coordinated and 1 lattice occluded water molecules (calculated weight loss 11.65 %); this observation was in good agreement with the single crystal structure of **CP2b**.

[{Co(μ-**L2**)$_2$ (H$_2$O)$_2$}.H$_2$O]$_{\propto}$**CP2c**was synthesized by adding carefully an aqueous solution of **L2**(40mg, 0.15 mmol) to a methanolic solution of Co(NO$_3$)$_2$.6H$_2$O (44 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks good looking block shaped pink crystals were obtained. The crystals were washed in distilled water and finally with methanol and characterized by elemental analysis, X-ray powder diffraction (PXRD) and FT-IR. Yield:~ 36.9 % (34 mg, 0.055 mmol). Elemental analysis calcd for **CP2c**, $C_{26}H_{26}CoN_4O_{10}$ (%): C 50.91, H 4.27, N 9.13; found: C 51.02, H 4.21, N 9.11. FT-I.R (KBr pellet): 3382, 3296, 1652s, 1610, 1598, 1541s, 1473s, 1419s, 1388s, 1317, 1269, 1199, 1164, 1110, 1080, 1051, 1031, 950, 896, 885, 835, 784m, 740, 673, 590, 451 cm^{-1}.

Thermogravimetric data analyses (Figure S9, supporting information) revealed a weight loss of 11.35 % that occurred within a temperature range of 38-150°C; this was attributed to the weight loss of 1 coordinated and 1 lattice occluded water molecules (calculated weight loss 11.73 %); this observation was in good agreement with the single crystal structure of **CP2c**.

[{Zn(μ-**L2**)$_2$(H$_2$O)}.(H$_2$O)(CH$_3$OH)]$_{\propto}$**CP2d**was synthesized by adding carefully an aqueous solution of **L2**(40mg, 0.15 mmol) to a methanolic solution of Zn(NO$_3$)$_2$.6H$_2$O (45 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks two colorless block shaped crystals were obtained. The crystals were washed in distilled water and finally with methanol and separately characterized by elemental analysis, X-ray powder diffraction (PXRD) and FT-IR. Yield:~37.8 % (35 mg, 0.056 mmol). Elemental analysis calcd for **CP2d**, $C_{27}H_{26}ZnN_4O_9$ (%): C 52.65, H 4.25, N 9.10; found: C 52.29, H 3.89, N 8.79. FT-I.R (KBr pellet): 3473, 3328, 3269, 1685s, 1667s, 1613s, 1577s, 1541s, 1434s, 1395s, 1323, 1292, 1262, 1203, 1177, 827, 768, 730, 701, 674 cm^{-1}.

Thermogravimetric data analyses (Figure S10, supporting information) of **CP2d** revealed a weight loss of 10.54 % that occurred within a temperature range of 45-112 °C; this was attributed to the weight loss of 1 coordinated and 1 lattice occluded water and 1 methanol molecules (calculated weight loss

11.04 %); this observation was in good agreement with the single crystal structure of **CP2d**.

$[\{Cd(\mu\text{-}\mathbf{L2})_2(H_2O)\}.(H_2O)(CH_3OH)]_\infty$**CP2e**was synthesized by adding carefully an aqueous solution of **L2** (40mg, 0.15 mmol) to a methanolic solution of $Cd(NO_3)_2.4H_2O$ (46.7 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks good looking block shaped crystals were obtained. The crystals were washed in distilled water and finally with methanol and separately characterized by elemental analysis, X-ray powder diffraction (PXRD) and FT-IR. Yield:~ 34.6 %(37 mg, 0.051 mmol). Elemental analysis calcd for**CP2e**, $C_{28}H_{32}CdN_4O_{11}$ (%): C 47.17, H 4.52, N 7.86; found: C 47.21, H 3.95, N 7.56.FT-I.R (KBr pellet): 3458, 3368, 3254, 3075, 1666s, 1614s, 1541s, 1485, 1395s, 1327s, 1246, 1190m, 1049, 1023m, 835, 813, 767s, 742m, 703, 671 cm^{-1}.

Thermogravimetric data analyses (Figure S11, supporting information) of **CP2e** revealed a weight loss of 16.84 % that occurred within a temperature range of 28-181 °C; this was attributed to the weight loss of 0.5 coordinated, 1 solvated water and 1 methanol molecules (calculated weight loss 16.55 %); this observation was in good agreement with the single crystal structure of **CP2e**.

$[\{(Cl)_2(H_2O)_2Cd_2(\mu\text{-}\mathbf{L2})_2\}.3H_2O]_\infty$**CP2f** was synthesized by adding carefully an aqueous solution of **L2** (40mg, 0.15 mmol) to a methanolic solution of $CdCl_2$ (27.5 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks good looking block shaped crystals were obtained. The crystals were washed in distilled water and finally with methanol and separately characterized by elemental analysis, X-ray powder diffraction (PXRD) and FT-IR. Yield:~29 %(38 mg, 0.043 mmol). Elemental analysis calcd for **CP2f**, $C_{26}H_{28}Cd_2Cl_2N_4O_{11}$ (%): C 35.97, H 3.25, N 6.45; found: C 36.49, H 3.02, N 6.48.FT-I.R (KBr pellet): 3298, 3261, 3058, 1685s, 1604s, 1552m, 1521m, 1508m, 1400, 1325s, 1274, 1178, 1107, 1029m, 835, 898, 864, 833, 784s, 730m, 717, 649, 432 cm^{-1}.

Thermogravimetric data analyses (Figure S12, supporting information) of **CP2f** revealed a weight loss of 11.78 % that occurred within a temperature range of 28-100 °C; this was attributed to the weight loss of 2 coordinated and 3occluded water molecules (calculated weight loss 11.90 %); this observation was in good agreement with the single crystal structure of **CP2f**.

Cation Separation.

The experiments for Cu^{II} separation were performed under different conditions namely I, II and III as described below.

Condition I. In a typical experiment, a methanolic solution (15 ml) containing $Cu(NO_3)_2$ (18.28 mg, 0.07 mmol), $Co(NO_3)_2$ (44.06 mg, 0.15 mmol) and $Zn(NO_3)_2$ (45.03 mg, 0.15 mmol) was layered over an aqueous solution (10 ml) of **L2** (40 mg, 0.15 mmol) in a 25 ml beaker and the resulting solution was allowed to undergo slow evaporation at room temperature. After two weeks, good quality crystals of **CP2a** and **CP2b** appeared concomitantly in the beaker. When the volume of the solution became ~5 ml, the crystals were separated and washed with methanol. The filtrate along with the washings was evaporated to dryness and subjected to atomic absorption spectroscopy (AAS).

Condition II. In a typical experiment, a methanolic solution (15 ml) containing $Cu(NO_3)_2$ (9.14 mg, 0.035 mmol), $Co(NO_3)_2$ (44.06 mg, 0.15 mmol) and $Zn(NO_3)_2$ (45.03 mg, 0.15 mmol) was layered over an aqueous solution (10 ml) of **L2** (40 mg, 0.15 mmol) in a 25 ml beaker and the resulting solution was allowed to undergo slow evaporation at room temperature. After two weeks, good quality crystals of **CP2a** and **CP2b** appeared concomitantly in the beaker. When the volume of the solution became ~5 ml, the crystals were separated and washed with methanol. The filtrate along with the washings was evaporated to dryness and subjected to atomic absorption spectroscopy (AAS).

Condition III. In a typical experiment, a methanolic solution (15 ml) containing $Cu(NO_3)_2$ (4.5 mg, 0.017 mmol), $Co(NO_3)_2$ (44.06 mg, 0.15 mmol) and $Zn(NO_3)_2$ (45.03 mg, 0.15 mmol) was layered over an aqueous solution (10 ml) of **L2** (40 mg, 0.15 mmol) in a 25 ml beaker and the resulting solution was allowed to undergo slow evaporation at room temperature. After two weeks, good quality crystals of **CP2a** and **CP2b** appeared concomitantly in the beaker. When the volume of the solution became ~5 ml, the crystals were separated and washed with methanol. The filtrate along with the washings was evaporated to dryness and subjected to atomic absorption spectroscopy (AAS).

Single crystal X-ray Crystallography.

Single crystal X-ray diffraction data were collected using MoKα (λ = 0.7107 Å) radiation on a BRUKER APEX II diffractometer equipped with CCD area detector. Data collection, data reduction, structure solution/refinement were carried out using the software package of APEX II. All the structures (**L1H**, **CP1a-CP1f** and **CP2a-CP2f**) were solved by direct methods and refined in a routine manner. In all the cases, nonhydrogen atoms were treated anisotropically. Whenever possible, the hydrogen atoms were located on a difference Fourier map and refined. In other cases, the hydrogen atoms were geometrically fixed. CCDC No. 989153- 989165 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Powder X-ray diffraction.

PXRD data were collected using Bruker AXS D8 Advance Powder (Cu Kα_1 radiation, λ = 1.5406 Å) Diffractometer equipped with super speed LYNXEYE detector. The sample was prepared by making a thin film of finely powdered sample (~30 mg) over a glass slide. The experiment was carried out with a scan speed of 0.3 sec/step (step size = 0.02˚) for the scan range of 5-35˚ 2θ.

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† Electronic Supplementary Information (ESI) available: Molecular plots and H-bonding parameters of coordination polymers, TGA, PXRD, elemental analysis, AAS, CIFcheck reports. See DOI: 10.1039/b000000x/

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Table 1. Crystallographic Data.

Crystal parameters	**L1H**	**CP1a**	**CP1b**	**CP1c**
CCDC No	989165	989153	989154	989155
empirical formula	C13 H9 N2 O3	C26 H26 Cu N4 O10	C26 H26 Co N4 O10	C26 H26 N4 O10 Zn
formula weight	242.23	618.05	613.44	619.88
crystal size/mm	0.21 X 0.08 X 0.06	0.28 X 0.08 X 0.05	0.30 X 0.22 X 0.08	0.50 X 0.22 X 0.16
crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
space group	*Pbcn*	$P2_1/n$	$P2_1/n$	*P-1*
a /Å	9.4072(3)	7.943(3)	7.7617(2)	9.3173(6)
b /Å	12.7350(3)	12.822(5)	12.4624(3)	10.4833(6)
c /Å	17.8919(5)	13.509(5)	13.3308(4)	14.0375(8)
$\alpha/^0$	90.00	90.00	90.00	97.468(2)
$\beta/^0$	90.00	90.626(12)	101.2430(10)	96.161(2)
$\gamma/^0$	90.00	90.00	90.00	91.980(2)
volume/Å^3	2143.46(10)	1375.8(9)	1264.73(6)	1350.01(14)
Z	8	2	2	2
D_{calc}/g cm^{-3}	1.501	1.492	1.611	1.525
F(000)	1008	638	634	640
μMoKα /mm^{-1}	0.109	0.858	0.748	0.975
temperature/K	296(2)	296(2)	296(2)	296(2)
R_{int}	0.0503	0.0447	0.0250	0.0132
range of h, k, l	-13/13,-17/17,-24/22	-11/11,-18/19,-17/19	-11/11,-18/18,-19/18	-12/13,-15/12,-20/20
θmin/max/°	2.28 / 29.46	2.19 / 32.31	2.26 / 32.29	1.47 / 32.33
Reflectionscollected/unique/ observed [I>2σ(I)]	38464 / 2967 / 1907	20886 / 4556/ 2825	23878 / 4051 / 3495	21168 /7990/6404
data/restraints/parameters	2967 /0/ 176	4556/0/199	4051 /0/200	7990/1/370
goodness of fit on F^2	1.007	1.043	0.878	1.056
final R indices [I>2σ(I)]	R_1 = 0.0526 wR_2= 0.1295	R_1 = 0.0456 wR_2= 0.1069	R_1 = 0.0320 wR_2 = 0.1034	R_1 = 0.0522 wR_2 =0.1759
R indices (all data)	R_1= 0.0965 wR_2 =0.1543	R_1=0.0980 wR_2 =0.1362	R_1= 0.0412 wR_2 = 0.1170	R_1=0.0677 wR_2 =0.1944

Table1. Contd……

Crystal parameters	**CP1d**	**CP1e**	**CP1f**
CCDC No	989156	989157	989158
empirical formula	C26 H22 Cd N4 O9	C26 H26 Cd N4 O10	C26H26 Fe N4 O10
formula weight	646.88	666.91	610.36
crystal size/mm	0.14 X 0.14 X 0.06	0.67 X 0.11 X 0.10	0.28 X 0.08 X 0.40
crystal system	Triclinic	Monoclinic	Monoclinic
space group	*P-1*	$P\ 2_1/n$	$P\ 2_1/n$
a /Å	8.7935(9)	7.90160(10)	7.7788(3)
b /Å	12.2071(13)	12.7481(2)	12.5459(4)
c /Å	12.6146(13)	13.5560(2)	13.3501(5)
$\alpha/^0$	96.023(4)	90.00	90.00
$\beta/^0$	103.536(4)	101.9350(10)	101.4830(10)
$\gamma/^0$	96.686(4)	90.00	90.00
volume/Å^3	1295.2(2)	1335.98(3)	1276.79(8)
Z	2	2	2
D_{calc}/g cm^{-3}	1.659	1.658	1.588
F(000)	652	676	632
μMoKα /mm^{-1}	0.905	0.883	0.659
temperature/K	296(2)	296(2)	296(2)
R_{int}	0.0150	0.0161	0.0234
range of h, k, l	-12/11,-16/17,-17/17	-12/12,-18/19,-20/20	-10/11,-18/18,-20/19
θmin/max/°	1.68 / 30.14	2.22 / 32.99	2.25 / 32.18
Reflectionscollected/unique/ observed [I>2σ(I)]	23897 /7034/6319	28656 / 4653 / 3893	19371 / 4090 / 3540
data/restraints/parameters	7034/0/369	4653 /0/203	4090 /0/200
goodness of fit on F^2	1.187	0.139	1.082
final R indices [I>2σ(I)]	R_1 = 0.0304 wR_2 =0.0893	R_1 = 0.0218 wR_2 = 0.0639	R_1 = 0.0323 wR_2 = 0.0934
R indices (all data)	R_1=0.0365 wR_2 =0.1004	R_1= 0.2980 wR_2 = 0.0777	R_1= 0.0405 wR_2 = 0.1048

Table1. Contd……

Crystal parameters	**CP2a**	**CP2b**	**CP2c**
CCDC No	989159	989160	989161
empirical formula	C26 H30 CuN4 O12	C26 H26 Cu N4 O10	C26 H26 Co N4 O10
formula weight	654.08	618.05	613.44
crystal size/mm	0.16 X 0.13 X 0.05	0.26 X 0.09 X 0.07	0.77 X 0.37 X 0.12
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	$P\ 2_1/c$	$P\ 2_1/n$	$P\ 2_1/n$
a /Å	8.8359(6)	9.0273(8)	8.7930(10)
b /Å	19.4935(13)	9.6688(8)	9.8082(11)
c /Å	8.0415(5)	15.3406(12)	15.5768(18)
$\alpha/^{0}$	90.00	90.00	90.00
$\beta/^{0}$	96.394(2)	99.176(3)	100.664(3)
$\gamma/^{0}$	90.00	90.00	90.00
volume/Å^3	1376.47(16)	1321.84(19)	1320.2(3)
Z	2	2	2
D_{calc}/g cm^{-3}	1.578	1.553	1.543
F(000)	678	638	634
μMoKα /mm^{-1}	0.867	0.892	0.716
temperature/K	296(2)	296(2)	100(2)
R_{int}	0.0337	0.0603	0.0184
range of h, k, l	-12/12,-28/26,-12/11	-10/11,-12/13,-21/21	-12/12,-12/14,-23/19
θmin/max/°	2.09 / 32.25	2.50 / 30.03	2.91/ 32.11
Reflectionscollected/unique/ observed [I>2σ(I)]	24406 / 4462 / 3541	16730 /3543/2501	19416/ 4287 / 4036
data/restraints/parameters	4462 /0/212	3543/0/191	4287 /0/200
goodness of fit on F^2	1.126	1.113	1.049
final R indices [I>2σ(I)]	R_1 = 0.0410 wR_2 =0.1103	R_1 = 0.0586 wR_2 =0.1359	R_1 = 0.0252 wR_2 =0.0720
R indices (all data)	R_1= 0.0614 wR_2 = 0.1325	R_1=0.1039 wR_2 =0.1714	R_1= 0.0252 wR_2 = 0.0710

Table1. Contd……

Crystal parameters	**CP2d**	**CP2e**	**CP2f**
CCDC No	989162	989163	989164
empirical formula	C27 H26 N4 O9 Zn	C28 H31 Cd N4 O11	C26H28Cd2Cl2N4O11
formula weight	615.89	711.97	868.22
crystal size/mm	1.00 X 0.14 X 0.10	1.00 X 0.12 X 0.08	0.24 X 0.21 X 0.16
crystal system	Triclinic	Monoclinic	Monoclinic
space group	*P-1*	*C2/c*	*C2/c*
a /Å	10.6479(4)	20.3394(16)	16.5778(8)
b /Å	11.0165(5)	10.1426(7)	16.9789(8)
c /Å	12.9533(5)	14.9680(9)	21.8040(10)
$\alpha/^0$	106.997(2)	90.00	90.00
$\beta/^0$	96.481(2)	104.500(5)	94.606(2)
$\gamma/^0$	106.063(2)	90.00	90.00
volume/$Å^3$	1364.96(10)	2989.5(4)	6117.4(5)
Z	2	4	8
D_{calc}/g cm^{-3}	1.499	1.582	1.885
F(000)	636	1452	3440
μMoKα /mm^{-1}	0.961	0.797	1.631
temperature/K	293(2)	296(2)	296(2)
R_{int}	0.0144	0.0201	0.0260
range of h, k, l	-16/16,-14/17,-16/18	-30/31, -13/14, -20/23	-20/24, -25/25, -32/26
θmin/max/°	1.68 / 33.98	2.26/34.06	1.87/32.18
Reflectionscollected/unique/ observed [$I>2\sigma(I)$]	48913 /8582/7322	33276/5412/4925	45949/9876/7674
data/restraints/parameters	8582/0/391	5412/0/200	9876/0/421
goodness of fit on F^2	1.014	1.120	1.023
final R indices [$I>2\sigma(I)$]	R_1 = 0.0359 wR_2 =0.1010	R_1 = 0.0253 wR_2 =0.0690	R_1 = 0.0443 wR_2 =0.1552
R indices (all data)	R_1=0.0438 wR_2 =0.1067	R_1=0.0300 wR_2 =0.0715	R_1=0.0611 wR_2 =0.1746

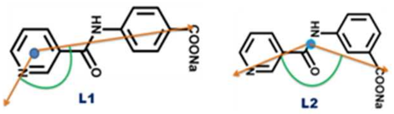
Table 2. Crystallographic and structural information.

Ligand and CPs	Structural information		Space group	Asymmetric unit content	Relative Orientation of pyridyl N and amide -->C=O	Dihedral angle between the terminal aromatic rings	Ligating angle	Network topology	Hydrogen bonding involving amide moiety	Lattice occluded Solvent molecules
L1H			*Pbcn*	1 fully occupied molecule of **L1**.	*syn*	16.02	132.55		N…$O_{carboxylate}$[N…O =2.653(2)- 3.012(2)Å; ∠N-H…O = 162.9°-165.1°];	
CP1a	**ISOMORPHOUS**	**ISOSTRUCTURAL**	$P2_1/n$	0.5Cu^{II}+1 **L1**+1 coordinated H_2O+1 solvated H_2O	*anti*	36.43	101.20	1D looped chain	N-H…$O_{solvate}$ [N…O =2.932(3) Å ; ∠N-H…O = 179(3)°] O-$H_{coord.wate}$…O [O…O =2.806(3)-2.956(4)Å; ∠O-H…O = 166(4)-168(5)°]	1 H_2O
CP1b			$P2_1/n$	0.5Co^{II}+1 **L1** + 1 coordinated H_2O + 1 solvated H_2O	*anti*	52.31	104.12	1D looped chain	N-H…$O_{solvate}$ [N…O =2.842(16)Å ; ∠N-H…O = 172(2)°] O-$H_{coord.wate}$…O[O…O =2.821(15) Å; ∠O-H…O = 176(2)]	1 H_2O
CP1e			$P2_1/n$	0.5Cd^{II}+ 1 **L1**+ 1 coordinated H_2O + 1 solvated H_2O	*anti*	51.94	104.61	1D looped chain	N-H…$O_{solvate}$ [N…O =2.896(18) Å ; ∠N-H…O = 171°] O-$H_{coord.wate}$…O [O…O =2.839(18)Å; ∠O-H…O = 179(3)] O-$H_{solvate}$…O[O…O =2.994(2)Å; ∠O-H…O = 176(2)]	1 H_2O
CP1f			$P2_1/n$	0.5Fe^{II}+ 1 **L1**++1 coordinated H_2O + 1 solvated H_2O	*anti*	50.56	104.35	1D looped chain	N-H…$O_{solvate}$ [N…O =2.850(15) Å ; ∠N-H…O = 172.3°] O-$H_{coord.wate}$…O[O…O =2.825(14)Å; ∠O-H…O = 175(2)] O-$H_{solvate}$…O[O…O =2.923(15)Å; ∠O-H…O = 170(2)]	1 H_2O
CP2a			$P\ 2_1/c$	0.5Cu^{II}+ 1 **L2**+1 coordinated H_2O + 2 solvated H_2O	*syn*	64.98	149.43	1D looped chain	N-H…$O_{solvate}$ [N…O =2.838(2) Å ; ∠N-H…O = 157.9°] O-$H_{solvate}$…O[O…O =2.794(2)Å]	2 H_2O
CP2e			*C2/c*	0.5Cd^{II}+ 1 **L2**+1/2 coordinated H_2O + 1 solvated H_2O +1 methanol	*Anti*	66.82	130.90	1D looped chain	N-H…$O_{solvate}$ [N…O =2.896(18)Å ; ∠N-H…O = 177.3°] O-$H_{coord\ water}$…O[O…O =2.746(17)Å; ∠O-H…O = 146.0]	1 H_2O + 1CH_3OH

Table 2. Contd……..

CPs	Structural information	Space group	Asymmetric unit content	Relative Orientation of pyridyl N and amide -- >C=O	Dihedral angle between the terminal aromatic rings	Ligating angle	Network topology	Hydrogen bonding involving amide moiety	Lattice occluded Solvent molecules
CP2b	**Isomorphous**	*P2$_1$/n*	0.5Cu^{II}+1 **L2** + 1 coordinated H_2O + 1 solvated H_2O.	*syn*	21.33	136.00	2D sheet	N-H…O$_{carbxylate}$ [N…O =3.006(4)Å ; ∠N-H…O = 161(5)°] O-$_{solvate}$…O[O…O =2.725(4)Å]	1 H_2O
CP2c		*P2$_1$/n*	0.5Co^{II}+ 1 **L2** + 1 coordinated H_2O + 1 solvated H_2O	*syn*	20.53	134.70	2D sheet	N-…O$_{carbxylate}$ [N…O =2.964(10)Å ; ∠N-H…O = 161.8°] O-$_{solvate}$…O[O…O =2.732(12)Å; ∠O-H…O = 176(2)°]	2H_2O
CP1c		*P-1*	1 Zn^{II}+ 2 **L1** + 1 coordinated H_2O + 3 solvated H_2O	All *syn*	13.91/ 3.76	129.08/ 134.83	Inter digited 1D chain	N-H…O$_{carbxylate}$ [N…O =2.834(3)Å ; ∠N-H…O = 158.3°] N-H…O$_{solvate}$[N…O =2.875(4)Å ; ∠N-H…O = 163.3°] O-$_{solvate}$…O[O…O =2.790(3)-2.829(5)Å]	3 H_2O
CP1d		*P-1*	1 Cd^{II}+ 2 **L1**+ 1 coordinated H_2O + 2 solvated H_2O	*anti/syn*	70.87/ 46.68	109.61/ 127.09	2D corrugated sheet	N-…O$_{amide}$[N…O =2.918(3); ∠N-H…O = 161.4°]; N-O$_{solvate}$[N…O =2.986(7)Å ; ∠N-H…O = 163(4)°]O-$_{olvate}$…O[O…O =2.763(4)Å]	2 H_2O
CP2d		*P-1*	1 Zn^{II}+2 **L2 + 1** coordinated H_2O + 1 solvated H_2O + 1 solvated methanol	*anti/syn*	11.17/ 25.66	125.27/ 142.91	1D polymeric tape	N-H…O$_{methanol}$ [N…O =2.968(2)Å ; ∠N-H…O = 167(2)°]; N-H..O$_{solvated}$[N…O =3.037(2)Å ; ∠N-H…O = 163.8°] O-H$_{solvate}$…O [O..O =2.825(19)Å; ∠O-H…O = 158.3°]	1 H_2O + 1CH_3OH
CP2f		*C2/c*	2 Cd^{II}+ 2 chloride + 2 **L2** +2 coordinated H_2O + 3 solvated H_2O	All *anti*	2.44/ 7.83	127.19/ 127.87	1D looped chain	N-H…O$_{solvate}$[N…O =3.064(3)Å ; ∠N-H…O = 164.3°] O-H$_{solvate}$…O[O…O =2.701(6)-2.934(4)Å]	3 H_2O

Determination of Ligating angle.



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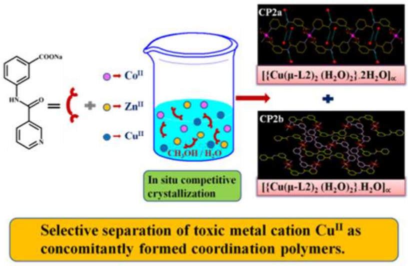
Coordination polymers derived from pyridyl carboxylate ligands having amide backbone: An attempt towards selective separation of Cu^{II} cation following *in situ* crystallization under competitive conditions Mithun Paul and Parthasarathi Dastidar* *CrystEngComm*. **2014, 00, 000.**		Selective separation of Cu^{II} ions in the form of concomitantly formed coordination polymers **CP2a** and **CP2b** in aqueous phase was achieved using a pyridyl carboxylate based functional ligand under competitive conditions.