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Is Metal Metathesis a Framework-Templating Strategy to Synthesize Coordination Polymers? Transmetallation Studies involving Flexible ligands

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The Coordination Polymer (CP) of *bis*(3-pyridyl)butanediamide with $Cu(ClO_4)_2$ is a 2D network (**CP-3-Cu**), which showed two-fold parallel interpenetration; whereas with $Cd(ClO_4)_2$ it is a 1D network containing rectangular loops (**CP-4-Cd**). The metal metathesis of **CP-4-Cd** with Cu(II) resulted in isomorphous replacement of the Cd(II) centre with Cu(II). Transmetallation reaction resulted in retaining the structural features of **CP-4-Cd** even in case of flexible ligand. The CP formed *via* transmetallation couldn't be synthesized from the direct reaction of *bis*(3-pyridyl)butanediamide and $Cu(ClO_4)_2$. The transmetallation kinetic studies are performed with Atomic Absorption Spectrophototmeter (AAS) and Wavelength Dispersive X-Ray Fluorescence (WDXRF).

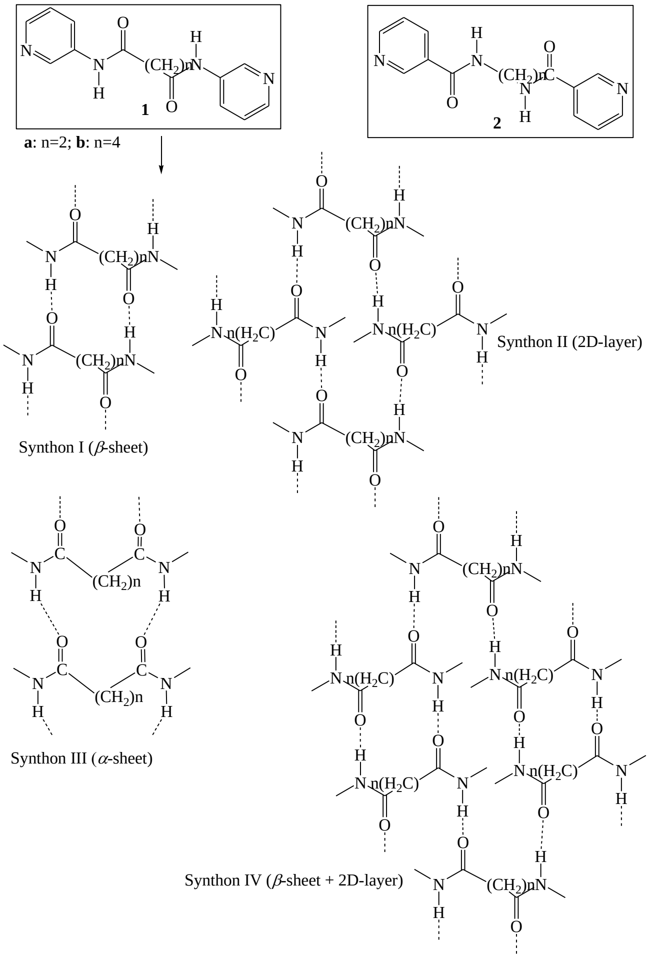
Introduction

Crystal engineering of coordination polymers (CP) have attracted considerable attention over a decade because of their potential applications such as in gas storage, separation, and catalysis. The most important application of the CPs in energy-related technologies (e.g., H_2, CH_4, CO_2) has been explored widely. [1] Other potential applications of CPs are in the areas of molecular sensing, host guest chemistry, catalysis, luminescence, and biotechnology.[2] Applications in these other fields of interest are becoming increasingly reliant on the development of CPs that possess complex chemical functionality that can impart sophisticated chemical and physical properties to these materials.

The supramolecular structure of CPs can be in principle controlled through judicious selection of metal nodes and organic linkers. The direct synthesis of CPs with desired functionalities are often difficult to achieve and are dependent on many parameters such as various coordination geometries of the metal center, nature and ligating topologies of the ligands used, metal-to-ligand ratio, nature of the counter anions and various experimental conditions such as solvents, temperature and crystallization methods.[3] The post-synthetic approaches are useful when the direct methods to synthesize the CPs do not give the expected product in crystalline form, desired framework topology or functions. The post-synthetic modifications of the CPs involving exchange of free guest molecules or counterions or removal of free/ weakly bound solvent molecules has been studied frequently.[4] The modification or selective replacement of integral parts (nodes and linkers) of the frameworks can be a route to synthesize the CPs that cannot be obtained by direct synthesis. While the post-synthetic modifications involving the linkers are studied in depth by many researchers[5]; the transmetalation/framework-metal metathesis studies in CPs are still in its infancy.[6] This may be attributed to the belief that the properties of CPs change by modifying the linkers of a framework rather than the metal node which is usually regarded as an inert structural element. However, transmetallation/framework-metal metathesis may lead to CPs with novel or enhanced properties and features. Huang *et al.* have studied the fluorescence properties on the pre- and post-metal ion exchanged CPs and found that central metal ions have great influence on the fluorescence signal & play more important roles than skeleton structures.[6b] Zhou and co-workers have demonstrated the robustness and enhanced gas adsorption properties when a Zn_2-paddlewheel in a MOF was substituted by Cu_2-paddlewheel.[6f] Recently, Brozek and Dinca have shown that the post-synthetic metal metathesis on $[Zn_4O(1,4\text{-benzenedicarboxylate})_3]_n$ resulted in MOFs with redox reactivity.[6h]

CPs derived from hydrogen bond functionalized ligands have the possibility of forming varied hydrogen bond synthons within the networks and have the ability to recognize the counter anions and various guest molecules *via* hydrogen bonding interactions.[7] The pyridyl based *exo* bidentate ligands having amide moieties are able to form coordination networks and can further assemble into higher dimensional architectures *via* hydrogen bond interactions. The amide-based ligands are exploited by some of the leading research groups to form CPs, where the networks recognize each other by amide-to-amide hydrogen bonding.[8] Nevertheless, continuous effort should be devoted to improve our understanding on CPs *via* "pre-design" as well as post-synthetic modification strategy. The post-synthetic approaches should be a more controlling synthetic strategy to generate desired materials because we will have the knowledge about the structure and properties of the precursor materials. The modifications on those precursor materials will direct the construction of a designed structure.

In the present work, we have exploited a pyridyl-based flexible ligand **1** having amide moieties in the spacer to form CPs (Scheme 1). The hydrogen-bond capable backbone involving amides will provide the network recognition process required for forming robust supramolecular architecture while the flexibility in the spacer will give enough opportunity to change the geometry in the event of variation in any of the components of the CPs. The structure of the CPs of different metal centres (Cu(II) and Cd(II)) is analyzed in order to determine the role of metal centre in forming the CPs. Further, the transmetallation approaches are used on the synthesized CPs and the kinetics of framework-metal metathesis is studied. Recently, we have reported the effect of changing the counter anion on the geometry of the network. The flexible alkyl chain resulted in modulating the conformation, thereby affected the guest uptake properties of the CP.[8f]



Scheme 1: *bis*-pyridylalkane diamides and their hydrogen bond synthons

Experimental section

General

Infra-red spectrum was recorded in FTIR ABB Bomen MB-3000. Elemental analyses were obtained with a Thermo finnigan, Italy, Model FLASH EA 1112 series. Powder X-ray diffraction (XRD) data were recorded with a Rigaku miniflex ll, λ =1.54, Cu Kα. Atomic Absorption Spectra (AAS) was measured using AA-7000, Shimadzu. Wavelength Dispersive X-Ray Fluorescence (WD-XRF) was measured using S8 TIGER, Make: Bruker, Germany; with X-Ray tube of 4KW with 'Rhodium' target and a high volatage/tube current: 60kv/64 mA.

Synthesis of ligand **1b**: The ligand **1b** was synthesized according to a literature procedure.[9] 3-Amino pyridine (2 mmol) was added to 40 mL of a pyridine solution of adipic acid (1 mmol), and the solution was stirred for 15 min. To this solution was added triphenyl phosphite (2 mmol), and the mixture was refluxed for 5 h. The volume of the solution was reduced to 5 mL by distilling out the pyridine, and a white precipitate was obtained. The solid was filtered, washed with water, and dried under vacuum. Yield: 70%. Mp: 216-220°C. FTIR (KBr, cm^{-1}): 3301(w), 3247(m), 3178(m), 3108(m), 3039(m), 2947(vs), 2917(s), 2875(m), 1690(vs), 1580(vs), 1550(s), 1478(m), 1419(vs), 1378(m), 1281(vs), 1157(s), 1132(w), 1034(m), 943(m), 910(w), 856(w), 810(s), 735(w), 701(m), 625(w), 578(w).

Synthesis of **CP-3-Cu**, $\{[Cu(\mathbf{1b})_2(H_2O)_2](ClO_4)_2•2(H_2O)\}_n$:The ligand **1b** (596 mg, 2.0 mmol) dissolved in 15ml of 1:1 mixture of water-Ethanol solvent system. To the above solution, 10 ml ethanolic solution of $Cu(ClO_4)_2.6H_2O$ (370.1 mg, 1.0 mmol) was added. The resulted blue precipitate was dissolved by adding few drops of water. The solution was filtered and kept for slow evaporation. Blue-colored crystals were formed after 8-10 days in 80% yield. Anal. Calcd (%)for $C_{32}H_{44}CuCl_2N_8O_{16}$:C, 41.27; H, 4.72; N 12.03 Found: C, 41.27; H, 4.55; N, 11.63 FTIR (KBr, cm^{-1}): 3564(s), 3278(s), 3201 (w), 3101(w), 2931(w), 2862(w), 1674(s), 1612(w), 1589(w), 1550(vs), 1488(m), 1427(s), 1365(w), 1296 (m), 1242(w), 1195(w), 1103(vs), 956(w), 918(w), 810(m), 702(m), 624(m), 555(w).

Synthesis of **CP-4-Cd**, $\{[(Cd(\mathbf{1b})_2(H_2O)_2](ClO_4)_2•2(H_2O)\}_n$: Microwave assisted technique was used wherein ligand **1b** (59.6 mg, 0.2 mmol) and $Cd(ClO_4)_2.6H_2O$ (41.94 mg, 0.1 mmol) was taken 5ml of 1:1 mixture of water-Ethanol into a specially designed microwave test tube. The reaction mixture was irradiated for 10 minutes at 90℃, at medium stirring rate and 100 psi pressure. White crystals suitable for single crystal XRD were formed after keeping the solution for a day. Anal. Calcd (%)for $C_{32}H_{44}CdCl_2N_8O_{16}$:C, 39.22; H, 4.53; N 11.43 Found: C, 41.69; H, 4.57; N, 10.69; The calculated percentages are based on the molecular formula from the single crystal XRD. **CP-4-Cd** was crystallized from ethanol. If we include the free ethanol molecules, we can account for the observed elemental percentage (Table S1). FTIR (KBr, cm^{-1}): 3865(s),3841(s), 3741(vs), 3672(m), 3649(m), 3618(m), 3564(w), 3317(vs), 1674(vs), 1527(vs), 1481(s), 1419(s), 1326(w), 1288(m), 1164(w), 1103(vs), 956(w), 802(w), 771(s), 702(w), 624(m), 563(m).

Synthesis of **CP-4-Cu**: Metal-metathesis reaction was performed on **CP-4-Cd** wherein crystals of **CP-4-Cd** were immersed into 0.1 M ethanolic solution of $Cu(ClO_4)_2.6H_2O$. The white crystals slowly turned blue crystals. The crystals were analyzed by IR, Powder XRD, AAS and WD-XRF spectroscopy.

Single Crystal X-ray Crystallography: Single crystal data for **CP-3-Cu** and **CP-4-Cd** were collected on a Xcalibur, Sapphire 3

X-ray diffractometer that uses graphite monochromated Mo Kα radiation (λ = 0.71073 Å) by the ω-scan method.[10] The structures were solved by direct methods and refined by least square methods on F^2 using SHELX-97.[11] In both structures, the disorder in the perchlorate group was modelled (one of the oxygens over two positions for CP-3-Cu and two of the oxygens over two positions (each) to obtain the lowest residual factors and optimum goodness of fit with convergence of refinement. Non-hydrogen atoms were refined anisotropically except the disordered perchlorate oxygens (O4/O4') in CP-3-Cu and the lattice water molecule (O2w) and the disordered perchlorate oxygens (O5/O5A and O6/O6A) in CP-4-Cd. In the final difference Fourier maps there was no significant peaks >1 e/Å^3. All hydrogen atoms except for the water molecule (O2w) in the asymmetric unit of CP-4-Cd were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. The crystal data and structure refinements of **CP-3-Cu** and **CP-4-Cd** are summarized in Table 1. (CCDC 963405-963406)

Table 1. Crystal Data and Structure Refinement Parameters of **CP-3-Cu** and **CP-4-Cd**

CP	**CP-3-Cu**	**CP-4-Cd**
Formula	$C_{32}H_{44}Cl_2CuN_8O_{16}$	$C_{32}H_{44}CdCl_2N_8O_{16}$
Mol. Wt.	931.19	980.05
Crystal System	Orthorhombic	Triclinic
Space Group	$P\ 2_1\ 2_1\ 2$	$P\ \bar{1}$
a/Å	11.3423(3)	9.0727(2)
b/Å	19.2826(7)	9.0760(2)
c/Å	9.5549(3)	15.3648(3)
α/°	90	106.099(2)
β/°	90	90.817(2)
γ/°	90	93.146(2)
V/Å^3	2089.74(11)	1213.17(4)
Z	2	1
$D_{calcd.}$/g cm^{-3}	1.480	1.341
T/K	296(2)	296(2)
Theta (°) range for data used	3.50 to 24.98	3.51 to 25.0
R_{int}	0.0428	0.0411
Reflections with I > 2σ(I)	2989	3982
No. of Parameters refined	270	255
Final R (with I > 2σ(I))	$R_1{}^a = 0.0679$; $wR_2{}^b = 0.1726$	$R_1{}^a = 0.0595$; $wR_2{}^b = 0.1679$
GOF on F^2	0.972	1.023

${}^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ${}^bwR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

Results and discussion

Structural Description of CP-3-Cu and CP-4-Cd: The geometry of the ligand **1b** (Figure 1) in the **CP-3-Cu** and **CP-4-Cd** give the insight into the agility of the ligand to assemble according to the requirement of the other components of the CPs. The size of the metal centre is the deciding factor in arranging the CPs. In **CP-3-Cu**, the two neighboring Cu(II) centers are separated by a distance of 14.831 Å, whereas in **CP-4-Cd**, Cd(II) are separated by a distance of 17.955 Å. The flexibility of the butyl chain in **1b** resulted in changing the ligand length required for Cu(II) center and Cd(II) centre. In **CP-3-Cu**, the butyl chain adopts *gauche-anti-gauche* conformation, whereas in **CP-4-Cd**, it adopts all *anti* conformation. This in turn affected the overall geometry of the CPs. In **CP-4-Cd**, the ligand behaves as a longer "rigid" analogue of 3,3'-bipyridine. In **CP-3-Cu**, the ligand adopts a wavy type of geometry with more of the hydrocarbon chain "clustered" in the spacer. The presence of two amide groups resulted in self-complementary amide-to-amide hydrogen bonds in both the CPs, even in the presence of counter anions and free water molecules.

The structural features of the **CP-3-Cu** and **CP-4-Cd** are as follows: **Two-Dimensional Coordination Network of (4,4)-Topology having two-Fold Parallel Interpenetration: CP-3-Cu** crystallizes in the orthorhombic space group $P2_12_12$. The Cu(II) centre adopts a distorted-octahedral geometry; where coordination environment of Cu(II) included four molecules of **1b** in the equatorial position (Cu-N: 2.023Å, 2.027Å) and two H_2O molecules in the axial positions (Cu-O: 2.480Å). The wavy-shape to the ligand due to *gauche-anti-gauche* conformation result in the formation of a highly corrugated 2D-network with (4,4) topology (Figure 2a).

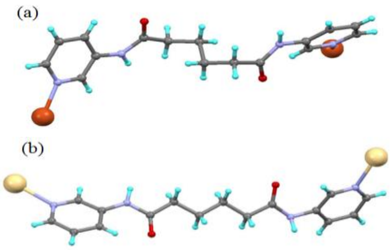


Figure 1: Geometry of the ligand **1b** in (a) **CP-3-Cu** and (b) **CP-4-Cd**; Notice the conformation of the butyl chain in each case.

The (4,4)-layers has rhomboidal-shaped cavities with diagonal-to-diagonal distances of 22.530Å × 19.216Å and the coordinated H_2O molecules point into the cavities. Two such (4,4)-layers interpenetrate in parallel mode (Figure 2b). The ligands in **CP-3-Cu** interact with each other *via* amide-to-amide hydrogen bonds (Figure 2c). The hydrogen bond pattern in case of amide groups represent the Synthon IV (Scheme 2). Biradha *et al.* obtained a similar structure with ligand **2** and $Cu(ClO_4)_2$, where the amide-to-amide hydrogen bonds are present between the two interpenetrated layers; the continuity of the amide hydrogen bonds throughout the network is hindered by water molecules and counter anions.[8d] Whereas in **CP-3-Cu**, the amide-to-amide hydrogen bond is present throughout the structure and is not interfered by counter anions and H_2O molecules.

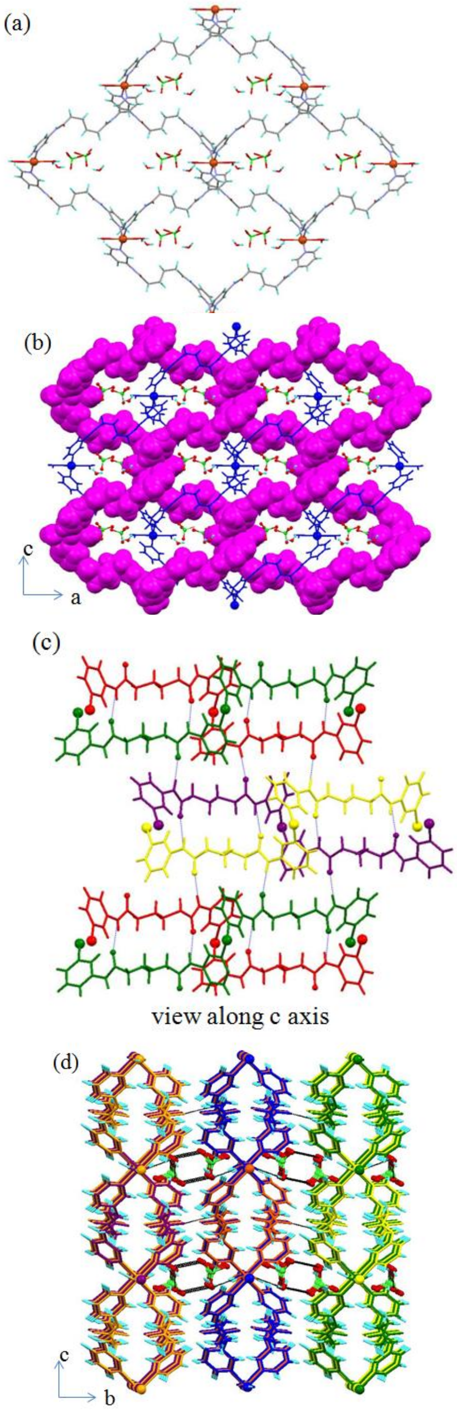


Figure 2: Illustration of the crystal structure of **CP-3-Cu**; (a) part of the 2D-layer of (4,4) topology (C = Grey; N = Blue; O = Red; Cu = Brown; P = Orange; F = Yellow); (b) Two-fold parallel interpenetration of the layers (One layer is shown in space fill mode (pink) and another is shown in ball and stick mode (Blue)); (c) Amide-to-amide hydrogen bonds (Each (4,4)-layer is shown in different color; Three pairs of interpenetrated layers are shown); (d) Side-view of the interpenetrated layers (Three pairs of interpenetrated layers are shown)

Looped One-Dimensional Coordination Network - Role of Metal Centre: The effect of metal centre on the geometry of the CP was studied by analyzing the structure of **CP-4-Cd**, which crystallizes in the triclinic $P\bar{1}$ space group. The coordination environment of Cd(II) centre included four molecules of the **1b** are present in the equatorial sites and two H_2O occupy the axial sites (Cd-N: 2.306Å, 2.311Å, 2.365Å, 2.404Å; Cd-O: 2.341Å, 2.349Å) (Figure 3a). The butyl chain in spacer of **1b** adopts *anti-anti-anti* conformation (Figure 1b), which resulted in stretching the ligand **1b** to its maximum length and hence linear geometry of the ligand is seen. The geometry of the ligand in **CP-4-Cd** is similar to that of *cis*- arranged 3,3'-bipyridine. The *cis*- arranged 3,3'-bipyridine is reported to form 1D-chains with Zn(II), Co(II) and Ni(II) whereas with Hg(II), it forms a dinuclear macrocyclic structure.[12]

The network formed in **CP-4-Cd** can be described as a 1D chain with rectangular loops. The longer length of the ligand 1b compared to that of 3,3'-bipyridine and larger size of the Cd(II) centre resulted in generating overall features of the reported structures (i.e. 1D looped chain). The rectangular loops in **CP-4-Cd** have a dimensions of 17.923Å × 5.176Å, where, the amide groups are involved in self-complementary hydrogen bond. The adjacent chains are held together by the hydrogen bond interaction between the amide N-H & ClO_4^- and between amide C=O & H_2O(Figure 3b). The π•••π interaction between the pyridyl groups are also responsible for holding the adjacent chains.

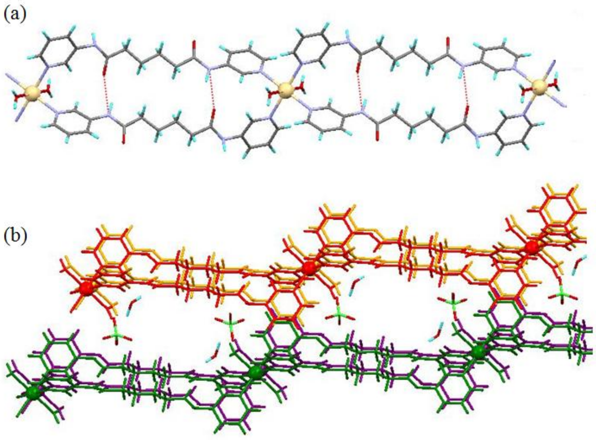


Figure 3: Illustration of the crystal structure of **CP-4-Cd**; (a) part of the 1D-looped chain (C = Grey; N = Blue; O = Red; Cu = Brown; P = Orange; F = Yellow; (b) packing of the 1D-chains via hydrogen bonding between the amide groups, water molecules and counter anions.

The 1D-looped chain with intra-chain amide-to-amide hydrogen bond observed in case of **CP-4-Cd** is similar to the reported structures by Dastidar and co-workers involving *bis*(3-pyridyl)terephthalamide with Cu(II) salts, where the ligand has a "rigid" phenyl spacer in between the *bis*-amide *bis*-pyridyl moieties.[13] This shows the ability of the "flexible" alkyl chain spacer of the ligand **1b**, when involved in forming CP with a larger metal center (i.e. Cd(II)), in mimicking the structural features obtained by a ligand involving "rigid" phenyl spacer.

Transmetallation Studies on the CPs: The response of the flexible spacer of ligand **1b** during the formation of the CPs on changing the metal centre has further prompted us to study their post-synthetic transformations. The transmetallation studies were performed on **CP-3-Cu** and **CP-4-Cd** to analyze whether the flexibility in the spacer will be able to change the geometry of the CPs on changing the metal centre or the robustness of the precursor CP will not allow any modification on the skeletal structure during metal metathesis.

CP-4-Cd

CP-4-Cd on metal metathesis reaction with Cu; after 10 min of reaction

CP-4-Cd on metal metathesis reaction with Cu; after 7 hrs of reaction

Figure 4: Crystal Morphology of CP-4-Cd on transmetallation reaction with Cu(II)

The transmetallation study on **CP-4-Cd** with $Cu(ClO_4)_2$ showed complete exchange of Cd(II) centre with Cu(II). The crystal color changed rapidly from white to blue, while the crystal morphology remained the same throughout the ion exchange process (Figure 4). The powder X-ray diffraction (PXRD) pattern of the resulting **CP-4-Cu** is similar to that of the parent compound **CP-4-Cd** (Figure 5). The Wavelength Dispersive X-ray Fluorescence (WD-XRF) shows the complete replacement of the framework Cd^{2+} ions by Cu^{2+} ions (Figure S12-S13).

The kinetics of the ion exchange process of Cd^{2+} by Cu^{2+} was monitored by AAS (Figure 6). Nearly 50% of the framework Cd^{2+} ions were replaced by Cu^{2+} within 1 h, and 97% of the Cd^{2+} ions were exchanged by Cu^{2+} within 10 hrs. The transmetallation study on CP-3-Cu and CP-4-Cu with $Cd(ClO_4)_2$ was very slow; negligible exchange was observed even after three months.

Powder XRD. The powder XRDs of CPs were analyzed along with the calculated powder XRD of CP-3-Cu and CP-4-Cd (Figure S4-S7). The structural differences of CP-3-Cu and CP-4-Cu is evident from these analysis (Figure S9). The powder XRD reflects the similarity in the structures of CP-4-Cd and CP-4-Cu. So we can relate that the structure of CP-4-Cu is isomorphous to that of CP-4-Cd. The direct reaction of ligand 1b with that of $Cu(ClO_4)_2$ always resulted in the formation of CP-3-Cu. The synthesis of CP-4-Cu is possible only by using transmetallation technique.

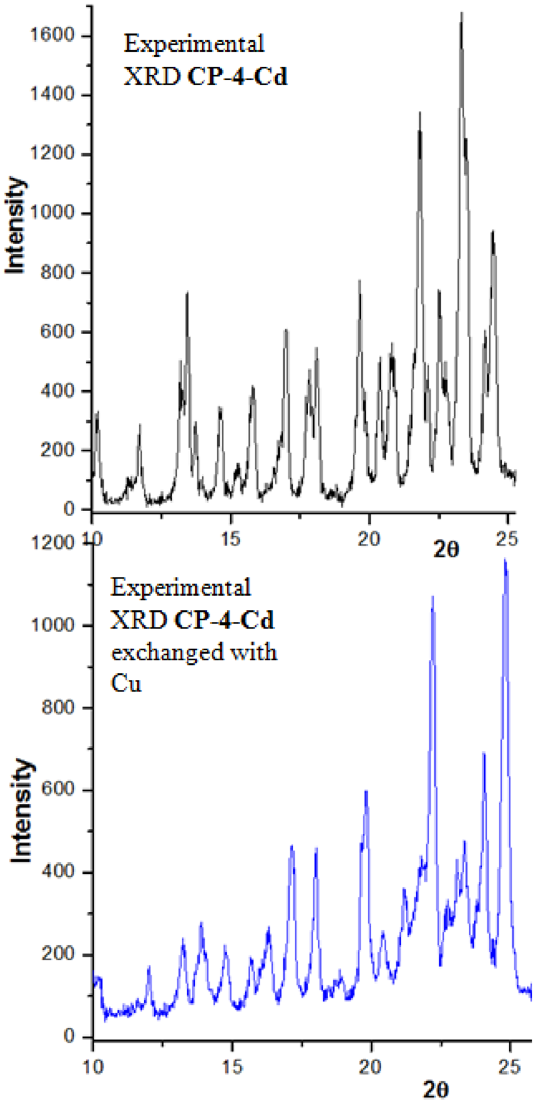


Figure 5: Powder X-ray diffraction profiles for the parent (**CP-4-Cd**) and ion exchanged material (**CP-4-Cu**) demonstrating the maintenance of the framework integrity

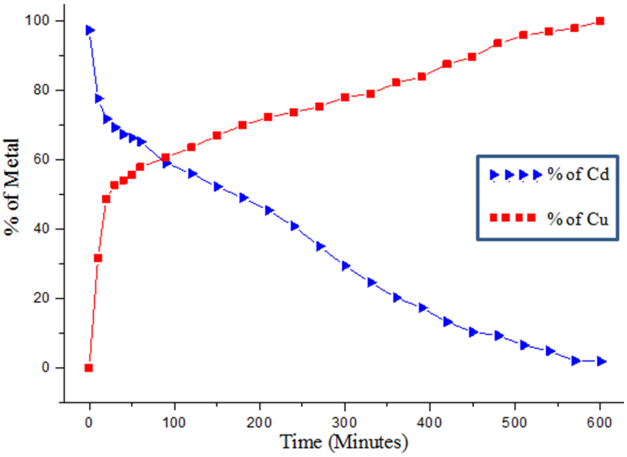


Figure 6: Kinetic profile of framework metal ion exchange of Cd(II) with Cu(II)

Conclusions

The metal centre was shown to play an important role in assembling the components during the formation of CPs: the size of the Cu(II) and Cd(II) centre being one of the major deciding factor in adjusting the conformation of the butyl spacer of the ligand. The transmetallation studies have shown us that despite having flexible framework, the metal exchange reaction proceeded without changing the structure of the CPs. This may be attributed to the fact that the looped-chain of **CP-4-Cd** has N-H•••O hydrogen bonds within the loops, which made the network robust. Further the CP synthesized *via* post-synthetic metal exchange could not be obtained from the direct reaction of the metal centre and the ligand. We have successfully synthesized with a framework-templating strategy by using the CP of Cd(II)-Flexible Ligand as a template, that may pre-assemble the flexible ligand in place.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Crystallographic data; PXRD patterns, IR, , AAS, WDXRF, and other supplementary material.]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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