CrystEngComm



View Article Online

PAPER



Cite this: *CrystEngComm*, 2014, **16**, 7815

Received 8th April 2014, Accepted 13th June 2014

DOI: 10.1039/c4ce00733f

www.rsc.org/crystengcomm

Introduction

Spontaneous self-assembly¹ 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 a Cu^{II}-diamondoid network derived from three dimensionally linked rod-like segments, namely 4,4',4'',4'''tetracyanotetraphenyl methane. Because of the remarkable advancement of single crystal X-ray diffraction techniques and the highly crystalline nature of CPs, it has been possible to study the structures of CPs at the molecular level enabling 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 properties,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

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

Mithun Paul and Parthasarathi Dastidar*

A series of coordination polymers (CPs) derived from pyridyl carboxylate ligands equipped with a 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. The effect of the ligating topology of these two positional isomers (L1 and L2) on the resultant supramolecular architecture of the corresponding CPs was investigated. The results indicate that most of the CPs display a 1D looped chain topology. Following *in situ* crystallization technique, attempts were made to separate environmentally toxic metal cation Cu^{II} in the form of the corresponding Cu^{II} CPs from a complex mixture of cations (Cu^{II}, Zn^{II} and Co^{II}) using both the ligands, while L1 was unsuccessful, L2 could indeed separate the Cu^{II} cation. The coordinating ability of the pyridyl and carboxylate moieties on the selective separation of cations was investigated. The results indicate that the selective separation of Cu^{II} followed the Irving–Williams series. Atomic absorption spectroscopy revealed that ~97% of Cu^{II} could be separated by this technique.

ditopic and tritopic ligands having *non-innocent* (hydrogen bond equipped) backbones.¹¹ Thus, various bis-pyridyl ligands having amide or urea functionality were exploited in generating intriguing structures like an 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 adsorption¹⁴ and solvent extraction.¹⁵ While chelating agents like hydroxyoximes, β -diketones, *etc.*, have been used in solvent extraction,16 solid sorbent mediated cation separation¹⁷ 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;

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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. CCDC 989153–989165. For the ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ce00733f

for example, drinking water containing copper concentrations more than 2 mg L^{-1} 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 pollutants²⁰ (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 the *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 polymers 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 the selective separation of Cu^{II} in the form of the corresponding coordination polymers. The reasons for obtaining the selective formation of Cu^{II} coordination polymers in this competitive conditions were: (a) the stability constants of Cu^{II} compounds were expected to be more than that of Co^{II} and Zn^{II} as per the Irving-Williams series,²² (b) pyridyl N atoms being a soft base as per the HSAB principle did not react to a significant extent with the relatively harder acids, such as Co^{II} and Zn^{II}, compared to the borderline Cu^{II} metal centre under competitive conditions.

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

Herein, we report the syntheses and single crystal structures of two new ligands, 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 the selective separation of Cu^{II} from a complex mixture of cations.

Results and discussion

The pyridyl-carboxy-amide ligands L1H and L2H were synthesized by reacting nicotinoyl chloride with the corresponding amino benzoic acid in a dichloromethane (DCM)-THF mixture under refluxing conditions. 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. The 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 lists the crystal data. Certain crystallographic and structural parameters are given in Table 2.

Single crystal structure of the free ligand L1H

Colorless blocked shaped crystals of L1H belong 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 (Fig. 1).



Table 1 Crystallographic data

Crystal parameters	L1H	CP1a	CP1b	CP1c
CCDC no.	989165	989153	989154	989155
Empirical formula	$C_{13}H_9N_2O_3$	$C_{26}H_{26}CuN_4O_{10}$	$C_{26}H_{26}CoN_4O_{10}$	$C_{26}H_{26}N_4O_{10}Zn$
Formula weight	242.23	618.05	613.44	619.88
Crystal size/mm	0.21 imes 0.08 imes 0.06	0.28 imes 0.08 imes 0.05	0.30 imes 0.22 imes 0.08	0.50 imes 0.22 imes 0.16
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	Phcn	$P2_a/n$	$P2_{a}/n$	PĪ
a/Λ	9 4072(3)	7 943(3)	77617(2)	9 3173(6)
h/λ	127250(2)	12 822(5)	12 4624(2)	10 4922(6)
	12.7330(3) 17.9010(5)	12.022(3) 12.00(5)	12.2209(4)	14.0275(9)
	17.8919(5)	13.509(5)	13.3308(4)	14.0375(8)
$\alpha/3$	90.00	90.00	90.00	97.468(2)
βlo	90.00	90.626(12)	101.2430(10)	96.161(2)
γ/ ⁰	90.00	90.00	90.00	91.980(2)
Volume/A ³	2143.46(10)	1375.8(9)	1264.73(6)	1350.01(14)
Ζ	8	2	2	2
$D_{\rm calc}/{\rm g~cm}^{-3}$	1.501	1.492	1.611	1.525
F(000)	1008	638	634	640
$\mu MoK\alpha/mm^{-1}$	0.109	0.858	0.748	0.975
Temperature/K	296(2)	296(2)	296(2)	296(2)
R.	0.0503	0.0447	0.0250	0.0132
$\mathbf{R}_{\mathrm{int}}$	-12/12 $-17/17$ $-24/22$	_11/11 _19/10 _17/1	-11/11 - 10/10 - 10/10	
$\alpha \min \max \alpha $	13/13, 17/17, 24/22	11/11, 10/19, 17/1	19 11/11, 10/10, 19/10	1.47/20.22
7 IIIII/IIIax/°	2.28/29.46	2.19/32.31	2.20/32.29	1.4//32.33
Reflections collected/unique/	38 464/296//190/	20886/4556/2825	23 8/8/4051/3495	21 168//990/6404
observed $[I > 2\sigma(I)]$				
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 <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0526$	$R_1 = 0.0456$	$R_1 = 0.0320$	$R_1 = 0.0522$
	$wR_2 = 0.1295$	$wR_2 = 0.1069$	$wR_2 = 0.1034$	$wR_2 = 0.1759$
R indices (all data)	$R_1 = 0.0965$	$R_1 = 0.0980$	$R_1 = 0.0412$	$R_1 = 0.0677$
	$wR_2 = 0.1543$	$wR_2 = 0.1362$	$wR_2 = 0.1170$	wR ₂ =0.1944
Crystal parameters	CP1d	C	P1e	CP1f
CCDC no.	989156	9	89157	989158
Empirical formula	$C_{26}H_{22}CdN_4O_9$	C	$L_{26}H_{26}CdN_4O_{10}$	C26H26FeN4O10
Formula weight	646.88	6	66.91	610.36
Crystal size/mm	0.14 imes 0.14 imes 0.0	06 0	$.67 \times 0.11 \times 0.10$	0.28 imes 0.08 imes 0.40
Crystal system	Triclinic	Ν	Ionoclinic	Monoclinic
Space group	PĪ	Р	$2_1/n$	$P2_1/n$
$a/\dot{\Delta}$	8 7935(9)	7	90160(10)	7 7788(3)
h/Λ	$12\ 2071(13)$, 1	2 7481(2)	12 5459(4)
	12.2071(13) 12.6146(13)	1	2.5560(2)	12.3439(4) 12.2501(5)
c/A	12.0140(13)	1	0.00	13.3301(3)
	96.023(4)	9	0.00	90.00
$\beta \beta$	103.536(4)	1	01.9350(10)	101.4830(10)
γ/0 	96.686(4)	9	0.00	90.00
Volume/A ³	1295.2(2)	1	335.98(3)	1276.79(8)
Ζ	2	2		2
$D_{\rm calc}/{\rm g~cm}^{-3}$	1.659	1	.658	1.588
F(000)	652	6	76	632
$\mu \text{ MoK}\alpha/\text{mm}^{-1}$	0.905	0	.883	0.659
Temperature/K	296(2)	2	96(2)	296(2)
n	0.0150	0	.0161	0.0234
Kint		-17/17 -	12/12, -18/19, -20/20	-10/11, -18/18, -20/19
Range of h. k. l	-12/11, $-16/17$.	+//+/	22/22, 20/23, 20/20	0.05/20.10
Rint Range of h, k, l $\theta \min/\max^{\circ}$	-12/11, -16/17, 1.68/30.14	2	.22/32.99	4.43/3/.18
Rint Range of h, k, l $\theta \min/\max^{0}$	-12/11, -16/17, 1.68/30.14 23.897/7034/631	2 9 2	.22/32.99 8.656/4653/3893	2.23/32.18
κ_{int} Range of h, k, l $\theta \min/\max/^{\circ}$ Reflections collected/unique/ ϕ heaving $[l \ge 2\pi/\ell]$	-12/11, -16/17, 1.68/30.14 23897/7034/631	9 2	.22/32.99 8 656/4653/3893	2.25/32.18 19 371/4090/3540
K_{int} Range of h, k, l θ min/max/° Reflections collected/unique/ observed $[I > 2\sigma(I)]$	-12/11, -16/17, 1.68/30.14 23 897/7034/631	9 2	.22/32.99 8 656/4653/3893	2.25/32.18 19 371/4090/3540
Rint Range of h , k , l θ min/max/° Reflections collected/unique/ observed $[I > 2\sigma(I)]$ Data/restraints/parameters	-12/11, -16/17, 1.68/30.14 23 897/7034/631 7034/0/369	9 2 4	.22/32.99 8 656/4653/3893 653/0/203	2.25/32.18 19 371/4090/3540 4090/0/200
Rint Range of h , k , l θ min/max/° Reflections collected/unique/ observed $[I > 2\sigma(I)]$ Data/restraints/parameters Goodness of fit on F^2	-12/11, -16/17, 1.68/30.14 23 897/7034/631 7034/0/369 1.187	9 2 9 4 0	.22/32.99 8 656/4653/3893 653/0/203 .139	2.25)32.18 19371/4090/3540 4090/0/200 1.082
Rint Range of h , k , l θ min/max/° Reflections collected/unique/ observed $[I > 2\sigma(I)]$ Data/restraints/parameters Goodness of fit on F^2 Final R indices $[I > 2\sigma(I)]$	$\begin{array}{c} -12/11, \ -16/17, \\ 1.68/30.14 \\ 23897/7034/631 \\ \hline 7034/0/369 \\ 1.187 \\ R_1 = 0.0304 \end{array}$	9 2 9 4 0 <i>R</i>	$\begin{array}{l} & 22/32.99 \\ 8 \ 656/4653/3893 \\ & 653/0/203 \\ & .139 \\ & v_1 = 0.0218 \end{array}$	$2.25(32.18)$ $19371/4090/3540$ $4090/0/200$ 1.082 $R_1 = 0.0323$
K_{int} Range of h, k, l θ min/max/° Reflections collected/unique/ observed $[I > 2\sigma(l)]$ Data/restraints/parameters Goodness of fit on F^2 Final R indices $[I > 2\sigma(l)]$	$-12/11, -16/17,$ $1.68/30.14$ $23897/7034/631$ $7034/0/369$ 1.187 $R_1 = 0.0304$ $wR_2 = 0.0893$	9 2 9 4 0 <i>R</i> w	$22/32.998 656/4653/3893653/0/203.139P_1 = 0.0218P_2 = 0.0639$	$2.25(32.18)$ $19 371/4090/3540$ $4090/0/200$ 1.082 $R_1 = 0.0323$ $wR_2 = 0.0934$
K_{int} Range of h, k, l θ min/max/° Reflections collected/unique/ observed $[I > 2\sigma(I)]$ Data/restraints/parameters Goodness of fit on F^2 Final R indices $[I > 2\sigma(I)]$ R indices (all data)	$-12/11, -16/17, \\1.68/30.14 \\23897/7034/631 \\7034/0/369 \\1.187 \\R_1 = 0.0304 \\wR_2 = 0.0893 \\R_1 = 0.0365$	9 2 9 2 4 0 <i>R</i> ww <i>R</i>	22/32.99 8 656/4653/3893 653/0/203 .139 $t_1 = 0.0218$ $t_2 = 0.0639$ $t_1 = 0.2980$	$2.25(32.18)$ $19 371/4090/3540$ $4090/0/200$ 1.082 $R_1 = 0.0323$ $wR_2 = 0.0934$ $R_1 = 0.0405$

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Table 1 (continued)

Crystal parameters	CP2a	CP2b	CP2c
CCDC no.	989159	989160	989161
Empirical formula	$C_{26}H_{30}CuN_4O_{12}$	$C_{26}H_{26}CuN_4O_{10}$	C26H26CoN4O10
Formula weight	654.08	618.05	613.44
Crystal size/mm	0.16 imes 0.13 imes 0.05	$0.26 \times 0.09 \times 0.07$	0.77 imes 0.37 imes 0.12
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
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)
α /°	90.00	90.00	90.00
$\beta/^{\circ}$	96.394(2)	99.176(3)	100.664(3)
γ/°	90.00	90.00	90.00
Volume/Å ³	1376.47(16)	1321.84(19)	1320.2(3)
Z	2	2	2
$D_{\rm calc}/{\rm g~cm}^{-3}$	1.578	1.553	1.543
<i>F</i> (000)	678	638	634
$\mu \text{ MoK}\alpha/\text{mm}^{-1}$	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
$\theta \min/\max/^{\circ}$	2.09/32.25	2.50/30.03	2.91/32.11
Reflections collected/unique/ observed $[I > 2\sigma(I)]$	24 406/4462/3541	16730/3543/2501	19 416/4287/4036
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 <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0410$	$R_1 = 0.0586$	$R_1 = 0.0252$
	$wR_2 = 0.1103$	$wR_2 = 0.1359$	$wR_2 = 0.0720$
R indices (all data)	$R_1 = 0.0614$	$R_1 = 0.1039$	$R_1 = 0.0252$
	$wR_2 = 0.1325$	$wR_2 = 0.1714$	$wR_2 = 0.0710$
Crystal parameters	CP2d	CP2e	CP2f
CCDC no.	989162	989163	989164
CCDC no. Empirical formula	989162 C ₂₇ H ₂₆ N ₄ O ₉ Zn	989163 C ₂₈ H ₃₁ CdN ₄ O ₁₁	989164 $C_{26}H_{28}Cd_2Cl_2N_4O_{11}$
CCDC no. Empirical formula Formula weight	989162 C ₂₇ H ₂₆ N ₄ O ₉ Zn 615.89	989163 C ₂₈ H ₃₁ CdN ₄ O ₁₁ 711.97	989164 $C_{26}H_{28}Cd_2Cl_2N_4O_{11}$ 868.22
CCDC no. Empirical formula Formula weight Crystal size/mm	989162 $C_{27}H_{26}N_4O_9Zn$ 615.89 1.00 × 0.14 × 0.10	$\begin{array}{l} 989163 \\ {\rm C_{28}H_{31}CdN_4O_{11}} \\ 711.97 \\ 1.00 \times 0.12 \times 0.08 \end{array}$	$\begin{array}{c} 989164 \\ {\rm C_{26}H_{28}Cd_2Cl_2N_4O_{11}} \\ 868.22 \\ 0.24 \times 0.21 \times 0.16 \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system	989162 C ₂₇ H ₂₆ N ₄ O ₉ Zn 615.89 1.00 × 0.14 × 0.10 Triclinic	989163 $C_{28}H_{31}CdN_4O_{11}$ 711.97 1.00 × 0.12 × 0.08 Monoclinic	$\begin{array}{c} 989164 \\ {\rm C_{26}H_{28}Cd_2Cl_2N_4O_{11}} \\ 868.22 \\ 0.24 \times 0.21 \times 0.16 \\ {\rm Monoclinic} \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group	989162 $C_{27}H_{26}N_4O_9Zn$ 615.89 1.00 × 0.14 × 0.10 Triclinic <i>P</i> I	989163 $C_{28}H_{31}CdN_4O_{11}$ 711.97 1.00 × 0.12 × 0.08 Monoclinic C2/c	989164 $C_{26}H_{28}Cd_2Cl_2N_4O_{11}$ 868.22 0.24 × 0.21 × 0.16 Monoclinic C2/c
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å	989162 $C_{27}H_{26}N_4O_9Zn$ 615.89 1.00 × 0.14 × 0.10 Triclinic <i>P</i> I 10.6479(4)	989163 $C_{28}H_{31}CdN_4O_{11}$ 711.97 1.00 × 0.12 × 0.08 Monoclinic C2/c 20.3394(16)	989164 $C_{26}H_{28}Cd_2Cl_2N_4O_{11}$ 868.22 0.24 × 0.21 × 0.16 Monoclinic C2/c 16.5778(8)
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å	989162 $C_{27}H_{26}N_4O_9Zn$ 615.89 1.00 × 0.14 × 0.10 Triclinic <i>P</i> I 10.6479(4) 11.0165(5)	989163 $C_{28}H_{31}CdN_4O_{11}$ 711.97 1.00 × 0.12 × 0.08 Monoclinic C2/c 20.3394(16) 10.1426(7)	$\begin{array}{c} 989164 \\ C_{26}H_{28}Cd_2Cl_2N_4O_{11} \\ 868.22 \\ 0.24 \times 0.21 \times 0.16 \\ Monoclinic \\ C2/c \\ 16.5778(8) \\ 16.9789(8) \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å	989162 $C_{27}H_{26}N_4O_9Zn$ 615.89 1.00 × 0.14 × 0.10 Triclinic <i>P</i> I 10.6479(4) 11.0165(5) 12.9533(5)	989163 $C_{28}H_{31}CdN_4O_{11}$ 711.97 1.00 × 0.12 × 0.08 Monoclinic C2/c 20.3394(16) 10.1426(7) 14.9680(9)	$\begin{array}{c} 989164 \\ C_{26}H_{28}Cd_2Cl_2N_4O_{11} \\ 868.22 \\ 0.24 \times 0.21 \times 0.16 \\ Monoclinic \\ C2/c \\ 16.5778(8) \\ 16.9789(8) \\ 21.8040(10) \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/\circ	989162 $C_{27}H_{26}N_4O_9Zn$ 615.89 1.00 × 0.14 × 0.10 Triclinic <i>P</i> 1 10.6479(4) 11.0165(5) 12.9533(5) 106.997(2)	989163 $C_{28}H_{31}CdN_4O_{11}$ 711.97 1.00 × 0.12 × 0.08 Monoclinic C2/c 20.3394(16) 10.1426(7) 14.9680(9) 90.00	$\begin{array}{c} 989164 \\ C_{26}H_{28}Cd_2Cl_2N_4O_{11} \\ 868.22 \\ 0.24 \times 0.21 \times 0.16 \\ Monoclinic \\ C2/c \\ 16.5778(8) \\ 16.9789(8) \\ 21.8040(10) \\ 90.00 \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/\circ β/\circ	989162 $C_{27}H_{26}N_4O_9Zn$ 615.89 1.00 × 0.14 × 0.10 Triclinic <i>P</i> 1 10.6479(4) 11.0165(5) 12.9533(5) 106.997(2) 96.481(2)	989163 $C_{28}H_{31}CdN_4O_{11}$ 711.97 1.00 × 0.12 × 0.08 Monoclinic C2/c 20.3394(16) 10.1426(7) 14.9680(9) 90.00 104.500(5)	$\begin{array}{c} 989164 \\ C_{26}H_{28}Cd_2Cl_2N_4O_{11} \\ 868.22 \\ 0.24 \times 0.21 \times 0.16 \\ Monoclinic \\ C2/c \\ 16.5778(8) \\ 16.9789(8) \\ 21.8040(10) \\ 90.00 \\ 94.606(2) \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/\circ β/\circ γ/\circ	$\begin{array}{l} 989162 \\ C_{27}H_{26}N_4O_9Zn \\ 615.89 \\ 1.00 \times 0.14 \times 0.10 \\ Triclinic \\ P\bar{1} \\ 10.6479(4) \\ 11.0165(5) \\ 12.9533(5) \\ 106.997(2) \\ 96.481(2) \\ 106.063(2) \end{array}$	989163 $C_{28}H_{31}CdN_4O_{11}$ 711.97 1.00 × 0.12 × 0.08 Monoclinic C2/c 20.3394(16) 10.1426(7) 14.9680(9) 90.00 104.500(5) 90.00	$\begin{array}{c} 989164 \\ C_{26}H_{28}Cd_2Cl_2N_4O_{11} \\ 868.22 \\ 0.24 \times 0.21 \times 0.16 \\ Monoclinic \\ C2/c \\ 16.5778(8) \\ 16.9789(8) \\ 21.8040(10) \\ 90.00 \\ 94.606(2) \\ 90.00 \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/\circ β/\circ γ/\circ Volume/Å ³	$\begin{array}{c} 989162 \\ C_{27}H_{26}N_4O_9Zn \\ 615.89 \\ 1.00 \times 0.14 \times 0.10 \\ Triclinic \\ P\bar{1} \\ 10.6479(4) \\ 11.0165(5) \\ 12.9533(5) \\ 106.997(2) \\ 96.481(2) \\ 106.063(2) \\ 1364.96(10) \end{array}$	989163 $C_{28}H_{31}CdN_4O_{11}$ 711.97 1.00 × 0.12 × 0.08 Monoclinic C2/c 20.3394(16) 10.1426(7) 14.9680(9) 90.00 104.500(5) 90.00 2989.5(4)	$\begin{array}{c} 989164 \\ C_{26}H_{28}Cd_2Cl_2N_4O_{11} \\ 868.22 \\ 0.24 \times 0.21 \times 0.16 \\ Monoclinic \\ C2/c \\ 16.5778(8) \\ 16.9789(8) \\ 21.8040(10) \\ 90.00 \\ 94.606(2) \\ 90.00 \\ 6117.4(5) \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ Volume/Å ³ Z	$\begin{array}{c} 989162 \\ C_{27}H_{26}N_4O_9Zn \\ 615.89 \\ 1.00 \times 0.14 \times 0.10 \\ Triclinic \\ P\bar{1} \\ 10.6479(4) \\ 11.0165(5) \\ 12.9533(5) \\ 106.997(2) \\ 96.481(2) \\ 106.063(2) \\ 1364.96(10) \\ 2 \end{array}$	$\begin{array}{c} 989163 \\ C_{28}H_{31}CdN_4O_{11} \\ 711.97 \\ 1.00 \times 0.12 \times 0.08 \\ Monoclinic \\ C2/c \\ 20.3394(16) \\ 10.1426(7) \\ 14.9680(9) \\ 90.00 \\ 104.500(5) \\ 90.00 \\ 2989.5(4) \\ 4 \end{array}$	$\begin{array}{c} 989164 \\ C_{26}H_{28}Cd_2Cl_2N_4O_{11} \\ 868.22 \\ 0.24 \times 0.21 \times 0.16 \\ \text{Monoclinic} \\ C2/c \\ 16.5778(8) \\ 16.9789(8) \\ 21.8040(10) \\ 90.00 \\ 94.606(2) \\ 90.00 \\ 6117.4(5) \\ 8 \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ Volume/Å ³ Z $D_{calc}/g cm^{-3}$	$\begin{array}{c} 989162 \\ C_{27}H_{26}N_4O_9Zn \\ 615.89 \\ 1.00 \times 0.14 \times 0.10 \\ Triclinic \\ P\bar{1} \\ 10.6479(4) \\ 11.0165(5) \\ 12.9533(5) \\ 106.997(2) \\ 96.481(2) \\ 106.063(2) \\ 1364.96(10) \\ 2 \\ 1.499 \end{array}$	$\begin{array}{c} 989163 \\ C_{28}H_{31}CdN_4O_{11} \\ 711.97 \\ 1.00 \times 0.12 \times 0.08 \\ Monoclinic \\ C2/c \\ 20.3394(16) \\ 10.1426(7) \\ 14.9680(9) \\ 90.00 \\ 104.500(5) \\ 90.00 \\ 2989.5(4) \\ 4 \\ 1.582 \end{array}$	$\begin{array}{c} 989164 \\ C_{26}H_{28}Cd_2Cl_2N_4O_{11} \\ 868.22 \\ 0.24 \times 0.21 \times 0.16 \\ \text{Monoclinic} \\ C2/c \\ 16.5778(8) \\ 16.9789(8) \\ 21.8040(10) \\ 90.00 \\ 94.606(2) \\ 90.00 \\ 6117.4(5) \\ 8 \\ 1.885 \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ Volume/Å ³ Z $D_{calc}/g cm^{-3}$ F(000)	$\begin{array}{c} 989162 \\ C_{27}H_{26}N_4O_9Zn \\ 615.89 \\ 1.00 \times 0.14 \times 0.10 \\ Triclinic \\ P\bar{1} \\ 10.6479(4) \\ 11.0165(5) \\ 12.9533(5) \\ 106.997(2) \\ 96.481(2) \\ 106.063(2) \\ 1364.96(10) \\ 2 \\ 1.499 \\ 636 \end{array}$	$\begin{array}{c} 989163 \\ C_{28}H_{31}CdN_4O_{11} \\ 711.97 \\ 1.00 \times 0.12 \times 0.08 \\ Monoclinic \\ C2/c \\ 20.3394(16) \\ 10.1426(7) \\ 14.9680(9) \\ 90.00 \\ 104.500(5) \\ 90.00 \\ 2989.5(4) \\ 4 \\ 1.582 \\ 1452 \end{array}$	$\begin{array}{c} 989164 \\ C_{26}H_{28}Cd_2Cl_2N_4O_{11} \\ 868.22 \\ 0.24 \times 0.21 \times 0.16 \\ \text{Monoclinic} \\ C2/c \\ 16.5778(8) \\ 16.9789(8) \\ 21.8040(10) \\ 90.00 \\ 94.606(2) \\ 90.00 \\ 6117.4(5) \\ 8 \\ 1.885 \\ 3440 \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ Volume/Å ³ Z $D_{calc}/g cm^{-3}$ F(000) μ MoK α /mm ⁻¹	$\begin{array}{c} 989162 \\ C_{27}H_{26}N_4O_9Zn \\ 615.89 \\ 1.00 \times 0.14 \times 0.10 \\ Triclinic \\ P\bar{1} \\ 10.6479(4) \\ 11.0165(5) \\ 12.9533(5) \\ 106.997(2) \\ 96.481(2) \\ 106.063(2) \\ 1364.96(10) \\ 2 \\ 1.499 \\ 636 \\ 0.961 \end{array}$	989163 $C_{28}H_{31}CdN_4O_{11}$ 711.97 $1.00 \times 0.12 \times 0.08$ Monoclinic C2/c 20.3394(16) 10.1426(7) 14.9680(9) 90.00 104.500(5) 90.00 2989.5(4) 4 1.582 1452 0.797	$\begin{array}{c} 989164\\ C_{26}H_{28}Cd_2Cl_2N_4O_{11}\\ 868.22\\ 0.24\times0.21\times0.16\\ Monoclinic\\ C2/c\\ 16.5778(8)\\ 16.9789(8)\\ 21.8040(10)\\ 90.00\\ 94.606(2)\\ 90.00\\ 6117.4(5)\\ 8\\ 1.885\\ 3440\\ 1.631\\ \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ Volume/Å ³ Z $D_{calc}/g cm^{-3}$ F(000) μ MoK α /mm ⁻¹ Temperature/K	$\begin{array}{c} 989162 \\ C_{27}H_{26}N_4O_9Zn \\ 615.89 \\ 1.00 \times 0.14 \times 0.10 \\ Triclinic \\ P\bar{1} \\ 10.6479(4) \\ 11.0165(5) \\ 12.9533(5) \\ 106.997(2) \\ 96.481(2) \\ 106.063(2) \\ 1364.96(10) \\ 2 \\ 1.499 \\ 636 \\ 0.961 \\ 293(2) \end{array}$	989163 $C_{28}H_{31}CdN_4O_{11}$ 711.97 $1.00 \times 0.12 \times 0.08$ Monoclinic C2/c 20.3394(16) 10.1426(7) 14.9680(9) 90.00 104.500(5) 90.00 2989.5(4) 4 1.582 1452 0.797 296(2)	$\begin{array}{c} 989164\\ C_{26}H_{28}Cd_2Cl_2N_4O_{11}\\ 868.22\\ 0.24\times0.21\times0.16\\ Monoclinic\\ C2/c\\ 16.5778(8)\\ 16.9789(8)\\ 21.8040(10)\\ 90.00\\ 94.606(2)\\ 90.00\\ 6117.4(5)\\ 8\\ 1.885\\ 3440\\ 1.631\\ 296(2)\\ \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ Volume/Å ³ Z $D_{calc}/g cm^{-3}$ F(000) μ MoK α /mm ⁻¹ Temperature/K R_{int}	$\begin{array}{c} 989162 \\ C_{27}H_{26}N_4O_9Zn \\ 615.89 \\ 1.00 \times 0.14 \times 0.10 \\ Triclinic \\ P\bar{1} \\ 10.6479(4) \\ 11.0165(5) \\ 12.9533(5) \\ 106.997(2) \\ 96.481(2) \\ 106.063(2) \\ 1364.96(10) \\ 2 \\ 1.499 \\ 636 \\ 0.961 \\ 293(2) \\ 0.0144 \end{array}$	989163 $C_{28}H_{31}CdN_4O_{11}$ 711.97 $1.00 \times 0.12 \times 0.08$ Monoclinic C2/c 20.3394(16) 10.1426(7) 14.9680(9) 90.00 104.500(5) 90.00 2989.5(4) 4 1.582 1452 0.797 296(2) 0.0201	$\begin{array}{c} 989164\\ C_{26}H_{28}Cd_2Cl_2N_4O_{11}\\ 868.22\\ 0.24\times0.21\times0.16\\ Monoclinic\\ C2/c\\ 16.5778(8)\\ 16.9789(8)\\ 21.8040(10)\\ 90.00\\ 94.606(2)\\ 90.00\\ 6117.4(5)\\ 8\\ 1.885\\ 3440\\ 1.631\\ 296(2)\\ 0.0260\\ \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ Volume/Å ³ Z $D_{calc}/g cm^{-3}$ F(000) μ MoK α /mm ⁻¹ Temperature/K R_{int} Range of h, k, l	$\begin{array}{l} 989162\\ C_{27}H_{26}N_4O_9Zn\\ 615.89\\ 1.00\times0.14\times0.10\\ Triclinic\\ P\bar{1}\\ 10.6479(4)\\ 11.0165(5)\\ 12.9533(5)\\ 106.997(2)\\ 96.481(2)\\ 106.063(2)\\ 1364.96(10)\\ 2\\ 1.499\\ 636\\ 0.961\\ 293(2)\\ 0.0144\\ -16/16, -14/17, -16/18\\ \end{array}$	$\begin{array}{c} 989163\\ C_{28}H_{31}CdN_4O_{11}\\ 711.97\\ 1.00 \times 0.12 \times 0.08\\ Monoclinic\\ C2/c\\ 20.3394(16)\\ 10.1426(7)\\ 14.9680(9)\\ 90.00\\ 104.500(5)\\ 90.00\\ 2989.5(4)\\ 4\\ 1.582\\ 1452\\ 0.797\\ 296(2)\\ 0.0201\\ -30/31, -13/14, -20/23\\ \end{array}$	$\begin{array}{c} 989164\\ C_{26}H_{28}Cd_2Cl_2N_4O_{11}\\ 868.22\\ 0.24\times0.21\times0.16\\ Monoclinic\\ C2/c\\ 16.5778(8)\\ 16.9789(8)\\ 21.8040(10)\\ 90.00\\ 94.606(2)\\ 90.00\\ 6117.4(5)\\ 8\\ 1.885\\ 3440\\ 1.631\\ 296(2)\\ 0.0260\\ -20/24, -25/25, -32/26\\ \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ Volume/Å ³ Z $D_{calc}/g cm^{-3}$ F(000) μ MoK α /mm ⁻¹ Temperature/K R_{int} Range of h, k, l θ min/max/°	$\begin{array}{l} 989162\\ C_{27}H_{26}N_4O_9Zn\\ 615.89\\ 1.00 \times 0.14 \times 0.10\\ Triclinic\\ P\bar{1}\\ 10.6479(4)\\ 11.0165(5)\\ 12.9533(5)\\ 106.997(2)\\ 96.481(2)\\ 106.063(2)\\ 1364.96(10)\\ 2\\ 1.499\\ 636\\ 0.961\\ 293(2)\\ 0.0144\\ -16/16, -14/17, -16/18\\ 1.68/33.98\\ \end{array}$	$\begin{array}{c} 989163\\ C_{28}H_{31}CdN_4O_{11}\\ 711.97\\ 1.00 \times 0.12 \times 0.08\\ Monoclinic\\ C2/c\\ 20.3394(16)\\ 10.1426(7)\\ 14.9680(9)\\ 90.00\\ 104.500(5)\\ 90.00\\ 2989.5(4)\\ 4\\ 1.582\\ 1452\\ 0.797\\ 296(2)\\ 0.0201\\ -30/31, -13/14, -20/23\\ 2.26/34.06\\ \end{array}$	$\begin{array}{c} 989164\\ C_{26}H_{28}Cd_2Cl_2N_4O_{11}\\ 868.22\\ 0.24\times0.21\times0.16\\ Monoclinic\\ C2/c\\ 16.5778(8)\\ 16.9789(8)\\ 21.8040(10)\\ 90.00\\ 94.606(2)\\ 90.00\\ 6117.4(5)\\ 8\\ 1.885\\ 3440\\ 1.631\\ 296(2)\\ 0.0260\\ -20/24, -25/25, -32/26\\ 1.87/32.18\\ \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ Volume/Å ³ Z $D_{calc}/g cm^{-3}$ F(000) μ MoK α /mm ⁻¹ Temperature/K R_{int} Range of h, k, l θ min/max/° Reflections collected/unique/	$\begin{array}{l} 989162\\ C_{27}H_{26}N_4O_9Zn\\ 615.89\\ 1.00 \times 0.14 \times 0.10\\ Triclinic\\ P\bar{1}\\ 10.6479(4)\\ 11.0165(5)\\ 12.9533(5)\\ 106.997(2)\\ 96.481(2)\\ 106.063(2)\\ 1364.96(10)\\ 2\\ 1.499\\ 636\\ 0.961\\ 293(2)\\ 0.0144\\ -16/16, -14/17, -16/18\\ 1.68/33.98\\ 48913/8582/7322\\ \end{array}$	$\begin{array}{c} 989163\\ C_{28}H_{31}CdN_4O_{11}\\ 711.97\\ 1.00 \times 0.12 \times 0.08\\ Monoclinic\\ C2/c\\ 20.3394(16)\\ 10.1426(7)\\ 14.9680(9)\\ 90.00\\ 104.500(5)\\ 90.00\\ 2989.5(4)\\ 4\\ 1.582\\ 1452\\ 0.797\\ 296(2)\\ 0.0201\\ -30/31, -13/14, -20/23\\ 2.26/34.06\\ 33276/5412/4925\\ \end{array}$	$\begin{array}{c} 989164\\ C_{26}H_{28}Cd_2Cl_2N_4O_{11}\\ 868.22\\ 0.24\times0.21\times0.16\\ Monoclinic\\ C2/c\\ 16.5778(8)\\ 16.9789(8)\\ 21.8040(10)\\ 90.00\\ 94.606(2)\\ 90.00\\ 6117.4(5)\\ 8\\ 1.885\\ 3440\\ 1.631\\ 296(2)\\ 0.0260\\ -20/24, -25/25, -32/26\\ 1.87/32.18\\ 45949/9876/7674\\ \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ Volume/Å ³ Z $D_{calc}/g cm^{-3}$ F(000) μ MoK α /mm ⁻¹ Temperature/K R_{int} Range of h, k, l θ min/max/° Reflections collected/unique/ observed $[I > 2\sigma(I)]$	$\begin{array}{l} 989162\\ C_{27}H_{26}N_4O_9Zn\\ 615.89\\ 1.00 \times 0.14 \times 0.10\\ Triclinic\\ P\bar{1}\\ 10.6479(4)\\ 11.0165(5)\\ 12.9533(5)\\ 106.997(2)\\ 96.481(2)\\ 106.063(2)\\ 1364.96(10)\\ 2\\ 1.499\\ 636\\ 0.961\\ 293(2)\\ 0.0144\\ -16/16, -14/17, -16/18\\ 1.68/33.98\\ 48913/8582/7322 \end{array}$	989163 $C_{28}H_{31}CdN_4O_{11}$ 711.97 1.00 × 0.12 × 0.08 Monoclinic C2/c 20.3394(16) 10.1426(7) 14.9680(9) 90.00 104.500(5) 90.00 2989.5(4) 4 1.582 1452 0.797 296(2) 0.0201 -30/31, -13/14, -20/23 2.26/34.06 33 276/5412/4925	$\begin{array}{c} 989164\\ C_{26}H_{28}Cd_2Cl_2N_4O_{11}\\ 868.22\\ 0.24\times0.21\times0.16\\ Monoclinic\\ C2/c\\ 16.5778(8)\\ 16.9789(8)\\ 21.8040(10)\\ 90.00\\ 94.606(2)\\ 90.00\\ 6117.4(5)\\ 8\\ 1.885\\ 3440\\ 1.631\\ 296(2)\\ 0.0260\\ -20/24, -25/25, -32/26\\ 1.87/32.18\\ 45949/9876/7674\\ \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ Volume/Å ³ Z $D_{calc}/g cm^{-3}$ F(000) μ MoK α /mm ⁻¹ Temperature/K R_{int} Range of h, k, l θ min/max/° Reflections collected/unique/ observed $[I > 2\sigma(I)]$ Data/restraints/parameters	$\begin{array}{c} 989162\\ C_{27}H_{26}N_4O_9Zn\\ 615.89\\ 1.00\times0.14\times0.10\\ Triclinic\\ P\bar{1}\\ 10.6479(4)\\ 11.0165(5)\\ 12.9533(5)\\ 106.997(2)\\ 96.481(2)\\ 106.063(2)\\ 1364.96(10)\\ 2\\ 1.499\\ 636\\ 0.961\\ 293(2)\\ 0.0144\\ -16/16, -14/17, -16/18\\ 1.68/33.98\\ 48913/8582/7322\\ \end{array}$	$\begin{array}{c} 989163\\ C_{28}H_{31}CdN_4O_{11}\\ 711.97\\ 1.00 \times 0.12 \times 0.08\\ Monoclinic\\ C2/c\\ 20.3394(16)\\ 10.1426(7)\\ 14.9680(9)\\ 90.00\\ 104.500(5)\\ 90.00\\ 2989.5(4)\\ 4\\ 1.582\\ 1452\\ 0.797\\ 296(2)\\ 0.0201\\ -30/31, -13/14, -20/23\\ 2.26/34.06\\ 33276/5412/4925\\ \\ 5412/0/200\\ \end{array}$	$\begin{array}{c} 989164\\ C_{26}H_{28}Cd_2Cl_2N_4O_{11}\\ 868.22\\ 0.24\times0.21\times0.16\\ Monoclinic\\ C2/c\\ 16.5778(8)\\ 16.9789(8)\\ 21.8040(10)\\ 90.00\\ 94.606(2)\\ 90.00\\ 6117.4(5)\\ 8\\ 1.885\\ 3440\\ 1.631\\ 296(2)\\ 0.0260\\ -20/24, -25/25, -32/26\\ 1.87/32.18\\ 45949/9876/7674\\ 9876/0/421\\ \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å c/Å a/° $\beta/°$ $\gamma/°$ Volume/Å ³ Z $D_{calc}/g cm^{-3}$ F(000) μ MoK α /mm ⁻¹ Temperature/K R_{int} Range of h, k, l θ min/max/° Reflections collected/unique/ observed $[I > 2\sigma(I)]$ Data/restraints/parameters Goodness of fit on F^2	$\begin{array}{c} 989162\\ C_{27}H_{26}N_4O_9Zn\\ 615.89\\ 1.00 \times 0.14 \times 0.10\\ Triclinic\\ P\bar{1}\\ 10.6479(4)\\ 11.0165(5)\\ 12.9533(5)\\ 106.997(2)\\ 96.481(2)\\ 106.063(2)\\ 1364.96(10)\\ 2\\ 1.499\\ 636\\ 0.961\\ 293(2)\\ 0.0144\\ -16/16, -14/17, -16/18\\ 1.68/33.98\\ 48913/8582/7322\\ \end{array}$	$\begin{array}{c} 989163\\ C_{28}H_{31}CdN_4O_{11}\\ 711.97\\ 1.00 \times 0.12 \times 0.08\\ Monoclinic\\ C2/c\\ 20.3394(16)\\ 10.1426(7)\\ 14.9680(9)\\ 90.00\\ 104.500(5)\\ 90.00\\ 104.500(5)\\ 90.00\\ 2989.5(4)\\ 4\\ 1.582\\ 1452\\ 0.797\\ 296(2)\\ 0.0201\\ -30/31, -13/14, -20/23\\ 2.26/34.06\\ 33276/5412/4925\\ \\\hline 5412/0/200\\ 1.120\\ \end{array}$	$\begin{array}{c} 989164\\ C_{26}H_{28}Cd_2Cl_2N_4O_{11}\\ 868.22\\ 0.24\times0.21\times0.16\\ Monoclinic\\ C2/c\\ 16.5778(8)\\ 16.9789(8)\\ 21.8040(10)\\ 90.00\\ 94.606(2)\\ 90.00\\ 6117.4(5)\\ 8\\ 1.885\\ 3440\\ 1.631\\ 296(2)\\ 0.0260\\ -20/24, -25/25, -32/26\\ 1.87/32.18\\ 45949/9876/7674\\ \\ 9876/0/421\\ 1.023\\ \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ Volume/Å ³ Z $D_{calc}/g cm^{-3}$ F(000) μ MoK α /mm ⁻¹ Temperature/K R_{int} Range of h, k, l θ min/max/° Reflections collected/unique/ observed $[I > 2\sigma(I)]$ Data/restraints/parameters Goodness of fit on F^2 Final R indices $[I > 2\sigma(I)]$	$\begin{array}{l} 989162\\ C_{27}H_{26}N_4O_9Zn\\ 615.89\\ 1.00 \times 0.14 \times 0.10\\ Triclinic\\ P\bar{1}\\ 10.6479(4)\\ 11.0165(5)\\ 12.9533(5)\\ 106.997(2)\\ 96.481(2)\\ 106.063(2)\\ 1364.96(10)\\ 2\\ 1.499\\ 636\\ 0.961\\ 293(2)\\ 0.0144\\ -16/16, -14/17, -16/18\\ 1.68/33.98\\ 48\ 913/8582/7322\\ \\ 8582/0/391\\ 1.014\\ R_1 = 0.0359\\ \end{array}$	$\begin{array}{l} 989163\\ C_{28}H_{31}CdN_4O_{11}\\ 711.97\\ 1.00 \times 0.12 \times 0.08\\ Monoclinic\\ C2/c\\ 20.3394(16)\\ 10.1426(7)\\ 14.9680(9)\\ 90.00\\ 104.500(5)\\ 90.00\\ 2989.5(4)\\ 4\\ 1.582\\ 1452\\ 0.797\\ 296(2)\\ 0.0201\\ -30/31, -13/14, -20/23\\ 2.26/34.06\\ 33276/5412/4925\\ \\\hline 5412/0/200\\ 1.120\\ R_1=0.0253\\ \end{array}$	$\begin{array}{l} 989164\\ C_{26}H_{28}Cd_2Cl_2N_4O_{11}\\ 868.22\\ 0.24\times0.21\times0.16\\ Monoclinic\\ C2/c\\ 16.5778(8)\\ 16.9789(8)\\ 21.8040(10)\\ 90.00\\ 94.606(2)\\ 90.00\\ 6117.4(5)\\ 8\\ 1.885\\ 3440\\ 1.631\\ 296(2)\\ 0.0260\\ -20/24, -25/25, -32/26\\ 1.87/32.18\\ 45949/9876/7674\\ 9876/0/421\\ 1.023\\ R_1=0.0443\\ \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ Volume/Å ³ Z $D_{calc}/g cm^{-3}$ F(000) μ MoK α /mm ⁻¹ Temperature/K R_{int} Range of h, k, l θ min/max/° Reflections collected/unique/ observed $[I > 2\sigma(I)]$ Data/restraints/parameters Goodness of fit on F^2 Final R indices $[I > 2\sigma(I)]$	989162 $C_{27}H_{26}N_4O_9Zn$ 615.89 1.00 × 0.14 × 0.10 Triclinic $P\overline{1}$ 10.6479(4) 11.0165(5) 12.9533(5) 106.997(2) 96.481(2) 106.063(2) 1364.96(10) 2 1.499 636 0.961 293(2) 0.0144 -16/16, -14/17, -16/18 1.68/33.98 48 913/8582/7322 8582/0/391 1.014 $R_1 = 0.0359$ $wR_2 = 0.1010$	$\begin{array}{l} 989163\\ C_{28}H_{31}CdN_4O_{11}\\ 711.97\\ 1.00 \times 0.12 \times 0.08\\ Monoclinic\\ C2/c\\ 20.3394(16)\\ 10.1426(7)\\ 14.9680(9)\\ 90.00\\ 104.500(5)\\ 90.00\\ 2989.5(4)\\ 4\\ 1.582\\ 1452\\ 0.797\\ 296(2)\\ 0.0201\\ -30/31, -13/14, -20/23\\ 2.26/34.06\\ 33276/5412/4925\\ \\\hline 5412/0/200\\ 1.120\\ R_1 = 0.0253\\ wR_2 = 0.0690\\ \end{array}$	$\begin{array}{l} 989164\\ C_{26}H_{28}Cd_2Cl_2N_4O_{11}\\ 868.22\\ 0.24\times0.21\times0.16\\ Monoclinic\\ C2/c\\ 16.5778(8)\\ 16.9789(8)\\ 21.8040(10)\\ 90.00\\ 94.606(2)\\ 90.00\\ 6117.4(5)\\ 8\\ 1.885\\ 3440\\ 1.631\\ 296(2)\\ 0.0260\\ -20/24, -25/25, -32/26\\ 1.87/32.18\\ 45949/9876/7674\\ 9876/0/421\\ 1.023\\ R_1=0.0443\\ wR_2=0.1552\\ \end{array}$
CCDC no. Empirical formula Formula weight Crystal size/mm Crystal system Space group a/Å b/Å c/Å $a/^{\circ}$ $\beta/^{\circ}$ $\gamma/^{\circ}$ Volume/Å ³ Z $D_{calc}/g cm^{-3}$ F(000) μ MoK α /mm ⁻¹ Temperature/K R_{int} Range of h, k, l θ min/max/ $^{\circ}$ Reflections collected/unique/ observed $[I > 2\sigma(I)]$ Data/restraints/parameters Goodness of fit on F^2 Final R indices $[I > 2\sigma(I)]$ R indices (all data)	989162 $C_{27}H_{26}N_4O_9Zn$ 615.89 1.00 × 0.14 × 0.10 Triclinic $P\overline{1}$ 10.6479(4) 11.0165(5) 12.9533(5) 106.997(2) 96.481(2) 106.063(2) 1364.96(10) 2 1.499 636 0.961 293(2) 0.0144 -16/16, -14/17, -16/18 1.68/33.98 48 913/8582/7322 8582/0/391 1.014 $R_1 = 0.0359$ $wR_2 = 0.1010$ $R_1 = 0.0438$	$\begin{array}{l} 989163\\ C_{28}H_{31}CdN_4O_{11}\\ 711.97\\ 1.00 \times 0.12 \times 0.08\\ Monoclinic\\ C2/c\\ 20.3394(16)\\ 10.1426(7)\\ 14.9680(9)\\ 90.00\\ 104.500(5)\\ 90.00\\ 2989.5(4)\\ 4\\ 1.582\\ 1452\\ 0.797\\ 296(2)\\ 0.0201\\ -30/31, -13/14, -20/23\\ 2.26/34.06\\ 33276/5412/4925\\ \hline\\ 5412/0/200\\ 1.120\\ R_1 = 0.0253\\ wR_2 = 0.0690\\ R_1 = 0.0300\\ \end{array}$	$\begin{array}{l} 989164\\ C_{26}H_{28}Cd_2Cl_2N_4O_{11}\\ 868.22\\ 0.24\times0.21\times0.16\\ Monoclinic\\ C2/c\\ 16.5778(8)\\ 16.9789(8)\\ 21.8040(10)\\ 90.00\\ 94.606(2)\\ 90.00\\ 6117.4(5)\\ 8\\ 1.885\\ 3440\\ 1.631\\ 296(2)\\ 0.0260\\ -20/24, -25/25, -32/26\\ 1.87/32.18\\ 45949/9876/7674\\ 9876/0/421\\ 1.023\\ R_1=0.0443\\ wR_2=0.1552\\ R_1=0.0611\\ \end{array}$

Single crystal structures of the coordination polymers

SXRD analyses of the coordination polymers revealed that CP1a, CP1b, CP1e and CP1f were isomorphous displaying the

identical space group $P2_1/n$ with near identical cell dimensions. It was observed that CP2a and CP2e crystallizing in different space groups ($P2_1/c$ and C2/c, respectively) were

Table 2 Crystallographic and structural information

Lattice occluded solvent molecules		$1H_2O$	$1H_2O$	$1 H_2 004 F$	$1H_2O$	$2H_2O$	1H ₂ O + 1CH ₃ OH
Hydrogen bonding involving the amide moiety	$ \begin{array}{l} \mathrm{N} \cdots \mathrm{O}_{\mathrm{arboxylate}} \left[\mathrm{N} \cdots \mathrm{O} = 2.653(2) - 3.012(2) \ \mathring{A}; \\ \angle \mathrm{N} - \mathrm{H} \cdots \mathrm{O} = 162.9^{\mathrm{o}-165.10} \right]; \end{array} $	N-H…O _{solvate} [N…O = 2.932(3) Å; ∠N-H…O = 179(3)°] O-H _{coord} water…O [O…O = 2.806(3)-2.956(4) Å; ∠O-H…O = 166(4)-168(5)°]	$ \begin{array}{l} N-H\cdots O_{\text{solvate}}\left[N\cdots O=2.842(16)\ \mathring{A}; \\ \angle N-H\cdots O=172(2)^{\circ}\right] O-H_{\text{coord wate}}\cdots O\left[O\cdots O=2.821(15)\ \mathring{A}; \\ \angle O-H\cdots O=176(2)\right] \end{array} $	N-H…O _{solvate} [NO = 2.896(18) Å; ∠N-H…O = 1710] O-H _{coold} water…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)]	$ \begin{array}{l} \overline{N}-H\cdots O_{solvate}\left[\overline{N}\cdots O_{1}\right] = 2.850(15) \ \mathring{A}; \\ \angle N-H\cdots O = 172.3^{\circ} \right] O-H_{coord water}\cdots O \left[\overline{O}\cdots O = 2.825(14) \ \mathring{A}; \\ \angle O-H\cdots O = 175(2) \right] O-H_{solvate}\cdots O \left[\overline{O}\cdots O = 2.923(15) \ \mathring{A}; \\ \angle O-H\cdots O = 170(2) \right] \end{array} $	$\frac{N-H\cdots O_{\text{solvate}}[N\cdots O=2.838(2) \text{ Å};}{\sum N-H\cdots O=157.9^{\circ}] \text{ O}-H_{\text{solvate}}\cdots \text{ O} [O\cdots O=2.794(2) \text{ Å}]}$	$\begin{split} & N-H\cdots O_{solvate} \left[N\cdots O = 2.896(18) \ \mathring{A}; \\ & \angle N-H\cdots O = 177.3^{\circ} \right] O-H_{coord \ water} \cdots O \ \left[O\cdots O = 2.746(17) \ \mathring{A}; \\ & \angle O-H\cdots O = 146.0 \right] \end{split}$
Network topology		1D looped chain	1D looped chain	1D looped chain	1D looped chain	1D looped chain	1D looped chain
Ligating angle	132.55	101.20	104.12	104.61	104.35	149.43	130.90
Dihedral angle between the terminal aromatic rings	16.02	36.43	52.31	51.94	50.56	64.98	66.82
Relative orientation of pyridyl N and amide >C==O	uńs	anti	anti	anti	anti	uńs	anti
Asymmetric unit content	1 fully occupied molecule of L1	$0.5Cu^{II} + 1 L1 + 1$ coordinated $H_2O + 1$ solvated H_2O	$0.5 \text{Co}^{\text{II}} + 1 \text{ L1} + 1$ coordinated $\text{H}_2\text{O} + 1$ solvated H_2O	0.5Cd ^{II} + 1 L1 + 1 coordinated H ₂ O + 1 solvated H ₂ O	$0.5 \text{Fe}^{\text{II}} + 1 \text{ L1} + 1$ coordinated $\text{H}_2\text{O} + 1$ solvated H_2O	0.5Cu ^{II} + 1 L2 + 1 coordinated H ₂ O + 2 solvated H ₂ O	$0.5Cd^{II} + 1L2 + 1/2$ coordinated H ₂ O + 1 solvated H ₂ O + 1 methanol
Space group	Pbcn	al $P2_1/n$	al $P2_1/n$	I P2 ₁ /n	I P2 ₁ /n	al <i>P</i> 2 ₁ / <i>c</i>	al <i>C2/c</i>
Structural information		Isomorphous Isostructur	Isomorphous Isostructur	Isomorphous Isostructur	Isomorphous Isostructur	Isostructur	Isostructur
Ligand and CPs	L1H	CP1a	CP1b	CP1e	CP1f	CP2a	CP2e

Table 2 (continued)

	Structural	Space		Relative orientation of pyridyl N and amide	Dihedral angle between the terminal	Ligating	Network		Lattice occluded solvent
CPs	information	group	Asymmetric unit content	>C==0	aromatic rings	angle	topology	Hydrogen bonding involving amide moiety	molecules
CP2b	Isomorphous	$P2_1/n$	0.5Cu ^{II} + 1 L2 + 1 coordinated H ₂ O + 1 solvated H ₂ O	uńs	21.33	136.00	2D sheet	$\begin{split} \mathrm{N-H}\cdots \mathrm{O}_{\mathrm{carbyylate}}\left[\mathrm{N}\cdots \mathrm{O}=3.006(4)~\mathring{\mathrm{A}};\right.\\ \mathcal{\angle}\mathrm{N-H}\cdots \mathrm{O}=161(5)^{\circ}\right]~\mathrm{O}_{\mathrm{solvate}}\cdots \mathrm{O}\left[\mathrm{O}\cdots \mathrm{O}=2.725(4)~\mathring{\mathrm{A}}\right] \end{split}$	$1H_2O$
CP2c	Isomorphous	$P2_1/n$	$0.5 \text{CO}^{\text{II}} + 1 \text{ L2} + 1 \text{ coordinated}$ $\text{H}_2\text{O} + 1 \text{ solvated} \text{ H}_2\text{O}$	uńs	20.53	134.70	2D sheet	$\begin{array}{l} N^{-}\cdotsO_{\operatorname{carbxylate}}\left[N\cdotsO=2.964(10)\ \mathring{\mathbf{A}};\\ \angleN^{-}H\cdotsO=161.8^{\circ}\right]O^{-\operatorname{solvate}}\cdotsO\left[O\cdotsO=2.732(12)\ \mathring{\mathbf{A}};\\ \angleO^{-}H\cdotsO=176(2)^{\circ}\right] \end{array}$	$2H_2O$
CP1c		P-1	1 Zn^{II} + 2 L1 + 1 coordinated H ₂ O + 3 solvated H ₂ O	All syn	13.91/3.76	129.08/ 134.83	Inter digited 1D chain	$\begin{split} & N-H\cdots O_{earbyJate} \left[\dot{N}^{}O = 2.834(3) \ \dot{A}; \\ & \angle N-H\cdots O = 158.3^{\circ} \right] N-H\cdots O_{solvate} \left[N\cdots O = 2.875(4) \ \dot{A}; \\ & \angle N-H\cdots O = 163.3^{\circ} \right] O_{solvate} \cdots O \left[O\cdots O = 2.790(3) - 2.829(5) \ \dot{A} \right] \end{split}$	$3H_2O$
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	$\begin{split} & N^{-}\cdotsO_{\mathrm{amide}}\left[N\cdotsO=2.918(3);\right.\\ & \boldsymbol{\angle N}-H\cdotsO=161.4^{\circ}]; \; N^{-}O_{\mathrm{solvate}}\left[N\cdotsO=2.986(7)\; \mathring{\mathrm{A}};\right.\\ & \boldsymbol{\angle N}-H\cdotsO=163(4)^{\circ}]O_{-\mathrm{olvate}}\cdotsO\left[O\cdotsO=2.763(4)\; \mathring{\mathrm{A}}\right] \end{split}$	$2H_2O$
CP2d		P-1	1 $Zn^{II} + 2 L2 + 1$ coordinated H ₂ O + 1 solvated H ₂ O + 1 solvated methanol	anti/syn	11.17/25.66	125.27/ 142.91	1D polymeric tape	$ \begin{split} & N-H\cdots \mathbf{O}_{\mathrm{methanol}}\left[\tilde{N}\cdots \mathbf{O}=2.968(2)\ \mathring{\mathbf{A}}; \\ & \boldsymbol{\angle}N-H\cdots O=167(2)^\circ\right]; N-H\cdots O_{\mathrm{solvated}}\left[N\cdots O=3.037(2)\ \mathring{\mathbf{A}}; \\ & \boldsymbol{\angle}N-H\cdots O=163.8^\circ\right] O-H_{\mathrm{solvate}}\cdots O\left[O\cdots O=2.825(19)\ \mathring{\mathbf{A}}; \\ & \boldsymbol{\angle}O-H\cdots O=158.3^\circ\right] \end{split} $	1H ₂ O + 1CH ₃ OH
CP2f		C2/c	$2 \text{ Cd}^{II} + 2 \text{ chloride} + 2 \text{ L2} + 2 \text{ coordinated} \text{ H}_2\text{O} + 3 \text{ solvated} \text{ H}_2\text{O}$	All <i>anti</i>	2.44/7.83	127.19/ 127.87	1D looped chain	$\begin{split} & N-H\cdots \mathbf{O}_{\text{solvate}}\left[N\cdots \overset{\circ}{O}=3.064(3) \ \overset{\circ}{A}; \\ & \angleN-H\cdotsO=164.3^{\circ}\right]O-H_{\text{solvate}}\cdotsO\left[O\cdotsO=2.701(6)\text{-}2.934(4) \ \overset{\circ}{A}\right] \end{split}$	3H ₂ O]
Detern	nination of liga	ating an	Igle.	HN COONA					



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

isostructural with the crystals of **CP1a**, **CP1b**, **CP1e** and **CP1f**. Thus, we describe below the crystal structure of **CP1a** only.

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 the 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 ligating sites (pyridyl N and carboxylate O) to generate a 1D looped chain topology. The Cu^{II} metal center displayed an almost perfect octahedral geometry wherein the equatorial sites were occupied by the O atoms of two water molecules and the carboxylate moiety, and the axial sites were coordinated by the 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 (Fig. 2).

Crystal structures of [{Cu(μ -L2)₂ (H₂O)₂}·H₂O]_{\propto}CP2b and [{Co(μ -L2)₂ (H₂O)₂}·H₂O]_{\propto}CP2c

SXRD data revealed that CP2b and CP2c were isomorphous displaying the identical space group $P2_1/n$ having a near identical cell dimension. Thus, we describe 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* the pyridyl N atom, one fully occupied water molecule coordinated to the metal center and a fully occupied lattice occluded water molecule.



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

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 bidentate pyridyl-carboxylate ligands coordinated to the adjacent metal centers in such a way that a highly non-planar 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 (Fig. 3).

Crystal structure of $[{Zn(\mu-L1)_2(H_2O)} \cdot 3H_2O]_{\infty}CP1c$

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 in 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 a 1D polymeric chain resembling comb-like structure. The coordination environment of Zn^{II} may be considered as a highly distorted octahedron wherein the equatorial positions were coordinated by the O atoms of the two carboxylates and one water molecule, whereas the axial positions were occupied by the pyridyl N and carboxylate O atoms. The 1D comblike polymeric chains were packed in inter-digited fashion resulting in bilayer structures which were further packed in parallel fashion though out of 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



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

neighbouring chain *via* N-H···O and O-H···O interactions (Fig. 4).

Crystal structure of $[{Cd(\mu-L1)_2(\mu-L1)_3(H_2O)} \cdot 2H_2O]_{x}$ 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 a 2D corrugated sheet network weaved with a looped structure generated due to the 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



Fig. 4 Crystal structure illustration of **CP1c**: 1D comb-like polymeric chains packed in inter-digited fashion displaying occluded solvent water molecules (red balls) sustained by hydrogen bonding.

found to be involved in hydrogen bonding with the lattice occluded water molecules resulting in an overall 3D hydrogen bonded network (Fig. 5).

Crystal structure of $[{Zn(\mu-L2)_2(H_2O)} \cdot (H_2O)(CH_3OH)]_{x}CP2d$

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 a 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 (Fig. 6).

Crystal structure of [{(Cl)₂(H₂O)₂Cd₂(µ-L2)₂}·3H₂O]_∞ CP2f

The coordination polymer **CP2f** crystallized in the centrosymmetric monoclinic space group C2/c. The asymmetric unit contained two ligand molecules, two Cd^{II} metal centers, two



Fig. 5 Crystal structure illustration of **CP1d**: (a) a non-planar 2D network weaved with a looped structure formed *via* metal-ligand coordination; (b) the 2D network represents a corrugated sheet.

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Fig. 6 Crystal structure illustration of **CP2d**; (a) 1D polymeric tape formed from two parallel running 1D chains cross-linked by metallamacrocycles (green); (b) the overall 3D network sustained by H-bonding interactions displaying lattice occluded water and methanol molecules.

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 to 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 M2L2 type macrocycles. The macrocycles were further propagated in 1D via the $Cd^{II}(\mu-Cl)_2$ -Cd^{II} bridge. Both the metal centers displayed a 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 (Fig. 7).

The crystalline phase purity of the coordination polymers CP1b, CP1c, CP1f, CP2a, CP2b, CP2c, CP2e, and CP2f were established by PXRD analyses (see the ESI†); in the case of CP1e, there appeared to be an extra phase as a few peaks within the region of $10-17^{\circ} 2\theta$ 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 a new crystalline phase in the bulk materials. The PXRD pattern in CP2d



Fig. 7 Crystal structure illustration of **CP2f**: (a) 1D looped chain coordination polymer propagated *via* the Cd^{II}(μ -Cl)₂-Cd^{II} bridge; (b) the overall 3D network sustained by H-bonding interactions displaying lattice occluded water molecules (red balls).

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 the syn conformation for Npy/>C=O, whereas the coordination polymers displaying looped architecture (CP1a, CP1b, CP1e and CP1f) showed the anti conformation understandably required to attain the looped coordination mode resulting in similar ligating angles (~101-109°) in these CPs. Interestingly, CP1d displayed both the syn and anti Npy/>C=O conformations in the two crystallographically independent ligand molecules. A detailed examination of the structure of CP1d revealed that the ligand having the anti Npy/>C=O conformation was responsible for making the loop, whereas the other ligand displaying the syn conformation connected the looped structure resulting in an overall 2D corrugated sheet. The effect of the Npy/>C=O conformation on the resulting coordination architecture was clear in the case of CP1c wherein the ligands displaying the syn conformation was unable to form a looped structure (Scheme 2), instead it generated comblike 1D polymeric chain.

In the case of L2 derived coordination polymers, the coordinating sites, *i.e.* pyridyl N and carboxylate, were in 3-positions in the aromatic rings making the ligating topology dependent on both the N_{amide}-C_{phenyl} and C_{pyridyl}-C_{carbonyl} bond rotation; as a result the N_{py}/>C=O conformation become irrelevant and thus, both the *syn* and *anti* N_{py}/>C=O conformations were observed in the coordination polymers having a 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 cases, in situ crystallization of the coordination polymers was 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 mixtures 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}) and CP1c (Zn^{II}) but failed to display the one to one correspondence with any of the individual simulated patterns thereby proving it unsuccessful in the selective separation of Cu^{II} (see the ESI[†]). 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 an excellent correspondence with that of the physical mixture of CP2a and CP2b as obtained concomitantly during their synthesis under 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 the 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)



Fig. 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.

were reasonably crystalline and the major peaks matched well with that of the 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 ran atomic absorption spectroscopy measurements on the supernatant liquid after removing the crystals of CP2a and CP2b. Interestingly, up to 97% of Cu^{II} could be separated selectively (see the ESI†). Thus, in the case of L1, Irving–Williams series did not seem to be operative, whereas in the case of L2 the 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 a selective separation was unsuccessful in the case of L1 clearly indicated that the 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 represent one of the rare attempts to separate toxic metal cations 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 a 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 α_1 radiation, $\lambda = 1.5406$ Å) diffractometer. The TEM images were recorded with a Jeol instrument using carbon coated 300 mesh Au grids at 200 kV. The mass spectrum was recorded on a QTOF Micro YA263. NMR spectra (¹H and ¹³C) were recorded using a 300 MHz BrukerAvance DPX300 spectrometer. The copper content in a sample was estimated using a Shimadzu AA-6300 atomic absorption spectrometer (AAS) fitted with a double beam monochromator.

Synthetic procedure for ligand L1H and L2H

In a 250 ml 2-neck round bottom flask 100 ml DCM, 5 mmol triethylamine (700 μ l) and 5 mmol (890 mg) acid chloride (nicotinoyl or isonicotinoyl) were mixed. 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 with further purification.

Characterization data of L1H

Yield: 1.0 g, ~57%; m.p: >300 °C after crystallization from DMF/EtOH/H₂O (1 : 2: 2 v/v). Anal. data calcd. 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*). ¹³C 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 calcd. 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, 1H); 7.70 (d, J = 7.6, 1H); 8.06 (d, J = 7.6, 1H); 8.44 (s, 1H); 8.00 (t, J = 5.6, 1H); 8.86 (s, 1H); 8.98 (d, J = 2, 1H); 9.39 (d, J = 8.8, 1H); 11.11 (s, 1H). ¹³C 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(µ-L1)₂ (H₂O)₂}·H₂O]_∞CP1a was synthesized by carefully adding an aqueous solution of L1 (40 mg, 0.15 mmol) to a methanolic solution of Cu(NO₃)₂·3H₂O (36.57 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks well formed 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, 0.055 mmol). Elemental analysis calcd. for CP1a, C₂₆H₂₆CuN₄O₁₀ (%): C 50.53, H 4.24, N 9.07; found: C 50.22, H3.93, N 8.86. FT-IR (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 (Fig. S1, ESI†) 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**.

 $[{Co(\mu-L1)_2 (H_2O)_2}\cdot H_2O]_{\infty} CP1b$ was synthesized by carefully adding an aqueous solution of L1 (40 mg, 0.15 mmol) to a methanolic solution of $Co(NO_3)_2 \cdot 6H_2O$ (44 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks well formed 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, 0.052 mmol). 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-IR (KBr pellet): 3487, 3047, 1643, 1622s, 1606s, 1527s, 1388s, 1344m, 1195, 1172m, 896, 831, 788m, 698, 644, 533, 507 cm⁻¹.

Thermogravimetric data analyses (Fig. S2, ESI[†]) 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(µ-L1)₂(H₂O)]·3H₂O]_∞CP1c was synthesized by carefully adding an aqueous solution of L1 (40 mg, 0.15 mmol) to a methanolic solution of Zn(NO₃)₂·6H₂O (45 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks well formed 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, 0.058 mmol). Elemental analysis calcd. for CP1c, C₂₆H₂₆ZnN₄O₁₀ (%): C 50.38, H 4.23, N 9.04; found: C 50.57, H 4.02, N 8.71. FT-IR (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 (Fig. S3, ESI[†]) 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**.

 $[{Cd(\mu-L1)_2(\mu-L1)_3(H_2O)}] \cdot 2H_2O]_{\infty}CP1d$ and [{Cd(µ- $L1_2(H_2O_2)$. H_2O_{α} CP1e were synthesized by carefully adding an aqueous solution of L1 (40 mg, 0.15 mmol) to a methanolic solution of Cd(NO₃)₂·4H₂O (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, C₂₆H₂₂CdN₄O₉·2H₂O (%): C 46.82, H 3.93, N 8.40; found: C 46.33, H 3.29, N 8.34 and for CP1e. H₂O, C₂₆H₂₆CdN₄O₁₀·H₂O (%): C 45.59, H 4.12, N 8.18; found: C 45.73, H 3.85, N 8.03. FT-IR (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 (Fig. S4, ESI[†]) 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 (Fig. S5, ESI[†]) 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(H₂O)₂}·H₂O]_∞CP1f was synthesized by carefully adding an aqueous solution of L1 (40 mg, 0.15 mmol) to a methanolic solution of Fe(ClO₄)₂·xH₂O (36.3 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks well formed 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, C₂₆H₂₆FeN₄O₁₀ (%): C 51.16, H 4.29, N 9.18; found: C 50.87, H 4.02, N 8.71. FT-IR (KBr pellet): 3487, 3058, 1602, 1558, 1527s, 1334m, 1245, 788s cm⁻¹.

Thermogravimetric data analyses (Fig. S6, ESI†) 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**.

 $(H_2O)_2$ ·2 $H_2O]_{\infty}$ CP2a $[{Cu(\mu-L2)_2}]$ and $[{Cu(\mu-L2)_2}]$ $(H_2O)_2$ \cdot $H_2O]_{\alpha}$ CP2b were synthesized by carefully adding an aqueous solution of L2 (40 mg, 0.15 mmol) to a methanolic solution of Cu(NO₃)₂·3H₂O (36.57 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks 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, C26H30CuN4O12 (%): C 47.74, H 4.62, N 8.57; found: C 48.32, H 4.42, N 8.66 and CP2b, C₂₆H₂₆CuN₄O₁₀ (%): C 50.53, H 4.24, N 9.07; found: C 50.74, H 4.22, N 9.07. FT-IR (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 (Fig. S7, ESI[†]) 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 (Fig. S8, ESI[†]) of CP2b revealed a 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 (H₂O)₂}·H₂O]_∞CP2c was synthesized by carefully adding an aqueous solution of L2 (40 mg, 0.15 mmol) to a methanolic solution of Co(NO₃)₂·6H₂O (44 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks well formed 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, C₂₆H₂₆CoN₄O₁₀ (%): C 50.91, H 4.27, N 9.13; found: C 51.02, H 4.21, N 9.11. FT-IR (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 (Fig. S9, ESI[†]) 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(H₂O)]·(H₂O)(CH₃OH)]_∞CP2d was synthesized by carefully adding an aqueous solution of L2 (40 mg, 0.15 mmol) to a methanolic solution of Zn(NO₃)₂·6H₂O (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, C₂₇H₂₆ZnN₄O₉ (%): C 52.65, H 4.25, N 9.10; found: C 52.29, H 3.89, N 8.79. FT-IR (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 (Fig. S10, ESI[†]) 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**.

 $[{Cd(\mu-L2)_2(H_2O)}\cdot(H_2O)(CH_3OH)]_{\infty}$ CP2e was synthesized by carefully adding an aqueous solution of L2 (40 mg, 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 well formed 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, C₂₈H₃₂CdN₄O₁₁ (%): C 47.17, H 4.52, N 7.86; found: C 47.21, H 3.95, N 7.56. FT-IR (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 (Fig. S11, ESI[†]) 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(H₂O)₂Cd₂(µ-L2)₂}·3H₂O]_∞CP2f was synthesized by carefully adding an aqueous solution of L2 (40 mg, 0.15 mmol) to a methanolic solution of CdCl₂ (27.5 mg, 0.15 mmol) and the solution was left for slow evaporation at room temperature. After two weeks well formed 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, C₂₆H₂₈Cd₂Cl₂N₄O₁₁ (%): C 35.97, H 3.25, N 6.45; found: C 36.49, H 3.02, N 6.48.FT-IR (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 (Fig. S12, ESI[†]) 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 3 occluded 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(NO₃)₂ (18.28 mg, 0.07 mmol), Co(NO₃)₂ (44.06 mg, 0.15 mmol) and Zn(NO₃)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(NO₃)₂ (9.14 mg, 0.035 mmol), Co(NO₃)₂ (44.06 mg, 0.15 mmol) and Zn(NO₃)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 MoK α (λ = 0.7107 Å) radiation on a BRUKER APEX II diffractometer equipped with a 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 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 contain 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, 95 Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Powder X-ray diffraction

PXRD data were collected using a Bruker AXS D8 Advance Powder (Cu K α_1 radiation, $\lambda = 1.5406$ Å) diffractometer equipped with a super speed LYNXEYE detector. The sample was prepared by making a thin film from the 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° 2 θ .

Acknowledgements

PD thanks the Department of Science & Technology (DST), New Delhi, India for financial support. M.P thanks CSIR, New Delhi (grant no. 09/080(0693)/2010-EMR-I) for SRF. SXRD data were collected at the DBT-funded X-ray Diffraction Facility under the CEIB program in the Department of Organic Chemistry, IACS, Kolkata

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