

Structural diversity in the Cu(pyrazinecarboxylate)₂/CdCl₂ system: new one-, two- and three-dimensional mixed metal coordination polymers

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Four new inorganic–organic polymeric materials have been synthesized by reacting the metal containing building block, Cu(pyzca)₂, with cadmium chloride. All resulting polymers have both metals incorporated in the structure and display a variety of structural motifs, ranging from one-dimensional chains to complicated three-dimensional networks. The first compound, [Cu(Pyzca)₂(H₂O)CdCl₂(H₂O)·H₂O]_n (**1**) is a one-dimensional double chain. The next two compounds, [Cu(Pyzca)₂(H₂O)₂Cd₂Cl₄(H₂O)₂]_n (**2**) and [Cu(Pyzca)₂(H₂O)Cd₂Cl₄(H₂O)₂·3H₂O]_n (**3**), assemble in a two-dimensional brick-wall network, while the fourth, [Cu(Pyzca)₂Cd₂Cl₄]_n (**4**), features an intricate three-dimensional network. Synthesis, X-ray structure determinations, and the influence of water molecules coordinated to the copper centers on the coordination geometry and overall extended structure are discussed.

Introduction

Research into the chemistry of coordination polymers has evolved rapidly in the last several years. In these polymeric materials a metal ion, a segment of an inorganic structural motif, or an entire well-defined inorganic structure^{1–14} are linked together by a rigid or flexible organic moiety to create an infinite organic–inorganic hybrid framework. Attributes of both the inorganic and organic moieties (*e.g.* available coordination sites and coordination preference, ligand flexibility and denticity) are transmitted to the extended structure, hence the great potential for complexity and functionality of these materials.^{15–19} A careful selection of ligand, metal center and reaction conditions can confer control over the topology of the resulting frameworks. Pyridinecarboxylates bind well to metal centers and, therefore, have been extensively employed in the construction of metal–organic networks in the role of organic linker.^{20–36} Their functionalized homologues, the pyrazinecarboxylates, although less used,^{37–43} are another class of very good ligands for the construction of new framework materials because of their extensive bonding versatility. In pyrazinecarboxylates, two coordination sites (neutral and/or charged) chelate the metal center while the remaining donor sites can further participate in the assembly of a polymeric structure by an exo-binding mode to other metal centers or by supra-molecular interactions with nearby H-bonding donors. In this context, we have intensively employed 2-pyrazinecarboxylic acid (abbreviated PyzcaH) and 2-methylpyrazine-5-carboxylic acid (abbreviated MePyzcaH) as organic spacers. Our two-step approach is to attach the pyrazinecarboxylates to a metal center and construct a building block which is subsequently reacted with a second metal center and assembled into an infinite bimetallic structure. The attraction of bimetallic coordination polymers is that the simultaneous presence of two different metals can potentially give rise to more complex physical properties and structural diversity. Several building blocks of the general formula (M(RPyzca)₂(H₂O)_x, M = Mn, Co, Cu, Zn; R = H, CH₃; x = 0, 1, 2)^{44–48} have been successfully incorporated into the extended frameworks of new bimetallic coordination polymers. One system we have recently focused on is CdX₂/Cu(Pyzca)₂, Cu(MePyzca)₂(H₂O) (X = halide), which has proven to be a rich source of interesting and novel extended inorganic–organic framework materials.^{49,50} In this paper we report four new coordination polymers obtained from the Cu(pyzca)₂/CdCl₂ synthetic system: the one-dimensional

double-chain compound [Cu(Pyzca)₂(H₂O)CdCl₂(H₂O)·H₂O]_n (**1**), two two-dimensional brick-wall motif polymers, [Cu(Pyzca)₂(H₂O)₂Cd₂Cl₄(H₂O)₂]_n (**2**) and [Cu(Pyzca)₂(H₂O)Cd₂Cl₄(H₂O)₂·3H₂O]_n (**3**), and the three-dimensional [Cu(Pyzca)₂Cd₂Cl₄]_n (**4**), featuring a more complicated structure.

Results and discussion

Hydrothermal reaction of CdCl₂ with anhydrous Cu(Pyzca)₂ in sealed tubes yields a series of four new mixed-metal inorganic/organic materials displaying different dimensionalities. All four compounds can be viewed as being based on a purely inorganic Cd–Cl backbone, present either as dimeric units (**1**) or polymeric chains (**2–4**) of Cl-bridged Cd²⁺ centers, which are further linked into infinite arrays by the metal–organic Cu(Pyzca)₂ (hydrated or anhydrous) units. The cadmium atoms are invariably in an octahedral coordination environment, while the copper centers have either a square pyramidal or a 4 + 2 pseudo-octahedral sphere of coordination.

Boiling a 1 : 2 solution of Cu(pyzca)₂ and CdCl₂ in water for 2 h followed by cooling leads to the precipitation of plentiful blue crystals of **1** after several hours of sitting at room temperature. X-Ray single crystal analysis shows that the structure of **1** consists of one-dimensional double chains comprised of [Cd₂Cl₃N₂(H₂O)] dimeric units linked by Cu(pyzca)₂(H₂O) groups (Fig. 1 and 2). The Cd atoms in the centrosymmetric dimer lie in a *mer*-{CdCl₃N₂O} coordination sphere with two bridging and one terminal chlorines, two *para*-nitrogens from two pyrazinecarboxylate rings, and one molecule of water. The nitrogen donors are situated *trans* to one another. Whereas the starting material Cu(Pyzca)₂ is anhydrous with a square planar geometry, the copper center in compound **1** is apically coordinated by a water molecule, resulting in a square pyramidal coordination environment. The presence of water molecules in both the metal–organic Cu(pyzca)₂(H₂O) part (O5) and in the inorganic Cd–Cl part (O6) plus an additional water of crystallization between the chains (O7) results in extensive hydrogen bonding and assemblage of the double chains into three dimensions. Both hydrogen atoms of the copper-bound water molecule (O5) are involved in hydrogen bonds with non-chelating carboxylic oxygens (O2 and O4) on two adjacent double chains. The Cd-bound water (O6) also links two adjacent chains through bifurcated O–H···O and O–H···Cl hydrogen bonding, as well as by H-bonding *via* the interstitial H₂O. In all, seven distinct hydrogen bonds are

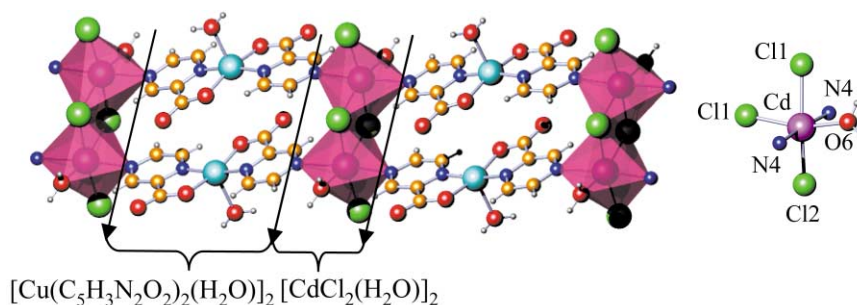


Fig. 1 View of a double chain in **1**, showing the coordination environment around cadmium and copper. The cadmium centered, edge sharing octahedra are pink. Cu atoms are light blue; Cd, purple; Cl, green; O, red; N, dark blue; C, orange.

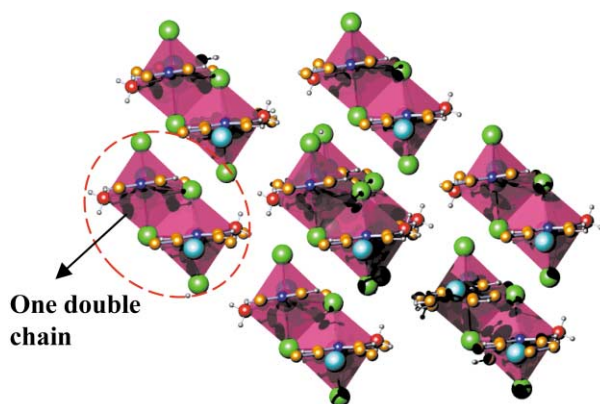


Fig. 2 Packing of the double chains in **1**.

present and serve to increase the dimensionality of the compound from one to three.

Boiling a 1 : 2 solution of CdCl_2 and $\text{Cu}(\text{Pyzca})_2$ in water followed by filtering the cooled solution and layering with either acetone or acetonitrile afforded two new two-dimensional coordination polymers, **2** and **3**, depending on the layering solvent. When the filtrate is layered with acetone, small blue crystals precipitate at the acetone–water interface after several hours. Single crystal analysis revealed a two-dimensional network for **2**, composed of distorted brick wall layers (Fig. 3(a)). The layers consist of one-dimensional $[\text{CdCl}_2\text{ON}]_n$ chains (Fig. 3(c)) connected by hydrated $\text{Cu}(\text{Pyzca})_2$ units (Fig. 3(b)). The cadmium centers are crystallographically identical and lie in pseudo-octahedral $\text{cis-}\{\text{Cd}(\mu_2\text{-Cl})_4\text{NO}\}$ coordination spheres. The nitrogen donor is provided by a pyrazine ring and the oxygen from a coordinated molecule of water. The inorganic chains run along the crystallographic *a* axis and consist of edge-sharing cadmium-centered octahedra. Consecutive octahedra are related by a center of inversion and form the biotetrahedral repeat unit in the inorganic chains (Fig. 3(c)). The copper in the metal–organic bridging $\text{Cu}(\text{pyzca})_2$ part is axially coordinated by two molecules of water, and lies in a distorted (4 + 2) octahedral coordination environment.

The resulting two-dimensional layers are not flat, but are slightly corrugated, as shown in Fig. 4. There are no intralayer water molecules of crystallization. Hydrogen bonds between the axial water molecule attached to copper and a water and a chlorine on a neighboring cadmium center, as well as hydrogen bonds between the Cd-coordinated water molecule and both carboxylic oxygens from a neighboring $\text{Cu}(\text{Pyzca})_2$ unit assemble the layers into a three-dimensional structure.

In an effort to produce larger single crystals of **2**, other layering solvents were tried. Interestingly, when the filtrate is layered with acetonitrile, larger blue blocklike crystals did indeed result, however, X-ray single crystal analysis showed them to be the new compound **3**, which, although possessing a similar 2D network, has important structural differences. The structural architecture of **3** is similar to that of compound **2**, consisting of two-dimensional distorted brick wall layers based

on one-dimensional $[\text{CdCl}_2\text{ON}]_n$ chains of edge-sharing cadmium centered octahedra. Two crystallographically inequivalent cadmium atoms were located, both of which have the same $\text{cis-}\{\text{CdCl}_4\text{NO}\}$ coordination environment, also identical to the coordination sphere already discussed for compound **2**. The inorganic chains are held together by monohydrated $\text{Cu}(\text{Pyzca})_2(\text{H}_2\text{O})$ units, with the copper centers in a square pyramidal geometry, rather than six-coordinate distorted octahedral as found in **2** (Fig. 5). The primary difference between **2** and **3** is the water content and the extensive hydrogen bonding pattern in **3**. Whereas **2** contains no uncoordinated water molecules between the layers, in the structure of **3** three crystallographically inequivalent uncoordinated water molecules crystallize between the layers. These waters occupy an infinite channel between the layers (Fig. 6(a)) and are organized by hydrogen bonds into one-dimensional strand running parallel to the inorganic chains (Fig. 6(b)). The water molecules that compose the strand act as H-bonding donors and acceptors and bridge the layers. A total of twelve distinct hydrogen bonds exist in **3**, connecting the layers into a full three-dimensional network. The explanation for the solvent-induced crystallization of a different compound is not clear to us at this time.

Reaction of CdCl_2 and $\text{Cu}(\text{Pyzca})_2$ under hydrothermal conditions yielded aquamarine plate crystals of **4**, the fourth compound in the $\text{Cu}(\text{Pyzca})_2/\text{CdCl}_2$ system. X-Ray single crystal analysis revealed a fully three-dimensional framework composed of one-dimensional inorganic $[\text{CdCl}_2\text{ON}]_n$ edge-sharing octahedral chains linked into three dimensions by anhydrous $\text{Cu}(\text{Pyzca})_2$ units. There is one crystallographically unique cadmium center, again in a $\{\text{Cd}(\mu_2\text{-Cl})_4\text{NO}\}$ octahedral coordination sphere, sharing an edge with two neighboring octahedra (Fig. 7). Every pair of edge sharing octahedra is related to the neighboring pair by a center of inversion, generating a repeat sequence of four octahedra rather than two as found in **2** and **3**. The framework expands in three-dimensions through the anhydrous copper pyrazinecarboxylate, $\text{Cu}(\text{Pyzca})_2$. As depicted in Fig. 8, every $\text{Cu}(\text{Pyzca})_2$ unit is connected to four different $[\text{CdCl}_2\text{NO}]_n$ chains. The chains situated above and below the plane of the pyrazinecarboxylate ligands have two points of attachment with each $\text{Cu}(\text{Pyzca})_2$ unit: one through a donating free carboxylic oxygen and the other through a chlorine atom coordinated to the copper (Cu-Cl bond length is 2.7593(7) Å). The linkage with the other two chains is achieved *via* the two *para*-nitrogen atoms, from the pyrazinecarboxylates. Hence, all copper atoms in the structure have a 4 + 2 pseudo-octahedral coordination sphere composed of two oxygens and two nitrogens provided by the chelating pyrazinecarboxylates situated in the equatorial plane and two chlorine atoms occupying the axial positions. Conversely, each repeating unit in the $[\text{CdCl}_2\text{ON}]_n$ chain is attached to eight $\text{Cu}(\text{Pyzca})_2$ units. As shown in Fig. 9, the inorganic chains pack in a pseudohexagonal fashion (each chain surrounded by six neighboring ones), joined together by a web of anhydrous $\text{Cu}(\text{Pyzca})_2$ units.

The use of $\text{Cu}(\text{pyzca})_2$ as a building block for bimetallic coordination polymers has led to the synthesis of frame-

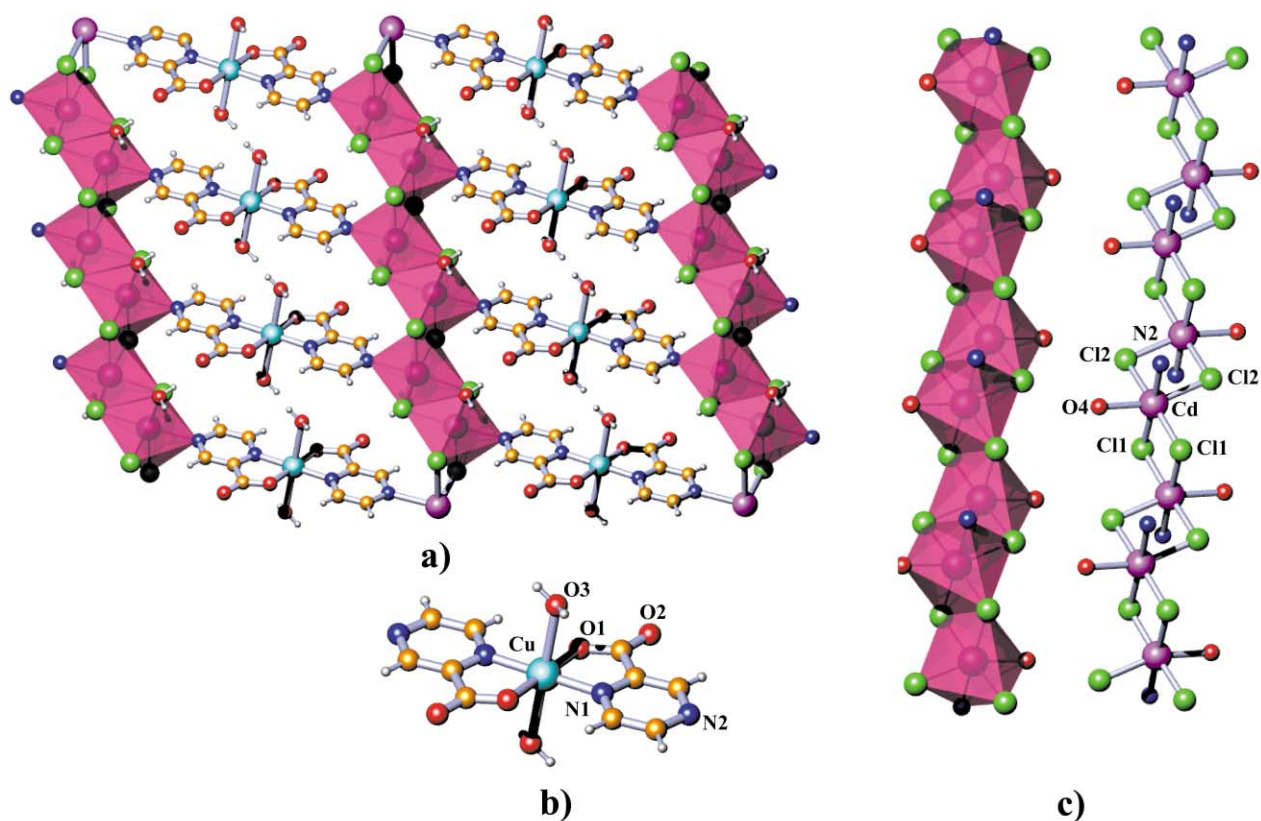


Fig. 3 (a) A two-dimensional distorted brick wall layer in **2**. (b) The hydrated $\text{Cu(Pyzca)}_2(\text{H}_2\text{O})_2$ unit, with the octahedral copper in the center. (c) The inorganic chains in **2**, represented as edge sharing octahedra (left) and balls and sticks (right), showing the coordination sphere around cadmiums. Cu atoms are light blue; Cd, purple; Cl, green; O, red; N, dark blue; C, orange.

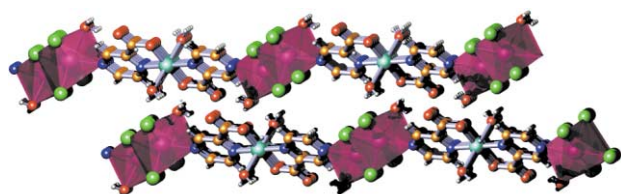


Fig. 4 View of two corrugated layers in **2**.

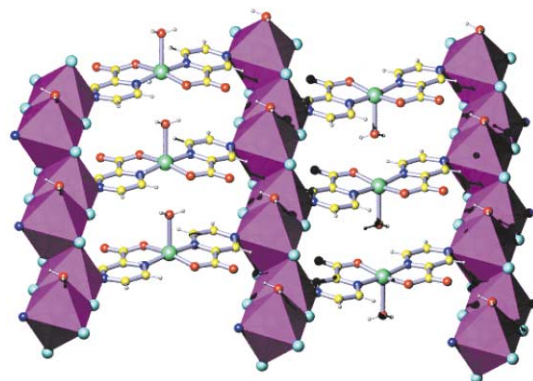
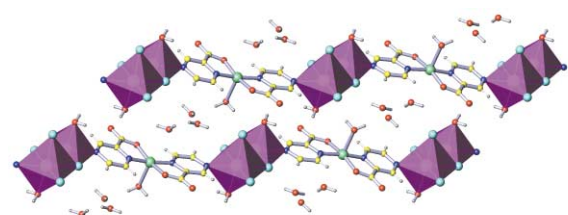
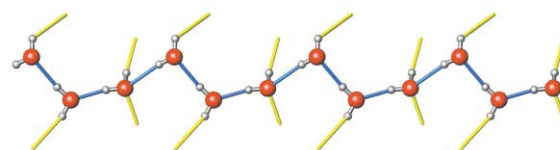


Fig. 5 One distorted brick wall layer in **3**, with mono-hydrated $\text{Cu(Pyzca)}_2(\text{H}_2\text{O})$ units linking the inorganic chains of edge sharing octahedra. Cu atoms are green; Cd centered octahedra, purple; Cl, blue; O, red; N, dark blue; C, yellow.

work materials displaying a large diversity of structural motifs. Theoretically, the polymer architecture can be propagated through the nonchelating *para* nitrogen donors on the pyrazine rings, the non-chelating carboxylic oxygen, and the acceptor axial free sites on the copper. While all three modes of binding are observed in **4**, for **1**, **2** and **3** the assertion is only true in the case of the *para* nitrogen atoms. Since all the reactions were carried out in water, the capability of the coppers to



a)



b)

Fig. 6 (a) View parallel to the stacked layers in **3**, showing the interstitial strand of water molecules and the inorganic chains. (b) Detail of the interstitial strand of water molecules. Hydrogen bonds linking the waters together are represented in blue; hydrogen bonds from the strand to layers above and below are represented in yellow.

participate in propagation is affected by the number of molecules of water coordinated to the metal. In this context, the copper containing building block can assemble in the framework in three different ways: in its anhydrous form, Cu(Pyzca)_2 , the monohydrated form, $\text{Cu(Pyzca)}_2(\text{H}_2\text{O})$, or dihydrated, $\text{Cu(Pyzca)}_2(\text{H}_2\text{O})_2$. The degree of hydration has a significant influence on the dimensionality and architecture of the resulting frameworks. Anhydrous Cu(Pyzca)_2 is capable of acting as a donor and acceptor of coordinative bonds, and thus can expand the framework in all three directions. Indeed Cu(Pyzca)_2 , as found in compound **4**, is involved in a complex

Table 1 Crystallographic data for **1**, **2**, **3** and **4**

Empirical	1	2	3	4
Formula	C ₁₀ H ₁₂ CdCl ₂ CuN ₄ O ₇	C ₁₀ H ₁₄ Cd ₂ Cl ₄ CuN ₄ O ₈	C ₁₀ H ₁₈ Cd ₂ Cl ₄ CuN ₄ O ₁₀	C ₁₀ H ₆ Cd ₂ Cl ₄ CuN ₄ O ₄
<i>M_w</i>	547.08	748.39	784.42	676.33
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
<i>a</i> /Å	7.2898(7)	6.7082(11)	6.5901(6)	15.2485(11)
<i>b</i> /Å	11.0148(10)	8.1416(13)	9.2936(8)	9.0948(7)
<i>c</i> /Å	11.3154(11)	10.3645(17)	19.4373(17)	13.5787(10)
<i>α</i> /°	68.462(2)	76.568(3)	82.778(2)	90
<i>β</i> /°	88.051(2)	75.419(3)	86.121(2)	102.0960(10)
<i>γ</i> /°	84.854(2)	86.280(3)	72.191(2)	90
<i>V</i> /Å ³	841.73(14)	532.83(15)	1123.88(17)	1841.3(2)
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>Z</i>	2	1	2	4
<i>D</i> _c /g cm ⁻³	2.159	2.332	2.318	2.440
<i>μ</i> (Mo-Kα)/mm ⁻¹	2.886	3.512	3.342	4.036
Reflections (measured)	7776	4887	10342	8027
<i>R</i> _{int}	0.0243	0.0281	0.0266	0.0280
Residuals: ^a <i>R</i> 1; <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0290; 0.0567	0.0292; 0.0580	0.0332; 0.0594	0.0222; 0.0471
all data	0.0355; 0.0580	0.0372; 0.0597	0.0440; 0.0614	0.0273; 0.0479

^a $R1 = \sum[|F_o| - |F_c|]/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ (*n* = no. refl.; *p* = no. refined parameters); $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where *P* is $[2F_c^2 + \max(F_o^2, 0)]/3$.

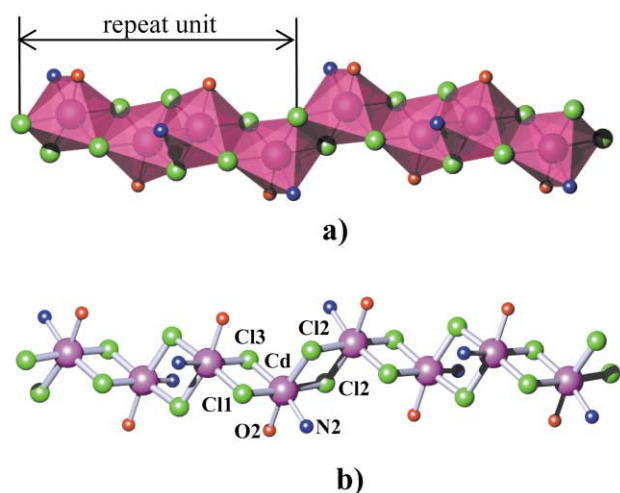


Fig. 7 The inorganic chains in **4**, shown as balls and sticks (a) and edge sharing octahedra (b). Cd atoms are purple; Cl, green; O, red; N, dark blue.

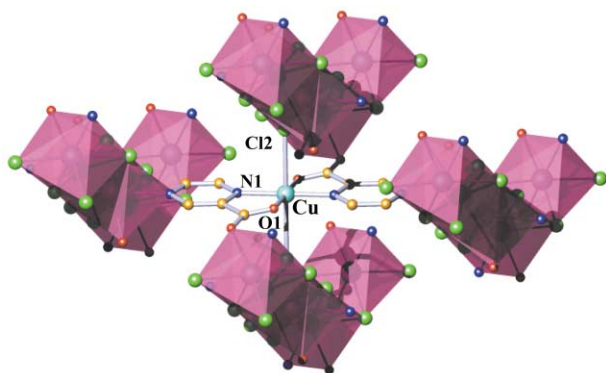


Fig. 8 Anhydrous Cu(Pyzca)₂ connecting four inorganic chains in **4**. Cu atoms are light blue; Cd, pink; Cl, green; O, red; N, dark blue; C, orange.

three-dimensional structure. It can also assemble in square-grid layers which are part of an overall three-dimensional framework, as reported in a previous work.⁴⁹ In the case of the monohydrated and dihydrated form, the capacity to link is reduced, and therefore the dimensionality of the coordination polymers is lower. Cu(Pyzca)₂(H₂O) and/or Cu(Pyzca)₂(H₂O)₂ act now as rigid linear bi-dentate ligands. Three-dimensionality

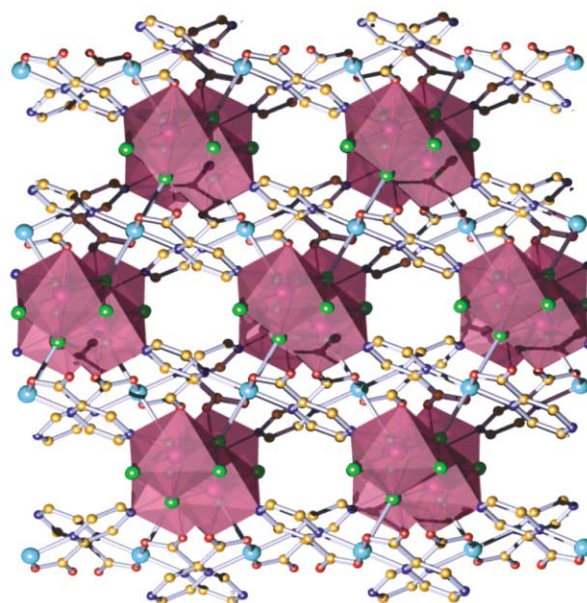


Fig. 9 The extended three-dimensional structure of **4**, viewed along the inorganic chain direction.

is achieved not *via* coordinative bonds but through the extensive hydrogen bonding which is generally present. The structures Cu(Pyzca)₂(H₂O) and/or Cu(Pyzca)₂(H₂O)₂ are incorporated in two-dimensional, networks (**2** and **3**) or simple one-dimensional chains (**1**). One way to accomplish our goal, which is to synthesize new high dimensional intricate framework materials, is to start with the anhydrous Cu(Pyzca)₂ and a non-coordinating solvent as a replacement for water. This work is underway.

Conclusions

Four new mixed-metal coordination polymers have been synthesized by the reaction of a copper containing building block, Cu(Pyzca)₂ and CdCl₂. Although originating from the same synthetic system, these new inorganic–organic materials display an impressive structural variety, ranging from one-dimensional double chains (**1**) to a three-dimensional framework (**4**). It was observed that the molecules of water coordinated to the copper centers have a significant influence on the coordination geometry and finally on the overall extended structure.

Experimental

Synthesis and general procedures

CdCl₂ (Alfa Aesar, 99%) and Cu(2-pyrazinecarboxylate)₂ (Aldrich, 97%) were used without further purification.

CAUTION: cadmium chloride is very toxic, and therefore should be handled with great care.

[Cu(Pyzca)₂(H₂O)₂CdCl₂(H₂O)·H₂O]_n (1). Cu(Pyzca)₂ (730 mg, 2 mmol), CdCl₂ (730 mg, 4 mmol) and water (10 ml) were mixed in a beaker and heated to boiling while stirring for 2 h. After the transparent solution was filtered, the filtrate was left at room temperature to evaporate. Blue crystals of **1** mixed with crystals of recrystallized Cu(pyzca)₂ grew overnight.

[Cu(Pyzca)₂(H₂O)₂Cd₂Cl₄(H₂O)₂]_n (2). Cu(Pyzca)₂ (730 mg, 2 mmol), CdCl₂ (730 mg, 4 mmol) and water (10 ml) were mixed in a beaker and heated to boiling while stirring for 2 h. The solution was filtered and acetone was carefully layered on the top of the filtrate. Blue transparent crystals grew at the interface of the two layers within two days.

[Cu(Pyzca)₂(H₂O)₂Cd₂Cl₄(H₂O)₂·3H₂O]_n (3). The procedure is identical to that used for compound **2**, except that acetonitrile was used instead of acetone. Blue transparent crystals grew within two days.

[Cu(Pyzca)₂Cd₂Cl₄]_n (4). Cu(Pyzca)₂ (68 mg, 0.2 mmol), CdCl₂ (73 mg, 0.4 mmol) and water (0.5 ml) were placed in a quartz tube. After reducing the pressure in the tube with a water aspirator, the tube was flame-sealed, heated to 130 °C at 1 °C min⁻¹ and held at that temperature for 24 h. The tube was then cooled to 70 °C at 1 °C min⁻¹ and held there for 7 h before turning off the furnace. In addition to brown crystals of a unidentified side product, aquamarine bar crystals of the title compound formed.

Crystallography

X-Ray intensity data for **1–4** were collected in ω scan mode at 293 K (**1,4**) or 190 K (**2,3**) on a Bruker SMART APEX CCD⁵¹ diffractometer equipped with graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å). For the triclinic compounds **1**, **2**, and **3**, the data collection covered the entire sphere of reciprocal space; for monoclinic **4** the data collection covered approximately $\frac{3}{4}$ of the sphere. The raw data frames were integrated with SAINT+,⁵¹ which also corrected for Lorentz and polarization effects. No crystal showed any indication of crystal decay while in the beam. An absorption correction based on the multiple measurement of equivalent reflections was applied to each data set with the program SADABS.⁵¹ All structures were solved by direct methods and refined against F^2 including all data, using SHELXTL.⁵² For the triclinic compounds **1**, **2** and **3**, the space group $P\bar{1}$ was assumed and confirmed by the successful refinement of the structures. For monoclinic **4**, the space group $C2/c$ was indicated by systematic absences and intensity statistics, and was eventually confirmed as correct. Non-hydrogen atoms in all structures were refined with anisotropic displacement parameters; hydrogen atoms attached to carbon were calculated and included as riding atoms. Water hydrogens could be located in all cases, and were refined with isotropic displacement parameters subject to an O–H distance restraint of 0.85(2) Å. Crystal data are summarized in Table 1 and selected bond lengths and angles are given in Table 2.

CCDC reference numbers 188220–188223.

See <http://www.rsc.org/suppdata/dt/b2/b212148b/> for crystallographic data in CIF or other electronic format.

Table 2 Interatomic distances (Å) and bond angles (°) with esds in parentheses for **1**, **2**, **3** and **4**

C ₁₀ H ₁₂ CdCl ₂ CuN ₄ O ₇ 1			
Cu–O(3)	1.935(2)	O(1)–Cu–O(5)	96.52(11)
Cu–O(1)	1.954(2)	O(3)–Cu–O(5)	95.92(11)
Cu–O(5)	2.198(3)	O(3)–Cu–O(1)	167.44(11)
Cu–N(1)	1.984(3)	O(6)–Cd–N(4)#1	87.65(10)
Cd–N(4)#1	2.424(3)	Cl(1)–Cd–Cl(1)#2	82.38(3)
Cd–N(2)	2.450(3)	N(2)–Cd–Cl(1)#2	98.36(7)
Cd–Cl(2)	2.5126(10)	O(6)–Cd–Cl(1)#2	80.37(8)
Cd–Cl(1)	2.5758(9)		
Cd–Cl(1)#2	2.6722(9)		
Cd–O(6)	2.260(3)		

Symmetry codes: (#1) $x - 1, y + 1, z - 1$; (#2) $-x, -y + 2, -z$.

C ₁₀ H ₁₄ Cd ₂ Cl ₄ CuN ₄ O ₈ 2			
Cu–O(1)	1.989(3)	O(1)–Cu–N(1)	82.89(12)
Cu–O(3)#1	2.391(3)	O(1)–Cu–O(3)	95.97(11)
Cu–N(1)	1.994(3)	O(1)–Cu–O(1)#1	180.00(16)
Cd–O(4)	2.407(3)	N(2)–Cd–Cl(2)#3	92.62(8)
Cd–N(2)	2.427(3)	O(4)–Cd–Cl(2)	160.53(7)
Cd–Cl(1)#2	2.5528(11)	Cl(1)–Cd–Cl(1)#2	86.69(3)
Cd–Cl(2)#3	2.5851(11)	Cl(1)–Cd–Cl(2)	100.25(3)
Cd–Cl(2)	2.6241(11)		
Cd–Cl(1)	2.6179(10)		

Symmetry codes: (#1) $-x, -y, -z + 1$; (#2) $-x + 1, -y + 1, -z + 2$; (#3) $-x, -y + 1, -z + 2$.

C ₁₀ H ₁₈ Cd ₂ Cl ₄ CuN ₄ O ₁₀ 3			
Cu–O(1)	1.943(3)	Cd(2)–O(7)	2.310(3)
Cu–O(3)	1.950(3)	Cd(2)–N(4)	2.428(3)
Cu–O(5)	2.321(4)		
Cu–N(1)	1.961(3)	O(3)–Cu–O(5)	89.92(13)
Cu–N(3)	1.963(3)	N(1)–Cu–O(5)	88.65(14)
Cd(1)–O(6)	2.344(3)	O(6)–Cd(1)–N(2)	84.53(11)
Cd(1)–N(2)	2.418(3)	Cl(2)–Cd(1)–Cl(1)	92.32(3)
Cd(1)–Cl(2)	2.5576(10)	N(2)–Cd(1)–Cl(2)#1	91.62(8)
Cd(1)–Cl(1)#1	2.5941(11)	O(7)–Cd(2)–N(4)	86.33(11)
Cd(1)–Cl(1)	2.5993(11)	N(4)–Cd(2)–Cl(4)	92.35(9)
Cd(1)–Cl(2)#2	2.6033(11)		

Symmetry codes: (#1) $-x + 2, -y + 3, -z + 2$; (#2) $-x + 1, -y + 3, -z + 2$.

C ₁₀ H ₆ Cd ₂ Cl ₄ CuN ₄ O ₄ 4			
Cu–O(1)	1.9453(17)	O(1)–Cu–N(1)	83.57(8)
Cu–N(1)	2.009(2)	O(1)–Cu–Cl(1)#1	86.21(6)
Cu–Cl(1)#1	2.7593(7)	N(1)–Cu–Cl(1)#1	89.86(7)
Cd–O(2)#2	2.368(2)	O(2)–Cd–N(2)#2	82.18(8)
Cd–N(2)	2.432(2)	Cl(3)–Cd–Cl(1)#3	93.72(2)
Cd–Cl(1)#3	2.6029(7)	N(2)–Cd–Cl(1)	89.92(6)
Cd–Cl(2)	2.6217(6)		
Cd–Cl(3)	2.6000(6)		

Symmetry codes: (#1) $x + 1/2, y + 1/2, z$; (#2) $-x + 1/2, y - 1/2, -z + 3/2$; (#3) $-x, -y, -z + 1$.

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