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New one- and two-dimensional cadmium iodide/pyrazinecarboxylate-based coordination polymers

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Abstract

Three new organic–inorganic coordination polymers, each adopting a different structural motif, were obtained from the CdI_2/pyrazinecarboxylic acid system. Syntheses and X-ray structural determinations are presented. The reaction between CdI_2 and 2-pyrazinecarboxylic acid (abbreviated pyzcaH) afforded a one-dimensional chain-like structure, $[CdI_2(PyzcaH)(H_2O)]_n$ (**1**). When 2-pyrazinecarboxylic acid was replaced by Cu(2-pyrazinecarboxylate)$_2$, the reaction yielded a two-dimensional framework polymer, $[CdI(Pyzca)(H_2O)]_n$ (**2**). The reaction of CdI_2 and 2-methylpyrazine-5-carboxylic acid (abbreviated MePyzcaH) resulted in the formation of a different coordination polymer, $[CdI(MePyzca)(H_2O)_{1.5}]_n$ (**3**), which adopts a one-dimensional chain structure. These new coordination polymers all assemble into three-dimensional structures via networks of hydrogen bonds.

Keywords: Cadmium; Cadmium halides; Coordination polymers; Framework materials; Hydrothermal synthesis

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1. Introduction

Diverse and useful physical properties as well as tremendous structural variety have prompted the recent surge in the design and synthesis of new hybrid organic–inorganic materials. These materials, in only a very short time, have become ubiquitous in the literature of coordination chemistry, where an impressive library of one-, two- and three-dimensional frameworks with various structural motifs has been reported to date [1–7]. However, full control over the overall product architecture (real crystal engineering) has not yet been achieved.

We have extensively employed the ligands 2-pyrazinecarboxylic acid (abbreviated PyzcaH) and 2-methylpyrazine-5-carboxylic acid (abbreviated MePyzcaH) in reactions with different transition metals, in particular copper and cadmium halides, to synthesize novel frameworks with an emphasis on creating mixed-metal and mixed-valent coordination polymers. Surprisingly, the transition metal/2-pyrazinecarboxylic acid system has proven to be a virtually inexhaustible source of new mono- and bi-metallic materials displaying an impressive diversity of structural motifs and dimensionalities [8–15]. The reason for this structural diversity is due to both the coordination chemistry of the metal centers and the complex binding capabilities of these exo-dentate ligands: the two nitrogen atoms and the two carboxylic oxygen atoms can act as donor atoms, capable of participating in strong coordinative bonds, oriented in various directions. At the same time the oxygen and the nitrogen atoms can also play the role of hydrogen-bonding acceptors, driving the formation of supramolecular assemblies [16–18]. The construction of new coordination polymers has been achieved by employing two related approaches: (i) direct reaction of the pure acids PyzcaH or MePyzcaH with metal salts; (ii) a two-step process whereby the metal center is first chelated by PyzcaH or MePyzcaH and subsequently employed as a building block for reaction with other metal salts. The preparation of the coordination polymers reported herein employed both methods. Three new materials have been synthesized and crystallographically characterized: $[CdI_2(PyzcaH)(H_2O)]_n$ (**1**), a chiral three-dimensional chain-based network, $[CdI(Pyzca)(H_2O)]_n$ (**2**), a brick wall-type layered structure, and $[CdI(MePyzca)(H_2O)_{1.5}]_n$ (**3**), a second chain-like framework.

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2. Experimental

2.1. Reagents

CdI_2 (Alfa Aesar, 99.5%), Cu(2-pyrazinecarboxylate)$_2$ (Aldrich, 97%), 2-pyrazinecarboxylic acid (Acros Organics, 99%) and 2-methylpyrazine-5-carboxylic acid (Avocado, 98%) were used without further purification. Cu(Mepyzca) was synthesized according to a method published previously [17].

2.2. Synthesis of $[CdI_2(PyzcaH)(H_2O)]_n$ (**1**)

2-Pyrazinecarboxylic acid (0.2 mmol, 0.024 g), CdI_2 (0.2 mmol, 0.073 g) and water (1 mL) were placed in a silica 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 and held at that temperature for 24 h. The mixture was then cooled to 70 °C at 1 °C/min, held at 70 °C for 7 h before shutting off the furnace. Yellowish crystals formed upon water evaporation at room temperature.

2.3. Synthesis of $[CdI(Pyzca)(H_2O)]_n$ (**2**)

The synthetic procedure is identical to that used for **1**. Cu(pyzca)$_2$ (0.2 mmol, 0.061 g), CdI_2 (0.4 mmol, 0.146 g) and water (1.3 mL) were placed in the silica tube. Yellow crystals formed at the completion of the reaction.

2.4. Synthesis of $[CdI(MePyzca)(H_2O)_{1.5}]_n$ (**3**)

The procedure is identical to that for **1**, except that 2-methylpyrazine-5-carboxylic acid (0.4 mmol, 0.055 g) has been used instead of PyzcaH and the volume of water is 1.3 mL. Yellowish crystals formed by the completion of the reaction.

2.5. X-ray crystallography

X-ray intensity data for **1**, **2** and **3** were collected at 293 K on a Bruker SMART APEX CCD diffractometer (Mo Kα, $\lambda = 0.71073$ Å), in ω scan mode [19]. For compound **1**, the data collection covered the entire sphere of reciprocal space; for **2** and **3** approximately 3/5 of the sphere was covered. The raw data frames were integrated into SHELX-format reflection files using SAINT+ [19], which also applied corrections for Lorentz and polarization effects. No crystal showed any indication of 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 [19]. All structures were solved by direct methods and refined against F^2 using SHELXTL [20], which was also the source of the neutral atom scattering factors used. For **1**, systematic absences indicated the space groups $P2_1$ or $P2_1/m$; intensity statistics indicated acentricity. A solution was obtained in the chiral space group $P2_1$, which was later verified using the ADDSYM program in PLATON [19]. Near the end of the refinement, the absolute structure (Flack) parameter was 0.35(2), indicating the crystal is a racemic (inversion) twin. The twinning was taken into account in subsequent refinement steps [20]. For **2**, systematic absences indicated the space groups $C2/c$ or Cc, the former of which was confirmed. Systematic absences in the intensity data for **3** were consistent with the space group

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

	1	**2**	**3**
Empirical formula	$C_{10}H_{12}Cd_2I_4N_4O_6$	$C_5H_5CdIN_2O_3$	$C_{12}H_{16}Cd_2I_2N_4O_7$
fw	1016.64	380.41	806.89
Crystal system	monoclinic	monoclinic	monoclinic
a (Å)	7.6002(11)	10.4253(4)	8.5549(5)
b (Å)	19.919(3)	14.6437(5)	12.7949(8)
c (Å)	8.0430(12)	12.7228(5)	18.8553(12)
α (°)	90.00	90.00	90.00
β (°)	113.794(2)	110.895(10)	90.664(10)
γ (°)	90.00	90.00	90.00
V (Å^3)	1114.1(3)	1814.59(12)	2063.7(2)
Space group	$P2_1$	$C2/c$	$P2_1/c$
Z value	2	8	4
ρ_{calc} (g/cm^3)	3.030	2.785	2.597
μ(Mo Kα) (cm^{-1})	0.7481	0.5779	0.5092
λ (Å)	0.71073	0.71073	0.71073
Temperature (°C)	20	20	20
Residuals[a] ($I > 2\sigma(I)$)			
$R1$	0.0250	0.0226	0.0334
$wR2$	0.0529	0.0481	0.0591
GOF	1.006	0.936	0.967

[a] $R1 = \sum \||F_o| - |F_c\|| / \sum |F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$; $\text{GOF} = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ (n = number of reflections; p = number of refined parameters); $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where P is $[2F_c^2 + \max(F_o^2, 0)]/3$.

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

$C_{10}H_{12}Cd_2I_4N_4O_6$, **1**			
Cd(1)–O(1)	2.462(5)	N(1)–Cd(1)–O(1)	68.77(18)
Cd(1)–N(1)	2.388(5)	O(1)–Cd(1)–I(2)	95.17(11)
Cd(1)–I(1)	3.0051(7)	I(2)–Cd(1)–I(1)	90.48(2)
Cd(1)–I(2)	2.8460(7)	I(2)–Cd(1)–I(3)	101.78(2)
Cd(1)–I(3)	2.8544(7)	N(1)–Cd(1)–I(3)	94.48(14)
Cd(1)–I(4)	3.0122(7)	I(3)–Cd(1)–I(4)	92.35(2)
Cd(2)–O(3)	2.462(5)	N(3)–Cd(2)–O(3)	68.82(17)
Cd(2)–N(3)	2.394(5)	O(3)–Cd(2)–I(1)	97.77(10)
Cd(2)–I(1)	2.8275(7)	I(1)–Cd(2)–I(2)	91.02(2)
Cd(2)–I(2)	2.9961(7)	N(3)–Cd(2)–I(3)	85.06(13)
Cd(2)–I(3)	3.0114(7)	I(4)–Cd(2)–I(3)	91.49(2)
Cd(2)–I(4)	2.8991(7)	I(1)–Cd(2)–I(3)	95.70(2)
$C_5H_5CdIN_2O_3$, **2**			
Cd–O(1)	2.2589(18)	O(1)–Cd–O(3)	84.96(7)
Cd–O(3)	2.320(2)	O(1)–Cd–N(2)	86.71(7)
Cd–N(1)	2.3853(18)	N(2)–Cd–O(3)	87.70(7)
Cd–N(2)	2.3566(18)	O(1)–Cd–N(1)	72.10(6)
Cd–I	2.7998(3)	I–Cd–I	92.003(8)
Cd–I	3.0583(3)	O(1)–Cd–I	85.93(5)
$C_{12}H_{16}Cd_2I_2N_4O_7$, **3**			
Cd(1)–O(1)	2.377(4)	O(1)–Cd(1)–N(1)	70.89(13)
Cd(1)–O(5)	2.310(5)	O(5)–Cd(1)–O(6)	83.36(19)
Cd(1)–O(6)	2.2.218(5)	O(6)–Cd(1)–I(2)	104.33(15)
Cd(1)–N(1)	2.356(4)	I(2)–Cd(1)–I(1)	98.701(17)
Cd(1)–I(1)	2.9261(6)	I(2)–Cd(1)–N(1)	95.47(11)
Cd(1)–I(2)	2.8556(6)	O(1)–Cd(2)–O(7)	88.08(16)
Cd(2)–O(1)	2.557(4)	O(1)–Cd(2)–I(1)	83.09(8)
Cd(2)–O(3)	2.256(3)	I(1)–Cd(2)–I(2)	93.945(16)
Cd(2)–O(7)	2.216(4)	O(3)–Cd(2)–N(3)	71.29(13)
Cd(2)–N(3)	2.392(4)		
Cd(2)–I(1)	2.8368(5)		
Cd(2)–I(2)	2.9385(6)		

$P2_1/c$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined as riding atoms. Water hydrogens for **1**–**3** and the 2-pyrazinecarboxylic acid protons on **1** were located in all cases in the Fourier maps, and refined with isotropic displacement parameters subjected 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.

3. Results and discussion

Two new polymeric compounds in the cadmium/iodine/2-pyrazinecarboxylate and cadmium/iodine/2-methylpyrazine-5-carboxylate system were synthesized hydrothermally by slow-cooling aqueous mixtures of the starting materials contained in sealed Pyrex tubes from 130 °C to room temperature over the course of one day. A third cadmium/iodine/2-pyrazinecarboxylate polymer was obtained by allowing the product solution from a hydrothermal reaction to evaporate to dryness at room temperature.

In an attempt to prepare mixed-metal organic–inorganic frameworks, CdI_2 was reacted with $Cu(pyzca)_2 \cdot (H_2O)_2$ in a 2:1 ratio in H_2O. This system yielded two different products: $\{[Cu(pyzca)_2]_2Cd_4I_8\}_n$ a mixed metal coordination polymer [14], and the novel compound **2**, which formed as large yellow block-like crystals. None of the copper present in the starting material was incorporated into the structure of **2**, instead the $Cu(pyzca)_2(H_2O)_2$ units acted solely as a source of the 2-pyrazinecarboxylato ligand. Reaction of CdI_2 with 2-pyrazinecarboxylic acid (pyzcaH) instead of $Cu(pyzca)_2(H_2O)_2$, in a 1:2 ratio under the same hydrothermal conditions again yielded two different products: the desired compound **2**, and a previously reported coordination polymer, $[CdI_2(C_4H_4\ N_2)]_n$ [21], obtained via the reductive decarboxylation of the 2-pyrazinecarboxylate ligand [8]. Changing the CdI_2:pyzcaH ratio to 1:1 yielded the same two compounds mentioned above. Interestingly, after the completion of the 1:1 reaction, the water was allowed to slowly evaporate from the reaction vessel. After several hours, colorless block crystals of the new compound **1** formed, containing the neutral form of the starting material ligand, the protonated acid. The crystallization upon water evaporation was not observed to take place in the previous systems. Extending the synthesis further by using 2-methylpyrazine-5-carboxylic acid (MepyzcaH), the methylated homologue of pyzcaH, resulted in no characterizable products from the reaction with CdI_2. However, reaction of CdI_2 with the copper-containing starting material Cu(Mepyzca)$_2$(H_2O)$_2$ as the 2-pyrazinecarboxylato supplier resulted in the synthesis of compound **3**.

3.1. Crystal structure of **1**, *[CdI_2(PyzcaH)(H_2O)]$_n$*

The structure of **1** consists of one-dimensional chains parallel to the crystallographic [0 0 1] direction, of composition Cd_2I_4(pyzcaH)$_2$ (Fig. 1). The cadmium centers lie in a {CdI_4ON} distorted octahedral geometry. Although chemically similar, two crystallographically different cadmium atoms, Cd1 and Cd2 (see Fig. 1), alternate along the chains. The coordination environment is the same for both centers. Four of the coordination sites are occupied by four crystallographically independent iodine atoms. The remaining two coordination sites are occupied by an oxygen atom and a nitrogen atom provided by a chelating 2-pyrazinecarboxylic acid ligand. The Cd–I, Cd–O, and Cd–N bond lengths are in the expected range (see Table 2). The one-dimensional polymer chains in **1** are propagated via iodine atoms, all four of which act as bridging atoms. The 2-pyrazinecarboxylic acid ligands play no role in propagating the chains, but instead extend outward on opposite sides of the chains, perpendicular to the chain direction. The arrangement of the chains is illustrated in Figs. 2(a) and (b). Two independent types of water molecules of crystallization, O5 and O6 (Fig. 3), are closely hydrogen-bonded to the chains as acceptors via the 2-pyrazinecarboxylic acid protons (O2–H2A···O5: H–A = 1.68(2) Å, D–A = 2.517(8) Å, D–H···A = 173(9)°; O4–H4A···O6: H–A = 1.72(5) Å, D–A = 2.516(7) Å, D–H···A = 158(13)°). These water molecules are further engaged as donors in a hydrogen bonding network which connects the one-dimensional chains into a three-dimensional structure. O5 is bound to a *para*-nitrogen atom (N2) of a protruding 2-pyrazinecarboxylic acid ligand (O5–H1W···N2: H–A = 1.92(2) Å, D–A = 2.762(8) Å, D–H···A = 177(8)°) and to an iodine

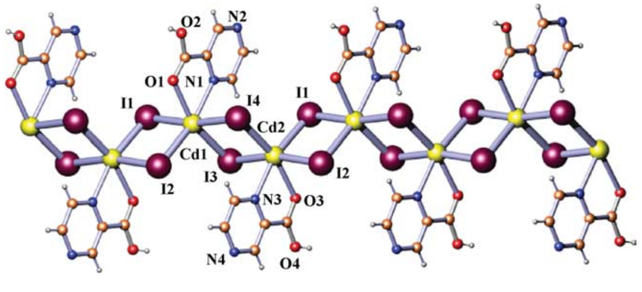

Fig. 1. View of the one-dimensional chains in **1**, showing the {CdI_4ON} coordination sphere of Cd.

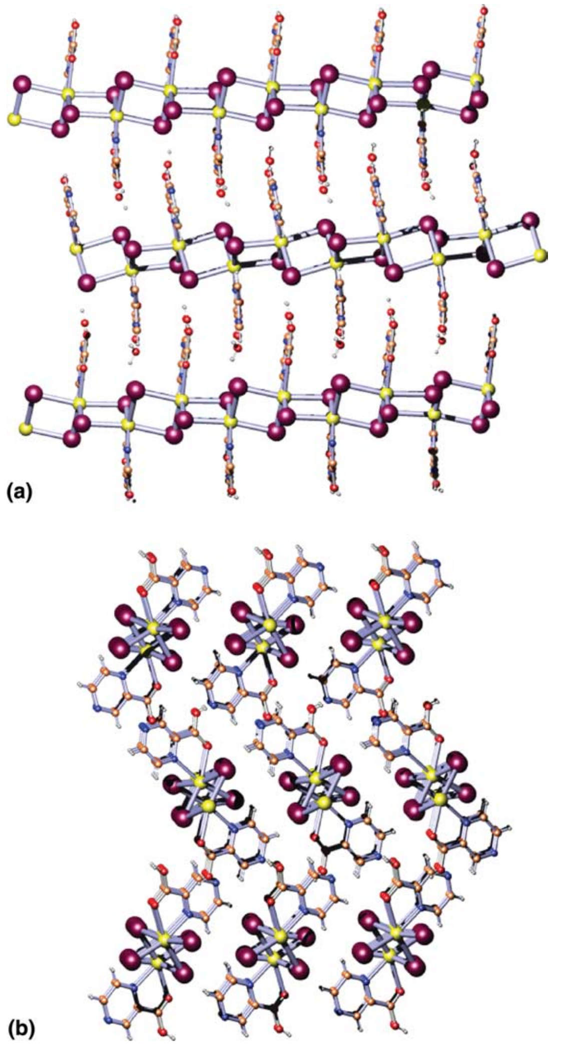

Fig. 2. Packing arrangement of the chains in **1**. (a) Perpendicular to the crystallographic (1 0 1) plane. (b) Down [1 0 0], the chain direction.

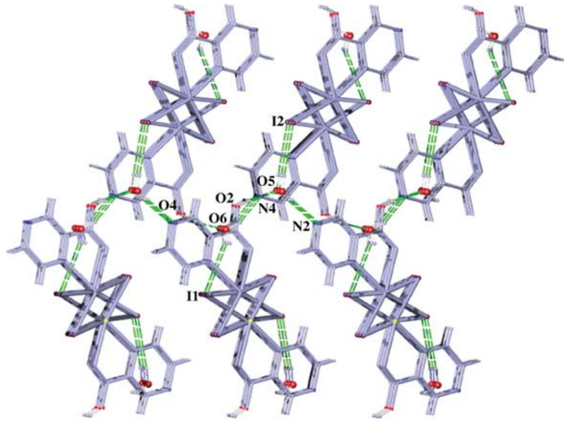

Fig. 3. Hydrogen bonding in **1**, giving rise to the three-dimensional framework. Hydrogen bonds are shown as green dashed lines.

atom, I1, originating on an adjacent chain (O5–H2W···I2: H–A = 2.74(3) Å, D–A = 3.559(6) Å, D–H···A = 165(8)°). Each such pair of connected chains is further linked to a third neighboring chain via hydrogen bonds between the O6 water, the other *para*-nitrogen atom and an iodine on the third chain (O6–H3W···N4: H–A = 2.02(6) Å, D–A = 2.784(9) Å, D–H···A = 147(9)°; O6–H4W···I1, H–A = 3.03(5) Å, D–A = 3.747(6) Å, D–H···A = 144(7)°).

3.2. Crystal structure of **2**, [CdI(Pyzca)(H_2O)]$_n$

Single crystal analysis of compound **2** revealed a layered, two-dimensional structure quite different than **1**. One crystallographically independent cadmium center is present, residing in a distorted {$CdI_2O_2N_2$} octahedral environment. As in **1**, a chelating 2-pyrazinecarboxylato ligand occupies two of the coordination sites. In **2**, however, only two iodine atoms coordinate to the metal center; the remaining coordination sites have been claimed by a *para*-nitrogen atom from a second 2-pyrazinecarboxylato ligand and an oxygen from a coordinated molecule of water (Fig. 4). In contrast to **1**, the two 2-pyrazinecarboxylato ligands in **2** do play a role in propagation of the polymeric chains. The cadmium centers are connected into one-dimensional strands that run along the crystallographic [0 1 0] direction by the pyzca ligands, and then further into a two-dimensional layer by the iodine atoms, that bridge the cadmium centers along [1 0 0], perpendicular to the strand direction. The layers lie parallel to the crystallographic (0 0 1) plane and adopt the well-known brick wall motif (Fig. 5). The cadmium centers at the corners of the bricks form an angle between 95° and 98° with the closest cadmium and the nitrogen in the pyrazine ring, hence causing a slight deviation from orthogonality of the bricks in the form of a bulge in the brick center. The dimension of the brick is approximately 4.1×14.6 Å^2. The layers stack along the [0 0 1] direction, and, as shown in Fig. 6, every other layer is rotated 180° around the stacking vector with respect to the layers above and below. As a result of this arrangement, no channels are present in the packed structure. Besides the coordinative bonds that hold the individual layers together, hydrogen bonds assemble the layers into a three-dimensional network (Fig. 6). Each of the coordinated water molecules forms two hydrogen bonds with two different uncoordinated carboxylic oxygen atoms: oxygen O3 in the same layer as the water (an intra-layer H-bond, O3–H5W···O2: H···A = 1.99(2) Å, D–A = 2.748(3) Å, D–H···A = 158(3)°) and oxygen O2 in adjacent layers (an inter-layer bond, O3–H6W···O2: H···A = 2.05(3) Å, D–A = 2.823(3) Å, D–H···A = 163(5)°). Since the coordinated H_2O molecules protrude from both faces of the centrosymmetric layers, the result is a three-dimensional hydrogen-bonded structure.

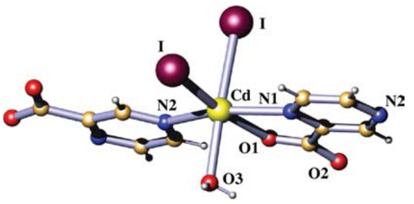

Fig. 4. {$CdI_2O_2N_2$} cadmium coordination environment in **2**.

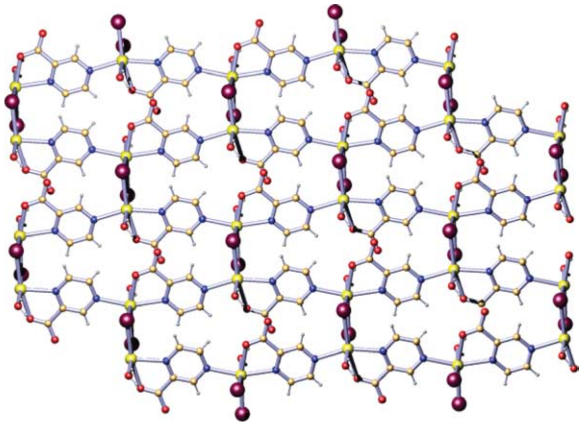

Fig. 5. Two-dimensional brick wall layer in **2**, viewed perpendicular to the crystallographic *ab* plane.

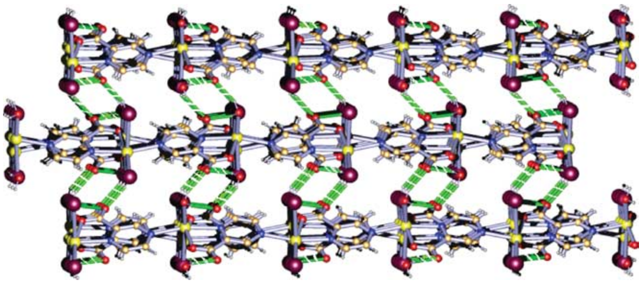

Fig. 6. Stacking of the two-dimensional layers in **2**. Hydrogen bond linkages between layers are shown as green dashed lines. The view is down the *a* axis.

3.3. Crystal structure of **3**, [CdI(MePyzca)(H_2O)$_{1.5}$]$_n$

Single crystal analysis of compound **3** revealed a one-dimensional chain as in **1**, with several important differences. The chains consist of two alternating crystallographically and chemically different cadmium atoms, Cd1 and Cd2. Both lie in a distorted {CdI_2O_3N} octahedral coordination environment, but composed of different donor types. The coordination sphere around Cd1 consists of two crystallographically different iodine atoms, a carboxylic oxygen and a nitrogen from a chelating 2-pyrazinecarboxylato ligand and two coordinated water molecules. The second cadmium, Cd2, is coordinated by two iodine atoms, one chelating 2-pyrazinecarboxylato oxygen and nitrogen, one water molecule and a bridging carboxylic oxygen from a 2-pyrazinecarboxylato ligand chelated to the adjacent Cd1 center. Hence, the one-dimensional chains are propagated both by iodine atoms and by one of the two 2-pyrazinecarboxylato ligands, which bridges every other pair of Cd1–Cd2 centers (Fig. 7). Unlike compound **1**, the 2-pyrazinecarboxylato ligands are all on the same side of the chains. The chains are further assembled in a three-dimensional framework by a complicated net of hydrogen bonds. Pairs of 1D chains are oriented centrosymmetrically such that the side of the chain featuring the H_2O molecules and that of the non-bridging carboxylic oxygen are facing each other (Fig. 8). Such an arrangement creates hydrogen bonds between both waters coordinated to the Cd1 centers and the water molecule on the Cd2 center as well as the carboxylic oxygen atoms (O5–H5WB···O3: H···A = 2.10(7) Å, D–A = 2.727(6) Å, D–H···A = 135(7)°; O6–H6WA···O2: H···A = 1.94(4) Å, D–A = 2.709(6) Å, D–H···A = 170(7)°; O7–H7WA···O4: H···A = 1.98(3) Å, D–A = 2.749(6) Å, D–H···A = 169(5)°). The pairs of chains so built are then linked to four neighboring chains by hydrogen bonds which involve the *para*-nitrogen atoms on the pyrazine rings (O6–H6WB···N2: H···A = 2.03(4) Å, D–A = 2.785(7) Å, D–H···A = 167(7)°; O7–H7WB···N4: H···A = 2.14(4) Å, D–A = 2.872(6) Å, D–H···A = 157(7)°) to generate the full three-dimensional structure of **3**.

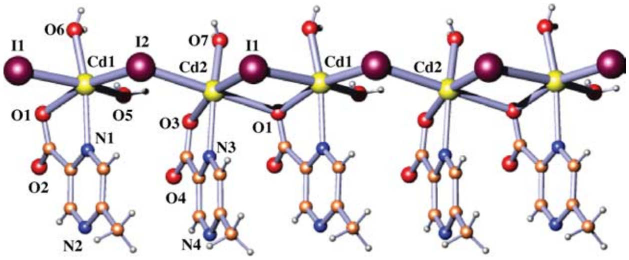

Fig. 7. View of the one-dimensional chains in **3** showing the $\{CdI_2O_3N\}$ coordination sphere of Cd.

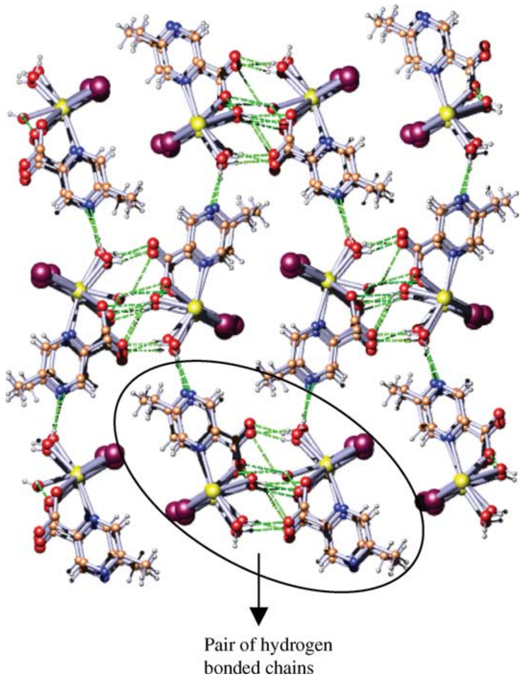

Fig. 8. Centrosymmetric linkage of pairs of chains in **3** via O–H···O hydrogen bonds, assembled further in a three-dimensional structure via O–H···N hydrogen bonds. Hydrogen bonds shown as green dashed lines.

4. Conclusions

In summary, the synthesis and the structural characterization of three new coordination polymers have been presented. Compounds **1** and **2** feature the same organic ligand, 2-pyrazinecarboxylate, in its protonated neutral acid form and in its deprotonated anion form, respectively, a difference which gives rise to markedly different architectures, a one-dimensional chain structure for **1** and a two-dimensional brick wall motif for **2**. This phenomenon points out the effect of pH in modifying coordination polymer architecture in this system. The necessity to satisfy charge balance requirements led to the more iodine-rich system **1**, and to the coordination of four iodides to the metal center, giving rise to the new $\{CdI_4ON\}$ cadmium coordination sphere. **3** contains the methylated form of the deprotonated 2-pyrazinecarboxylate ligand and is a one-dimensional chain. In all three compounds the cadmium centers are chelated by only one 2-pyrazinecarboxylate ligand, with iodide atoms, water molecules and *para*-nitrogen donors from the ligand completing the coordination spheres of cadmium. Though employing very similar coordinating species, the cadmium centers in the three structures feature three different pseudo-octahedral coordination spheres: $\{CdI_4ON\}$ in **1**, $\{CdI_2O_2N_2\}$ in **2**, and $\{CdI_2O_3N\}$ in **3**. While there are several examples of $\{CdI_2O_2N_2\}$ cadmium coordination environments [22–24], to the best of our knowledge, the $\{CdI_4ON\}$ and $\{CdI_2O_3N\}$ cadmium environments are the first such reported. In both one-dimensional structures **1** and **3** the ligands do not participate in the propagation of the chains. On the contrary, in **2**, the layers expand through the role of the 2-pyrazinecarboxylate ligands. As expected from hydrothermal reactions involving chemical species with hydrogen bonding donor and acceptor capabilities, the structures feature hydrogen bonding networks which serve to increase the system dimensionality to fully three-dimensional by linkage of polymeric structural subunits. The abovementioned facets demonstrate the variety and complexity of the CdI_2/pyrazinecarboxylate/H_2O system, and also underscore the difficulties in ab initio prediction of product architectures when dealing with a ligand with so many binding possibilities as 2-pyrazinecarboxylate.

5. Supplementary data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 183345–183347. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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