DOI: 10.1002/ejic.200800222

Pore-Size Tuning in Double-Pillared Metal-Organic Frameworks Containing Cadmium Clusters

Irán F. Hernández-Ahuactzi,[a] Herbert Höpfl,*[a] Victor Barba,[a] Perla Román-Bravo,[a] Luis S. Zamudio-Rivera,[b] and Hiram I. Beltrán[c]

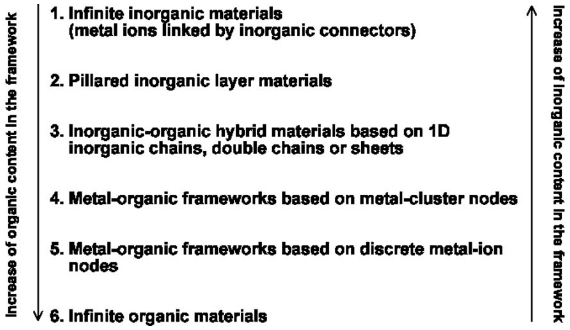
Keywords: Cadmium / Crystal engineering / Metal-organic frameworks / Self-assembly / Supramolecular chemistry

This contribution describes metal-organic frameworks based on cadmium-clusters that are capable of generating double-pillared architectures. A brief overview of the literature concerning such systems is presented together with the description of three new coordination polymers, $[\{[\mathrm{Cd_2}(\textit{trans}\text{-}1,2\text{-}a,a\text{-chdc})(\textit{trans}\text{-}1,2\text{-}e,e\text{-chdcH})_2(4,4'\text{-bpy})_2]\cdot 8H_2O\}_n]$ (**1**), $[\{\mathrm{Cd_2}(\textit{trans}\text{-}1,4\text{-}e,e\text{-chdc})(\textit{trans}\text{-}1,4\text{-}a,a\text{-chdc})(4,4'\text{-bpe})_2\}_n]$ (**2**) and $[\{[\mathrm{Cd_2}(\textit{cis,cis}\text{-}1,3,5\text{-chtc})(HCO_2)(H_2O)(4,4'\text{-bpy})_2]\cdot\mathrm{DMF}\cdot 4H_2O\}_n]$ (**3**) [1,2-chdc = 1,2-cyclohexanedicarboxylate, 1,4-chdc = 1,4-cyclohexanedicarboxylate, 1,3,5-chtc = 1,3,5-cyclohexanetricarboxylate, 4,4′-bpy = 4,4′-bipyridine and 4,4′-bpe = (*E*)-1,2-bis(4-pyridyl)ethylene]. Compound **1** has a double-pillared two-dimensional layer structure, while compounds **2** and **3** are double-pillared three-dimensional frameworks. All materials have been characterized by elemental analysis, IR spectroscopy, single-crystal X-ray diffraction and thermogravimetric analysis. The robustness of the open-frameworks found for compounds **1** and **3** has been examined by X-ray powder diffraction of dried samples, which showed that the crystal structure of the 2D coordination polymer **1** collapses whereas the 3D architecture of compound **3** remains intact.

Introduction

To date, a great deal of time and money has been dedicated to the development of new porous materials that might find applications in the (i) improvement of catalytic processes, mainly those related to the oil refining and exploitation industry, (ii) separation and storage of gaseous fuels (H_2, CH_4), contaminants (CO_2, SO_x, NO_x, etc.) and unstable chemicals, (iii) ion exchange, (iv) molecular transport and drug delivery, and (v) generation of materials having novel or improved optical, electrical and magnetic properties.[1]

In addition to the traditionally employed inorganic materials, such as metal oxides, aluminosilicates and metal phosphates, etc.,[2] the modern chemist can also make use of organic and inorganic-organic hybrid substances.[3] Indeed, a broad spectrum of substance classes with a variable content of inorganic and organic components is known, and, extending the proposal of Yaghi et al. for the differentiation of coordination polymers at different levels,[4] the currently available two- and three-dimensional frameworks can be classified into six families, as summarized in Scheme 1.



Scheme 1. Currently availabe 2D and 3D frameworks and their classification into six families in order of increasing organic content.

The extremes in Scheme 1 are occupied by purely inorganic (family 1) and organic materials (family 6). The metal ions in typical inorganic materials such as aluminosilicates and metal phosphates are connected by inorganic linkers, such as silicates, phosphates, sulfates, etc.,[2] whereas 2D and 3D frameworks based on organic substances connected through covalent unions are rare (family 6). Within this family, extended graphite and diamandoid architectures have received most attention.[5] Families 2–5 are inorganic-organic hybrid substances[3] and have been ordered accord-

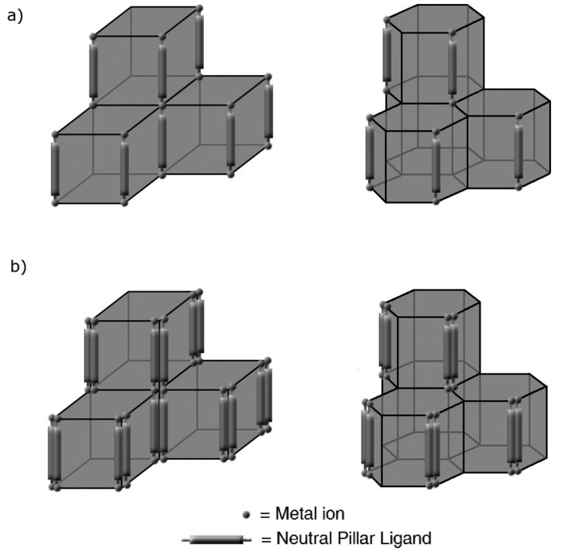
---

[a] Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos,
Av. Universidad 1001, C. P., 62209 Cuernavaca, Mexico
E-mail: hhopfl@ciq.uaem.mx
[b] Laboratorio de Síntesis Química y Electroquímica, Instituto Mexicano del Petróleo,
Eje Central Lázaro Cárdenas 152, Col. San Bartolo Atepehuacan, México D.F., Mexico
[c] Departamento de Ciencias Naturales, DCNI, Universidad Autónoma Metropolitana,
Cuajimalpa, Pedro Antonio de los Santos 84, 11850 México D.F., Mexico

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

ing to their degree of organic/inorganic content. Thus, family 2 contains materials in which 2D inorganic layers are bridged by organic pillars, generally difunctional ligands such as diamines, dicarboxylates, disulfonates, diphosphonates, etc., whereas in family 3 the organic components comprise two of the three dimensions of the material, thus reducing the organizational level induced by inorganic components to one dimension. In families 4 and 5, the inorganic component in the framework is reduced to the presence of metal ion clusters, also known as secondary building blocks, and single metal ions, respectively.

Tunable pore and channel sizes are required for many applications. Among the above-mentioned architectures, coordination polymers derived from metal clusters or discrete metal ions (families 4 and 5) have the advantage that they can be connected in three-dimensional space by ligands with different sizes, shapes and functionalities. In general, such three-dimensional architectures are assembled by one ligand type (homoleptic system) or a combination of two or more different ligands (heteroleptic system). The metal ions or clusters in heteroleptic systems are generally combined with anionic ligands to form neutral two-dimensional networks that are then cross-linked by neutral organic pillars (Scheme 2a). Carboxylates and amines are most commonly employed in these systems, particularly as their rigid aromatic analogues (Scheme 2).[6,7]



Scheme 2. Strategies for the generation of 3D metal-organic open-frameworks: (a) combination of metal ions with charged and/or neutral difunctional ligands to form a pillared-layer skeleton based on a square, rectangular or hexagonal grid; (b) introduction of double-pillared building bocks.

Despite the advantage such metal-organic frameworks have for the adjustment of the pore and channel size, one important handicap is their propensity to interpenetrate and catenate[8] and their generally lower thermal stability when compared to materials that are rich in inorganic components.[3l] A strategy to reduce the degree of interpenetration and enhance the thermal stability of the resulting materials might be to substitute the traditionally employed mono-pillared building blocks in 3D metal-organic frameworks[6,7] by a reinforced structural unit, for example a double-pillared building unit (Scheme 2b).[9,10]

Herein, we present three new examples of pillared metal-organic skeletons containing double-pillared building blocks. Metal-organic frameworks derived from cyclohexanecarboxylic acids are rare,[10c,11,12] probably due to their fluxionality when compared with aromatic, polyunsaturated or other types of rigid motifs.

Results and Discussion

Synthetic Procedures

Compound **1** was obtained from cadmium(II) nitrate, the potassium salt of *trans*-1,2-cyclohexanedicarboxylic acid (*trans*-1,2-chdcH$_2$) and 4,4′-bipyridine (4,4′-bpy) in a mixture of ethanol and water. The composition of the crystalline material was determined to be [{[Cd$_2$(*trans*-1,2-*a*,*a*-chdc)(*trans*-1,2-*e*,*e*-chdcH)$_2$(4,4′-bpy)$_2$]·8H$_2$O}$_n$]. For the preparation of compound **2**, cadmium(II) nitrate was combined with the potassium salt of *trans*-1,4-cyclohexanedicarboxylic acid (*trans*-1,4-chdcH$_2$) and *trans*-1,2-bis(4-

Table 1. Selected bond lengths [Å] and bond angles [°] for compounds **1**–**3**.[a]

1			
Cd(1)–O(1)	2.384(4)	O(1)–Cd(1)–O(2)	52.44(13)
Cd(1)–O(2)	2.527(4)	O(5)–Cd(1)–O(6)	54.96(14)
Cd(1)–O(5)	2.328(4)	O(5)–Cd(1)–O(1)	81.97(14)
Cd(1)–O(6)	2.402(4)	O(6)–Cd(1)–O(2#1)	88.42(13)
Cd(1)–O(2#1)	2.359(4)	O(2)–Cd(1)–O(2#1)	82.70(14)
Cd(1)–N(1)	2.283(4)	N(1)–Cd(1)–N(2)	176.34(17)
Cd(1)–N(2)	2.304(5)	N(1)–Cd(1)–O(1)	94.46(16)
		N(1)–Cd(1)–O(5)	91.17(17)
2			
Cd(1)–O(1)	2.326(4)	O(1)–Cd(1)–O(2)	55.20(14)
Cd(1)–O(2)	2.427(4)	O(3)–Cd(1)–O(4)	47.05(14)
Cd(1)–O(3)	2.246(4)	O(3)–Cd(1)–O(1)	88.06(15)
Cd(1)–O(4)	3.016(4)	O(2)–Cd(1)–O(4#2)	93.74(15)
Cd(1)–O(4#2)	2.241(4)	O(4)–Cd(1)–O(4#2)	82.40(15)
Cd(1)–N(1)	2.300(4)	N(1)–Cd(1)–N(2)	175.51(16)
Cd(1)–N(2)	2.347(4)	N(1)–Cd(1)–O(1)	93.12(15)
		N(1)–Cd(1)–O(3)	97.31(14)
3			
Cd(1)–O(1)	2.370(3)	O(1)–Cd(1)–O(2)	53.74(12)
Cd(1)–O(2)	2.473(4)	O(3)–Cd(1)–O(4)	50.64(14)
Cd(1)–O(3)	2.224(4)	O(3)–Cd(1)–O(2)	86.79(14)
Cd(1)–O(4)	2.662(4)	O(4)–Cd(1)–O(7)	79.78(14)
Cd(1)–O(7)	2.295(3)	O(7)–Cd(1)–O(1)	89.10(11)
Cd(1)–N(1)	2.364(5)	N(1)–Cd(1)–N(3)	170.61(16)
Cd(1)–N(3)	2.370(4)	N(1)–Cd(1)–O(1)	86.68(14)
Cd(2)–O(5)	2.271(4)	O(8)–Cd(2)–O(7)	52.46(12)
Cd(2)–O(6)	2.596(4)	O(5)–Cd(2)–O(6)	51.17(13)
Cd(2)–O(7)	2.479(3)	O(5)–Cd(2)–O(8)	80.83(14)
Cd(2)–O(8)	2.462(4)	O(9)–Cd(2)–O(7)	98.42(12)
Cd(2)–O(9)	2.299(4)	O(9)–Cd(2)–O(6)	81.33(15)
Cd(2)–N(2)	2.336(4)	N(2)–Cd(2)–O(5)	94.52(16)
Cd(2)–N(4)	2.327(4)	N(4)–Cd(2)–N(2)	160.62(14)

[a] Symmetry operators: #1: $-x + 3/2$, $-y + 3/2$, z; #2: $-x + 1$, $-y + 1$, $-z$.

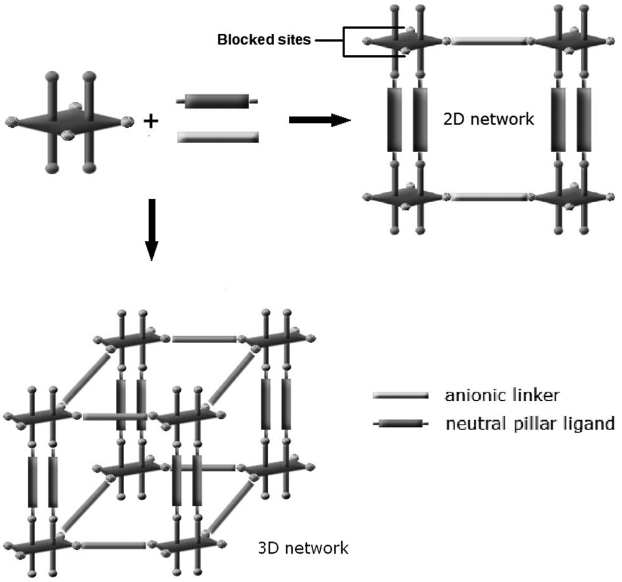
pyridyl)ethylene (4,4′-bpe) in a mixture of ethanol and water to give crystals of the composition [{Cd_2(*trans*-1,4-*e*,*e*-chdc)(*trans*-1,4-*a*,*a*-chdc)(4,4′-bpe)$_2$}$_n$]. Under hydrothermal reaction conditions (120 °C, 4 d), however, the same compound is formed in a significantly higher yield (70 vs. 44%). Compound **3**, [{[Cd_2(*cis*,*cis*-1,3,5-chtc)(HCO_2)(H_2O)(4,4′-bpy)$_2$]·DMF·4H_2O}$_n$], was obtained in crystalline form from cadmium(II) nitrate, the potassium salt of *cis*,*cis*-1,3,5-cyclohexanetricarboxylic acid (*cis*,*cis*-1,3,5-chtcH_2) and 4,4′-bipyridine (4,4′-bpy) in a mixture of dmf and ethanol. The formate moieties present in compound **3** are the result of alkaline-based solvent hydrolysis (dmf), as confirmed by a control reaction employing potassium formate as additional reagent (see Experimental Section). All three compounds were characterized by single-crystal X-ray diffraction, elemental analysis, IR spectroscopy and thermogravimetric analysis. Selected geometric parameters are summarized in Table 1, and crystallographic data can be found in the Experimental Section.

Crystallographic Studies

As shown by the crystal structures of compounds **1**–**3** and those of related coordination polymers,[7,10] cadmium(II) ions are ideal candidates for the preparation of pillared metal-organic open-frameworks using di- or oligocarboxylates as anionic, and bis(pyridyl)-type ligands as neutral, organic building blocks. In the coordination polyhedra typically found in such assemblies, the carboxylate groups occupy equatorial sites while the pyridyl groups are located in the axial positions. Thus, the carboxylate ligands generate two-dimensional metal-organic layers that are linked in the third dimension by diamine pillars. The resulting cadmium-based metal-organic frameworks contain either discrete metal ions having a distorted octahedral {CdO_4N_2} coordination geometry[7] or dinuclear {$Cd_2(\mu\text{-}O)_2O_6N_4$} metal clusters formed through the association of two {CdO_4N_2} polyhedra by the formation of Cd···O bonds.[10] Double-pillared 2D and 3D open-frameworks can be generated from building blocks with the latter characteristics, as shown by the structures reported previously[10] and the solid-state structures of compounds **1**–**3** (Scheme 3).

Compound **1** has a two-dimensional layer structure in which infinite 1D chains with the composition [{Cd_2(*trans*-1,2-*a*,*a*-chdc)(*trans*-1,2-*e*,*e*-chdcH)$_2$}$_n$] are linked by 4,4′-bpy to form a double-pillared 2D layer structure (Figure 1). Related 2D double-pillared layer structures with cadmium are almost unknown to date.[10b]

Interestingly, the anionic connectors (*trans*-1,2-chdc) are two different deprotonated conformational species: the monodeprotonated ligands that participate in the formation of the dinuclear metal clusters have the thermodynamically more stable *e*,*e* conformation, while the dianionic 1,2-chdc^{2-} linkers responsible for the generation of the infinite 1D chain have an *a*,*a* conformation. This is a rare phenomenon, and there are only a few examples known where conformational supramolecular isomerism occurs within the same crystal lattice.[13,14]



Scheme 3. Schematic representation of the synthetic route for the generation of double-pillared 2D and 3D open-frameworks based on a dinuclear {$M_2(\mu\text{-}O)_2O_6N_4$} metal cluster.

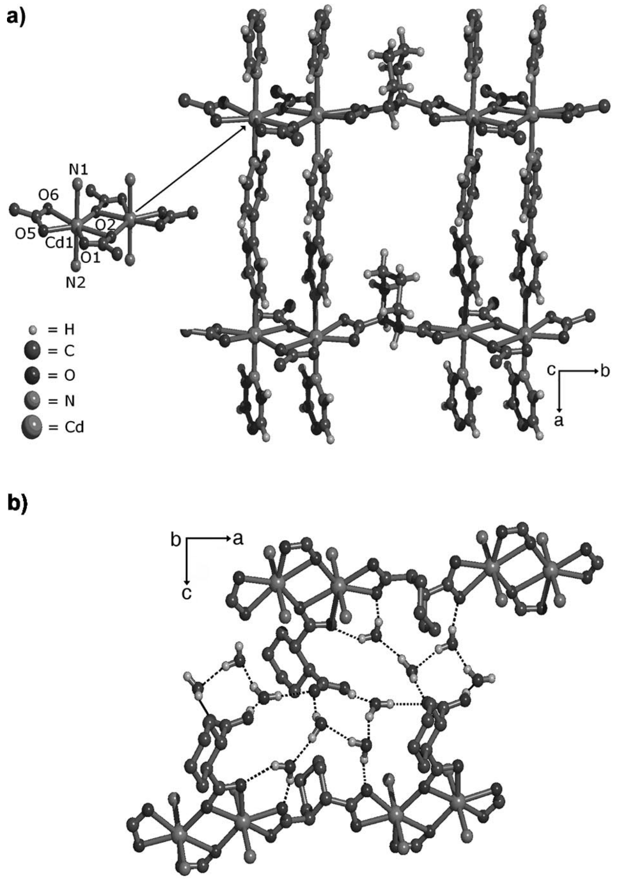


Figure 1. Different perspective views of the crystal lattice of [{[Cd_2(*trans*-1,2-*a*,*a*-chdc)(*trans*-1,2-*e*,*e*-chdcH)$_2$(4,4′-bpy)$_2$]·8H_2O}$_n$] (**1**). (a) A fragment of the crystal lattice showing the cadmium coordination geometry, the dinuclear {$Cd_2(\mu\text{-}O)_2O_6N_4$} metal cluster building block and the octanuclear constructional unit of the network. (b) Hydrogen-bonding patterns formed between the water molecules and the uncoordinated COOH groups of adjacent 2D layers.

Each cadmium atom within the dinuclear $\{Cd_2(\mu\text{-}O)_2O_6N_4\}$ metal clusters has a distorted pentagonal-bipyramidal environment in which five oxygen atoms are located in the equatorial and two nitrogen atoms in the axial positions [Cd–N1 2.304(5) and Cd–N2 2.283(4) Å]. The Cd–O distances for the terminal carboxylate groups [2.328(4) and 2.402(4) Å] indicate an almost isobidentate coordination mode. The corresponding Cd–O bond lengths for the bridging carboxylate groups are 2.384(4) Å for the monodentate oxygen atom, and 2.527(4) (Cd–O2) and 2.359(4) Å (Cd–O2′, symmetry operator: $-x + 3/2, -y + 3/2, z$) for the bridging oxygen atom. As indicated by the dihedral angle between the terminal carboxylate groups (29.8°), the dinuclear cadmium cluster is not completely planar, as might be expected, thus showing that it has some conformational flexibility. This distortion is probably due to the deviation from linearity of the carboxylate groups in the bridging *trans-a*,*a* conformer (approximately 164°).

The rectangular windows within the 2D layer structure have dimensions of 4.3×5.6 Å^2 (Figure 1a). The layers are organized in an ...ABABAB... fashion in the three-dimensional space, which means that the cyclohexane moieties of the monoprotonated ligands are located above and below the cavities (Figures S1–S3 in the Supporting Information). The water molecules present in the crystal lattice are located between the layers and participate as three-connected nodes in an extensive net of hydrogen-bonding interactions that also includes the COOH groups of the *trans*-1,2-*e*,*e*-chdcH ligands (O–H 0.84 Å; O···O 2.67–3.02 Å; O–H···O 142–179°; Figure 1b).

The dinuclear $\{Cd_2(\mu\text{-}O)_2O_6N_4\}$ clusters in compound **2**, which contains the 1,4-disubstituted isomer of cyclohexanedicarboxylic acid (*trans*-1,4-chdc) as building block, are linked in two dimensions [Cd–O1 2.326(4), Cd–O2 2.427(4), Cd–O3 2.246(4), Cd–O4 3.016(4), Cd–O4′ 2.241(4), Cd–N1 2.300(4) and Cd–N2 2.347(4) Å; symmetry operator: $-x + 1, -y + 1, -z$]. These infinite 2D networks have the composition $[\{Cd_2(\textit{trans}\text{-}1,4\text{-}e,e\text{-chdc})(\textit{trans}\text{-}1,4\text{-}a,a\text{-chdc})\}_n]$ and are bridged by bidentate 4,4′-bpe ligands to form a twofold interpenetrated 3D framework (Figure 2 and Figures S4–S6 in the Supporting Information). Again, the cyclohexanedicarboxylate connectors have two different conformations within the crystal lattice, namely *trans*-1,4-*e*,*e*-chdc and *trans*-1,4-*a*,*a*-chdc. Because of the larger Cd···Cd distance in the 1,4-cyclohexane derivative (11.35 Å for *trans*-1,4-*e*,*e*-chdc and 9.53 Å for *trans*-1,4-*a*,*a*-chdc vs. 9.03 Å for *trans*-1,2-*a*,*a*-chdc) and the use of the extended 4,4′-bpy homologue 4,4′-bpe (11.63 Å for 4,4′-bpy vs. 13.99 Å for 4,4′-bpe), the cavities of the rhombohedrally distorted hexadecanuclear boxes (angles: 59.6, 120.4 and 90°) in compound

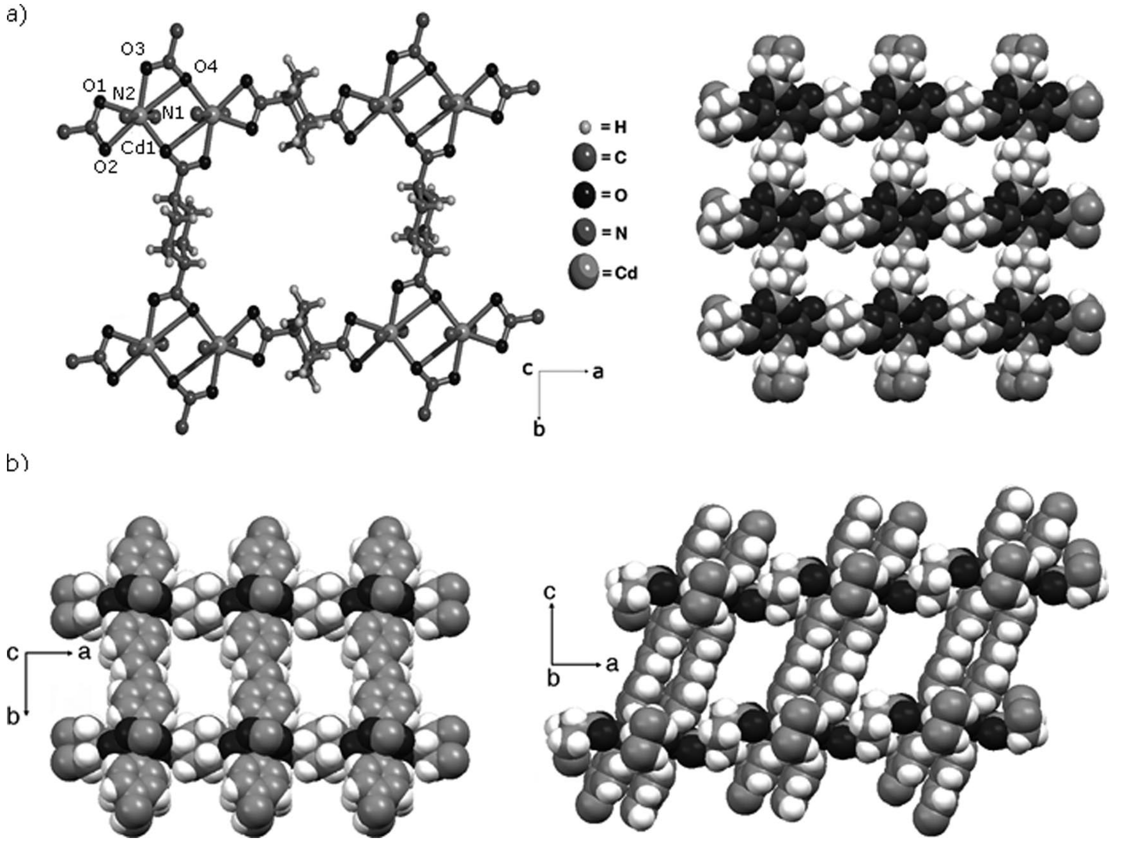


Figure 2. Different perspective views of the crystal lattice of $[\{Cd_2(\textit{trans}\text{-}1,4\text{-}e,e\text{-chdc})(\textit{trans}\text{-}1,4\text{-}a,a\text{-chdc})(4,4'\text{-bpe})_2\}_n]$ (**2**): (a) Dinuclear $\{Cd_2(\mu\text{-}O)_2O_6N_4\}$ metal cluster building block and repeating unit within the infinite 2D rectangular grid network with the composition $[\{Cd_2(\textit{trans}\text{-}1,4\text{-}e,e\text{-chdc})(\textit{trans}\text{-}1,4\text{-}a,a\text{-chdc})\}_n]$. (b) Channels generated by the cross-linking of the 2D layers shown in (a) by 4,4′-bpe double-pillars.

2 are larger: 3.8 × 7.8 Å^2 for the windows in the [{Cd_2(*trans*-1,4-*a*,*a*-chdc)(*trans*-1,4-*e*,*e*-chdc)}$_n$] layers, 4.7 × 7.1 Å^2 for the windows in the [{Cd_2(*trans*-1,4-*e*,*e*-chdc)(bpe)$_2$}$_n$] layers, and 4.2 × 6.3 Å^2 for the windows in the [{Cd_2(*trans*-1,4-*a*,*a*-chdc)(bpe)$_2$}$_n$] layers.

The most important contacts between the interpenetrated layers are C–H···O interactions formed between the oxygen atoms of the terminal carboxylate groups and some of the hydrogen atoms of the 4,4′-bpe ligands (C–H 0.95, C–H···O 2.36–2.38, O···O 3.28–3.30 Å; O–H···O 163–167°).

Similar twofold interpenetrated structures have been reported previously for two further cadmium complexes, namely [{Cd(1,4-bdc)(4,4′-bpy)}$_n$] (**4**)[10a] and [{[Cd(4,4′-bpdc)(4,4′-bpe)]·$2H_2O$}$_n$][7d] (**5**) (1,4-bdc = 1,4-benzenedicarboxylate and 4,4′-bpdc = biphenyl-4,4′-dicarboxylate) (Figure 3). Interestingly, there is also one report of a triple-pillared 3D skeleton, [{Cd(1,4-bdc)(4,4′-bpy)}$_n$] (**6**), and it should be noted that this structure is a true supramolecular isomer of compound **4** (Figure 3).[10d] Although the number of structures available so far is very limited, there are indications that double- and triple-pillared cadmium-based building blocks have a high potential for supramolecular synthesis (crystal engineering), including for pore-size tuning. While the combination of mononuclear {CdO_4N_2} nodes with carboxylates and bis(pyridyl) ligands has generated a large diversity of structures,[7] the likelihood of obtaining a predictable and steady pattern of 3D structural organization increases significantly for the dinuclear {Cd_2(μ-O)$_2O_6N_4$} node. This allows for the construction of open-framework series with varying pore sizes, as shown in Figure 3. The edges of the cavities within the 3D open-frameworks for the members of this compound class vary from 3.8 to 14.2 Å within the 2D layer and from 3.7 to 8.1 Å for the pillared arrays. Very few prototypes of metal-organic frameworks with a tunable pore size are known so far,[15] and it should be noted that most of them are architectures based on metal-cluster nodes.

Despite their similar chemical composition, the dinuclear {Cd_2(μ-O)O_7(H_2O)N_4} building blocks in compound **3** are somewhat different from those found for compounds **1** and **2** [{Cd_2(μ-O)$_2O_6N_4$}], thus giving rise to the formation of a very interesting 3D structural pattern. As can be seen from Figure 4a, the main differences arise from the inclusion of a water molecule in the coordination sphere of one of the cadmium atoms and the substitution of one of the two cyclohexanecarboxylate bridges by a formate bridge, thus eliminating the C_2 axis present in compounds **1** and **2**. A closer inspection of this coordination polyhedron shows that the metal cluster is stabilized by a strong, charge-assisted hydrogen-bonding interaction between the coordinated water molecule [Cd2–O9 2.299(4) Å] and the carboxylate group located at Cd1 (O–H 0.84, H···O 1.83, O···O 2.66 Å; O–H···O 169°). A similar interaction has been reported for [{[Cd_2(sb)$_2$(4,4′-bpy)$_2$(H_2O)]·$2H_2O$}$_n$] (sb = 2-sulfobenzoate).[16]

As can be seen from Figures 4a and b, the anionic *cis*,*cis*-1,3,5-chtc ligands and the formate-bridged cadmium nodes in compound **3** combine to form an undulating distorted honeycomb pattern with the composition [{Cd_2(*cis*,*cis*-1,3,5-chtc)(HCO_2)(H_2O)}$_n$]. This 2D layer can also be visualized as a combination of two 1D chains in which the dinuclear metal cluster nodes are first linked by two of the three carboxylate functions of the *cis*,*cis*-1,3,5-chtc connectors and then interconnected through the remaining carboxylate function. Besides the deviation from planarity, the irregularity of the hexagons with dimensions of 4.5 × 6.7 Å^2 is a consequence of their pentanuclear composition due to the

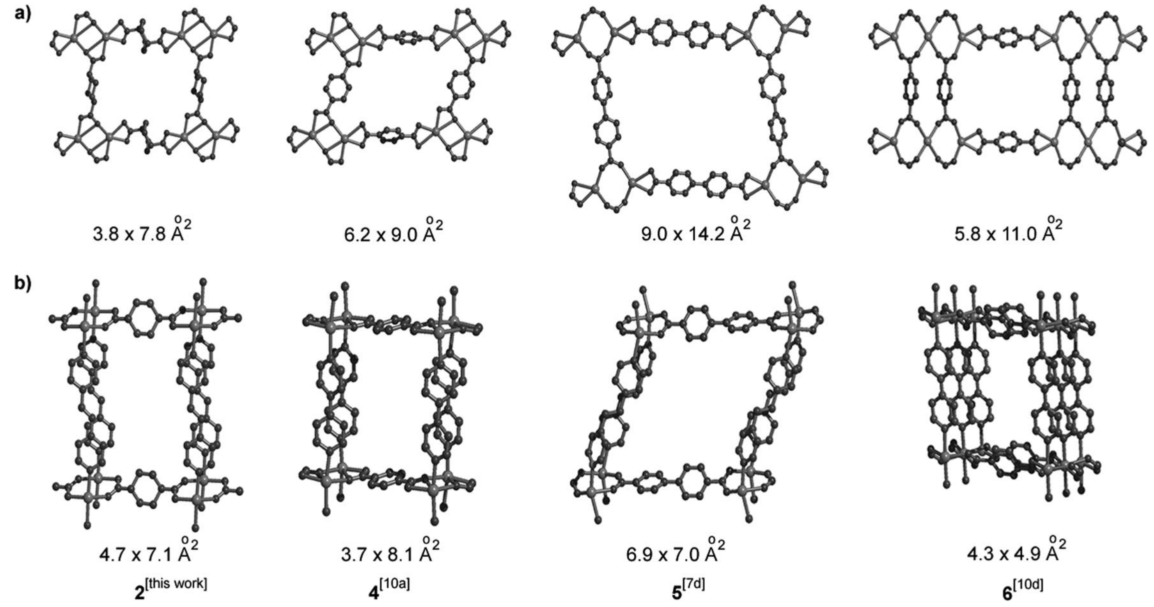


Figure 3. Double- (**2**, **4** and **5**) and triple-pillared (**6**) cadmium-based 3D metal-organic frameworks having variable pore sizes (effective cavity sizes are given). (a) View of the cavities within the 2D layer. (b) View showing the pillared-layer structure.

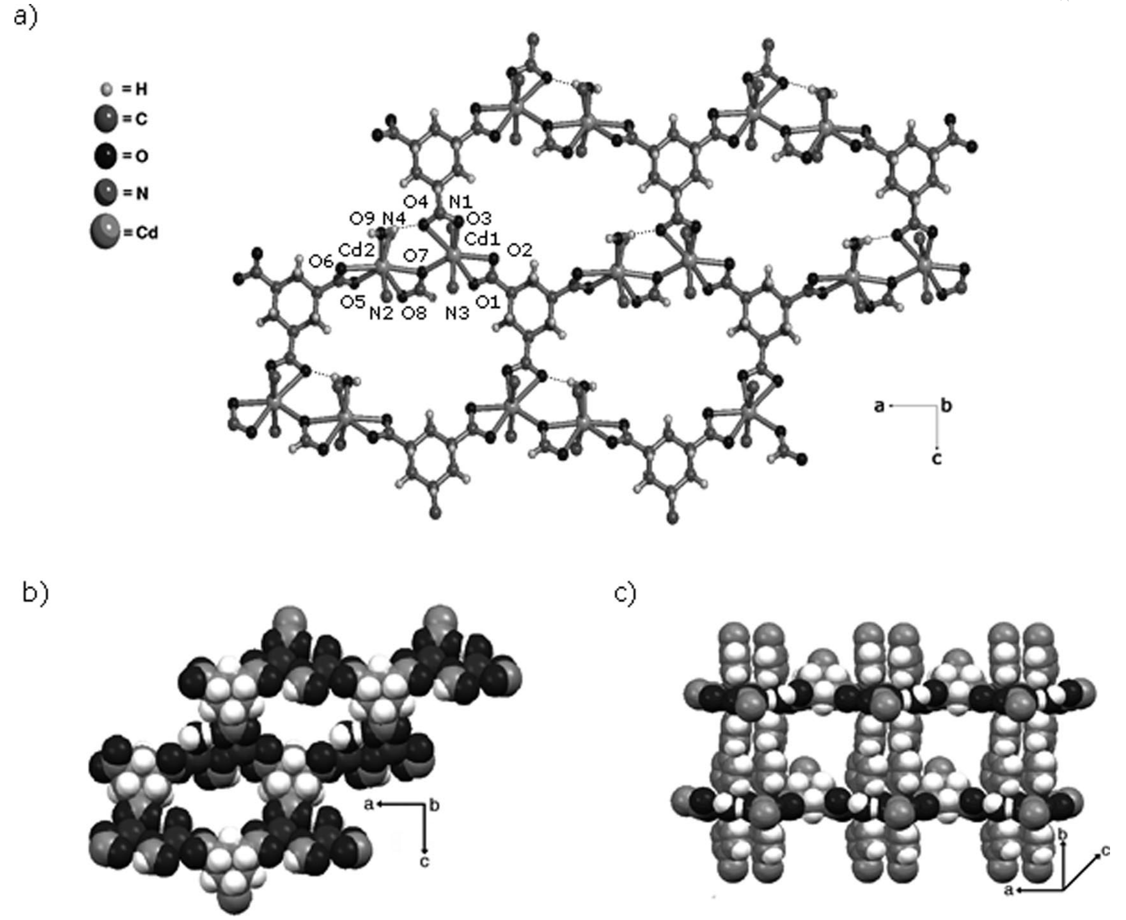


Figure 4. Different perspective views of the crystal lattice of [{[Cd$_2$(*cis*,*cis*-1,3,5-chtc)(HCO$_2$)(H$_2$O)(4,4′-bpy)$_2$]·DMF·4H$_2$O}$_n$] (**3**). (a), (b) Dinuclear {Cd$_2$(μ-O)O$_7$(H$_2$O)N$_4$} metal-cluster building block and repeating unit within the infinite 2D honeycomb pattern of the composition [{Cd$_2$(*cis*,*cis*-1,3,5-chtc)(HCO$_2$)(H$_2$O)}$_n$]. (c) Double-pillared octanuclear metal-ligand assembly related to those found in compounds **1** and **2**.

fact that three ligands are combined with two and a half metal clusters within a honeycomb.

Interestingly, octanuclear assemblies similar to those found in compounds **1** and **2** can be identified within the 3D architecture (Figures S7–S9 in the Supporting Information and Figure 4c). Their cavities have dimensions of 6.0×8.1 Å^2 and are penetrated by 4,4′-bpy double-pillars from cadmium atoms attached to neighbouring 2D layers to generate a self-interpenetrated 3D open-framework that is stabilized by π···π stacking interactions (centroid···centroid distances: 3.64 Å; Figure 5). Additional voids within the 3D skeleton are occupied by dmf and water molecules. As for compound **1**, the pyridyl groups of the bridging 4,4′-bpy ligand are twisted (23.7 and 28.3° for **3** vs. 37.9° for **1**), which apparently optimizes the π···π stacking interactions within the double-pillars (centroid···centroid distances: 3.70 and 3.79 Å for **1** vs. 3.79 and 3.95 Å for **3**). In contrast, the 4,4′-bpe ligands in compound **2** are almost planar (dihedral angle: 9.1°), with centroid···centroid distances of 3.87 Å.

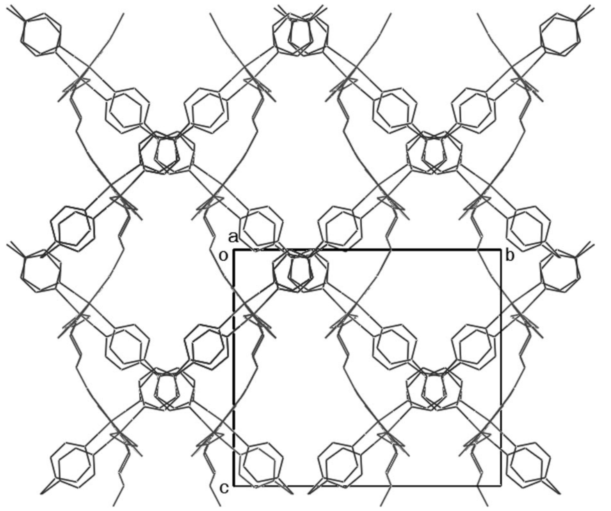


Figure 5. Representation of the self-interpenetrated framework of [{[Cd$_2$(*cis*,*cis*-1,3,5-chtc)(HCO$_2$)(H$_2$O)(4,4′-bpy)$_2$]·DMF·4H$_2$O}$_n$] (**3**).

IR Spectroscopy

In agreement with the crystal structures, the IR spectra of compounds **1**–**3** show intense bands due to the symmetric and asymmetric stretching vibrations of metal-coordinated chelating and/or bridging carboxylate groups (1416–1354 for ν_s and 1607–1559 cm^{-1} for ν_{as}).[17] Splitting of the bands is observed in all three cases, thus indicating at least two different coordination modes. The broad bands at 3429 and 3422 cm^{-1} for compounds **1** and **3** prove the presence of water molecules within the solid-state structures.

Thermal Stability

Thermogravimetric analyses (TGA) and measurements of the X-ray powder diffraction patterns (XRPD) were carried out to investigate the thermal stability of compounds **1**–**3**. As expected, the TGA curves for compounds **1** and **3** show three consecutive processes: crystal-lattice solvent evaporation, ligand pyrolysis or volatilization and inorganic residue formation. Since the crystal lattice of compound **2** is solvent-free, only the latter two processes are observed in this case.

The TGA curve for compound **1** shows an initial weight loss of 6.5% in the range from 70 to 200 °C corresponding to the removal of approximately 50% of the water molecules present in the crystal lattice (calcd. 6.03%), followed by a further weight loss of 28.15% in a relatively narrow temperature range (200–235 °C) due to further evaporation of solvent molecules and the pyrolysis and/or removal of part of the 1,2-chdc ligands and 4,4′-bpy pillars from the framework. In order to examine the robustness of the framework after evaporation of the solvent guest molecules, an X-ray powder diffractogram was recorded with a sample that had been treated thermally (120 °C for 1 h) and compared with the diffractogram of an untreated sample (Figure S10, Supporting Information). This comparison showed that the framework collapses after evaporation of the solvent guest molecules, which is not surprising since the coordination polymer is only two-dimensional (see above). However, the presence of clearly defined peaks within the XRPD pattern indicates that the resulting materials still conserves some crystallinity.

No weight loss occurs up to 320 °C during the TGA of compound **2**, at which point decomposition begins.

The TGA curve of compound **3** shows that weight loss starts already at room temperature. After a weight loss of 10.8% within the temperature range 20–120 °C, which corresponds to partial removal of the solvent molecules (dmf and two of the four water molecules, calcd. 11.4%), a very gradual weight loss of only 2.18%, which can be attributed to the elimination of an additional water molecule (calcd. 1.88%), occurs between 120 and 210 °C. A further significant weight loss of 26.2% takes place from 210 to 350 °C due to the elimination of the remaining crystal lattice water molecule, the coordinated water molecule and approximately 62.5% of the 4,4′-bpy pillars (calcd. 37%, observed 37%). The final disintegration of the framework starts at approximately 375 °C. Figure 6 shows the XRPD patterns of a sample of compound **3** that has been heated to 120 °C for 1 h. A comparison of the diffractograms shown in Figures 6a and b shows that they are in good agreement, thereby demonstrating that the 3D porous network is retained even in the absence of included guest molecules.

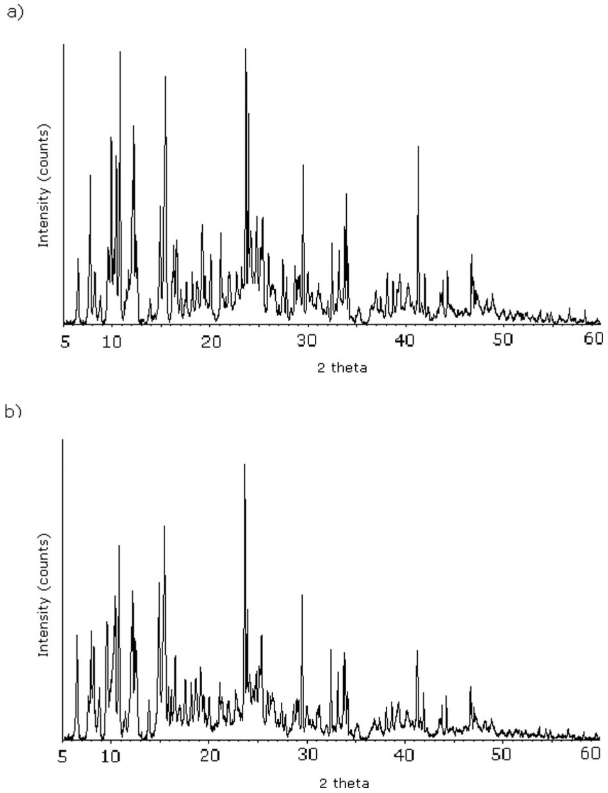


Figure 6. X-ray powder diffractograms of compound **3** before (a) and after (b) removal of solvent.

Conclusions

This contribution has shown that dinuclear cadmium clusters are ideal building blocks for the generation of double-pillared 2D and 3D open-frameworks. The simultaneous employment of carboxylate ligands and substituted pillars will probably allow for pore-size tuning in three dimensions and the generation of chiral cavities, which should stimulate a more profound and systematic exploitation of their potential.

Experimental Section

Instruments: IR spectra were recorded with a Bruker Vector 22 FT spectrophotometer. Elemental analyses were performed with Perkin–Elmer Series II 2400 and Elementar Vario ELIII instruments. Thermogravimetric analyses were performed under nitrogen (50 $mL\,min^{-1}$) at a heating rate of 10 $°C\,min^{-1}$ using a TA SDT Q600 apparatus.

X-ray Crystallographic Measurements: Powder X-ray diffraction analyses were carried out in the transmission mode with a Bruker

Table 2. Crystallographic data for compounds **1**–**3**.

	1[a]	**2**[a]	**3**[b]
Empirical formula	$C_{44}H_{48}Cd_2N_4O_{12}\cdot 8H_2O$	$C_{20}H_{20}CdN_2O_4$	$C_{30}H_{28}Cd_2N_4O_9\cdot dmf\cdot 4H_2O$
Formula mass [g mol^{-1}]	1193.79	464.78	958.52
Crystal size [mm]	0.06 × 0.18 × 0.20	0.16 × 0.23 × 0.32	0.16 × 0.21 × 0.32
Space group	*Pccn*	$P2_1/n$	$Pna2_1$
a [Å]	12.6415(8)	13.4099(18)	14.4979(16)
b [Å]	16.9860(10)	10.6761(14)	17.5125(19)
c [Å]	23.2415(14)	13.991(3)	15.4716(15)
α [°]	90	90	90
β [°]	90	115.708(2)	90
γ [°]	90	90	90
V [Å^3]	4990.6(5)	1804.8(5)	3928.2(7)
Z	4	4	4
μ [mm^{-1}]	0.932	1.239	1.153
$\rho_{calcd.}$ [g cm^{-3}]	1.589	1.711	1.621
θ limits [°]	$2 < \theta < 25$	$2 < \theta < 25$	$2 < \theta < 25$
hkl limits	–15 to 15, –20 to 20, –27 to 27	–15 to 15, –12 to 12, –16 to 16	–17 to 17, –20 to 20, –18 to 18
No. of collected reflections	45921	8705	36429
No. of independent reflections (R_{int})	4402 (0.105)	3146 (0.049)	6919 (0.041)
No. of observed reflections[c]	3594	2324	6856
R[c,d]	0.061	0.049	0.031
R_w[e,f]	0.121	0.101	0.078
No. of variables	344	244	495
GOOF	1.122	1.072	1.175
$\Delta\rho_{min}$ [e Å^{-3}]	–1.71	–0.71	–0.35
$\Delta\rho_{max}$ [e Å^{-3}]	0.97	0.73	0.70

[a] Data collection at T = 293 K. [b] Data collection at T = 100 K. [c] $I > 2\sigma(I)$. [d] $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$. [e] All data. [f] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

D8-Advance diffractometer equipped with a LynxEye detector ($\lambda_{Cu\text{-}K_{\alpha 1}}$ = 1.5406 Å; monochromator: germanium). Data were collected at room temperature in the 2θ range of 5–60° (step size: 0.01°; step time: 10 s). Single-crystal X-ray diffraction studies were carried out with a Bruker-AXS APEX diffractometer equipped with a CCD area detector ($\lambda_{Mo\text{-}K_\alpha}$ = 0.71073 Å; monochromator: graphite). Frames were collected at T = 100 (compounds **1** and **2**) or 293 K (compound **3**) by the ω/ϕ-rotation method ($\Delta\omega$ = 0.3°) at 10 s per frame (SMART[18a]). The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT[18b]). Structure solution, refinement, and data output were carried out with the SHELXTL-NT program package.[18c,18d] Non-hydrogen atoms were refined anisotropically. C–H hydrogen atoms were placed in geometrically calculated positions using a riding model. Except for the uncoordinated water molecules in compound **3**, all O–H hydrogen atoms were localized in the difference Fourier maps, and their atomic coordinates were freely refined. The O–H distance was fixed to 0.84 Å and the isotropic temperature factors to a value 1.5 times that of the corresponding oxygen atom. The most relevant crystallographic data are summarized in Table 2. CCDC-670458, -670459, -670460 for compounds **1**–**3**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation: Commercially available starting materials and solvents were used in all cases.

[{[Cd$_2$(*trans*-1,2-*a*,*a*-chdc)(*trans*-1,2-*e*,*e*-chdcH)$_2$(4,4′-bpy)$_2$]·8H$_2$O}$_n$] (1): *trans*-1,2-Cyclohexanedicarboxylic acid (0.050 g, 0.29 mmol) was dissolved in a mixture of ethanol and water (1:1, 10 mL) in the presence of potassium hydroxide (0.021 g, 0.38 mmol), and a solution of cadmium(II) nitrate tetrahydrate (0.059 g, 0.19 mmol) and 4,4′-bipyridine (0.030 g, 0.19 mmol) in ethanol (10 mL) was added. Crystals suitable for X-ray analysis formed after 1 week upon slow evaporation of the solvent at room temperature. Yield: 0.051 g (45%). IR (KBr): ṽ = 3429 (m), 2930 (m), 2856 (w), 1604 (s), 1562 (s), 1416 (s), 1391 (s), 1312 (m), 1255 (m), 1214 (m), 1111 (w), 1070 (w), 1008 (w), 900 (w), 809 (w), 726 (w), 629 (m), 492 (w) cm^{-1}. $C_{22}H_{32}CdN_2O_{10}$ (596.91): calcd. C 44.26, H 5.40, N 4.69; found C 44.47, H 5.03, N 4.47.

[{Cd$_2$(*trans*-1,4-*e*,*e*-chdc)(*trans*-1,4-*a*,*a*-chdc)(4,4′-bpe)$_2$}$_n$] (2). Method A: *trans*-1,4-Cyclohexanedicarboxylic acid (0.080 g, 0.46 mmol) was dissolved in ethanol (8 mL) in the presence of 2 equiv. of potassium hydroxide (0.052 g, 0.93 mmol), and a solution of cadmium(II) nitrate tetrahydrate (0.143 g, 0.46 mmol) and (*E*)-1,2-bis(4-pyridyl)ethylene (0.084 g, 0.46 mmol) in ethanol and water (7:1, 8 mL) was added. Crystals suitable for X-ray analysis formed after 4 d upon slow evaporation of the solvent at room temperature. Yield: 0.094 g (44%). **Method B:** For the reaction under hydrothermal conditions, *trans*-1,4-cyclohexanedicarboxylic acid (0.080 g, 0.46 mmol), potassium hydroxide (0.052 g, 0.93 mmol), cadmium(II) nitrate tetrahydrate (0.143 g, 0.46 mmol) and (*E*)-1,2-bis(4-pyridyl)ethylene (0.084 g, 0.46 mmol) were suspended homogeneously in water (12 mL). The suspension was then transferred to a pressure tube with PTFE bushing and heated to 120 °C for 4 d, after which time compound **1** had precipitated as colourless crystalline material. Yield: 0.150 g (70%). IR (KBr): ṽ = 3434 (m), 3051 (m), 2941 (w), 2857 (w), 1607 (s), 1571 (s), 1416 (s), 1290 (m), 1214 (w), 1016 (w), 981 (w), 836 (m), 777 (w), 732 (w), 554 (m), 468 (w) cm^{-1}. $C_{20}H_{20}CdN_2O_4$ (464.78): calcd. C 51.68, H 4.33, N 6.02; found C 51.57, H 4.03, N 6.25.

[{[Cd$_2$(*cis*,*cis*-1,3,5-chtc)(HCO$_2$)(H$_2$O)(4,4′-bpy)$_2$]·DMF·4H$_2$O}$_n$] (3). Method A: *cis*-*cis*-1,3,5-Cyclohexanetricarboxylic acid (0.040 g, 0.19 mmol) was dissolved in ethanol (8 mL) in the presence of 3 equiv. of potassium hydroxide (0.031 g, 0.56 mmol), and a solution of cadmium(II) nitrate tetrahydrate (0.114 g, 0.37 mmol) and

4,4′-bipyridine (0.058 g, 0.37 mmol) in dmf (8 mL) was added. Crystals suitable for X-ray analysis formed after 4 d upon slow evaporation of the solvent at room temperature. Yield: 0.038 g (42 %). **Method B:** The reaction was repeated under the same conditions as described above but in the presence of formic acid (1 mL). The product yield of compound **3** increased to 0.056 g (62 %). IR (KBr): $\tilde{\nu}$ = 3429 (s), 2924 (w), 1604 (s), 1559 (s), 1391 (s), 1354 (m), 1219 (w), 1074 (w), 1043 (w), 1006 (w), 806 (m), 629 (m), 490 (w) cm^{-1}. $C_{33}H_{43}Cd_2N_5O_{14}$ (958.52): calcd. C 41.35, H 4.49, N 7.30; found C 41.73, H 4.37, N 7.68.

Supporting Information (see footnote on the first page of this article): Additional figures with perspective views of the crystal lattices along *a*, *b* and *c* (Figures S1–S9); X-ray powder diffraction patterns of compound **1** (Figure S10); figures from this article in colour (Figures S11–S15).

Acknowledgments

This work was supported by the Consejo Nacional de Ciencia y Tecnología (CONACYT) and the Instituto Mexicano del Petróleo (IMP).

---

[1] For reviews see: a) P. J. Langley, J. Hulliger, *Chem. Soc. Rev.* **1999**, *28*, 279–291; b) M. Fujita, *Struct. Bonding* **2000**, *96*, 177–201; c) D. Braga, *J. Chem. Soc., Dalton Trans.* **2000**, 3705–3713; d) P. H. Dinolfo, J. T. Hupp, *Chem. Mater.* **2001**, *13*, 3113–3125; e) S. Feng, R. Xu, *Acc. Chem. Res.* **2001**, *34*, 239–247; f) B. Kesanli, W. Lin, *Coord. Chem. Rev.* **2003**, *246*, 305–326; g) C. Janiak, *Dalton Trans.* **2003**, 2781–2804; h) S.-L. Zheng, X.-M. Chen, *Aust. J. Chem.* **2004**, *57*, 703–712; i) J. L. C. Rowsell, O. M. Yaghi, *Angew. Chem. Int. Ed.* **2005**, *44*, 4670–4679; j) C. Sanchez, B. Julián, P. Belleville, M. Popall, *J. Mater. Chem.* **2005**, *15*, 3559–3592; k) U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastré, *J. Mater. Chem.* **2006**, *16*, 626–636.

[2] a) M. L. Occelli, H. C. Robson, *Zeolite Synthesis*, American Chemical Society, Washington, D.C., **1989**; b) A. K. Cheetham, G. Ferey, T. Loiseau, *Angew. Chem. Int. Ed.* **1999**, *38*, 3268–3292.

[3] For reviews see: a) O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474–478; b) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117–138; c) P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem. Int. Ed.* **1999**, *38*, 2638–2684; d) G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, *100*, 3483–3537; e) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658; f) G. Feréy, *Chem. Mater.* **2001**, *13*, 3084–3098; g) C. N. R. Rao, S. Natarajan, A. Choudhury, S. Neeraj, A. A. Ayi, *Acc. Chem. Res.* **2001**, *34*, 80–87; h) G. S. Papaefstathiou, L. R. MacGillivray, *Coord. Chem. Rev.* **2003**, *246*, 169–184; i) A. Erxleben, *Coord. Chem. Rev.* **2003**, *246*, 203–228; j) J. Y. Lu, *Coord. Chem. Rev.* **2003**, *246*, 327–347; k) C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew. Chem. Int. Ed.* **2004**, *43*, 1466–1496; l) G. Ferey, C. Mellot-Draznieks, C. Serre, F. Millange, *Acc. Chem. Res.* **2005**, *38*, 217–225; m) M. W. Hosseini, *Acc. Chem. Res.* **2005**, *38*, 313–323; n) J. R. Nitschke, *Acc. Chem. Res.* **2007**, *40*, 103–112; o) M. A. Pitt, D. W. Johnson, *Chem. Soc. Rev.* **2007**, *36*, 1441–1453; p) J. A. Thomas, *Chem. Soc. Rev.* **2007**, *36*, 856–868.

[4] A. C. Sudik, A. P. Cote, A. G. Wong-Foy, M. O'Keeffe, O. M. Yaghi, *Angew. Chem. Int. Ed.* **2006**, *45*, 2528–2533.

[5] a) H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Cote, R. E. Taylor, M. O'Keeffe, O. M. Yaghi, *Science* **2007**, *316*, 268–272; b) A. P. Cote, H. M. El-Kaderi, H. Furukawa, J. R. Hunt, O. M. Yaghi, *J. Am. Chem. Soc.* **2007**, *129*, 12914–12915.

[6] For references concerning mono-pillared metal-organic frameworks containing metals other than cadmium, see: a) M. Kondo, T. Okubo, A. Asami, S.-I. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka, K. Seki, *Angew. Chem. Int. Ed.* **1999**, *38*, 140–143; b) K. Seki, *Chem. Commun.* **2001**, 1496–1497; c) K. Seki, S. Takamizawa, W. Mori, *Chem. Lett.* **2001**, 332–333; d) L. Pan, H. Liu, X. Lei, X. Huang, D. H. Olson, N. J. Turro, J. Li, *Angew. Chem. Int. Ed.* **2003**, *42*, 542–546; e) S. Dalai, P. S. Mukerjee, E. Zangrando, F. Lloret, N. R. Chaudhuri, *J. Chem. Soc., Dalton Trans.* **2002**, 822–823; f) T. J. Prior, D. Bradshaw, S. J. Teat, M. J. Rosseinsky, *Chem. Commun.* **2003**, 500–501; g) F. S. Delgado, J. Sanchiz, C. Ruiz-Perez, F. Lloret, M. Julve, *CrystEngComm* **2003**, *5*, 280–284; h) S. Konar, F. S. Mukherjee, M. G. B. Drew, J. Ribas, N. R. Chaudhuri, *Inorg. Chem.* **2003**, *42*, 2545–2552; i) C.-B. Ma, F. Chen, C.-X. Zhang, M.-Q. Hu, C.-N. Chen, Q.-T. Liu, *Acta Crystallogr., Sect. C* **2004**, *60*, m285–m287; j) Y.-L. Wang, D.-Q. Yuan, W.-H. Bi, X. Li, X.-J. Li, F. Li, R. Cao, *Cryst. Growth Des.* **2005**, *5*, 1849–1855; k) B.-Q. Ma, K. L. Mulfort, J. T. Hupp, *Inorg. Chem.* **2005**, *44*, 4912–4914; l) C.-J. Li, S. Hu, W. Li, C.-K. Lam, Y.-Z. Zheng, M.-L. Tong, *Eur. J. Inorg. Chem.* **2006**, 1931–1935; m) B. Chen, S. Ma, F. Zapata, F. R. Fronczek, E. B. Lobkovsky, H.-C. Zhou, *Inorg. Chem.* **2007**, *46*, 1233–1236; n) A. Pichon, C. M. Fierro, M. Nieuwenhuyzen, S. L. James, *CrystEngComm* **2007**, *9*, 449–451.

[7] For references concerning mono-pillared metal-organic frameworks containing cadmium, see: a) L. R. MacGillivray, R. H. Groeneman, J. L. Atwood, *J. Am. Chem. Soc.* **1998**, *120*, 2676–2677; b) Z.-Y. Fu, X.-T. Wu, J.-C. Dai, L.-M. Wu, C.-P. Cui, S.-M. Hu, *Chem. Commun.* **2001**, 1856–1857; c) E. Suresh, K. Boopalan, R. V. Jasra, M. M. Bhadbhade, *Inorg. Chem.* **2001**, *40*, 4078–4080; d) F. A. A. Paz, Y. Z. Khimyak, A. D. Bond, J. Rocha, J. Klinowski, *Eur. J. Inorg. Chem.* **2002**, 2823–2828; e) J.-C. Dai, S.-M. Hu, X.-T. Wu, Z.-Y. Fu, W.-X. Du, H.-H. Zhang, R.-Q. Sun, *New J. Chem.* **2003**, *27*, 914–918; f) J.-H. Liao, C.-Y. Lai, C.-D. Ho, C.-T. Su, *Inorg. Chem. Commun.* **2004**, *7*, 402–404; g) R. Wang, M. Hong, D. Yuan, Y. Sun, L. Xu, J. Luo, R. Cao, A. S. C. Chan, *Eur. J. Inorg. Chem.* **2004**, 37–43; h) F. A. Almeida Paz, J. Klinowski, *Inorg. Chem.* **2004**, *43*, 3948–3954; i) J.-H. Liao, C.-D. Ho, *Acta Crystallogr., Sect. E* **2004**, *60*, m156–m158; j) X. Li, R. Cao, W. Bi, D. Yuan, D. Sun, *Eur. J. Inorg. Chem.* **2005**, 3156–3166; k) A. Thirumurugan, C. N. R. Rao, *J. Mater. Chem.* **2005**, *15*, 3852–3858; l) W.-G. Lu, L. Jiang, X.-L. Feng, T.-B. Lu, *Cryst. Growth Des.* **2006**, *6*, 564–571.

[8] a) S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494; b) L. Carlucci, G. Ciani, D. M. Proserpio, *Coord. Chem. Rev.* **2003**, *246*, 247–289.

[9] For references concerning double-pillared metal-organic frameworks containing metals other than cadmium, see: a) Z. Shi, L. Zhang, S. Gao, G. Yang, J. Hua, L. Gao, S. Feng, *Inorg. Chem.* **2000**, *39*, 1990–1993; b) J. Tao, M.-L. Tong, J.-X. Shi, X.-M. Chen, S. W. Ng, *Chem. Commun.* **2000**, 2043–2044; c) P. S. Mukherjee, S. Konar, E. Zangrando, T. Mallah, J. Ribas, N. R. Chaudhuri, *Inorg. Chem.* **2002**, *42*, 2695–2703; d) Z.-Y. Fu, X.-T. Wu, J.-C. Dai, S.-M. Hu, W.-X. Du, H.-H. Zhang, R.-Q. Sun, *Eur. J. Inorg. Chem.* **2002**, 2730–2735; e) C. Ma, C. Chen, Q. Liu, D. Liao, L. Li, L. Sun, *New J. Chem.* **2003**, *27*, 890–894; f) N. Hao, E. Shen, Y. Li, E. Wang, C. Hu, L. Xu, *Inorg. Chem. Commun.* **2004**, *7*, 510–512; g) H.-P. Jia, W. Li, Z.-F. Ju, J. Zhang, *Eur. J. Inorg. Chem.* **2006**, 4264–4270.

[10] For references concerning double-pillared metal-organic frameworks containing cadmium, see: a) J. Tao, M.-L. Tong, X.-M. Chen, *J. Chem. Soc., Dalton Trans.* **2000**, 3669–3674; b) J. Tao, X. Yin, Z.-B. Wei, R.-B. Huang, L.-S. Zheng, *Eur. J. Inorg. Chem.* **2004**, 125–133; c) Q. Fang, G. Zhu, M. Xue, J. Sun, G. Tian, G. Wu, S. Qiu, *Dalton Trans.* **2004**, 2202–2207; d) J.-C. Dai, X.-T. Wu, S.-M. Hu, Z.-Y. Fu, J.-J. Zhang, W.-X.

Du, H.-H. Zhang, R.-Q. Sun, *Eur. J. Inorg. Chem.* **2004**, 2096–2106; e) T. K. Maji, K. Uemura, H.-C. Chang, R. Matsuda, S. Kitagawa, *Angew. Chem. Int. Ed.* **2004**, *43*, 3269–3272.

[11] For metal-organic frameworks derived from 1,*x*-cyclohexanedicarboxylic acid, see: a) W. Uhl, T. Spies, W. Saak, *Eur. J. Inorg. Chem.* **1998**, 1661–1665; b) Y. Kim, D.-Y. Jung, *Chem. Commun.* **2002**, 908–909; c) M. Kurmoo, H. Kumagai, S. M. Hughes, C. J. Kepert, *Inorg. Chem.* **2003**, *42*, 6709–6722; d) Y. Qi, Y. Wang, C. Hu, M. Cao, L. Mao, E. Wang, *Inorg. Chem.* **2003**, *42*, 8519–8523; e) W. Bi, R. Cao, D. Sun, D. Yuan, X. Li, Y. Wang, X. Li, M. Hong, *Chem. Commun.* **2004**, 2104–2105; f) M. Inoue, T. Atake, H. Kawaji, T. Tojo, *Solid State Commun.* **2005**, *134*, 303–306; g) J. Chen, M. Ohba, D. Zhao, W. Kaneko, S. Kitagawa, *Cryst. Growth Des.* **2006**, *6*, 664–668; h) B. Chen, F. R. Fronczek, B. H. Courtney, F. Zapata, *Cryst. Growth Des.* **2006**, *6*, 825–828; i) A. Thirumurugan, M. B. Avinash, C. N. R. Rao, *Dalton Trans.* **2006**, 221–228; j) H. Kumagai, M. Akita-Tanaka, K. Inoue, K. Takahashi, H. Kobayashi, S. Vilminot, M. Kurmoo, *Inorg. Chem.* **2007**, *46*, 5949–5956.

[12] For metal-organic frameworks derived from 1,3,5-cyclohexanetricarboxylic acid, see: a) O. M. Yaghi, R. Jernigan, H. Li, C. E. Davis, T. L. Groy, *J. Chem. Soc., Dalton Trans.* **1997**, 2383–2384; b) L. Pan, E. B. Woodlock, X. Wang, *Inorg. Chem.* **2000**, *39*, 4174–4178; c) H. Kumagai, A.-M. Akita-Tanaka, K. Inoue, M. Kurmoo, *J. Mater. Chem.* **2001**, *11*, 2146–2151; d) M. P. Suh, K. S. Min, J. W. Ko, H. J. Choi, *Eur. J. Inorg. Chem.* **2003**, 1373–1379; e) X.-J. Liu, Q.-R. Fang, G.-S. Zhu, M. Xue, X. Shi, G. Wu, G. Tian, S.-L. Qiu, L. Fang, *Inorg. Chem. Commun.* **2004**, *7*, 31–34.

[13] L. Carlucci, G. Ciani, D. M. Proserpio, L. Spadacini, *CrystEngComm* **2004**, *6*, 96–101.

[14] For a review on supramolecular isomerism, see ref.[3e]

[15] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469–472.

[16] W. Su, W.-H. Bi, X. Li, R. Cao, *Acta Crystallogr., Sect. C* **2005**, *61*, m16–m18.

[17] G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **1980**, *33*, 227–250.

[18] a) *SMART, Bruker Molecular Analysis Research Tool*, version 5.618, Bruker Analytical X-ray Systems, **2000**; b) *SAINT-NT*, version 6.04, Bruker Analytical X-ray Systems, **2001**; c) G. Sheldrick, *SHELX86, Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, **1986**; d) *SHELXTL-NT*, version 6.10, Bruker Analytical X-ray Systems, **2000**.

Received: March 4, 2008