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Synthesis and Characterization of a Novel Cadmium–Organic Framework with Trimesic Acid and 1,2-Bis(4-pyridyl)ethane

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The hydrothermal reaction between $Cd(NO_3)_2$, trimesic acid (H_3BTC), 1,2-bis(4-pyridyl)ethane (BPE), and triethylamine under mild conditions yielded, after 3 days, a novel three-dimensional metal–organic framework, $[Cd_{1.5}(BTC)(BPE)(H_2O)_2]\cdot(H_2O)$, which has been characterized structurally using single-crystal and powder X-ray diffraction, elemental analysis, infrared and Raman spectroscopies, thermogravimetry, and differential scanning calorimetry. The structure exhibits a 2-fold interpenetration of identical $[Cd_{1.5}(BTC)(BPE)(H_2O)_2]$ single frameworks, described as an unusual $(9,{}_4^3)$ net. Crystal data: $Cd_{1.5}C_{21}H_{21}N_2O_9$, monoclinic, space group $C2/c$, with $a = 10.8264(5)$ Å, $b = 17.4563(5)$ Å, $c = 24.2605(11)$ Å, $\beta = 91.978(2)°$, $V = 4582.2(3)$ Å^3, and $Z = 8$.

Introduction

Since the seminal paper in which Hoskins and Robson[1] extrapolated the systematic approach of Wells[2] to the structure of solids to construct the first engineered diamondoid framework belonging to "a new class of scaffolding-like materials",[1] the field of crystal engineering of metal−organic framewoks (MOFs) has seen a great surge in research interest.[3] The driving force behind this work lies in the interesting architectures and potential applications of the products.[4]

In theory, the construction of novel MOFs requires multitopic organic ligands capable of forming one or more bridges and metal centers with one or more vacant coordinative sites. According to Pearson's classification,[5] Cd^{2+} cations are weak- to medium-strength acids able to coordinate simultaneously in solution to both hard oxygen-containing and soft nitrogen-containing organic bases. 1,3,5-Benzenetricarboxylic acid (H_3BTC, also known as trimesic acid) is a rigid, planar molecule that is soluble in a number of solvents. The three exo-carboxylic acid groups are arranged symmetrically around the benzene ring, forming a flat, trigonal molecule, which can be used as a building block in the construction of organic crystals and MOFs. In this context, H_3BTC has been extensively used in the synthesis of multidimensional MOFs with Ba^{2+},[6] Ca^{2+},[7] Cd^{2+},[8] Co^{2+},[9,10] Cu^{2+},[11] Er^{3+},[12,13] Fe^{2+} and Fe^{3+},[14] Mn^{2+},[10] Ni^{2+},[15] Pb^{2+},[16]

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Sr^{2+},[6] Ti^{4+},[17] Zn^{2+},[10,18] Ag^{+},[19] and Y^{3+}.[13] Furthermore, when chemical aggregates, like methylene groups, are selectively introduced between the two 4-pyridyl rings of large rodlike spacer ligands, such as the widely used 4,4′-bipyridine (4,4-bpy), the ligand acquires variable flexibility and functionality which can direct specific framework properties (dimensionality, void space, degree of interpenetration, and topology). 1,2-Bis(4-pyridyl)ethane (BPE)[20,21] is thus a good starting candidate for the study of the effect of their flexibility on the structural properties of the cadmium−organic frameworks (Cd−OFs). Hennigar et al.[20] showed that this ligand can adopt the gauche and anti conformations and that a variety of network topologies can occur.

We have demonstrated that the absence of triethylamine in reactive mixtures containing H_3BTC and BPE molecules leads, under optimized hydrothermal conditions,[22] to the synthesis of two novel layered structures, $[(BPEH_2)(H_2BTC)_2(H_3BTC)_2\cdot(H_2O)]$[23] and $[(BPEH_2)_2(H_2BTC)_4(H_3BTC)_4\cdot(H_2O)_{14}]$.[24] Following our recent interest in the synthesis and characterization of novel highly crystalline MOFs,[22,25] we report a novel mixed-ligand three-dimensional 2-fold interpenetrated Cd−OF containing H_3BTC and BPE residues, $[Cd_{1.5}(BTC)(BPE)(H_2O)_2]\cdot(H_2O)$ (**I**), synthesized from reactive mixtures identical to those used to isolate the previously mentioned organic crystals, but for the inclusion of triethylamine, a widely used proton-acceptor molecule and structure-directing agent.

Experimental Section

Synthesis. Reagents were acquired from commercial sources and used as received without further purification. Synthesis was carried out in a PTFE-lined stainless steel reaction vessel (8 cm^3, filling rate 70%) under autogenous pressure and static conditions. The compound proved to be air- and light-stable, as well as insoluble in water and solvents such as methanol, ethanol, acetone, dichloromethane, toluene, DMSO, and chloroform.

Typical Synthesis of $[Cd_{1.5}(BTC)(BPE)(H_2O)_2]\cdot(H_2O)$ (I). $Cd(NO_3)_2\cdot4H_2O$ (0.312 g, Aldrich) was dissolved in distilled water (ca. 3 cm^3) at ambient temperature, followed by the addition, with vigorous magnetic stirring, of BPE (0.125 g, Aldrich). A solution of H_3BTC (0.211 g, Aldrich) and triethylamine (TEA, 0.294 g, Avocado) in distilled water (ca. 3 cm^3) was added dropwise to the resulting white suspension. The final mixture, with a molar composition of 1.49:1.00:1.48:4.28:512 Cd^{2+}/BPE/H_3BTC/TEA/H_2O, was stirred thoroughly for 1 h at ambient temperature before being transferred to the reaction vessel, which was sealed and placed inside a preheated oven at 145 °C. The temperature profile used for the synthesis has already been reported.[22] From the crystalline white product, crystals suitable for single-crystal X-ray diffraction were manually harvested and preserved in a portion of the colorless autoclave solution. The microcrystalline powder was washed with ca. 50 cm^3 of distilled water and ca. 3×50 cm^3 of absolute ethanol and then air-dried at 70 °C.

Elemental composition found: C, 40.96; H, 3.48; and N, 4.12. Calcd (based on single-crystal data): C, 41.07; H, 3.44; and N, 4.56. Thermogravimetric analysis data (weight losses) and derivative thermogravimetric peaks (DTG; in italics inside the parenthesis): 20−160 °C, 6.7% (*88* °C); 250−305 °C, 8.6% (*283* °C); 350−435 °C, 55.3% (*397* and *425* °C). Differential scanning calorimetry (DSC) peaks: 93, 281, and 397 °C. Selected vibrational (FT-IR and FT-Raman in italics; cm^{-1}): ν(O−H, lattice and coordinated water), 3350, vs, vb; ν(C−H, aromatic compounds), (*3063*);

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ν_{asym}(C−H in −CH$_2$−), 2934, m (*2936*); ν_{sym}(C−H in −CH$_2$−), 2909, m (*2906*); overtones and combination bands for 1,3,5-trisubstituted benzene rings, 1966, w, 1873, w and 1717, s; ν_{asym}(−CO$_2$−), 1622, vs and 1556, vs; interactions between ν(C−C) and ν(C−N) for 4-monosubstituted pyridines, (*1550*, *1563*); ν(−C−H, aromatic compounds), 1528, m; from aromatic compounds with groups capable of donating electrons (e.g., carboxylate groups), 1502, m (*1501*); δ(−CH$_2$−), (*1416*); ν(C−H, aromatic compounds), (*1443*); ν_{sym}(−CO$_2$−), 1434, vs and 1367, vs; δ(O−H···O), 1335, m (*1330* and *1353*); ν(C−O), 1220, s and 1241, m (*1214*); ρ(C−H), 1180, s (*1188*); δ(−C−H, 4-monosubstituted pyridines), 1096, m and 1069, m (*1072*); δ(═C−H, aromatic compounds), 1016, s (*1018*); γ(O−H···O), 931, m; δ(C−O), 837, s (*841*); γ(═C−H, 4-monosubstituted pyridines), 813, s and 797, m (*813* and *798*); ω(C−H, substituted benzene rings), 758, m; γ(C−O), 735, m (*734*); depolarized δ(C═C) band for substituted aromatic rings, (*667*); γ(C−H, 1,3,5-trisubstituted benzene rings), 548, s (*548*); ρ[(C−O)-O], 491, s (*496*); γ(C−H, aromatic rings), 386, m.

Physical Measurements. Elemental analysis for carbon, hydrogen, and nitrogen was performed on an Exeter Analytical CE-440 elemental analyzer. Samples were combusted under an oxygen atmosphere at 975 °C for 1 min, with helium used as purge gas.

FT-IR spectra were collected from KBr pellets (Aldrich 99%+, FT-IR grade) using a Mattson 4000 at the University of Aveiro, Portugal. FT-Raman spectra were measured on a Bruker RFS 100 with a Nd:YAG coherent laser ($\lambda = 1064$ nm) in Aveiro.

Scanning electron microscopy images were obtained in Aveiro using an FEG-SEM Hitachi S4100 microscope, operating at 25 kV. Samples were prepared by deposition on aluminum sample holders and by carbon coating.

Thermogravimetric analysis was carried out using a Polymer Laboratories TGA 1500. Differential scanning calorimetry analysis was performed in Aveiro using a Shimadzu DSC-50. These thermoanalytical studies were always performed using a heating rate of 5 °C/min and a constant nitrogen flow of 25 cm^3/min.

Powder X-ray diffraction patterns were measured at ambient temperature using the step counting method (step, 0.5°; time, 460 s) on a STOE STADI-P high-resolution transmission diffractometer equipped with Ge(111)-monochromated Cu Kα radiation ($\lambda = 1.5406$ Å) and a position-sensitive detector covering a 6° 2θ angle (40 kV, 40 mA). Simulated powder patterns were based on single-crystal data and calculated using the STOE Win XPOW software package.[26]

Single-Crystal X-ray Crystallography. Suitable single crystals were mounted on a glass fiber using perfluoropolyether oil.[27] Data were collected at 180(2) K on a Nonius Kappa charge coupled device (CCD) area-detector diffractrometer (Mo Kα graphite-monochromated radiation, $\lambda = 0.7107$ Å) equipped with an Oxford Cryosystems cryostream and controlled by the Collect software package.[28] Images were processed using the software packages Denzo and Scalepack,[29] and the data were corrected for absorption by using the empirical method employed in Sortav.[30] Structures were solved by the direct methods of SHELXS-97[31] and refined by full-matrix least squares on F^2 using SHELXL-97.[32] Cavity dimensions were calculated by overlapping rigid spheres with van der Waals radii for each element: O, 1.52 Å; N, 1.55 Å; C, 1.7 Å; and Cd, 2.2 Å (hydrogen atoms were omitted in all cases for simplicity). Further details on single-crystal solution and refinement are given in the Supporting Information.

Table 1. Crystal Data and Structure Refinement Information for **I**

formula	$Cd_{1.5}C_{21}H_{21}N_2O_9$
fw	614.00
cryst syst	monoclinic
space group	*C*2/*c*
a (Å)	10.8264(5)
b (Å)	17.4563(5)
c (Å)	24.2605(11)
β (°)	91.978(2)
volume (Å^3)	4582.2(3)
Z	8
D_c (g cm^{-3})	1.780
μ(Mo Kα) (mm^{-1})	1.459
cryst size (mm)	0.23 × 0.12 × 0.05
cryst type	colorless plates
θ range	3.77−22.49°
index ranges	$-14 \leq h \leq 14$ $-22 \leq k \leq 22$ $-31 \leq l \leq 31$
reflns collected	14470
independent reflns	5145 ($R_{int} = 0.0499$)
final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0463$, $wR2 = 0.1106$
final *R* indices (all data)	$R1 = 0.0762$, $wR2 = 0.1203$
largest diff peak and hole	0.983 and −0.781 e Å^{-3}

Crystallographic data (excluding structure factors) for structure **I** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-230806. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, U.K. [Fax: (+44) 1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

Results and Discussion

Crystal Structure of [Cd$_{1.5}$(BTC)(BPE)(H$_2$O)$_2$]·(H$_2$O) (I). The reaction between H$_3$BTC and BPE under hydrothermal conditions gives rise to a highly crystalline product (see Experimental Section) formulated as [Cd$_{1.5}$(BTC)(BPE)(H$_2$O)$_2$]·(H$_2$O) (**I**) by single-crystal X-ray diffraction (Table 1) and elemental analysis. Despite minor differences between the simulated and the experimental high-resolution transmission X-ray powder patterns, phase purity and homogeneity were confirmed (Figure 1).

The structure contains two distinct repeating structural motifs, each containing a crystallographically unique Cd^{2+} cation in a distorted octahedral coordination geometry (Figure 2): Cd(1) is coordinated to two BTC^{3-} and two BPE ligands, {CdO$_4$N$_2$} (Figure 2a and Table 2), and Cd(2) has two water molecules occupying the apical positions, with two BTC^{3-} ligands and one BPE ligand forming the equatorial plane (Figure 2b and Table 2). The average Cd−O and Cd−N distances are ca. 2.35 and 2.27 Å, respectively, consistent with results for other Cd−OFs.[33] In particular, for the coordinated water molecules, the average Cd−O distance of ca. 2.32 Å is slightly above the typical results for crystal

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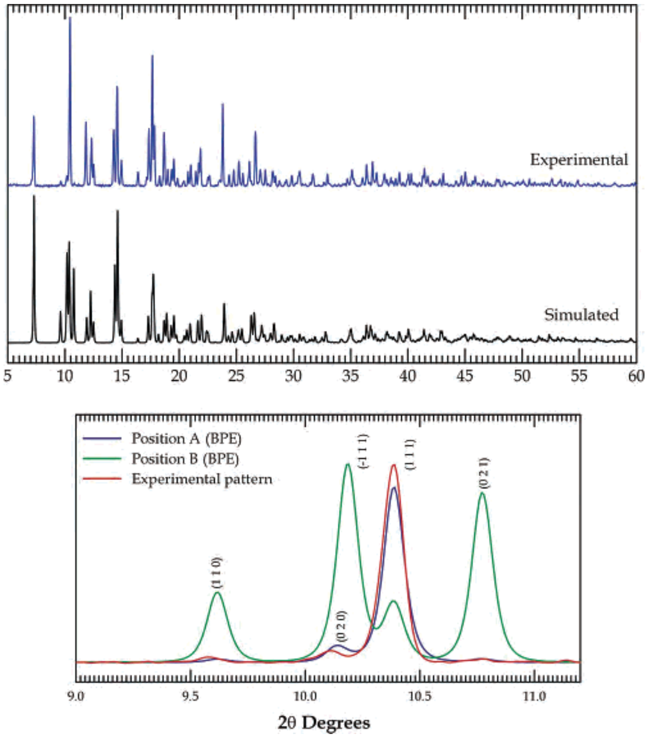

Figure 1. Simulated and experimental high-resolution (collected in transmission mode) powder X-ray diffraction patterns for **I**.

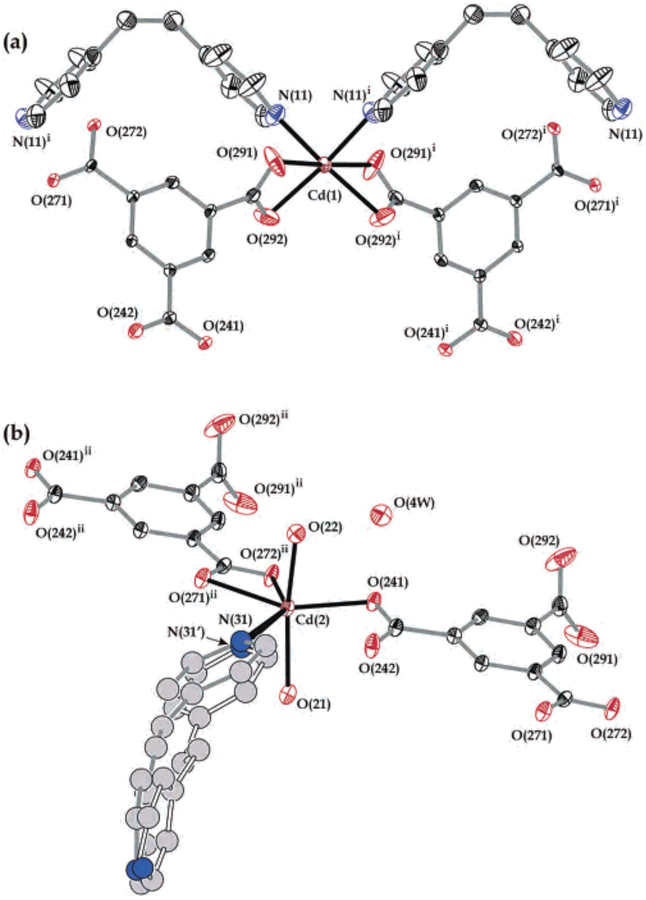

Figure 2. Schematic representation of the distorted octahedral coordination environments for the two crystallographically unique Cd^{2+} metal centers. H atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 30% probability level. The disordered BPE ligand coordinated to Cd(2) is represented in the ball-and-stick mode. For bond lengths (Å) and angles (deg), see Table 2. Symmetry codes used to generate equivalent atoms: (i) $-x, y, 1/2 - z$; (ii) $x - 1/2, 1/2 + y, z$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **I**

Cd(1)−N(11)	2.258(3)	N(11)−Cd(1)−N(11)^a	98.3(2)
Cd(1)−O(291)	2.395(4)	O(291)−Cd(1)−O(292)	53.86(16)
Cd(1)−O(292)	2.298(4)	O(291)−C(29)−O(292)	119.2(5)
C(29)−O(291)	1.231(7)	O(291)−Cd(1)−O(292)^a	127.9(2)
C(29)−O(292)	1.236(7)	O(291)−Cd(1)−N(11)	87.80(18)
Cd(2)−O(241)	2.297(3)	O(291)−Cd(1)−N(11)^a	90.77(15)
Cd(2)−O(271)^b	2.470(3)	O(291)^a−Cd(1)−N(11)^a	87.80(18)
Cd(2)−O(272)^b	2.346(3)	O(292)−Cd(1)−N(11)	93.83(19)
Cd(2)−O(21)	2.364(3)	O(292)−Cd(1)−N(11a)	142.11(17)
Cd(2)−O(22)	2.272(4)	O(271)^b−Cd(2)−O(272)^b	54.06(11)
C(24)−O(241)	1.268(5)	O(241)−Cd(2)−O(272)^b	85.75(11)
C(24)−O(242)	1.234(6)	O(271)^b−Cd(2)−N(31)	85.5(3)
C(27)−O(271)	1.252(6)	O(22)−Cd(2)−N(31)	88.1(3)
C(27)−O(272)	1.268(5)	O(21)−Cd(2)−N(31)	84.1(3)
Cd(2)−N(31)	2.276(6)	O(271)^b−Cd(2)−O(241)	138.63(11)
Cd(2)−N(31′)	2.281(6)		

^{a} Symmetry codes used to genterate equivalent atoms: $-x, y, 1/2 - z$. ^{b} Symmetry codes used to generate equivalent atoms: $x - 1/2, 1/2 + y, z$.

hydrates,[34] but it is in good agreement with related values reported for other Cd−OFs.[33]

An interesting feature of **I**, uncommon among highly crystalline MOFs, is the disordered nature of the BPE ligand coordinated to Cd(2) (Figure 2b). The two different positions for this ligand result in different X-ray powder diffraction patterns, particularly in the $9 \leq 2\theta° \leq 11$ region (Figure 1): position A indicates more strongly the reflection of the (1 1 1) plane family, while position B implies the presence of three strong reflections corresponding to the (1 1 0), (−1 1 1), and (0 2 1) families. In accordance with what is observed in the experimental high-resolution transmission PXRD pattern, microcrystalline **I** has a much higher population of position A of BPE than of position B (Figure 1), as opposed to the optimal ca. 1:1 ratio calculated during single-crystal analysis (see Supporting Information). This behavior was observed for other crystals (from the same and different batches), strongly indicating that other factors, such as the temperature, may be in the origin of such discrepancies between the PXRD patterns.

BTC^{3-} appears as a rigid, planar exo-tridentate bridging ligand, forming two coordinative η^3-syn,syn-chelates and one syn-unidentate bond (Figure 2). In fact, each BTC^{3-} effectively bridges three Cd^{2+} centers [one Cd(1) and two Cd(2)], imposing separations of Cd(1)···Cd(2), 9.5713(6) Å; Cd(1)···Cd(2),^{i} 9.5317(5) Å; and Cd(2)···Cd(2),^{i} 10.2705(2) Å (symmetry code: (i) $1/2 + x, -1/2 + y, z$). The coordination mode of the C(29) carboxylate group to Cd(1) can be considered as an almost symmetrical chelate, since the two Cd−O bonds are very similar (Table 2). Although the same is observed for the C(27) carboxylate group coordinated to Cd(2), C(24) appears connected in a uni-

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Table 3. Hydrogen-Bonding Geometry for **I** (in Å and deg)

D−H···A	d(D···A)	∠(D−H···A)
O(21)−H(21A)···O(241)^{a}	2.678(5)	160(4)
O(21)−H(21B)···O(272)^{b}	2.800(5)	128(4)
O(22)−H(22A)···O(271)^{c}	2.778(5)	170(4)
O(22)−H(22B)···O(4W)	2.682(5)	163(4)
O(4W)−H(4WA)···O(291)^{d}	2.703(6)	168(5)
O(4W)−H(4WB)···O(242)^{c}	2.743(6)	154(5)

$^{a-d}$ Symmetry codes used to generate equivalent atoms: (a) $1 - x$, $1 - y$, $2 - z$, (b) $3/2 - x$, $1/2 - y$, $2 - z$, (c) $2 - x$, $1 - y$, $2 - z$, and (d) $x + 1/2$, $y + 1/2$, z.

dentate fashion through the O(241) atom (Cd−O, 2.297(3) Å). All the carboxylate groups maintain the equivalence of the C−O bonds, with lengths in the 1.23−1.27 Å range. This is particularly unexpected for the C(24) group and is caused by the strong hydrogen bonds between O(242) and the free water molecule (Table 3).[35] Although the C(24) and C(27) carboxylate groups are approximately in the same plane as the benzene aromatic ring, with the average dihedral angle of less than ca. 5°, the C(29) group forms a ca. 50° angle with the same ring (Figure 2).

The BPE ligand acts as an effective inter-metallic bridge, always connecting the same type of metal centers: Cd(1) to Cd(1) and Cd(2) to Cd(2), imposing separations in Cd(1)···Cd(1)^{ii} of 13.6111(9) Å and in Cd(2)···Cd(2)^{iii} of 10.8264(5) Å (symmetry codes: (ii) $1 + x$, y, z; (iii) $2 - x$, y, $2.5 - z$). When coordinated to Cd(1), this spacer adopts the gauche conformation, as reported by Hennigar et al.[20] For Cd(2), the two possible BPE positions can be considered as intermediate between the anti and the gauche conformations,[20] with the average dihedral angles between the 4-pyridyl rings of ca. 53°.

The three-dimensional assembly of the two distinct Cd^{2+} repeating structural motifs shown in Figure 2 leads to the formation of a single framework, $[Cd_{1.5}(BTC)(BPE)(H_2O)_2]$, which contains compact triple-metallic layers formed by two external sheets of Cd(2) and one internal of Cd(1) (Figure 3). The latter metal centers are arranged in straight lines along the *a* axis and interconnected by the BPE bridges. These triple-metallic layers are pillared by the disordered BPE ligands, leading to the formation of cavities, the largest of which have a cross-section of ca. 5.2 × 8.5 Å and run along the *a* direction (Figure 3). The O(21) and O(22) water molecules coordinated to Cd(2) point toward the inside of the channels, which might facilitate their removal without the destruction of the crystal structure. Thus, **I** may be considered as containing *open* metal sites. There are other types of channels running along the other directions of the unit cell in $[Cd_{1.5}(BTC)(BPE)(H_2O)_2]$, the most prominent having cross-sections of ca. 3.2 × 3.0 Å and 3.8 × 16.3 Å (Figure 4).

As is usually found in MOFs containing large cavities, the voids within the $[Cd_{1.5}(BTC)(BPE)(H_2O)_2]$ single framework are too large to be left filled only by solvent molecules.

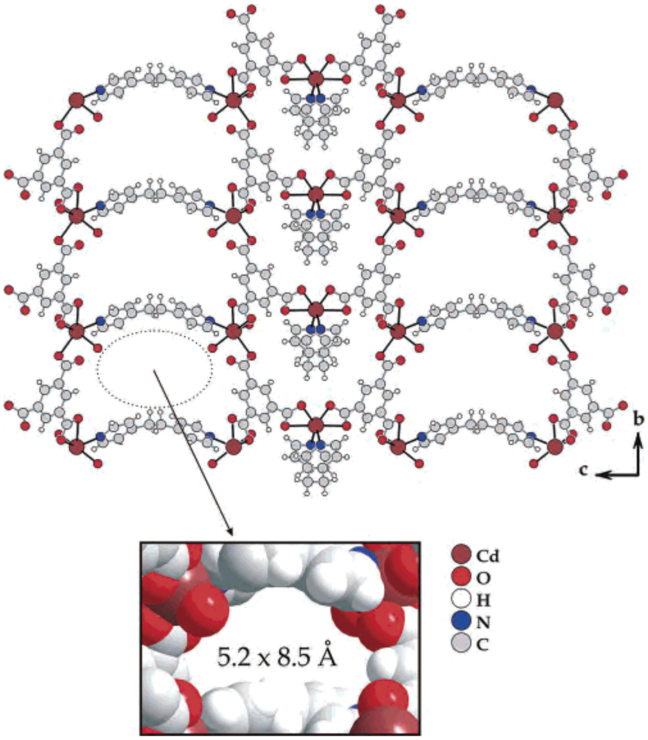

Figure 3. Projection of the $[Cd_{1.5}(BTC)(BPE)(H_2O)_2]$ single framework along the *a* direction, revealing the existence of large channels with cross-sections of ca. 5.2 × 8.5 Å. For clarity, uncoordinated water molecules have been omitted, and only one position for the disordered BPE ligand is represented.

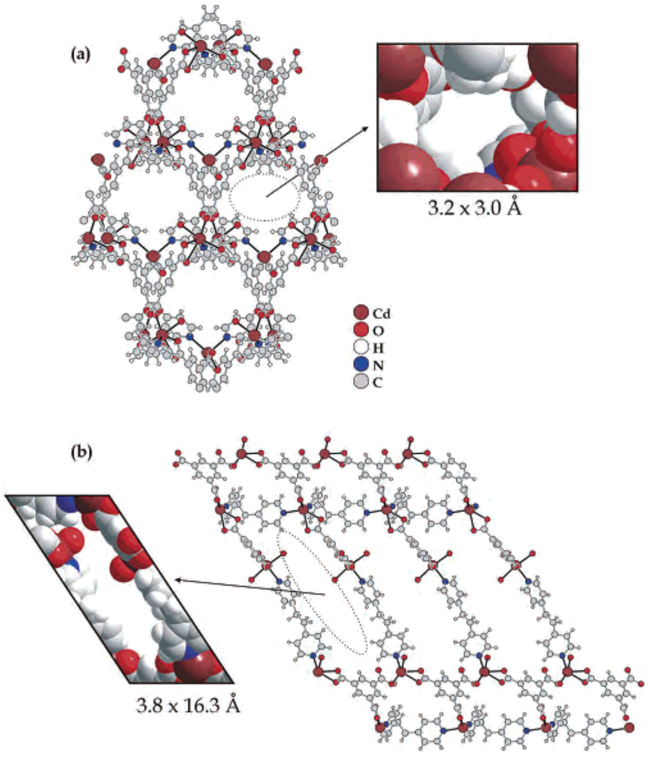

Figure 4. Two projections of the $[Cd_{1.5}(BTC)(BPE)(H_2O)_2]$ single framework, showing the presence of channels with a cross-section of (a) ca. 3.2 × 3.0 Å and (b) ca. 3.8 × 16.3 Å.

Consequently, **I** exhibits a 2-fold interpenetration of identical $[Cd_{1.5}(BTC)(BPE)(H_2O)_2]$ frameworks related by the 2-fold axis of *C*2/c (Figure 5). This loss of porosity was confirmed

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[35] Oldham, C. In *Comprehensive Coordination Chemistry*, 1st ed.; Wilkinson, S. G., Ed.; Pergamon Press: Elmsford, NY 1987; Vol. 2, p 435.

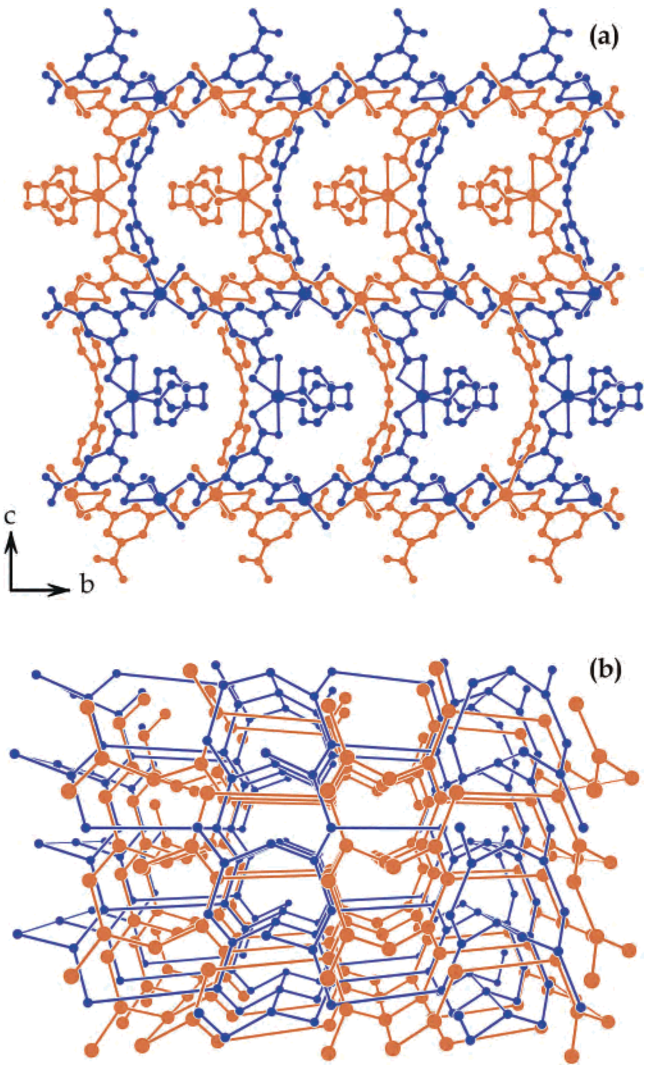

Figure 5. (**a**) Structure of **I** showing the 2-fold interpenetration of identical $[Cd_{1.5}(BTC)(BPE)(H_2O)_2]$ frameworks. (**b**) Topological representation of the two frameworks (with three- and four-connected nodes).

by N_2 adsorption isotherms, which gave a BET surface area of only 6.3 m^2/g.

Taking the Cd^{2+} cations and the BTC^{3-} anionic ligands as nodes for the $[Cd_{1.5}(BTC)(BPE)(H_2O)_2]$ framework, two different types of three-connected and one kind of four-connected node are observed, all characterized by the shortest topological circuits enclosing nine nodes (metallic bridges through BPE have been substituted by a connection between metals; the BTC^{3-} ligand was replaced by a three-connected node placed in the geometrical center of the aromatic ring). The topology of **I** can thus be described by an unusual $(9,{}^{3}_{4})$ net (Figure 5b).

Connections between the two interpenetrating $[Cd_{1.5}(BTC)(BPE)(H_2O)_2]$ open-frameworks are assured by the hydrogen-bonding network, which confers additional stability to the structure. The uncoordinated water molecule is engaged in three distinct strong O−H···O interactions: on one hand, it is bound to O(22) and O(291) from the same framework, and on the other to O(242) from the neighboring framework. The connection between the two frameworks is further established by two O(22)···O(271) interactions forming a typical $R_2^2(8)$ graph set and by the bifurcated interaction O(21)···{O(241),O(272)} described by an $R_2^2(6)$ graph set (Table 3 and Supporting Information).[36]

Thermal Analysis. Thermal decomposition proceeds with four distinct weight losses between ambient temperature and 600°C. The first weight loss is attributed to the gradual release of two-and-a-half water molecules (calculated: 6.8% for ca. 2.5 molecules per formula unit), probably incorporated due to incomplete drying. The second loss corresponds to the release of almost all the water molecules (calculated: 8.2%). We note that the crystallization water is released at the same time as the coordinated solvent, supporting the structural evidence of a very strong hydrogen-bonding network in **I**. Two consecutive decompositions suggest the total destruction of the framework by the oxidation of the organic component, leading to the formation of the stoichiometric amount of cadmium oxide as the residue (calculated: 29.2%). DSC analysis of **I** reveals only three major endothermic processes which are in good agreement with the DTG peaks. The DSC peak at 397 °C is not very well resolved, with two shoulders being clearly visible. This suggests oxidation of the organic component of **I** in several distinct steps.

Vibrational Spectroscopy. IR and Raman spectra confirm the presence of the organic ligands used in the syntheses (through the typical vibrations of substituted benzene and/or pyridine aromatic rings and the vibrational modes for carboxylic acid groups), as well as the extensive hydrogen-bonding network, which is present within the crystal structures and involves the coordinated and uncoordinated solvent molecules (e.g., through the presence of the ν(O−H), δ(O−H···O), and γ(O−H···O) vibrational modes).

The Δ values, defined by Deacon and Phillips as $\nu_{asym}(-CO_2^-)-\nu_{sym}(-CO_2^-)$,[37] give information concerning the coordination modes of the carboxylate groups. The calculated 122 and 255 cm^{-1} values are in very good agreement with the previously reported structure and indicate the presence of the chelating and unidentate coordination modes, respectively.[37]

Conclusions

In summary, we have demonstrated that, under mild and controlled hydrothermal conditions, the use of triethylamine as a proton acceptor in reactive mixtures containing trimesic acid and BPE leads to the formation of a novel 2-fold interpenetrated $(9,{}^{3}_{4})$ cadmium−organic framework, $[Cd_{1.5}(BTC)(BPE)(H_2O)_2]$, thermally stable up to ca. 350 °C. The structure contains disordered BPE organic molecules, acting as pillars between compact triple-metallic layers. Powder X-ray diffraction and simulations based on single-crystal results proved to be valuable for establishing which position for BPE is more common. Ongoing research is being focused on the use of more flexible pillars, such as 4,4′-trimethylene-dipyridine (which contains one more methylene group than BPE).

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Supporting Information Available: Crystallographic file in CIF format plus further details for crystal structure solution and refinement. Additional figures: PXRD comparison between the experimental pattern and simulations for positions A and B, SEM picture, and two schematic representations of the hydrogen-bonding network. This material is available free of charge via the Internet at http://pubs.acs.org.

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