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ARTICLE

Syntheses and Crystal Structures of Two Cadmium Methanetetrabenzoates Featured by Open Framework and Infinite Layers

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Abstract. Colorless single crystals of $Cd_2[\mu_8\text{-MTB}]\cdot 3H_2O\cdot DMF$ (**1**) were prepared in DMF/H_2O solution [**1**: space group *C*2/*c* (no. 15) with a = 1821.30(6), b = 2175.08(6), c = 1269.87(4) pm, β = 129.684(1)°]. The connection between the methane-*p*-benzoate tetraanions (MTB^{4-}) and the Cd^{2+} cations leads to a three-dimensional framework with channels extending along [$\bar{1}$10] and [110] with openings of 670 pm × 360 pm. The channel-like voids accommodate water molecules and *N*,*N*-dimethylformamide (DMF) molecules not bound to Cd^{2+}. Colorless single crystals of $[Cd_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2]\cdot 7DMF$ (**2**) were prepared in DMF in the presence of 2,2′-bipyridine [**2**: space group $P\bar{1}$ (no. 2) with a = 1224.84(4), b = 1418.85(5), c = 2033.49(4) pm, α = 85.831(2)°, β = 88.351(2)°, γ = 68.261(1)°]. The coordination of MTB^{4-} to Cd^{2+} results in infinite layers parallel to (001). The layers, not connected by any hydrogen bonds, contain small openings of about 320 pm × 340 pm.

Introduction

Porous coordination polymers, often called metal-organic frameworks (MOFs), have attracted much attention due to their potential application e.g. as catalyst,[1] ion exchanger,[2] and in gas storage and separation processes.[3] Hereby, polycarboxylate ligands are able to coordinate metal ions in flexible modes, resulting in various interesting complexes with one-, two, and three-dimensional structure motives.[4–8] Building blocks with tetrahedrally directed functional groups will very likely build up frameworks related to the structure of diamond. Such diamond-like frameworks, often called diamondoid, have been veryfied in the crystal structure of methanetetraacetic acid (3,3-bis(carboxymethyl)glutaric acid) and adamantane-1,3,5,7-tetracarboxylic acid.[9,10] These compounds feature interpenetrating networks. If it is possible to avoid interpenetrating structures, open frameworks will result. Common examples are the mineral melanophlogite and various porous silica modifications. A platinum coordination compound with adamantoid cages has been reported very recently.[11] Further three-dimensional and porous coordination polymers have been prepared using tetrahedral building units, like the anions of methanetetra-*p*-benzoic acid and tetrakis(4-carboxy-phenyl)-silane.[12–15] A few three-dimensional open frameworks have been reported for the connection between the methanetetra-*p*-benzoate anion (MTB^{4-}) and metal cations (Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Zr^{4+}, Pb^{2+}).[12,13,16–24] Several transition metal methane-*p*-benzoates show selective gas adsorption behavior for CO_2, H_2, and O_2.[12,17,18,19,25] Additionally, $[Ni_2(\text{cyclam})_2(\text{MTB})]\cdot 8H_2O\cdot 4DMF$ (DMF = dimethylformamide, cyclam = 1,4,8,11-tetraazacyclotetradecane) can be used to produce palladium nanoparticles, whereas $[Ni_4(\mu_6\text{-MTB})_2(\mu_2\text{-}H_2O)_4(H_2O)_4]\cdot 10DMF\cdot 11H_2O$ and $[Pb_4(\mu_8\text{-MTB})_2(H_2O)_4]\cdot 5DMF\cdot H_2O$ act as catalysts in Knoevenagel condensation reactions.[17,18,26]

Herein, we report on the crystal structures of two cadmium(II) methanetetra-*p*-benzoates with a three-dimensional open framework ($Cd_2[\mu_8\text{-MTB}]\cdot 3H_2O\cdot DMF$) and a two-dimensionally polymeric structure ($[Cd_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2]\cdot 7DMF$), respectively.

Results and Discussion

$Cd_2[\mu_8\text{-MTB}]\cdot 3H_2O\cdot DMF$ (1)

In $Cd_2[\mu_8\text{-MTB}]\cdot 3H_2O\cdot DMF$ (**1**) there are two crystallographically independent Cd^{2+} cations. Cd(1) occupies a crystallographic inversion center (Wyckoff position 4*c*), whereas Cd(2) lies on a twofold crystallographic axis of space-group *C*2/*c* (Wyckoff position 4*e*). Cd(1) is sixfold coordinated in a slightly distorted octahedral manner by four carboxylate oxygen atoms [2 × O(2), 2 × O(4)], from four crystallographically equivalent methanetetra-*p*-benzoate tetraanions (MTB^{4-}) and twice by the water molecule O(1w) (Figure 1a). The Cd–O distances range from 221.2(3) to 231.3(3) pm (Table 1, Table 2). The bond angles within the octahedron differ marginally from the ideal values, except the angles between the oxygen atoms O(2) and O(4). Thus, the octahedron can be described by D_{2d} symmetry in good approximation. Cd(2) is sur-

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Table 1. The coordination of Cd^{2+} in $Cd_2[\mu_8\text{-}MTB]\cdot 3H_2O\cdot DMF$ (**1**).

Distance /pm					
Cd(1)–O(2)	228.7(3)	2x	Cd(2)–O(1)	221.3(3)	2x
Cd(1)–O(4)	231.3(3)	2x	Cd(2)–O(3)	235.4(3)	2x
Cd(1)–O(1w)	221.2(3)	2x	Cd(2)–O(4)	241.1(3)	2x
Bond angle /°					
$O(1w)^{\#1}$–Cd(1)–O(1w)	180.0		$O(1)^{\#4}$–Cd(2)–O(3)	98.89(11)	
O(1w)–Cd(1)–O(2)	92.10(12)		$O(1)^{\#4}$–Cd(2)–$O(1)^{\#5}$	107.59(15)	
O(1w)–Cd(1)–$O(2)^{\#1}$	87.90(12)		$O(1)^{\#5}$–Cd(2)–O(4)	86.88(10)	
$O(1w)^{\#1}$–Cd(1)–$O(4)^{\#2}$	88.15(13)		$O(1)^{\#5}$–Cd(2)–O(3)	137.52(11)	
$O(1w)^{\#1}$–Cd(1)–$O(4)^{\#3}$	91.85(13)		$O(1)^{\#4}$–Cd(2)–O(4)	102.14(10)	
O(2)–Cd(1)–$O(4)^{\#2}$	99.12(10)		$O(3)^{\#6}$–Cd(2)–O(3)	81.94(16)	
O(2)–Cd(1)–$O(2)^{\#1}$	180.0		O(3)–Cd(2)–O(4)	54.85(10)	
O(2)–Cd(1)–$O(4)^{\#3}$	80.88(10)		O(3)–Cd(2)–$O(4)^{\#6}$	112.07(10)	
$O(4)^{\#2}$–Cd(1)–$O(4)^{\#3}$	180.00(16)		O(4)–Cd(2)–$O(4)^{\#6}$	164.78(13)	

Symmetry codes: #1: –x+0.5; –y+0.5; –z, #2: –x;–y;–z, #3: x+0.5;y+0.5;z, #4: –x+0.5;y–0.5;–z–0.5, #5: x–0.5;y–0.5;z, #6: –x–1;y;–z–0.5.

rounded by six carboxylate oxygen atoms stemming from four equivalent MTB^{4-} anions with bond lengths between 221.3(3) and 241.1(3) pm. The coordination polyhedron strongly deviates from an ideal octahedron as well as from an ideal trigonal prism (Figure 1b, Table 1). Thus the Cd(2) polyhedron can be best described as a distorted intermediate between an octahedral and a trigonal prismatic coordination. Employing the method of *Brese* and *O'Keeffe*[27] the bond valence sum for Cd(1) and Cd(2) is calculated to 2.24 and 1.97, respectively. Neighboring Cd(1) and Cd(2) polyhedra are linked by a common corner [O(4)] leading to sinusoidal infinite polyhedra chains along [101] (Figure 1c). The shortest Cd(1)···Cd(2) contact is 387.53(2) pm.

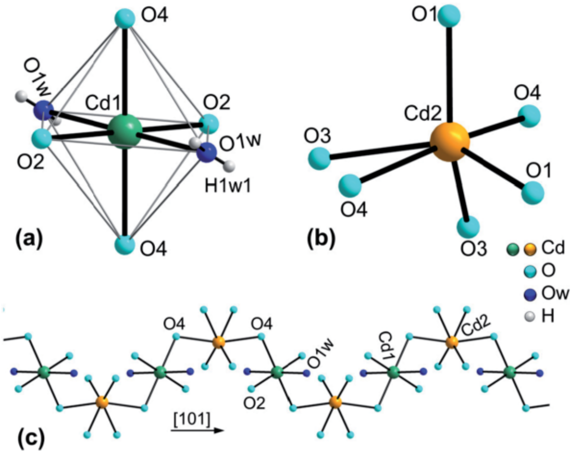

Figure 1. (a,b) The coordination environment of Cd(1) and Cd(2) in $Cd_2[\mu_8\text{-}MTB]\cdot 3H_2O\cdot DMF$ (**1**). (c) The connection between the Cd(1) and Cd(2) polyhedra leads to infinite chains (hydrogen atoms are omitted for clarity).

Chun et al.[20] reported on a tetragonal three-dimensionally connected cadmium methanetetra-p-benzoate complex ($[Cd_4(MTB)_2(DMF)_4]\cdot 4DMF\cdot 4H_2O$), in which the sevenfold coordinated Cd^{2+} cations form tetranuclear clusters and all carboxylate groups act as chelate ligands.

The tetraanion of the methanetetra-p-benzoic acid (MTB^{4-}) is situated on a twofold axis. The C–O bond lengths in the carboxylate groups are in the range between 124.7(5) and 127.6(5) pm. The carboxylate groups with C(8) are nearly coplanar to the C_6 rings [torsion angle 2.3(3)°] and the carboxylate groups with C(15) are slightly twisted by 9.7(4)°. Moreover, the phenyl rings are twisted against each other by 63.3(1)° to 74.2(2)°. Each MTB^{4-} anion connects eight cadmium cations and adopts a μ_8 coordination mode (Figure 2a). All carboxylate oxygen atoms are involved in the coordination

Table 2. Selected bond lengths and angles of the MTB^{4-} anion in $Cd_2[\mu_8\text{-}MTB]\cdot 3H_2O\cdot DMF$ (**1**).

Distance /pm			
C(8)–O(1)	127.6(5)	C(15)–O(3)	125.4(5)
C(8)–O(2)	124.7(5)	C(15)–O(4)	127.0(5)
C(5)–C(8)	151.0(5)	C(12)–C(15)	149.5(5)
C(1)–C(2)	154.5(4)	C(1)–C(9)	155.3(4)
Bond angle /°			
O(1)–C(8)–O(2)	124.9(3)	O(3)–C(15)–O(4)	120.9(4)
O(2)–C(8)–C(5)	119.1(3)	O(3)–C(15)–C(12)	120.0(4)
C(9)–C(1)–$C(9)^{\#7}$	108.6(4)	C(2)–C(1)–$C(2)^{\#7}$	107.5(4)
C(2)–C(1)–C(9)	110.02(18)	C(2)–C(1)–$C(9)^{\#7}$	110.34(18)

Symmetry code: #7: –x;y; –z + 0.5.

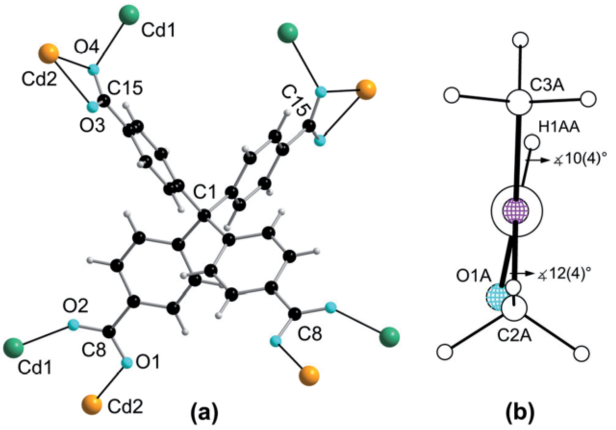

Figure 2. (a) The connection between the tetraanion of the methanetetra-*p*-benzoic acid (MTB^{4-}) and the Cd^{2+} cations in **1**. (b) Newman projection of the *N*,*N*-dimethylformamide (DMF) molecule along N(1A)–C(1A).

to Cd^{2+}. The carboxylate groups with C(15) are bonded to Cd(1) in a monodentate and to Cd(2) in a bidentate manner. The coordination leads to a μ_2-η^2:η^1 connection mode. Whereas the carboxylate groups with C(8) show only a monodentate coordination to Cd^{2+} with a μ_2-η^1:η^1 mode.

The cadmium centered polyhedra chains are linked by MTB^{4-} anions to an open three-dimensional framework (Figure 3, Figure 4). Each MTB^{4-} anion connects three Cd-polyhedra chains (Figure S1, Supporting Information). Channel-like voids extend along [$\bar{1}$10] and [110]. The openings of these channels are approximately 670 pm × 360 pm with van der Waals radii[28] of the framework atoms taken into account. The channels accommodate in a disordered manner water molecules [O(2w), O(3w)] and *N*,*N*-dimethylformamide (DMF) molecules not bound to Cd^{2+}. Figure 2b shows the Newman projection of the DMF molecule along the N(1A)–C(1A) bond. The torsion angles between C(2A)/O(1A) and C(3A)/O(1A) of 12(4)° and 170(2)° are comparable with values found in gaseous DMF.[29] The DMF molecules are only connected to the framework by weak C–H···O contacts to the phenyl rings (Table 3). Furthermore, the coordinated water molecule O(1w) acts as donator in medium and strong hydrogen bonds to the uncoordinated water molecules [O(2w), O(3w)] and to the carboxylate oxygen atom O(1). The water molecule O(2w) builds up a weak hydrogen bond to the DMF oxygen atom O(1A).

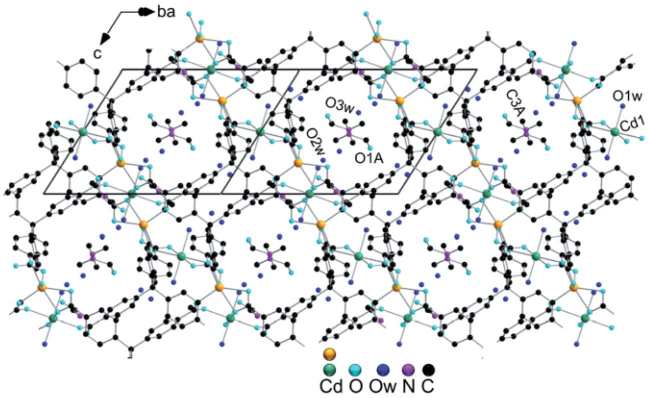

Figure 3. Crystal structure of $Cd_2[\mu_8\text{-MTB}]\cdot 3H_2O\cdot DMF$ (**1**) viewed from [$\bar{1}$10]. Hydrogen atoms are omitted for clarity.

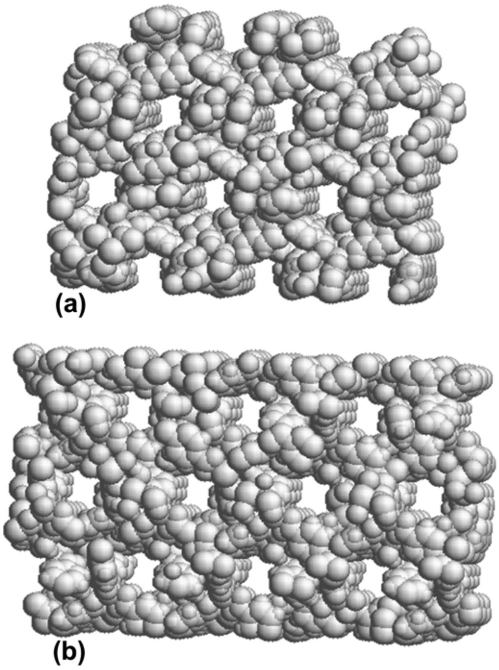

Figure 4. Space-filling model of the framework of **1**. (a) View along [$\bar{1}$10], (b) view along [110]. DMF molecules and uncoordinated water molecules are omitted.

Table 3. Hydrogen bonds in **1**.

	d(O···O) /pm	Angle (O–H···O) /°
O(1w)–H(1w1)···O(2w)	262.3(10)	143(1)
O(1w)–H(1w1)···O(3w)	258.2(10)	159(1)
O(1w)–H(2w1)···$O(1)_{MTB}$	269.8(5)	169(1)
O(2w)–H(2wB)···$O(1A)_{DMF}$	264.4(10)	136(1)
	d(C···O) /pm)	Angle (C–H···O) /°
$C(11)_{MTB}$–H(11A)···$O(1A)_{DMF}$	374.3(10)	147(1)

Table 4. The coordination of Cd^{2+} in $Cd_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2]\cdot 7DMF$ (**2**).

Distance /pm			
Cd(1)–O(1)	284.3(7)	Cd(2)–O(1)	227.0(6)
Cd(1)–O(2)	224.4(5)	Cd(2)–O(3)	225.1(5)
Cd(1)–O(3)	238.9(5)	Cd(2)–O(6)	266.9(6)
Cd(1)–O(4)	254.9(5)	Cd(2)–O(7)	246.3(6)
Cd(1)–O(5)	254.7(5)	Cd(2)–O(8)	234.3(6)
Cd(1)–O(6)	233.2(5)	Cd(2)–N(3)	231.5(7)
Cd(1)–N(1)	231.9(6)	Cd(2)–N(4)	234.8(8)
Cd(1)–N(2)	234.9(6)		
Bond angle /°			
O(2)–Cd(1)–N(2)	154.5(2)	N(3)–Cd(2)–N(4)	70.8(3)
$O(4)^{\#2}$–Cd(1)–$O(5)^{\#1}$	170.81(18)	$O(3)^{\#2}$–Cd(2)–$O(7)^{\#3}$	100.76(19)
N(1)–Cd(1)–$O(3)^{\#2}$	146.3(2)	$O(8)^{\#3}$–Cd(2)–$O(7)^{\#3}$	53.7(2)
$O(6)^{\#1}$–Cd(1)–N(2)	83.15(18)	O(1)–Cd(2)–N(4)	144.1(2)
$O(3)^{\#2}$–Cd(1)–$O(5)^{\#1}$	125.37(18)	$O(3)^{\#2}$–Cd(2)–N(3)	153.0(2)
N(2)–Cd(1)–O(1)	155.1(2)	$O(6)^{\#1}$–Cd(2)–$O(7)^{\#3}$	149.5(2)

Symmetry codes: #1: x+2;y–1;z, #2: x–1;y;z, #3: –x;–y+1; –z+1.

$[Cd_4\,(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2]\cdot 7DMF$ (2)

In **2**, the cadmium cations occupy general positions of space group $P\bar{1}$. Cd(1) is surrounded by two nitrogen atoms [N(1), N(2)] from the 2,2′-bipyridine (bipy) molecule (**I**) and six carboxylate oxygen atoms from three crystallographically equivalent MTB^{4-} anions. The Cd(1)–N distances are 231.9(6) and 234.9(6) pm, respectively (Table 4). The Cd(1)–O bond lengths to O(2), O(3), O(4), O(5), and O(6) are in the range between 224.4(5) and 254.9(5) pm, whereas the bond to O(1) is 284.3(7) pm. Although this Cd–O bond is weak, it is significantly shorter than the sum of the van der Waals radii. A similar situation was reported with several Cd complexes.[28,30,31–37] The resulting coordination (7+1) can be approximately described as a distorted two-capped octahedron. As seen in Figure 5a, the equatorial plane is spanned by N(1), O(3), O(4), and O(5) deviating slightly from planarity with an average and maximum deviation of 4.4(3) pm and 5.2(7) pm, respectively. The axial positions are occupied by the nitrogen atom N(2) and the carboxylate oxygen atom O(2).

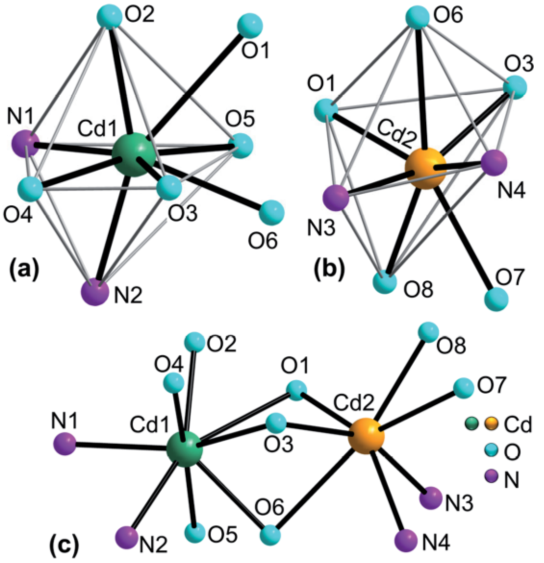

Figure 5. (a,b) The coordination spheres of Cd^{2+} in $[Cd_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2]\cdot 7DMF$ (**2**). (c) Connection between the Cd(1) and Cd(1) polyhedra.

Alternatively, the coordination polyhedron might also be considered as a monocapped pentagonal bipyramid with O(1) as the capping atom. However, the pentagonal equatorial plane through N(1), O(3), O(4), O(5) and O(6) deviates considerably from planarity [average 20.6(4) pm] with a maximum deviation of 35.3(6) pm for O(6). The coordination sphere of Cd(2) is built up by two nitrogen atoms [N(3), N(4)] from the 2,2′-bipyridine molecule (**II**) and five carboxylate oxygen atoms [O(1), O(3), O(6), O(7), O(8)] stemming from four crystallographically equivalent MTB^{4-} anions. The coordination environment (cn = 7) forms a strongly distorted monocapped octahedron with O(7) as the capping atom (Figure 5b). The bond lengths are 231.5(7) and 234.8(8) pm for Cd(2)–N and 225.1(5)–266.9(6) pm for Cd(2)–O. The bond angles within the Cd(1) and Cd(2) polyhedra differ significantly from those in an ideal octahedron (Table 4). According to *Brese* and *O'Keeffe*[27] the bond valence sum for Cd(1) and Cd(2) was calculated to 2.14 and 2.15, respectively.

As shown in Figure 5c, neighboring Cd(1) and Cd(2) polyhedra share a common face [O(1), O(3), O(6)] leading to dimeric polyhedra units. The Cd(1)···Cd(2) distance is 347.32(7) pm.

The methanetetra-*p*-benzoate anion (MTB^{4-}) lies on a general crystallographic position. The phenyl rings within the MTB^{4-} anion are twisted against each other by 58.4(2)° to 87.4(2)°. As seen in Figure 6 each tetraanion bridges seven cadmium cations. All carboxylate groups are bound to Cd(2) in a monodentate manner, except the COO^- group with C(29), which coordinates in a bidentate mode only to Cd(2). The Cd(1) cations are exclusively bidentately coordinated by the carboxylate groups. Thus, the carboxylate group with C(29) coordinates in a μ_1-η^2 mode, whereas the remaining carboxylate groups show a μ_2-η^2:η^1 connection. The C–O bonds are between 121.4(12) and 128.7(9) pm (Table 5). The carboxylate groups with C(8) and C(15) are slightly tilted to the C_6 rings [torsion angles 7.0(5)°, 3.9(4)°], whereas the carboxylate

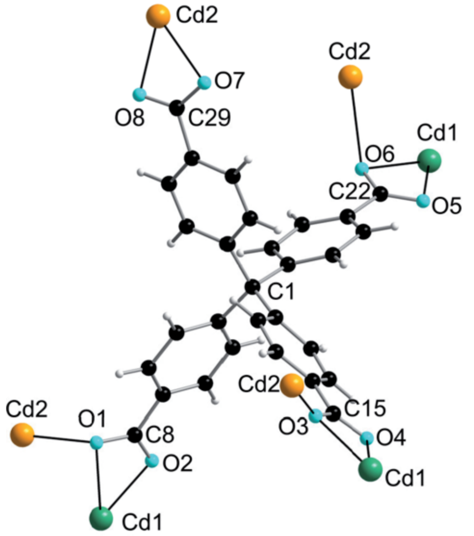

Figure 6. The connection between the $[MTB]^{4-}$ tetraanion and the cadmium cations in **2**.

Table 5. Selected bond lengths and angles of the MTB^{4-} anion and the 2,2′-bipyridine molecules in $Cd_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2]\cdot 7DMF$ (**2**).

Distance /pm			
MTB^{4-}			
C(8)–O(1)	124.9(10)	C(22)–O(5)	124.9(10)
C(8)–O(2)	128.3(10)	C(22)–O(6)	127.5(9)
C(15)–O(3)	128.7(9)	C(29)–O(7)	125.5(11)
C(15)–O(4)	124.3(9)	C(29)–O(8)	121.4(12)
C(5)–C(8)	148.9(10)	C(12)–C(15)	149.0(10)
C(19)–C(22)	151.7(10)	C(26)–C(29)	152.4(10)
C(1)–C(2)	156.0(9)	C(1)–C(16)	155.2(9)
C(1)–C(9)	152.7(9)	C(1)–C(23)	154.2(9)
2,2′-Bipyridine **I**			
N(1)–C(30)	133.5(11)	N(2)–C(39)	131.6(11)
N(1)–C(34)	135.4(10)	N(2)–C(35)	134.4(9)
C(33)–C(34)	138.3(11)		
2,2′-Bipyridine **II**			
N(3)–C(40)	132.2(12)	N(4)–C(49)	132.4(13)
N(3)–C(44)	134.1(11)	N(4)–C(45)	135.0(11)
C(44)–C(45)	149.9(13)		
Bond angle /°			
MTB^{4-}			
O(1)–C(8)–O(2)	123.3(7)	O(5)–C(22)–O(6)	123.4(7)
O(3)–C(15)–O(4)	120.9(7)	O(7)–C(29)–O(8)	123.5(8)
O(1)–C(8)–C(5)	119.1(7)	O(3)–C(15)–C(12)	118.5(6)
O(5)–C(22)–C(19)	119.8(7)	O(7)–C(29)–C(26)	118.2(8)
C(9)–C(1)–C(23)	113.5(5)	C(9)–C(1)–C(2)	101.8(5)
C(23)–C(1)–C(2)	113.1(6)	C(9)–C(1)–C(16)	113.1(6)
C(23)–C(1)–C(16)	102.7(5)	C(2)–C(1)–C(16)	113.1(5)
2,2′-Bipyridine **I/II**			
N(1)–C(34)–C(35)	116.1(7)	N(2)–C(35)–C(34)	116.5(6)
N(3)–C(44)–C(45)	116.9(7)	N(4)–C(45)–C(44)	116.1(8)

groups with C(22) and C(29) are twisted by 23.9(3)° and 15.5(5)°.

The two crystallographically independent 2,2′-bipyridine molecules (**I**, **II**) are planar with small torsion angles between the C_5N rings of 1.9(3)° and 3.3(3)°, respectively

In **2**, the coordination of the MTB^{4-} tetraanions to the Cd(2) cations leads to infinite layers extending in the (001) plane (Figure 7 and Figure 8) with honeycomb-like pattern. The connection between Cd(1) and MTB^{4-} leads to a stabilization of the structure by compensating the resulting negative charge of the layers. Each MTB^{4-} anion is linked to four dimeric Cd(1)/Cd(2) polyhedra units (Figure S2, Supporting Information). The 2,2′-bipyridine molecules bound to Cd^{2+} are not essential for the two-dimensionally infinite connection, but they complete the Cd coordination sphere. This obviously prevents from formation of a three-dimensional framework. The 2,2′-bipyridine molecule **I** extends into the openings of the layer acting as void filling group (Figure 7). The cavities along [001] (see inset in Figure 7) have dimensions of about 320 pm × 340 pm (inclusive van der Waals radii[28]).

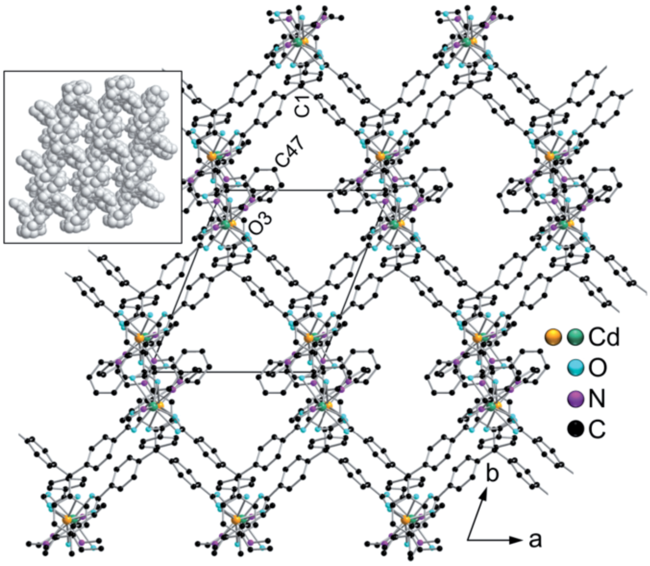

Figure 7. Crystal structure of $[Cd_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2]\cdot 7DMF$ (**2**) viewed on (001). Hydrogen atoms and uncoordinated DMF molecules are omitted for clarity. The inset shows a space-filling model including hydrogen atoms.

The layers are stacked in a **…**AA**…** sequence along the [001] direction. Neighboring layers are not connected by any interlayer hydrogen bonds. On the other hand, the layers are confined by the 2,2′-bipyridine molecules (**I**) coordinated to Cd(1) pointing towards the interlayer space. As seen in Figure 9, the 2,2′-bipyridine molecules (**I**) are parallel to the 2,2′-bipyridine molecules (**I**) of the neighboring layer along [$\bar{1}$10]. The distance between these 2,2′-bipyridine molecules is 348 pm indicating a very close π–π interaction between the bipyridine rings, which additionally stabilizes the crystal structure.[38,39] Within each layer, neighboring 2,2′-bipyridine molecules (**II**) bound to Cd(2) are parallel to each other with a distance of 345 pm. There are five crystallographically independent DMF molecules (**I**–**V**) not bound to Cd^{2+}, which are situated within the layers as well as intercalated between adjacent layers (Figure 8, Figure S3, Supporting Information). The partly disordered DMF molecules form weak and medium C-H···O hydrogen bonds to the phenyl rings of MTB^{4-} and to the C_5N-rings of the 2,2′-bipyridine molecules (Table 6). Some C–N–C–O torsion angles of the DMF molecules [0(3)°-12(4)°], differ considerably from the values found in gaseous DMF

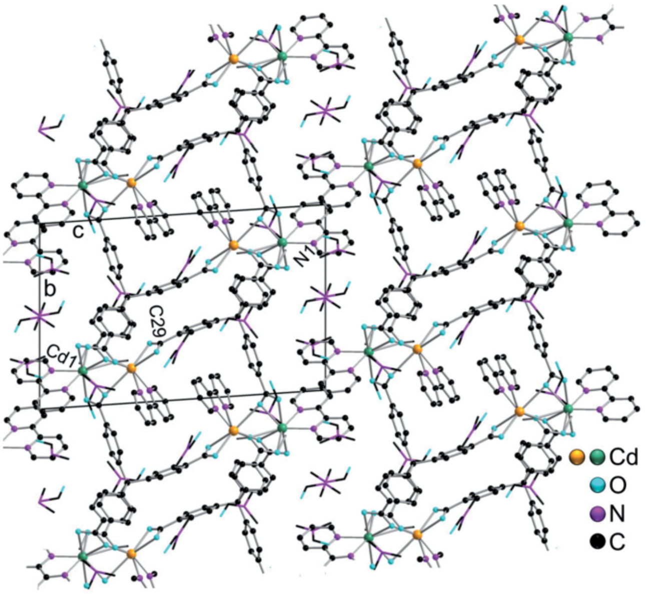

Figure 8. View along [100] in **2**. DMF molecules are drawn as sticks. Hydrogen atoms are omitted for clarity.

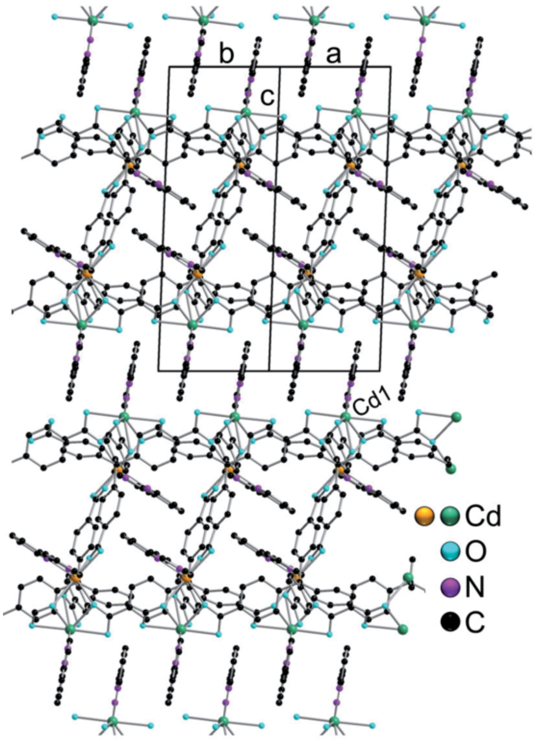

Figure 9. Crystal structure of **2** viewed from [110]. Hydrogen atoms and uncoordinated DMF molecules are omitted for clarity.

(Figure S4, Supporting Information).[29] The small torsion angles of 4(2)° in DMF **II** and 0(3)° in DMF **III** are probably caused by the formation of strong C–H···O hydrogen bonds with short C···O contacts.

Table 6. Hydrogen bonds in **2**.

	d(C···O) /pm	<(C–H···O) /°
$C(24)_{MTB}$–H(24A)···$O(1DA)_{DMF–I}$	338.6(16)	147(1)
$C(21)_{MTB}$–H(21A)···$O(1DA)_{DMF–I}$	356.6(15)	168(1)
$C(4)_{MTB}$–H(4A)···$O(1DB)_{DMF–II}$	351.4(12)	157(1)
$C(6)_{MTB}$–H(6A)···$O(1DE)_{DMF–V}$	355(2)	132(1)
$C(40)_{MTB}$–H(40A)···$O(1DE)_{DMF–V}$	320(3)	123(1)
$C(47)_{bipy}$–H(47A)···$O(1DA)_{DMF–I}$	327.6(17)	124(1)
$C(31)_{bipy}$–H(31A)···$O(1DB)_{DMF–II}$	326.4(19)	170(1)
$C(37)_{bipy}$–H(37A)···$O(1DC)_{DMF–III}$	318(3)	142(1)
$C(38)_{bipy}$–H(38A)···$O(1DD)_{DMF–IV}$	377(3)	154(1)
$C(48)_{bipy}$–H(48A)···$O(1DD)_{DMF–IV}$	388(3)	134(1)

Conclusions

We reported on the synthesis and structural properties of $Cd_2[\mu_8\text{-MTB}]\cdot 3H_2O\cdot DMF$ (**1**) and $[Cd_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2]\cdot 7DMF$ (**2**). In **1** the connection between the Cd^{2+} cations and the MTB^{4-} tetra-anions leads to an open three-dimensional framework with channels along [$\bar{1}$10] and [110]. The channels accommodate uncoordinated DMF and water molecules. Compound **2** was synthesized with 2,2′-bipyridine as an additional ligand. The Cd^{2+} cations are linked by MTB^{4-} anions to form infinite layers parallel to (001). The layers contain small openings. The 2,2′-bipyridine molecules act as N-donor ligands completing the coordination environment of Cd^{2+}. π–π interactions between 2,2′-bipyridine rings of neighboring layers obviously contribute to stabilize the structure. The results confirm that ligands with tetrahedrally directed functional groups favor the formation of diamondoid arrangements as expected and encourage further use of these buildings blocks in the synthesis of open framework structures.

Experimental Section

Synthesis of Tetrakis(4-bromophenyl)methane:[40] Tetraphenylmethane (54 mmol) synthesized as described elsewhere,[41] was slowly dropped in 60 mL bromine in a round-bottomed flask under ice-cooling and stirred for 45 min. Afterwards, 150 mL ethanol was added (cooling with ice). The precipitate formed was collected by filtering and dried. The solid was dissolved in 500 mL $CHCl_3$ and washed with aqueous Na_2SO_3 solution. The organic phase was distilled and the white product formed was recrystallized from a dioxane/ acetonitrile mixture. Yield 63 %. EA: (molecular weight 636.01): C 46.46 (calcd. 47.21); H 2.30 (2.54); Br 51.24 % (50.25 %). **^{1}H NMR** ([D_6]DMSO): δ (ppm) = 6.99, 7.37. **^{13}C NMR** ([D_6]DMSO): δ (ppm) = 63.6, 120.8, 131.1, 132.4, 144.4.

Synthesis of Methanetetra-*p*-benzoic Acid (H_4MTB):[42] The reaction was carried out in an argon atmosphere. Tetrakis(4-bromophenyl) methane (7.9 mmol) was dissolved in 500 mL dried THF. Buthyllithium was slowly dropped into the THF solution at –70 °C. The solution was stirred for 10 min. Afterwards, CO_2 was introduced for 2 h into the solution whilst stirring and the reaction mixture was meanwhile slowly heated to room temperature After adding of half concentrated HCl the THF was distilled. The white residue was dissolved in aqueous NaOH and filtered through diatomaceous earth. The filtrate was acidified with HCl. The formed precipitate of methanetetra-*p*-benzoic acid [tetrakis(4-carboxyphenyl)methane] was collected and dried. Yield: 71 %. EA: (molecular weight 496.46): C 68.78 (calcd. 70.16); H 4.51 % (4.06 %). **^{1}H NMR** ([D_6]DMSO): δ (ppm) = 7.29, 7.85; **^{13}C NMR** ([D_6]DMSO): δ (ppm) = 65.2, 128.9, 129.3, 130.5, 149.8, 166.9.

$Cd_2[\mu_8\text{-MTB}]\cdot 3H_2O\cdot DMF$ (1):[42] H_4MTB (0.2 mmol) and $Cd(NO_3)_2\cdot 4H_2O$ (0.4 mmol) were dissolved in 5 mL DMF (*N*,*N*-dimethylformamide) and 2 mL deionized water. The mixture was kept at about 50 °C in a drying oven. After several days, colorless crystals of **1** appeared.

$[Cd_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2]\cdot 7DMF$ (2):[42] H_4MTB (0.2 mmol), 2,2′-bipyridine (0.8 mmol), and $Cd(NO_3)_2\cdot 4H_2O$ (0.4 mmol) were dissolved in 7 mL DMF. The mixture was kept at about 70 °C in a drying oven. Colorless crystals of **2** appeared after several days.

X-ray Diffraction: The intensity data were collected with a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.[43–45] The structures were solved by direct methods (SHELXS[46]) and refined by full-matrix least-squares techniques against $|F_o|^2$ (SHELXL-97[46]). The hydrogen atoms bound to the water

Table 7. Crystallographic data.

	1	2
Empirical formula	$C_{32}H_{29}NCd_2O_{12}$	$C_{119}H_{113}N_{15}Cd_4O_{23}$
Crystal system	monoclinic	triclinic
Space group	$C2/c$ (no.15)	$P\bar{1}$ (no.2)
Lattice constants		
a /pm	1821.30(6)	1224.84(4)
b /pm	2175.08(6)	1418.85(5)
c /pm	1269.87(4)	2033.49(4)
α /°	90	85.831(2)
β /°	129.684(1)	88.351(2)
γ /°	90	68.261(1)
Cell volume /nm^3	3.8714(2)	3.27391(17)
Formulas in unit cell	4	1
Formula weight /g·mol^{-1}	844.36	2570.84
Density (calcd.) /g·cm^{-3}	1.449	1.304
Wavelength /pm	71.073	
Absorption coefficient / mm^{-1}	1.153	0.709
Numerical absorption correction	min./max. transmittance 0.6841/0.7456	min./max. transmittance 0.6539/0.7456
Temperature /K	183 (2)	
Crystal size /mm	0.104 × 0.094 × 0.084	0.088 × 0.082 × 0.076
F(000)	1680	1308
Θ range /°	1.87–27.47	2.09–27.45
Limiting indices	h: –23/+23; k: –28/ +28; l: –16/+15	h: –15/14; k: –15/ +18; l: –26/+26
Reflections collected	13612	20389
Independent reflections	4427 (R_{int} = 0.0314)	14138 (R_{int} = 0.0341)
Structure refinement	Full-matrix least-squares on $|F|^2$	
Refined parameters	219	767
Goodness-of-fit on $|F|^2$	1.079	1.039
Residuals (all data)	R_1 = 0.0479, wR_2 = 0.1166	R_1 = 0.1191, wR_2 = 0.2633
Max. features in last Difference Fourier synthesis /e·nm^{-3}	1255 and –646	5869 and –2312

molecule O(1 W) of **1** were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically.[46] DIAMOND was used for structure representations.[47] Crystallographic data are compiled in Table 7.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1862572 for **1** and CCDC-1862573 for **2** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Crystal structure of compound **1** viewed from [101] (Figure S1). Connection between anions and cations in compound **2** (Figure S2) Crystal structure of **2** viewed on (001) (Figure S3). Newman projection of *N*,*N*-dimethylformamide (DMF) molecules in **2** (Figure S4). Bond lengths in **1** and **2** (Tables S1 and S2)

Keywords: Methanetetra-*p*-benzoic acid; Cadmium; Coordination polymer; Crystal structure; Metal-organic framework (MOF)

References

[1] L. Ma, C. Abney, W. Lin, *Chem. Soc. Rev.* **2009**, *38*, 1248–1258.
[2] M. Plabst, L. B. McCusker, T. Bein, *J. Am. Chem. Soc.* **2009**, *131*, 18112–18118.
[3] A. C. Sudik, N. W. Ockwig, A. R. Millward, A. P. Cote, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 7110–7118.
[4] M. O'Keeffe, O. M. Yaghi, *Chem. Rev.* **2012**, *112*, 675–702.
[5] R. Köferstein, C. Robl, *Z. Anorg. Allg. Chem.* **2015**, *641*, 1886–1891.
[6] D. Poleti, L. Karanović, *Acta Crystallogr., Sect. C* **1989**, *45*, 1716–1718.
[7] R. Köferstein, C. Robl, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1035–1037.
[8] Z.-J. Lin, J. Lü, M. Hong, R. Cao, *Chem. Soc. Rev.* **2014**, *43*, 5867–5895.
[9] O. Ermer, A. Eling, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 829–833.
[10] O. Ermer, *J. Am. Chem. Soc.* **1988**, *110*, 3747–3754.
[11] L. Cao, P. Wang, X. Miao, Y. Dong, H. Wang, H. Duan, Y. Yu, X. Li, P. J. Stang, *J. Am. Chem. Soc.* **2018**, *140*, 7005–7011.
[12] L. Ma, A. Jin, Z. Xie, W. Lin, *Angew. Chem. Int. Ed.* **2009**, *48*, 9905–9908.
[13] J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 8239–8247.
[14] M. Zhang, Y.-P. Chen, H.-C. Zhou, *CrystEngComm* **2013**, *15*, 9544–9552.
[15] R. P. Davies, R. Less, P. D. Lickiss, K. Robertson, A. J. P. White, *Cryst. Growth Des.* **2010**, *10*, 4571–4581.
[16] X. Jiang, H.-Z. Kou, *RSC Adv.* **2015**, *15*, 89052–89055.
[17] Y. E. Cheon, M. P. Suh, *Chem. Eur. J.* **2008**, *14*, 3961–3967.
[18] M. Almáši, V. Zeleňák, M. Opanasenko, J. Čejka, *Dalton Trans.* **2014**, *43*, 3730–3738.
[19] Y. E. Cheon, M. P. Suh, *Chem. Commun.* **2009**, 2296–2298.
[20] H. Chun, D. Kim, D. N. Dybtsev, K. Kim, *Angew. Chem. Int. Ed.* **2004**, *43*, 971–974.
[21] H. Furukawa, F. Gándara, Y.-B. Zhang, J. Jiang, W. L. Queen, M. R. Hudson, O. M. Yaghi, *J. Am. Chem. Soc.* **2014**, *136*, 4369–4381.
[22] M. Almáši, V. Zeleňák, R. Gyepes, S. Bourrelly, M. V. Opanasenko, P. L. Llewellyn, J. Čejka, *Inorg. Chem.* **2018**, *57*, 1774–1786.
[23] X. Jiang, H.-Z. Kou, *Chem. Commun.* **2016**, *52*, 2952–2955.
[24] M. Almáši, V. Zeleňák, A. Zukal, J. Kuchár, J. Čejka, *Dalton Trans.* **2016**, *45*, 1233–1242.
[25] M. Almáši, V. Zeleňák, R. Gyepes, A. Zukal, J. Čejka, *Colloids Surf. A* **2013**, *437*, 101–107.
[26] M. Almáši, V. Zeleňák, M. V. Opanasenko, J. Čejka, *Catal. Lett.* **2018**, *148*, 2263–2273.
[27] N. E. Brese, M. O'Keeffe, *Acta Crystallogr., Sect. B* **1991**, *47*, 192–197.
[28] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.
[29] G. Schultz, I. Hargittai, *J. Phys. Chem.* **1993**, *97*, 4966–4969.
[30] S.-Z. Hu, Z.-H. Zhou, B. E. Robertson, *Z. Kristallogr.* **2009**, *224*, 375–383.
[31] T. C. Stamatatos, E. Katsoulakou, V. Nastopoulos, C. P. Raptopoulou, E. Manessi-Zoupa, S. P. Perlepes, *Z. Naturforsch. B* **2003**, *58*, 1045–1054.
[32] Q. Shi, R. Cao, D.-F. Sun, M.-C. Hong, Y.-C. Liang, *Polyhedron* **2001**, *20*, 3287–3293.
[33] W. Clegg, J. T. Cressey, A. McCamley, B. P. Straughan, *Acta Crystallogr., Sect. C* **1995**, *51*, 234–235.
[34] A. Tahli, Ü. Köc, R. F. M. Elshaaeawy, A. C. Kautz, C. Janiak, *Crystals* **2016**, *6*, 23.
[35] J. K. Shiba, R. Bau, *Inorg. Chem.* **1978**, *17*, 3484–3488.
[36] C. Gagnon, A. L. Beauchamp, D. Tranqui, *Can. J. Chem.* **1979**, *57*, 1372–1376.
[37] M. A. Romero, M. N. Moreno, J. Ruiz, M. P. Sanchez, F. Nieto, *Inorg. Chem.* **1986**, *25*, 1498–1501.
[38] M. O. Sinnokrot, E. F. Valeev, C. D. Sherrill, *J. Am. Chem. Soc.* **2002**, *124*, 10887–10893.
[39] L. Han, H.-M. Luo, Q.-H. Meng, Y.-F. Luo, R.-H. Zeng, *Acta Crystallogr., Sect. E* **2010**, *66*, o68–o69.
[40] T. J. Zimmermann, T. J. J. Müller, *Synthesis* **2002**, *9*, 1157–1162.
[41] M. Grimm, B. Kirste, H. Kurreck, *Angew. Chem.* **1986**, *98*, 1095–10099.
[42] S. Harms, Dissertation, Universität Jena, Germany, **2010**.
[43] COLLECT, Data Collection Software; Nonius B. V., Netherlands, **1998**.
[44] Z. Otwinowski, W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode*, in *Methods in Enzymology*, vol. 276, *Macromolecular Crystallography*, Part A (Eds.: C. W. Carter, R. M. Sweet), Academic Press, San Diego, USA, **1997**, pp. 307–326.
[45] SADABS 2.10, Bruker-AXS inc., Madison, WI, USA, **2002**.
[46] G. M. Sheldrick, *Acta Crystallogr., Sect. C* **2015**, *71*, 3–8.
[47] Diamond – Crystal and Molecular Structure Visualization, Crystal Impact H. Putz and K. Brandenburg GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany.

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Syntheses and Crystal Structures of Two Cadmium Methanetetrabenzoates Featured by Open Framework and Infinite Layers