

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

Sven Harms^[a], Roberto Köferstein^[b], Helmar Görls^[a], and Christian Robl^{*[a]}

Abstract: Colourless single crystals of $\text{Cd}_2[\mu_8\text{-MTB}]\cdot 3\text{H}_2\text{O}\cdot \text{DMF}$ (**1**) were prepared in DMF/ H_2O solution. **1**: Space group C2/c (no. 15) with $a = 1821.30(6)$, $b = 2175.08(6)$, $c = 1269.87(4)$ pm, $\beta = 129.684(1)^\circ$. 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 $670 \text{ pm} \times 360 \text{ pm}$. The channel-like voids accommodate water molecules and *N,N*-dimethylformamide (DMF) molecules not bound to Cd^{2+} . Colourless single crystals of $[\text{Cd}_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2]\cdot 7\text{DMF}$ (**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, $\alpha = 85.831(2)^\circ$, $\beta = 88.351(2)^\circ$, $\gamma = 68.261(1)^\circ$. 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 $320 \text{ pm} \times 340 \text{ pm}$.

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 verified in the crystal structure of methanetetraacetic acid

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-carboxyphenyl)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 behaviour for CO_2 , H_2 , and O_2 .^[12,17–19, 25] Additionally, $[\text{Ni}_2(\text{cyclam})_2(\text{MTB})_2]\cdot 8\text{H}_2\text{O}\cdot 4\text{DMF}$ (DMF = dimethylformamide, cyclam = 1,4,8,11-tetraazacyclotetradecane) can be used to produce palladium nanoparticles, whereas $[\text{Ni}_4(\mu_8\text{-MTB})_2(\mu_2\text{-H}_2\text{O})_4(\text{H}_2\text{O})_4]\cdot 10\text{DMF}\cdot 11\text{H}_2\text{O}$ and $[\text{Pb}_4(\mu_8\text{-MTB})_2(\text{H}_2\text{O})_4]\cdot 5\text{DMF}\cdot \text{H}_2\text{O}$ 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 ($\text{Cd}_2[\mu_8\text{-MTB}]\cdot 3\text{H}_2\text{O}\cdot \text{DMF}$) and a two-dimensionally polymeric structure ($[\text{Cd}_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2]\cdot 7\text{DMF}$), respectively.

Results and Discussion

$\text{Cd}_2[\mu_8\text{-MTB}]\cdot 3\text{H}_2\text{O}\cdot \text{DMF}$ (**1**)

In $\text{Cd}_2[\mu_8\text{-MTB}]\cdot 3\text{H}_2\text{O}\cdot \text{DMF}$ (**1**) there are two crystallographically independent Cd^{2+} cations. Cd(1) occupies a crystallographic inversion center (Wyckoff position 4c), whereas Cd(2) lies on a twofold crystallographic axis of space-group C2/c (Wyckoff position 4e). Cd(1) is six-fold coordinated in a slightly distorted octahedral manner by four carboxylate oxygen atoms [2x O(2), 2x 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). 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)

* Prof. Dr. C. Robl
Fax: +49-3641-948152
E-mail: crr@uni-jena.de

[a] Institute of Inorganic and Analytical Chemistry
Friedrich-Schiller-University Jena
Humboldtstrasse 8, 07743 Jena, Germany

[b] Institute of Chemistry, Inorganic Chemistry
Martin Luther University Halle-Wittenberg
Kurt-Mothes-Strasse 2
06120 Halle, Germany

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/zaac.201900089> or from the author.

(3,3-bis(carboxymethyl)glutaric acid) and adamantane-1,3,5,7-

is surrounded by six carboxylate oxygen atoms stemming from four equivalent MTB⁴⁻ 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. Neighbouring 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.

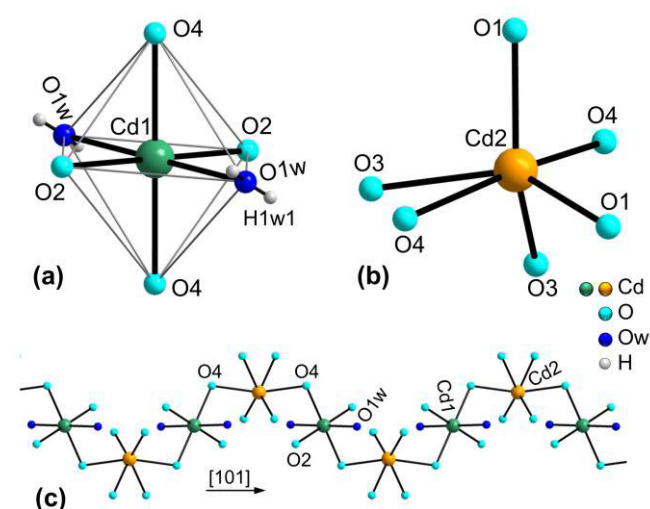


Figure 1. (a,b) The coordination environment of Cd(1) and Cd(2) in Cd₂[μ₈-MTB]·3H₂O·DMF (1). (c) The connection between the Cd(1) and Cd(2) polyhedra leads to infinite chains (hydrogen atoms are omitted for clarity).

Table 1. The coordination of Cd²⁺ in Cd₂[μ₈-MTB]·3H₂O·DMF (1)

Distances (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 angles (°)					
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

Chun et al.^[20] reported on a tetragonal three-dimensionally connected cadmium methanetetra-p-benzoate complex ([Cd₄(MTB)₂(DMF)₄]·4DMF·4H₂O) in which the seven-fold coordinated Cd²⁺ cations form tetranuclear clusters and all carboxylate groups act as chelate ligands.

The tetraanion of the methanetetra-p-benzoic acid (MTB⁴⁻) is situated on a twofold axis. The C–O bond length 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 C₆ 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 MTB⁴⁻ anion connects eight cadmium cations and adopts a μ₈ coordination mode (Figure 2a). All carboxylate oxygen atoms are involved in the coordination to Cd²⁺. 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 μ₂-η²:η¹ connection mode. Whereas the carboxylate groups with C(8) show only a monodentate coordination to Cd²⁺ with a μ₂-η¹:η¹ mode.

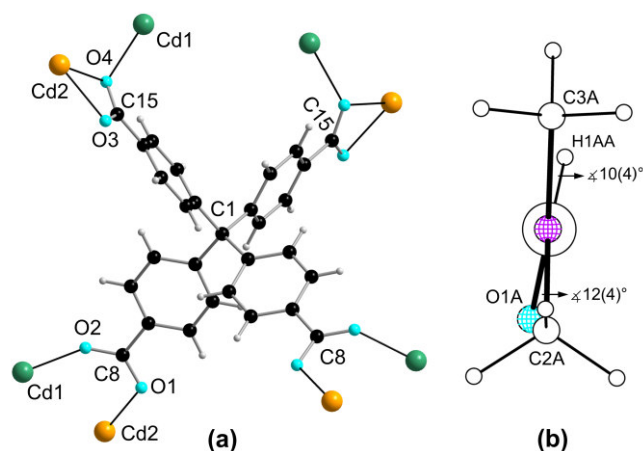


Figure 2. (a) The connection between the tetraanion of the methanetetra-p-benzoic acid (MTB⁴⁻) and the Cd²⁺ cations in (1). (b) Newman projection of the *N,N*-dimethylformamide (DMF) molecule along N(1A)–C(1A).

Table 2. Selected bond lengths and angles of the MTB⁴⁻ anion in Cd₂[μ₈-MTB]·3H₂O·DMF (1)

Distances (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 angles (°)			
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

The cadmium centered polyhedra chains are linked by MTB⁴⁻ anions to an open three-dimensional framework (Figures 3, 4). Each MTB⁴⁻ 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 Cd²⁺. 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 donor 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).

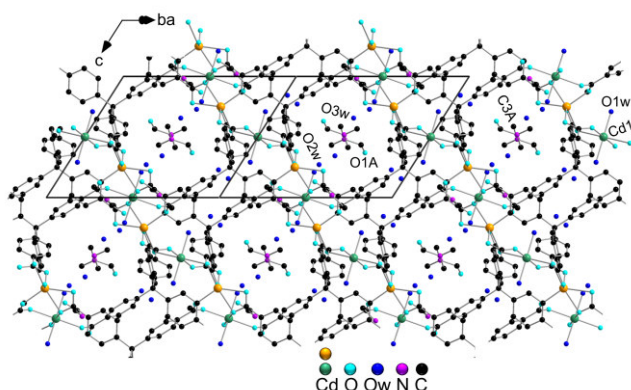


Figure 3. Crystal structure of Cd₂[μ₈-MTB]·3H₂O·DMF (1) viewed from $[\bar{1}10]$. Hydrogen atoms are omitted for clarity.

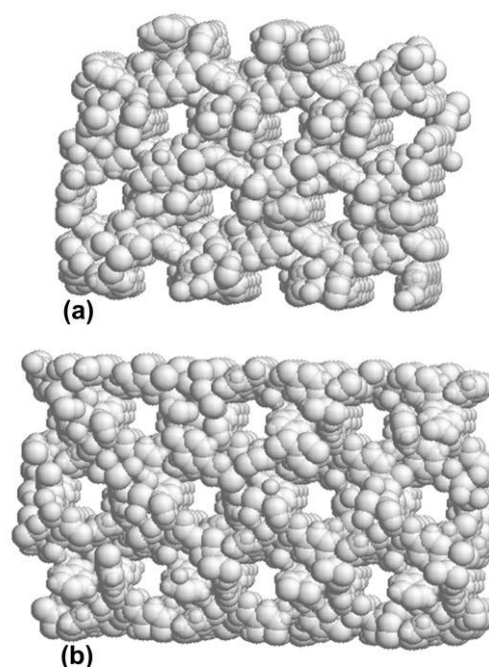


Figure 4. Space-filling model of the framework of 1. (a) view along $[\bar{1}10]$, (b) view along $[110]$. DMF molecules and uncoordinated water molecules are omitted.

Table 3. Hydrogen bonds in 1

	O...O Distance (pm)	O–H...O Angle (°)
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)

	C...O Distance (pm)	C–H...O Angle (°)
C(11) _{MTB} –H(11A)···O(1A) _{DMF}	374.3(10)	147(1)

[Cd₄(2,2'-bipy)₄(μ₇-MTB)₂]·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 different but crystallographically equivalent MTB⁴⁻ 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 – 37] The resulting coordination (7+1) can be approximately described as a distorted two-capped octahedron. As seen in Fig. 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). 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 MTB⁴⁻ anions. The coordination environment (cn = 7) forms a strongly distorted monocapped octahedron with O(7) as the capping atom (Fig. 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 *Breese* 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 Fig. 5c, neighbouring 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.

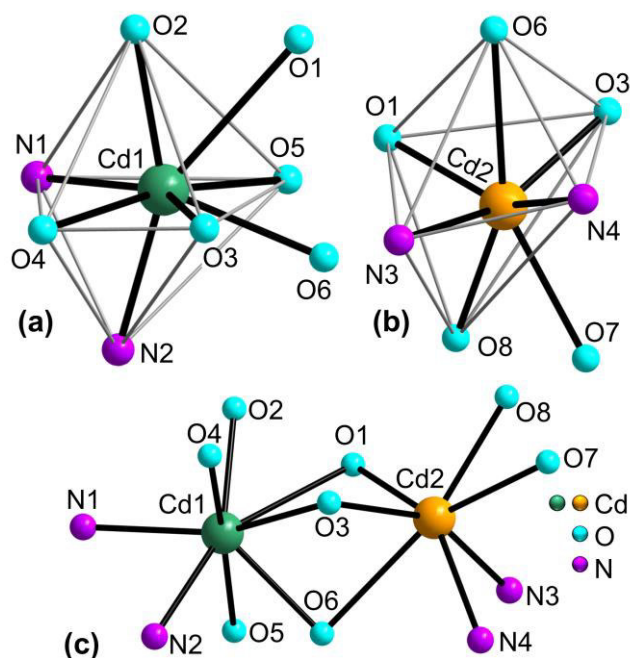


Figure 5. (a,b) The coordination spheres of Cd²⁺ in [Cd₄(2,2'-bipy)₄(μ₇-MTB)₂]₂·7DMF (2). (c) Connection between the Cd(1) and Cd(2) polyhedra.

Table 4. The coordination of Cd²⁺ in Cd₄(2,2'-bipy)₄(μ₇-MTB)₂·7DMF (2)

Distances (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 angles (°)			
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

The methanetetrakis-p-benzoate anion (MTB⁴⁻) lies on a general crystallographic position. The phenyl rings within the MTB⁴⁻ 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 μ₁-η² mode, whereas the remaining carboxylate groups show a μ₂-η²:η¹ 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 C₆ rings (torsion angles 7.0(5)°, 3.9(4)°), whereas the carboxylate 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 C₅N-rings of 1.9(3)° and 3.3(3)°, respectively

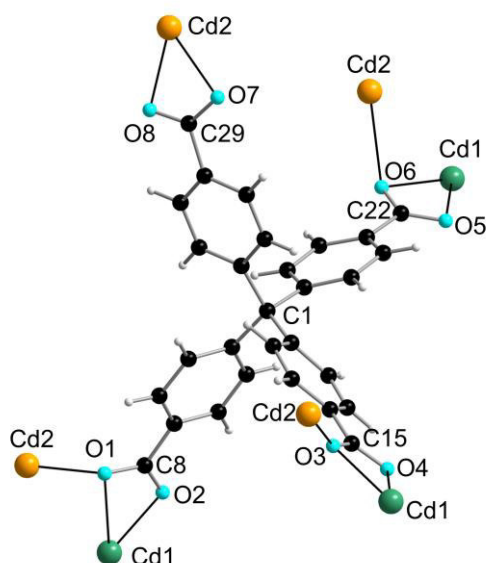


Figure 6. The connection between the $[\text{MTB}]^{4-}$ tetraanion and the cadmium cations in **2**.

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

Distances (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 angles (°)

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)

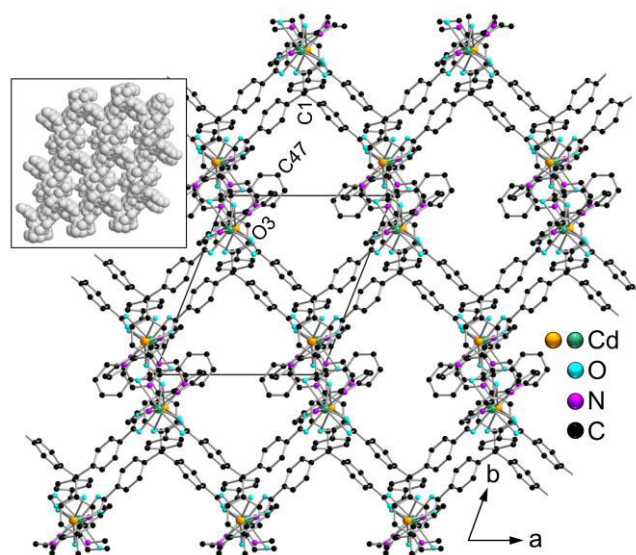


Figure 7. Crystal structure of $[\text{Cd}_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2] \cdot 7\text{DMF}$ (**2**) viewed on (001). Hydrogen atoms and uncoordinated DMF molecules are omitted for clarity. The inset shows a space-filling model including hydrogen atoms.

In **2**, the coordination of the MTB^{4-} tetraanions to the $\text{Cd}(2)$ cations leads to infinite layers extending in the (001) plane (Figure 7 and 8) with honeycomb-like pattern. The connection between $\text{Cd}(1)$ 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 $\text{Cd}(1)/\text{Cd}(2)$ 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]). The layers are stacked in a ...AA... sequence along the [001] direction. Neighbouring 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 neighbouring layer along $[110]$. 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, neighbouring 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 Cd²⁺, which are situated within the layers as well as intercalated between adjacent layers (Figure 8, S3, Supporting Information). The partly disordered DMF molecules form weak and medium C–H...O hydrogen bonds to the phenyl rings of MTB⁴⁻ and to the C₅N-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 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.

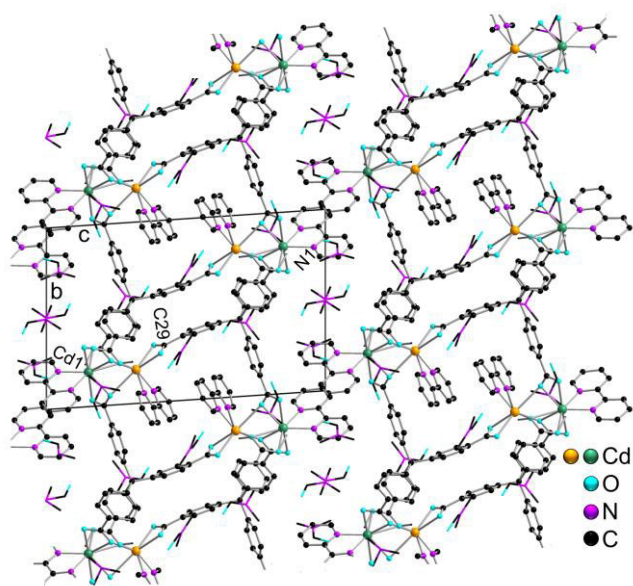


Figure 8. View along $[100]$ in **2**. DMF molecules are drawn as sticks. Hydrogen atoms are omitted for clarity.

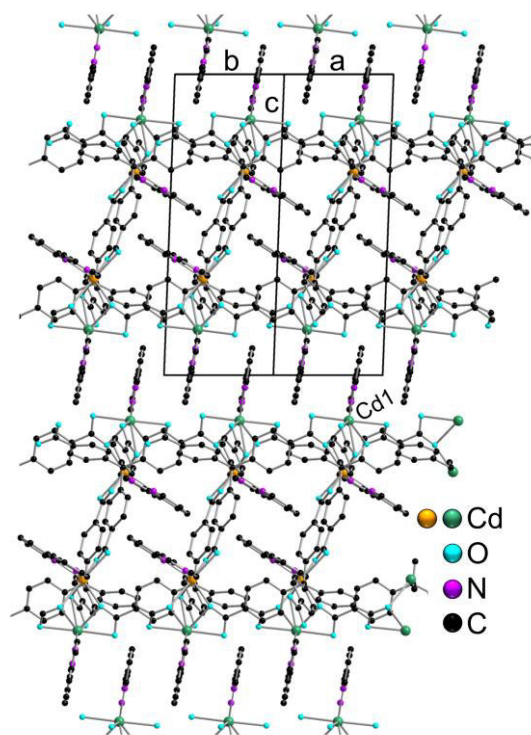


Figure 9. Crystal structure of **2** viewed from $[110]$. Hydrogen atoms and uncoordinated DMF molecules are omitted for clarity.

Table 6. Hydrogen bonds in **2**

	C...O Distance (pm)	C–H...O Angle (°)
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 Cd₂[μ₈-MTB]·3H₂O·DMF (**1**) and [Cd₄(2,2'-bipy)₄(μ₇-MTB)₂]·7DMF (**2**). In **1** the connection between the Cd²⁺ cations and the MTB⁴⁻ tetraanions leads to an open three-dimensional framework with channels along $[110]$ 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 neighbouring layers obviously contribute to stabilize the structure. The results confirm that ligands with tetrahedrally directed functional groups favour the formation of diamondoid frameworks as expected and encourage further use of these buildings blocks.

Experimental Section

Synthesis of Tetrakis(4-bromophenyl)methane^[40]

54 mmol tetraphenylmethane, synthesized as described elsewhere^[41], were 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 in a dioxane/ acetonitrile mixture. Yield: 63 %. Elemental analysis: (molecular weight 636.01): C 46.46 (calcd. 47.21); H 2.30 (2.54); Br 51.24 (50.25). $^1\text{H-NMR}$ (DMSO-d_6): δ (ppm) = 6.99, 7.37; $^{13}\text{C-NMR}$ (DMSO-d_6): δ (ppm) = 63.6, 120.8, 131.1, 132.4, 144.4.

Synthesis of Methanetetrakis-p-benzoic acid (H_4MTB)^[42]

The reaction was carried out under argon atmosphere. 7.9 mmol tetrakis(4-bromophenyl)methane was dissolved in 500 ml dried THF. Butyllithium 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 under stirring and the reaction mixture was meanwhile slowly heated to RT. 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 methanetetrakis-p-benzoic acid [tetrakis(4-carboxyphenyl)methane] was collected and dried. Yield: 71 %. Elemental analysis: (molecular weight 496.46): C 68.78 (calcd. 70.16); H 4.51 (4.06). $^1\text{H-NMR}$ (DMSO-d_6): δ (ppm) = 7.29, 7.85; $^{13}\text{C-NMR}$ (DMSO-d_6): δ (ppm) = 65.2, 128.9, 129.3, 130.5, 149.8, 166.9.

$\text{Cd}_2[\mu_6\text{-MTB}]\cdot 3\text{H}_2\text{O}\cdot \text{DMF}$ (1**)^[42]**: 0.2 mmol H_4MTB and 0.4 mmol $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ 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, colourless crystals of **1** appeared.

$[\text{Cd}_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2]\cdot 7\text{DMF}$ (2**)^[42]**: 0.2 mmol H_4MTB , 0.8 mmol 2,2'-bipyridine, and 0.4 mmol $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ were dissolved in 7 ml DMF. The mixture was kept at about 70°C in a drying oven. Colourless crystals of **2** appeared after several days.

The intensity data were collected on 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 molecule O(1W) 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. Further crystallographic data have been

deposited at the Cambridge Crystallographic Data Centre under CCDC-1862572 for **1**, and CCDC-1862573 for **2** containing the supplementary crystallographic data excluding structure factors; this data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Table 7. Crystallographic Data

Compound	1	2
Empirical formula	$\text{C}_{32}\text{H}_{29}\text{NCd}_2\text{O}_{12}$	$\text{C}_{119}\text{H}_{113}\text{N}_{15}\text{Cd}_4\text{O}_{23}$
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)
Lattice constants	$a = 1821.30(6)$ pm $b = 2175.08(6)$ pm $c = 1269.87(4)$ pm $\beta = 129.684(1)^\circ$	$a = 1224.84(4)$ pm $b = 1418.85(5)$ pm $c = 2033.49(4)$ pm $\alpha = 85.831(2)^\circ$ $\beta = 88.351(2)^\circ$ $\gamma = 68.261(1)^\circ$
Cell volume	$3.8714(2)$ nm ³	$3.27391(17)$ nm ³
Formulas in unit cell	4	1
Formula weight	844.36 g mol ⁻¹	2570.84 g mol ⁻¹
Density (calc.)	1.449 g cm ⁻³	1.304 g cm ⁻³
Wavelength	71.073 pm	
Absorption coefficient	1.153 mm ⁻¹	0.709 mm ⁻¹
Numerical absorption correction	min./max. transmittance $0.6841/0.7456$	min./max. transmittance $0.6539/0.7456$
Temperature	183 (2) K	
Crystal size (mm)	$0.104 \times 0.094 \times 0.084$	$0.088 \times 0.082 \times 0.076$
F (000)	1680	1308
Θ -range	$1.87^\circ - 27.47^\circ$	$2.09^\circ - 27.45^\circ$
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 ($R_{\text{int}} = 0.0314$)	14138 ($R_{\text{int}} = 0.0341$)
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	1255 and -646 e $\cdot\text{nm}^{-3}$	5869 and -2312 e $\cdot\text{nm}^{-3}$

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

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 and O. M. Yaghi, *Chem. Rev.* **2012**, 112, 675–702.
- [5] R. Köferstein and C. Robl, *Z. Anorg. Allg. Chem.* **2015**, 641, 1886–1891.
- [6] D. Poletti and L. Karanović, *Acta Cryst.* **1989**, C45, 1716–1718.
- [7] R. Köferstein and 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 and A. Eling, *Angew. Chem. Int. Ed.* **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, *Cryst. Eng Comm.* **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 and H.-Z. Kou, *RSC Adv.* **2015**, 15, 89052–89055.
- [17] Y. E. Cheon and M. P. Suh, *Chem. Eur. J.* **2008**, 3961–3967.
- [18] M. Almáši, V. Zelenák, M. Opanasenko, J. Čejka, *Dalton Trans.* **2014**, 43, 3730–3738.
- [19] Y. E. Cheon and M. P. Suh, *Chem. Comm.* **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. Gandara, 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. Zelenák, 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. Comm.* **2016**, 52, 2952–2955.
- [24] M. Almáši, V. Zelenák, A. Zukal, J. Kuchár, J. Čejka, *Dalton Trans.* **2016**, 45, 1233–1242.
- [25] M. Almáši, V. Zelenák, R. Gyepes, A. Zukal, J. Čejka, *Colloids Surf. A.* **2013**, 437, 101–107.
- [26] M. Almáši, V. Zelenák, M. V. Opanasenko, J. Čejka, *Catal. Lett.* **2018**, 148, 2263–2273.
- [27] N. E. Brese and M. O’Keeffe, *Acta Cryst.* **1991**, B47, 192–197.
- [28] A. Bondi, *J. Phys. Chem.* **1964**, 68, 441–451.
- [29] G. Schultz and 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.* **2003**, 58b, 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 Cryst.* **1995**, C51, 234–235.
- [34] A. Tahlil, Ü. Köc, R. F. M. Elshaaawy, A. C. Kautz, C. Janiak, *Crystals* **2016**, 6, 23.
- [35] J. K. Shiba and R. Bau, *Inorg. Chem.* **1978**, 12, 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 Cryst.* **2010**, E66, o68–o69.
- [40] T. J. Zimmermann and 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, Univ. Jena, Germany, **2010**.
- [43] COLLECT, Data Collection Software; Nonius B.V., Netherlands, **1998**.
- [44] Z. Otwinowski and 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 Cryst.* **2015**, C71, 3–8.
- [47] Diamond - Crystal and Molecular Structure Visualization, Crystal Impact H. Putz and K. Brandenburg GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany.

S. Harms, R. Köferstein, H. Görls, C. Robl, *Syntheses and Crystal Structures of Two Cadmium Methanetetraobenzoates Featured by Open Framework and Infinite Layers*, Z. Anorg. Allg. Chem. 645 (2019) 912–918. (**Highlighted as cover picture 07/2019**, DOI: 10.1002/zaac.201900089)

Syntheses and Crystal Structures of Two Novel Cadmium Methanetetra benzoate featured by Open Frameworks and infinite Layers

Sven Harms^[a], Roberto Köferstein^[b], Helmar Görls^[a], and Christian Robl^{*[a]}

^a Institute of Inorganic and Analytical Chemistry, Friedrich-Schiller-University Jena, Humboldtstrasse 8, 07743 Jena, Germany.

^b Institute of Chemistry, Inorganic Chemistry, Martin Luther University Halle-Wittenberg, Kurt-Mothes-Strasse 2, 06120 Halle, Germany.

* Corresponding author. E-mail address: crr@uni-jena.de

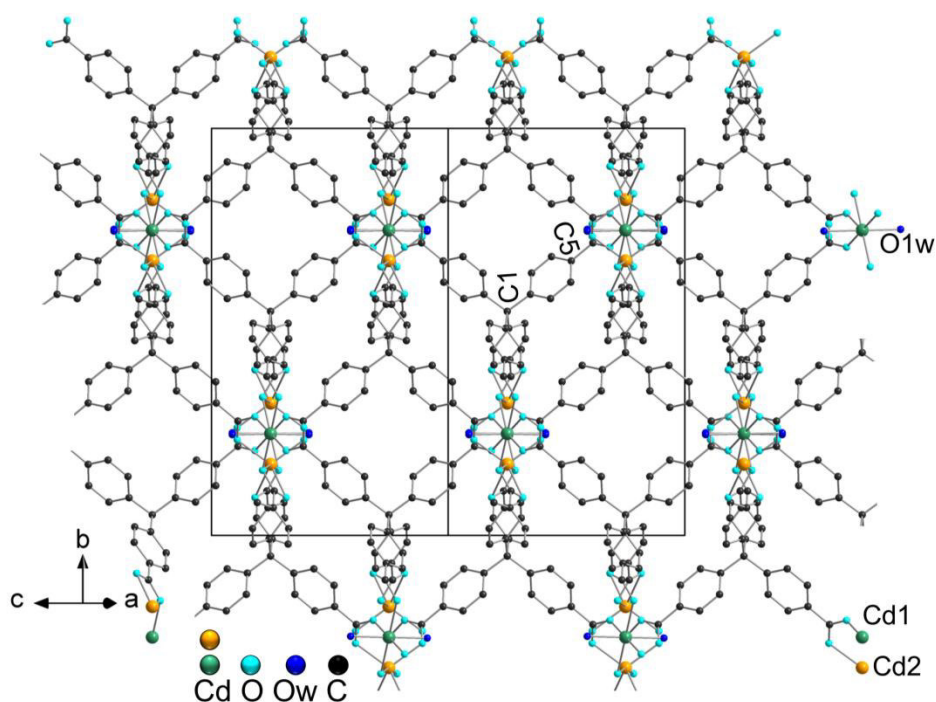


Figure S1. Connection between the MTB^{4-} anions and the Cd^{2+} cations in $\text{Cd}_2[\mu_8\text{-MTB}]\cdot 3\text{H}_2\text{O}\cdot \text{DMF}$ (**1**) viewed from [101]. Hydrogen atoms, uncoordinated water molecules [O(2w) and O(3w)] and DMF molecules are omitted for clarity.

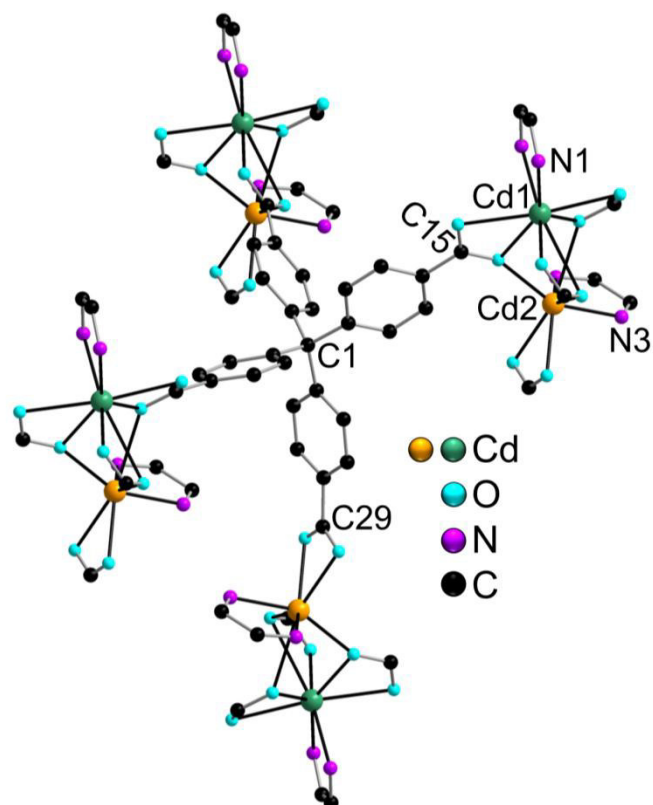


Figure S2. Connection between the MTB^{4-} anions and the dimeric Cd^{2+} polyhedra units in $[\text{Cd}_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2]\cdot 7\text{DMF}$ (**2**). Hydrogen atoms are omitted for clarity.

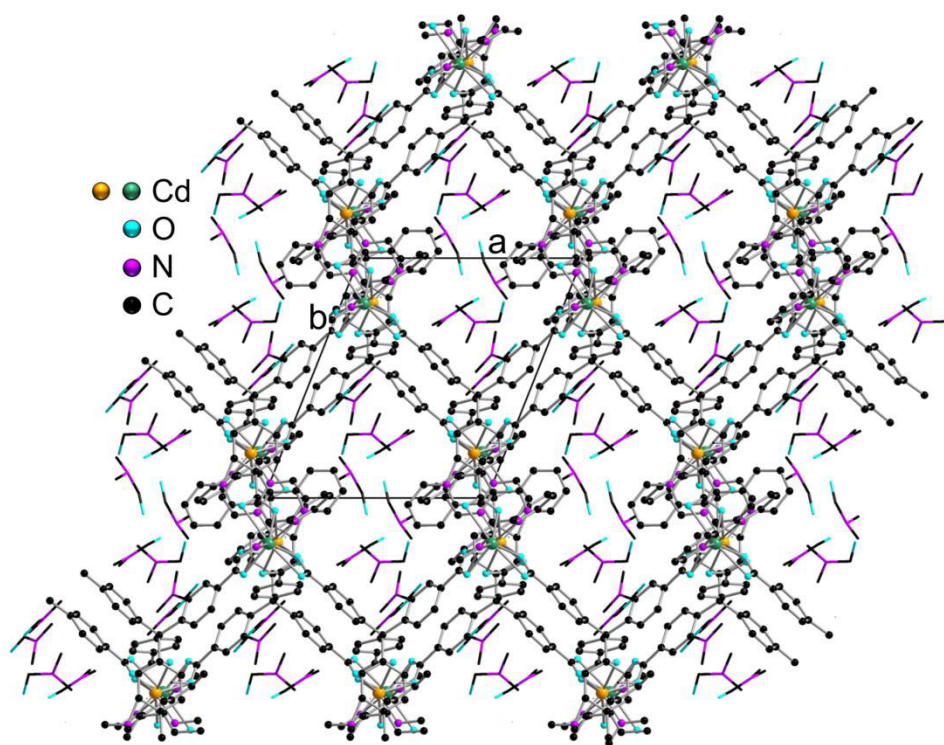


Figure S3. The crystal structure of $[\text{Cd}_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2]\cdot 7\text{DMF}$ (**2**) viewed along $[001]$. DMF molecules are drawn as sticks. Hydrogen atoms are omitted for clarity.

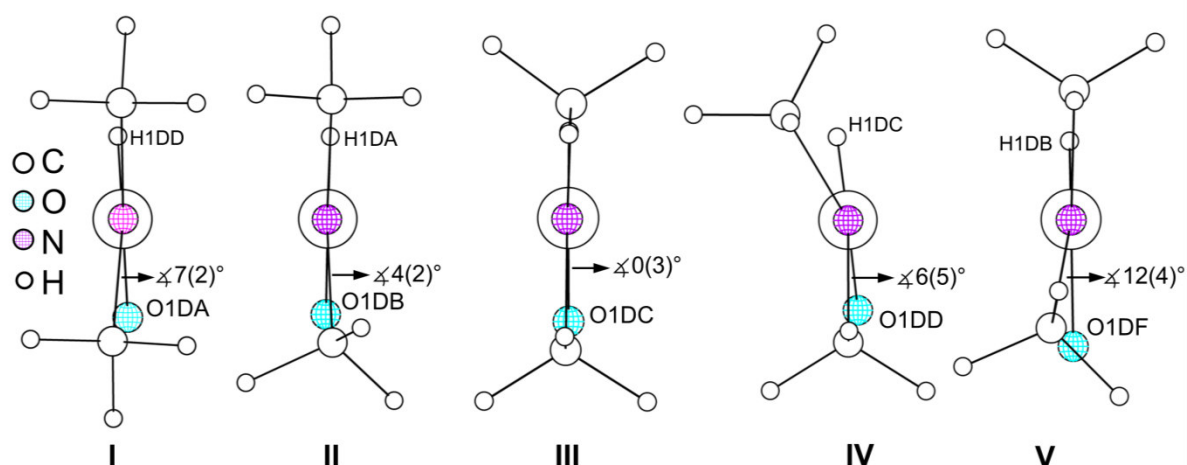


Figure S4. Newman projection of *N,N*-dimethylformamide (DMF) molecules along N–C in $[\text{Cd}_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2]\cdot 7\text{DMF}$ (**2**). The indicated values describe the smallest C–N–C–O torsion angle.

Table S1. Bond lengths (pm) of the MTB^{4-} anion and *N,N*-dimethylformamide (DMF) in $\text{Cd}_2[\mu_8\text{-MTB}]\cdot 3\text{H}_2\text{O}\cdot \text{DMF}$ (**1**)

Methanetetra- <i>p</i> -benzoate tetraanion (MTB^{4-})							
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)
C(2)–C(3)	139.3(5)	C(2)–C(7)	139.8(5)	C(3)–C(4)	139.0(5)	C(4)–C(5)	138.7(5)
C(5)–C(6)	138.8(5)	C(6)–C(7)	138.3(5)	C(9)–C(10)	138.8(5)	C(9)–C(14)	140.6(5)
C(10)–C(11)	139.4(5)	C(11)–C(12)	138.7(6)	C(12)–C(13)	138.7(5)	C(13)–C(14)	138.5(5)
<i>N,N</i> -dimethylformamide (DMF)							
O(1A)–C(1A)	1.20(2)	N(1A)–C(2A)	1.36(2)	N(1A)–C(3A)	1.45(2)	N(1A)–C(1A)	1.43(2)

Table S2. Bond lengths (pm) of the MTB^{4-} anion, 2,2'-bipyridine, and *N,N*-dimethylformamide (DMF) in $\text{Cd}_4(2,2'\text{-bipy})_4(\mu_7\text{-MTB})_2\cdot 7\text{DMF}$ (**2**)

Methanetetra- <i>p</i> -benzoate tetraanion (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)
C(2)–C(7)	138.3(10)	C(2)–C(3)	139.7(9)	C(3)–C(4)	138.8(10)	C(4)–C(5)	140.2(10)
C(5)–C(6)	138.7(10)	C(6)–C(7)	138.7(11)	C(9)–C(10)	139.9(9)	C(9)–C(14)	140.6(10)
C(10)–C(11)	137.8(10)	C(11)–C(12)	139.0(10)	C(12)–C(13)	139.0(10)	C(13)–C(14)	138.8(9)

C(16)–C(17)	138.3(11)	C(16)–C(21)	139.7(10)	C(17)–C(18)	139.6(10)	C(18)–C(19)	138.7(10)
C(19)–C(20)	138.5(11)	C(20)–C(21)	139.1(10)	C(23)–C(24)	138.7(11)	C(23)–C(28)	140.6(10)
C(24)–C(25)	139.2(10)	C(25)–C(26)	140.0(11)	C(26)–C(27)	139.0(12)	C(27)–C(28)	138.6(10)
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)	C(30)–C(31)	141.4(12)	C(31)–C(32)	135.0(13)	C(32)–C(33)	137.5(14)
C(34)–C(35)	148.8(12)	C(35)–C(36)	139.8(10)	C(36)–C(37)	136.4(14)	C(37)–C(38)	139.2(15)
C(38)–C(39)	138.6(13)						
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)	C(40)–C(41)	137.8(14)	C(41)–C(42)	137.6(15)	C(42)–C(43)	137.4(15)
C(43)–C(44)	138.4(12)	C(45)–C(46)	137.6(13)	C(46)–C(47)	137.3(16)	C(47)–C(48)	137.6(18)
C(48)–C(49)	140.3(16)						
<i>N,N</i> -dimethylformamide (DMF) (I)							
O(1DA)–C(1DA)	125.3(14)	N(1DA)–C(1DA)	129.6(14)	N(1DA)–C(2DA)	144.0(14)	N(1DA)–C(3DA)	153.0(18)
<i>N,N</i> -dimethylformamide (DMF) (II)							
O(1DB)–C(1DB)	119.3(13)	N(1DB)–C(1DB)	134.6(12)	N(1DB)–C(2DB)	144.1(13)	N(1DB)–C(3DB)	144.6(14)
<i>N,N</i> -dimethylformamide (DMF) (III)							
O(1DC)–C(1DC)	124(3)	N(1DC)–C(1DC)	131(2)	N(1DC)–C(2DC)	141(2)	N(1DC)–C(3DC)	144.6(19)
<i>N,N</i> -dimethylformamide (DMF) (IV)							
O(1DD)–C(1DD)	122(3)	N(1DD)–C(1DD)	138(4)	N(1DD)–C(2DD)	139(3)	N(1DD)–C(3DD)	140(3)
<i>N,N</i> -dimethylformamide (DMF) (V)							
O(1DE)–C(1DE)	136(3)	N(1DE)–C(1DE)	129(3)	N(1DE)–C(2DE)	146(3)	N(1DE)–C(3DE)	145(3)