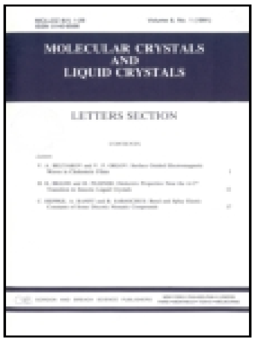

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Syntheses and Structures of Three Divalent Zn/Cd Metal–Organic Supramolecular Frameworks Constructed by 1, 2, 4-benzenetricarboxylate

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*Three novel metal–organic hybrid compounds, [Zn(H_2btc)$_2$(H_2O)$_2$]·2H_2O (**1**),[Cd(Hbtc) (H_2O)]n (**2**) and [Zn_3(btc)$_2$(phen)$_2$(H_2O)$_2$]n (**3**) (H3btc = 1,2,4-benzenetricarboxylate, phen = 1,10-phenanthroline), have been hydrothermally synthesized and their structures were determined by single-crystal X-ray diffraction. The structural motifs are multiforms from 0D, 3D, and 2D interpenetrating networks. It is found that the H3btc ligand exhibits multicoordinated modes. In these complexes, the carboxylates of btc and water molecules are involved in intermolecular hydrogen bondings to form the 3D molecular frameworks and reinforce the structural stability, which proves that noncovalent interactions like H-bond play an important role in instructing the supramolecular architectures.*

Keywords benzenetricarboxylate, multiform, hydrogen bonding

Introduction

Metal–organic hybrid compounds have attracted tremendous attentions not only owning to their intriguing structural diversity, but also because of their various potential applications in catalysis and adsorption[1–9]. The selection of appropriate ligands with certain features such as versatile coordination modes, variable hydrogen bondings, plays important roles in the synthesis of a desired framework[8]. It is noteworthy that the rigid benzene polycarboxylate linkers, such as 1,4-benzenedicarboxylate,1,3,5-benzenetricarboxylate, 1,2,4,5-benzenetetracarboxylate, and 1,2,4-benzenetricarboxylate are good candidates for the construction of novel metal–organic compounds due to their several promising advantages, of which the great diversity in binding modes of carboxylate groups is the key[10,11]. To date, a large number of rigid multidimensional coordination networks constructed from symmetric polycarboxylate have been reported[12–18]. In contrast, research on complexes of metal centers with the asymmetric 1,2,4-benzenetricarboxylate ligand is rarely reported.[19–23]

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Table 1. Crystallographic Data and Refinement Parameters for Compounds **1–3**

Complex	**1**	**2**	**3**
Empirical formula	$C_{18}H_{18}O_{16}Zn,2(H_2 O)$	$C_9H_6CdO_7$	$C_{42}H_{26}N_4O_{14}Zn_3$
Formula weight	591.70	338.55	1006.84
Crystal size (mm)	0.20 × 0.30 × 0.60	0.20 × 0.30 × 0.50	0.26 × 0.41 × 0.53
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P\,2_1/c$	P-1	P-1
a (Å)	12.3244(18)	7.0010(15)	7.764(2)
b (Å)	12.5965(18)	7.0532(15)	10.631(3)
c (Å)	7.4959(11)	10.107(2)	12.236(3)
α[°]	90.00	83.369(3)	87.966(4)
β[°]	103.654(2)	86.422(4)	77.721(5)
γ [°]	90.00	69.284(3)	69.272(4)
V, Å^3	1130.8(3)	463.56(17)	922.1(4)
Z	2	2	1
D_{calcd}, (Mg/m^3)	1.738	2.425	1.813
μ, mm^{-1}	1.179	2.379	2.019
F(000)	608	328	508
Ref. collected/unique	5883/2210(R_{int} = 0.045)	2276/1591(R_{int} = 0.045)	4813/3499(R_{int} = 0.075)
Parameters	192	155	294
$R1^a$	0.0358	0.0316	0.0497
$wR2^b$	0.0991	0.0846	0.1507
GOF	1.03	1.18	1.05
Min. / max. $\Delta\rho$ (e·Å^{-3})	−0.63/0.52	−0.80/1.11	−0.98/0.76

$^aR1 = \sum||F_o|-|F_c|| / \sum|F_o|$, $^b\, wR2 = [\sum[w(F_o^2-F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$

1,2,4-benzenetricarboxylic acid as an unsymmetrical benzene polycarboxylate exhibits more advantages in constructing novel topological features, which can be of benefit to the synthesis of the chiral, spiral and higher unsymmetrical metal–organic frameworks[24–26]. Furthermore, the introduction of another multidentate ligands containing *N*-donors such as phen may alter the dimensionality of these metal—organic hybrid complexes through binding metal centers[27,28]. Taking account of these, we choose 1,2,4-benzenetricarboxylic acid and 1,10-phenanthroline as the organic ligands to prepare novel metal–organic hybrid compounds. Herein, we report the synthesis and crystal structures of three new coordination polymers with multiforms from 0D, 2D–3D interpenetrating networks.

Experimental

General

1,2,4-benzenetricarboxylic acid(H_3btc) was purchased from Aldrich and used without further purification. All the other reagents were commercially available and used as received. Elemental analyses were recorded on a Perkin–Elmer 1400C analyzer. Infrared spectra were measured on a Nicolet Magna 750 FI-IR spectrometer using KBr pellets in the range of 4000–400 cm^{-1}.

Table 2. Selected bond lengths(Å) and angles(°) for three compounds

1					
Zn1-O2	2.0990 (15)	Zn1-O7	2.0527 (15)	Zn-O8	2.1130 (15)
O2-Zn1-O7	96.02 (6)	O2-Zn1-O8	85.34 (6)	O2-Zn1-O2$^{\mathrm{I}}$	180.00
O2-Zn1-O7$^{\mathrm{I}}$	83.98 (6)	O2-Zn1-O8$^{\mathrm{I}}$	94.66 (6)	O7-Zn1-O8	92.07 (6)
O7-Zn1-O7$^{\mathrm{I}}$	180.00	O7-Zn1-O8$^{\mathrm{I}}$	87.93 (6)	O8-Zn1-O8$^{\mathrm{I}}$	180.00
2					
Cd1-O1	2.667 (4)	Cd1-O2	2.354 (4)	Cd1-O5	2.401 (3)
Cd1-O4$^{\mathrm{II}}$	2.345 (3)	Cd1-O6$^{\mathrm{III}}$	2.274 (3)	Cd1-O3$^{\mathrm{IV}}$	2.337 (4)
Cd1-O1$^{\mathrm{V}}$	2.366 (4)	O1-Cd1-O2	51.51 (12)	O1-Cd1-O5	72.82 (11)
O1-Cd1-O4$^{\mathrm{II}}$	145.96 (12)	O1-Cd1-O6$^{\mathrm{III}}$	76.89 (12)	O1-Cd1-O3$^{\mathrm{IV}}$	123.10 (12)
O1-Cd1-O1$^{\mathrm{V}}$	70.95 (12)	O2-Cd1-O5	91.40 (12)	O2-Cd1-O4$^{\mathrm{II}}$	156.00 (13)
O2-Cd1-O6$^{\mathrm{III}}$	81.40 (12)	O1$^{\mathrm{V}}$-Cd1-O2	121.95 (13)	O4$^{\mathrm{II}}$-Cd1-O5	83.94 (11)
O5-Cd1-O6$^{\mathrm{III}}$	146.03 (12)	O3$^{\mathrm{IV}}$-Cd1-O5	92.20 (13)	O1$^{\mathrm{V}}$-Cd1-O5	77.20 (12)
O4$^{\mathrm{II}}$-Cd1-O6$^{\mathrm{III}}$	114.94 (12)	O3$^{\mathrm{IV}}$-Cd1-O4$^{\mathrm{II}}$	81.39 (12)	O1$^{\mathrm{V}}$-Cd1-O4$^{\mathrm{II}}$	80.02 (13)
O3$^{\mathrm{IV}}$-Cd1-O6$^{\mathrm{III}}$	117.43 (12)	O1$^{\mathrm{V}}$-Cd1-O6$^{\mathrm{III}}$	78.72 (13)	O1$^{\mathrm{V}}$-Cd1-O3$^{\mathrm{IV}}$	159.44 (12)
3					
Zn1-O1	2.177 (3)	Zn1-O3	2.070 (3)	Zn1-O4$^{\mathrm{VI}}$	2.078 (3)
Zn2-O6	2.002 (3)	Zn2-O7	2.686 (4)	Zn2-N1	2.096 (3)
Zn2-N2	2.192 (4)	Zn2-O2$^{\mathrm{IX}}$	2.006 (3)	Zn2-O5$^{\mathrm{IX}}$	2.058 (3)
O1-Zn1-O3	89.46 (11)	O1-Zn1-O4$^{\mathrm{VI}}$	87.71 (12)	O1-Zn1-O1$^{\mathrm{VII}}$	180.00
O1-Zn1-O3$^{\mathrm{VII}}$	90.54 (11)	O1-Zn1-O4$^{\mathrm{VIII}}$	92.29 (12)	O3-Zn1-O4$^{\mathrm{VI}}$	94.10 (11)
O3-Zn1-O3$^{\mathrm{VII}}$	180.00	O3-Zn1-O4$^{\mathrm{VIII}}$	85.90 (11)	O4$^{\mathrm{VI}}$-Zn1-O4$^{\mathrm{VIII}}$	180.00
O6-Zn2-O7	54.15 (12)	O6-Zn2-N1	144.77 (14)	O6-Zn2-N2	93.71 (13)
O2$^{\mathrm{IX}}$-Zn2-O6	104.82 (13)	O5$^{\mathrm{IX}}$-Zn2-O6	97.86 (13)	O7-Zn2-N1	93.60 (12)
O7-Zn2-N2	100.49 (13)	O2$^{\mathrm{IX}}$-Zn2-O7	153.45 (11)	O5$^{\mathrm{IX}}$-Zn2-O7	79.62 (12)
N1-Zn2-N2	77.24 (12)	O2$^{\mathrm{IX}}$-Zn2-N1	109.98 (13)	O5$^{\mathrm{IX}}$-Zn2-N1	88.34 (12)
O2$^{\mathrm{IX}}$-Zn2-N2	96.60 (13)				

[a] Symmetry Transformations used to generate equivalent atoms: (I) 1 - x, 1 - y, -z, (II) x, 1 + y, -1 + z, (III) x, 1 + y, z, (IV) -x, 1 - y, 1 - z, (V) 1 - x, 1 - y, 1 - z, (VI) -1 + x, y, z, (VII) -1 - x, -1 - y, 1 - z, (VIII) -x, -1- y, 1 - z, (IX) -x , -y, 1 - z.

Preparation of Complexes 1-3

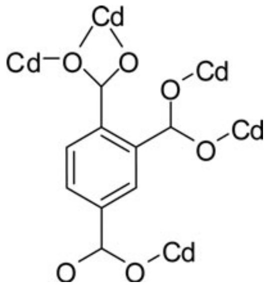
Synthesis of [Zn(H_2btc)$_2$(H_2O)$_2$]·2H_2O (1). H_3btc (105 mg, 0.5 mmol), NaOH (20 mg, 0.5 mmol), and Zn(OAc)$_2$·2H_2O (110 mg, 0.5 mmol) were stirred for 0.5 h in 20 mL of ethanol and water (1:1) mixed solvent then at 160°C for 4 days in a sealed 30 mL Teflon-lined stainless steel vessel under autogenous pressure. After the reaction mixture was slowly cooled to room temperature, the colorless crystals of 1 were produced (yield 43%,). Anal. Calcd. For $C_{18}H_{22}O_{18}Zn$: C, 36.53; H, 3.75. Found: C, 36.50; H, 3.78. IR (cm^{-1}, KBr): 3420(vs), 1702(w), 1619(s), 1591(s), 1495(w), 1394(s), 1358(s), 1081(w), 792(w), 675(w).

Synthesis of [Cd(Hbtc) (H_2O)]$_n$ (2). H_3btc (105 mg, 0.5 mmol) , NaOH (20 mg, 0.5 mmol) and Cd(OAc)$_2$·2H_2O,(133 mg, 0.5 mmol) were stirred for 0.5 h in 20 mL aqueous and ethanol mixed solution (1:1), then at 170°C for 5 days in a sealed 30 mL Teflon-lined stainless steel vessel under autogenous pressure. After the reaction mixture was slowly cooled to room temperature, the colorless crystals of 2 were produced (yield 51%,). Anal. Calcd. For $C_9H_6CdO_7$: C, 31.93; H, 1.79. Found: C, 31.91; H, 1.93. IR (cm^{-1}, KBr): 3350(bs), 1703(w),1613(s), 1586(s), 1491(w), 1390(s), 1352(s), 1086(w), 795(w), 674(w).

Synthesis of [Zn$_3$(btc)$_2$(phen)$_2$(H_2O)$_2$]$_n$ (3). **3** was produced in the same way as that of **1** except that phen (1.0 mmol, 0.201 g) was added. Zn(OAc)$_2$·2H_2O, 1,2,4-H_3btc, phen and NaOH with the ratio of 1:1:1:1 in basified aqueous and ethanol solution were heated at 160°C for 6 days, leading to the formation of compound 3(yield 58%,). Calcd. For $C_{42}H_{26}N_4O_{14}Zn_3$: C, 50.10; H, 2.60; N, 5.56. Found: C, 50.09; H, 2.64; N, 5.54%. 3344(s),

Table 3. Selected hydrogen bond lengths (Å) and angles (°) for complexes 1-3

D–H... A	D–H	H... A	D... A	∠DHA	A
1					
O4- H4... O2	0.79 (4)	1.87 (4)	2.645 (2)	168 (4)	$x, 3/2 - y, 1/2 + z$
O5- H5... O9	0.8200	1.7900	2.609 (3)	177.00	$-x, 1/2 + y, 1/2 -$ z
O7- H7A... O6	0.8200	1.9500	2.750 (3)	166.00	$1 + x, y, z$
O7- H7B... O1	0.79 (4)	2.22 (4)	2.832 (2)	134 (3)	
O8- H8A... O9	0.8200	1.9100	2.724 (2)	171.00	$1 - x, 1/2 + y, 1/2 - z$
O8- H8B... O3	0.82 (4)	1.94 (4)	2.753 (2)	168 (4)	$x, 3/2 - y, -1/2 + z$
O9- H9A... O8	0.77 (4)	1.99 (3)	2.712 (2)	156 (3)	$1 - x, 1 - y, -z$
O9- H9B... O1	0.84 (3)	1.87 (3)	2.695 (2)	168 (3)	$x, 1/2 - y, -1/2 + z$
2					
O5- H5B... O2	0.8500	1.7800	2.619 (5)	168.00	$-x, 1 - y, 1 - z$
O5- H5C... O6	0.8500	1.9100	2.748 (5)	168.00	$1 - x, -y, 1 - z$
O7- H7... O5	0.8200	1.7600	2.583 (4)	178.00	$x, -1 + y, 1 + z$
3					
O3- H3A... O5	0.75 (7)	2.48 (7)	2.939 (5)	121 (6)	$-1 + x, y, z,$
O3-H3A... O7	0.75 (7)	2.22 (6)	2.920 (5)	156 (6)	$-1 - x, -y, 1 - z$
O3-H3B... O2	0.89 (7)	1.83 (6)	2.693 (5)	165 (5)	
C10-H10... O1	0.9300	2.4400	3.325 (6)	158.00	$x, 1 + y, z$
C10-H10... O5	0.9300	2.4500	2.995 (5)	118.00	$-x, -y, 1 - z$
C15-H15... O3	0.9300	2.4100	3.097 (5)	131.00	$1 + x, 1 + y, -1 + z$



Scheme 1. The coordination mode of 1, 2, 4-btc ligand in **2.**

1619(s), 1586(m), 1501(m), 1433(m), 1406(s), 1379(sh), 1305(w), 1266(w), 1231(w), 835(w), 773(m), 724(m), 692(m).

X-ray Crystallography

X-ray data for complexes 1-3 were collected on a Bruker SMART 1K CCD diffractometer at 291 K employing graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The data were collected using SMART and reduced by the program SAINT.[29] The structure was solved by the direct method and refined by full-matrix least squares fitting on "$F^2{}_{obs}$" by SHELXTL-PC[30]. All nonhydrogen atoms were placed in geometrically calculated positions. The C-H hydrogen atoms were positioned geometrically and refined using a riding model with $d(\mathrm{CH_{aro}}) = 0.95$ Å, $U_{iso} = 1.2U_{eq}$ (C) for aromatic. The O-H hydrogen atoms were localized by difference Fourier maps and refined by fixing the bond lengths to 0.840(1) Å. The crystallographic data and selected bond lengths and angles are listed in Tables 1 and 2, respectively.

Results and Discussion

Compound 1 was prepared from a mixture of $Zn(OAc)_2{\cdot}2H_2O$, H_3btc and NaOH with the molar ratio of 1:2:2 in an aqueous and ethanol solution at 160°C for 4 days. The complex

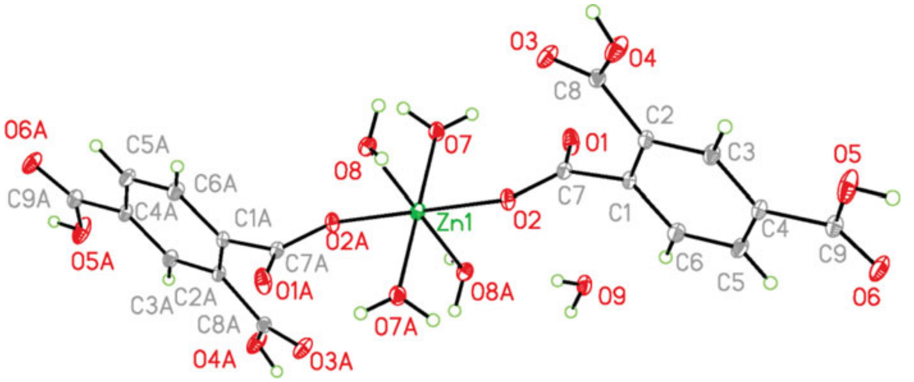


Figure 1. (a) Perspective view of complex **1** with the atom-numbering scheme (30% probability ellipsoids).

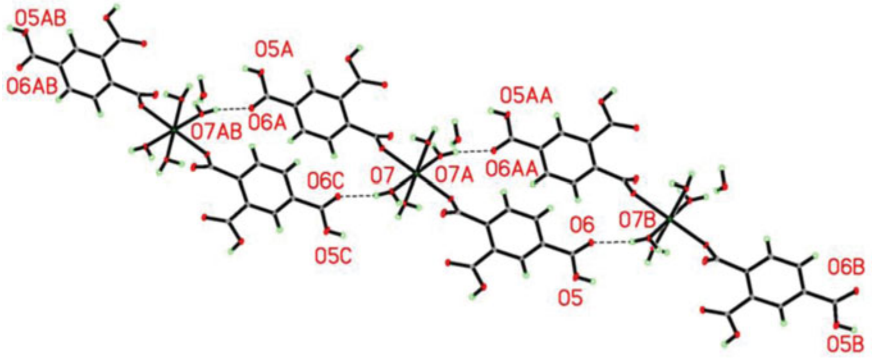


Figure 1. (b) The extended chain structure of in **1**, viewed down the *b*-axis.

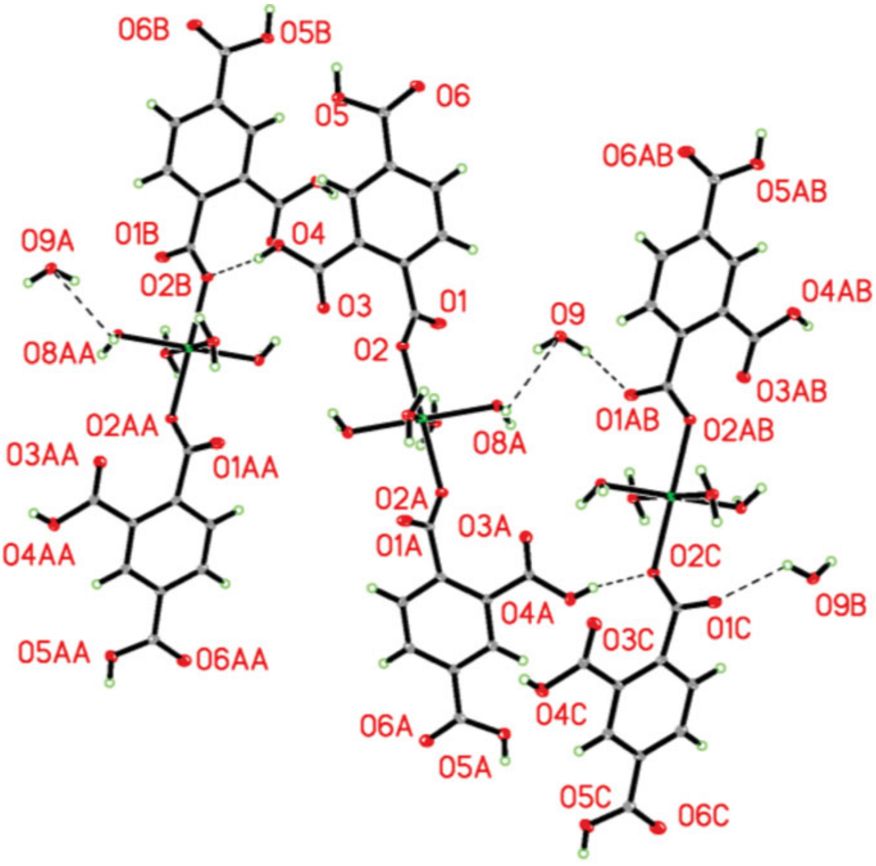


Figure 1. (c) The extended layer structure of **1**, viewed down the *c*-axis.

1 $[Zn(H_2btc)_2(H_2O)_4]\cdot 2H_2O$ crystallizes in the monoclinic system, with space group $P\ 2_1/c$. The least unit of the complex consists of one central metal Zn(II), two btc ligand, four coordinated water molecules and two lattice water molecules, as shown in Fig. 1. The Zn center is six-coordinated by six oxygen atoms, whose coordination geometry can

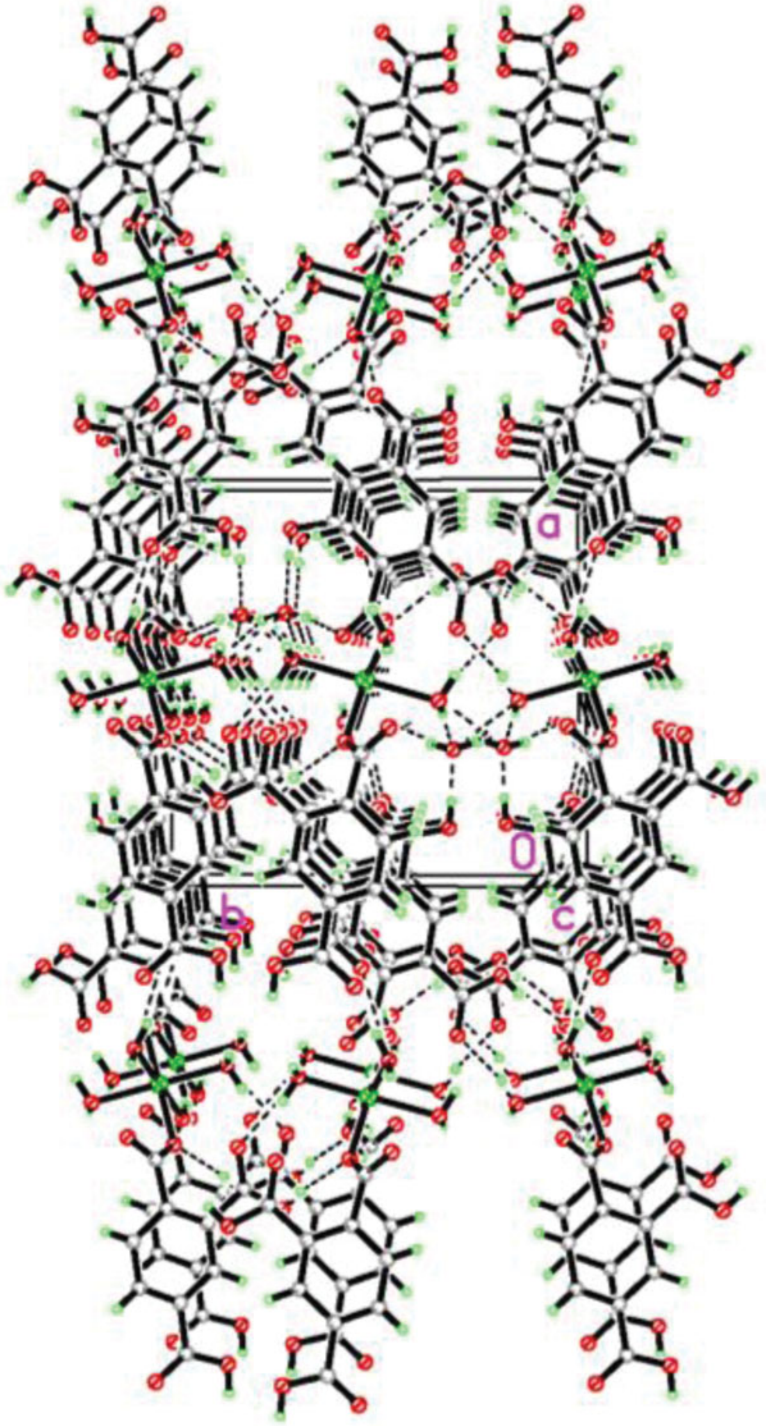


Figure 1. (d) 3D supramolecular network of **1** viewed down the *b*-axis.

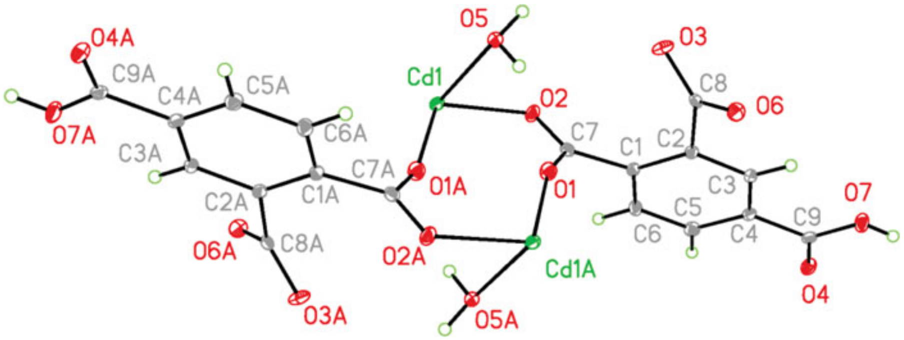


Figure 2. (a) Perspective view of complex **2** with the atom-numbering scheme (30% probability ellipsoids).

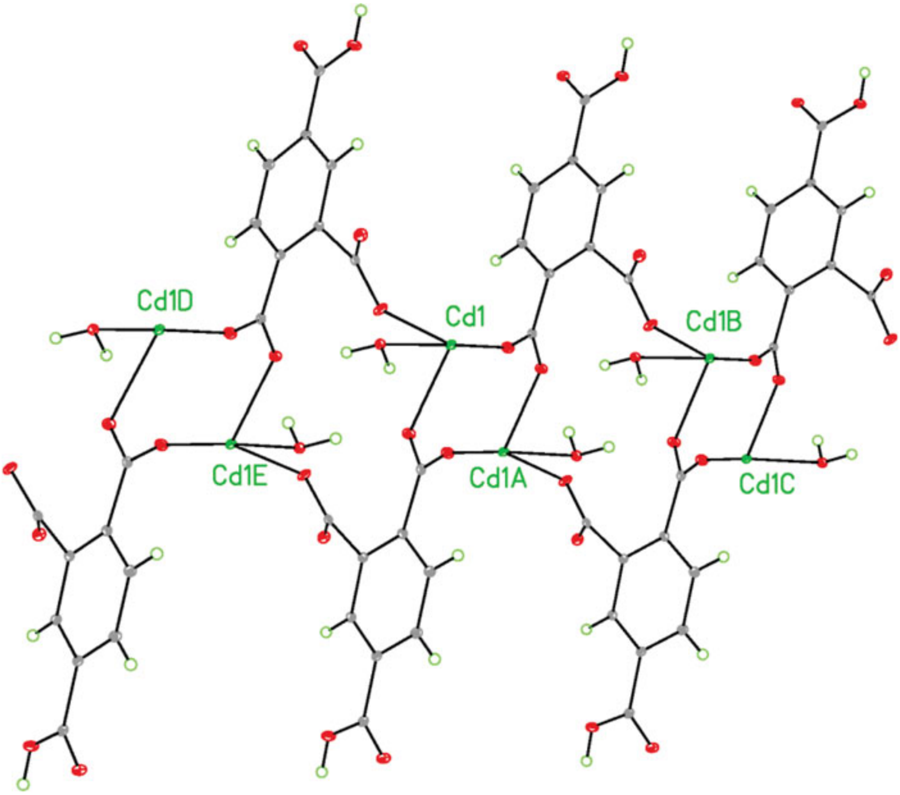


Figure 2. (b) The extended chain structure of in **2.**

be described as distorted octahedron geometry. Two oxygen atoms are from two different btc ligands lying on the axial positions with the bond distances between the zinc ion and oxygen atoms of 2.0990(15) Å. The equatorial plane are occupied by the other four oxygen atoms from the coordinated water molecules with the Zn-O bonds ranging from 2.0527(15) to 2.1130(15). The Zn–O bond angles are varied from 83.98(6)° to 180°.

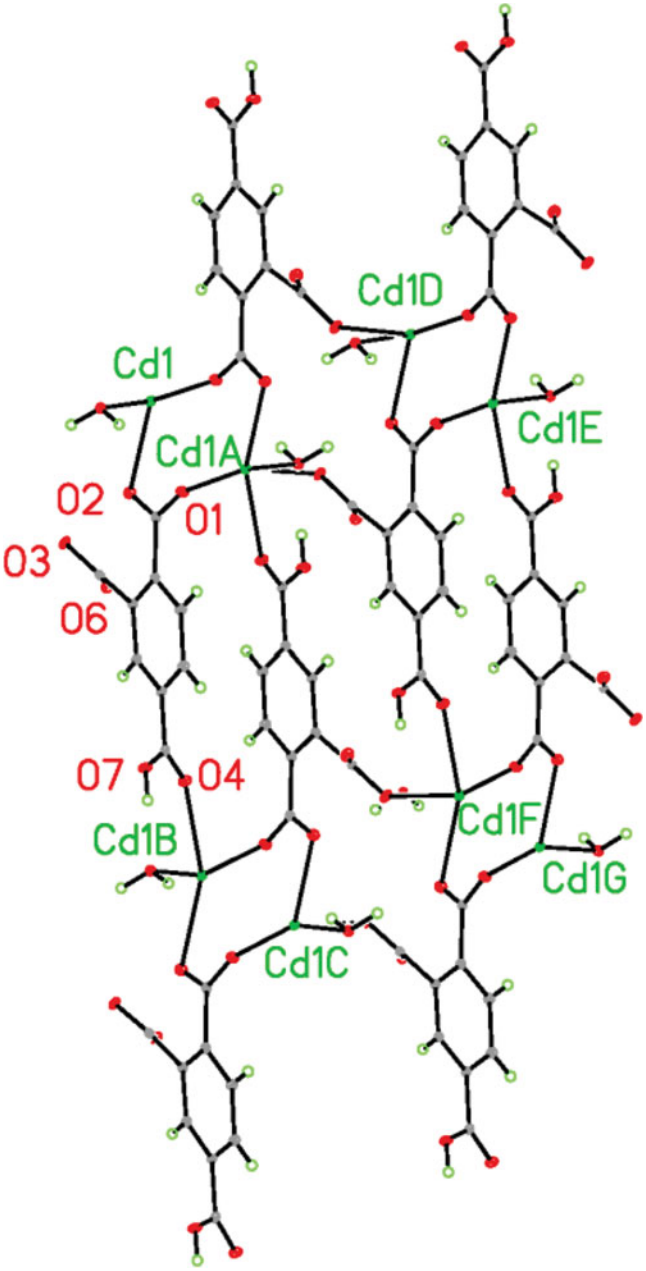


Figure 2. (c) The extended layer structure of in **2**, viewed down the *b*-axis.

All oxygen atoms of the ligand and water molecules of complex 1 participate in intermolecular hydrogen-bonding, constructing novel hydrogen-bonded supramolecule. Hydrogen bond lengths and angles are listed in Table 3.

In **1**, the packing structure shows a three-dimensional supramolecular network formed via intermolecular O-H· · · O hydrogen bonds. First, 1D-hydrogen-bonded network is linked

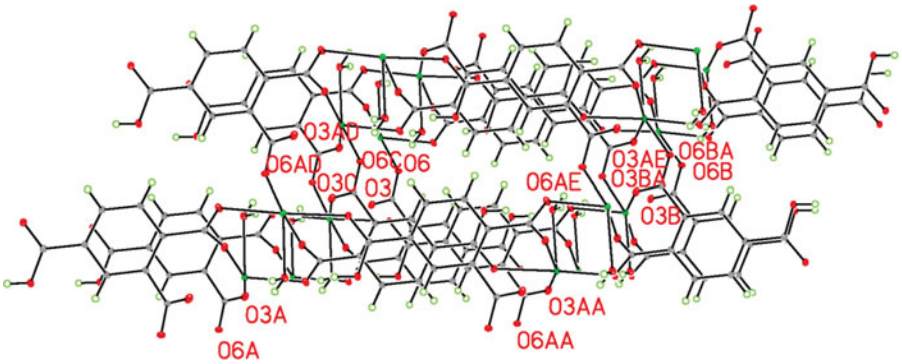


Figure 2. (d) Packing diagram of **2** viewed down the *b*-axis.

via hydrogen bond O7-H7··· O6 along *b*-axis (see Fig. 1(b)). The oxygen atom O6 of noncoordinated carboxylate and hydrogen H7 of the coordinated water molecular are engaged. Then 1D-hydrogen-bonded network are connected and spread through *c*-axis by hydrogen bonds, O4-H4··· O2, which is implicated with the noncoordinated oxygen atom O4 of the carboxylate and coordinated oxygen atom O2. Meanwhile, the hydrogen bonds O8-H8··· O9, and O9-H9··· O1 between the water molecules or carboxylates reinforce the structural stability (Fig. 1(c)). Further, the resulted 2D networks are eventually assembled into 3D supramolecules via hydrogen bondings O5-H5··· O9, O7-H7··· O1, and O8- H8··· O3 (Fig. 1(d)). It is quite interesting to note that the water molecules play an important role in the formation of hydrogen bonds. Especially, the free water molecule involved oxygen atom O9, participates in four types of hydrogen bonds, that is O9-H9b··· O1, O9-H9A··· O8, O5-H5··· O9 and O8-H8A··· O9.

The hydrothermal reaction of Cd(II) acetate, 1,2,4-benzenetricarboxylate and NaOH in basified aqueous and ethanol solution were heated at 170°C for 5 days producing compound 2. The X-ray diffraction analysis reveals that compound 2 consists of $[Cd_2(btc)_2(OH_2)_2]$

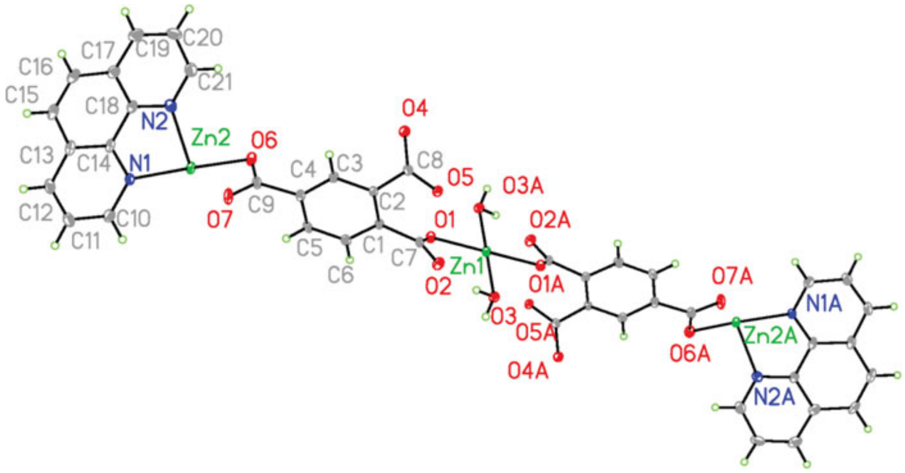


Figure 3. (a) Perspective view of complex **3** with the atom-numbering scheme (30% probability ellipsoids).

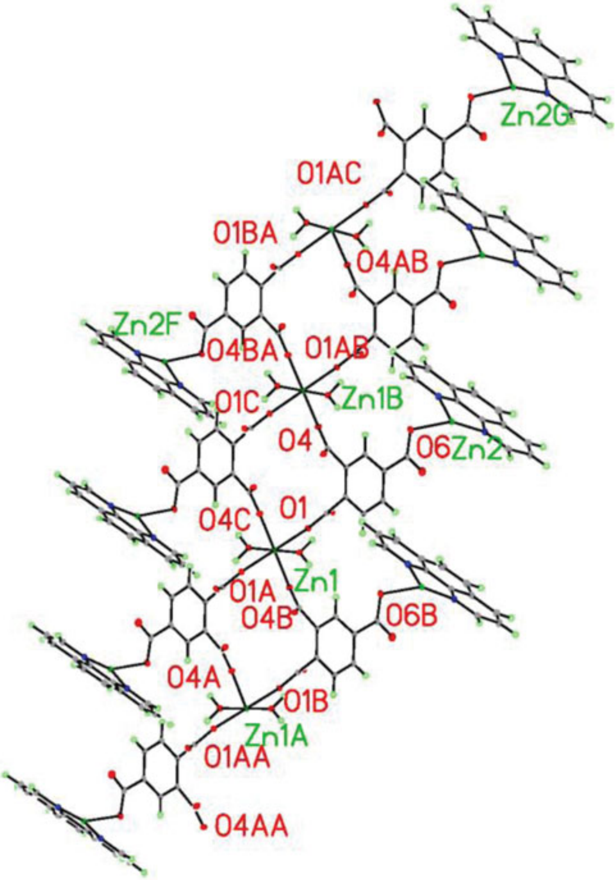


Figure 3. (b) The extended chain structure of in **3**.

dimers. There is one crystallographic unique Cd center in the structure of 2. The Cd center is seven-coordinated and displays a distorted pentagonal bipyramidal coordination geometry, which is completed by six carboxylic oxygen atoms from five btc ligands with the Cd-O bond length in the range of 2.274(3)–2.667(4) Å, and another oxygen atom from one coordinated water molecule(Cd-O = 2.401(3) Å). The O-Cd-O angles range from

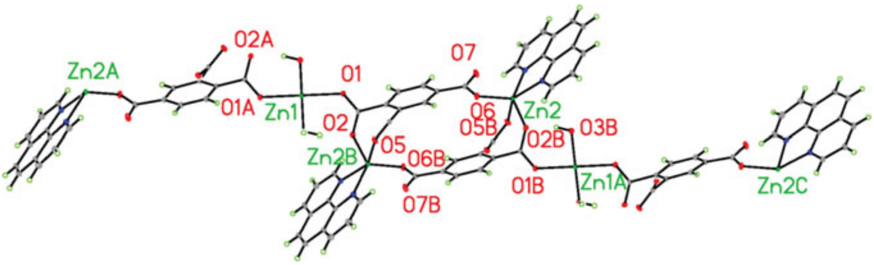


Figure 3. (c) The extended layer structure of in **3**, viewed down the *b*-axis.

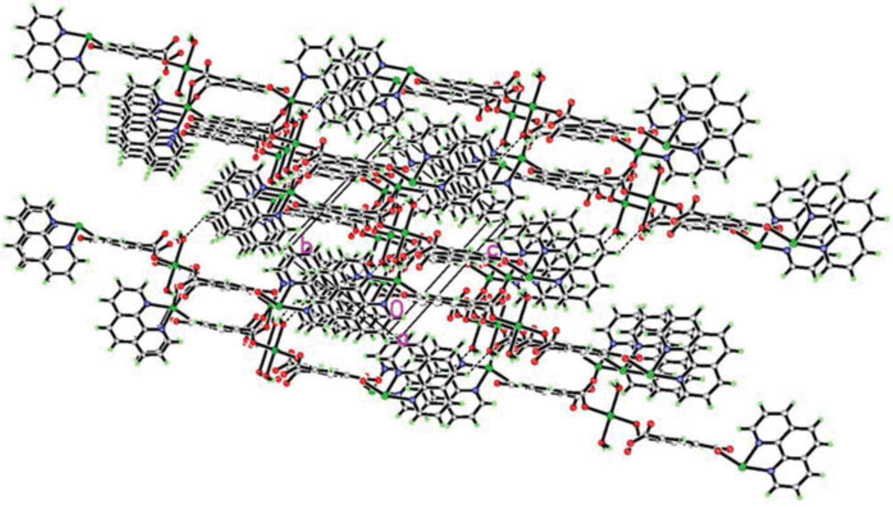
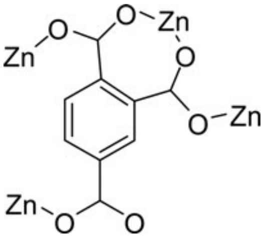


Figure 3. (d) 3D supramolecular network of **3** viewed down the *b*-axis.



Scheme 2. The coordination mode of 1, 2, 4-btc ligand in 3.

51.51(12)° to 156.00(13)°. The btc ligand exhibits an interesting connection mode with metal ions as shown in Scheme 1. Three carboxyl groups display three different kinds of coordination modes, that is, the monodentate, bidentate, and chelating–bridging tridentate mode. Based on these connection modes, every Cd1 and Cd1A center are linked by two btc ligands to form a dimer unit along *a*-axis (see Fig. 2(a)). Furthermore, the adjacent dimers are connected with each other to form a 2D lay parallel to the *b*-axis with two 2-carboxyl oxygen atoms of different btc ligands coordinating to two different Cd centers in the neighboring dimer, respectively (see Fig. 2(b)). Finally, these chains are extended to form a 3D network through Cd-O bonds involving 4-carboxyl oxygen atoms and Cd centers in parallelly adjacent lays (see Fig. 2(c)). Fig. 2(d) shows the packing arrangement of compound 2 along ac plane.

The hydrothermal reaction of Zn(II) acetate, 1,2,4-H_3btc, phen and NaOH with the ratio of 1:1:1:1 in basified aqueous and ethanol solution were heated at 160°C for 6 days forming compound 3. The complex 3 crystallizes in the triclinic system, with space group *P-1*. The fundamental unit is shown in Fig. 3(a). There are three crystallographically independent Zn(II) centers, which exhibit two different coordination environments. The first one is coordinated by four oxygen atoms from four different btc ligands and two oxygen atoms of coordinated water molecules to form an octahedral environment with Zn-O bond distances ranging from 2.070(3) –2.177(3) Å. The other two are coordinated by two nitrogen atoms from one phen (Zn–N = 2.096(3)– 2.192(4)Å) and three oxygen atoms from two btc ligands (Zn–O = 2.002(3) –2.686(4)Å) respectively to complete a distorted triangle bipyramid environment. The O(N)-Zn-O(N) angles vary from 54.15(12)° to 180.00°. Different from the coordination modes of btc in **2**, three carboxyl groups exhibit two different kinds of coordination modes in **3**, the monodentate and monodentate double-bridging mode, which is shown in **Scheme 2**. The most interesting structural feature of **3** is that the btc ligands link three Zn atoms into an infinite two-dimensional framework. Each unit involving three Zn centers are interconnected to form an infinite chain along the *a*-axis through Zn1-O bonds involving 2-carboxyl oxygen atoms and other Zn1 centers (see Fig. 3(b)), and the chains are further linked to form a 2D structure with 1-carboxyl and 2-carboxyl oxygen atoms of the same btc ligand coordinating to the same Zn2 center in the other units. Finally, the adjacent 2D layers are parallel with each other and construct a 3D framework via weak hydrogen bonding interactions with the coordinated H_2O molecules as acceptors and the C—H bond of the phen as donors (see Fig. 3(d)). The hydrogen bonding interactions enhance the stability of the compound and lead to a higher dimensional structure.

Conclusion

In this work, three metal–organic hybrid compounds, $[Zn(H_2btc)_2(H_2O)_2]\cdot 2H_2O$ (**1**), $[Cd(Hbtc)(H_2O)]_n$ (**2**), and $[Zn_3(btc)_2(phen)_2(H_2O)_2]n$ (**3**) have been hydrothermally synthesized and characterized. The structural motifs of these complexes are multiforms from 0D, 2D–3D interpenetrating networks. It is found that the H_3btc ligand exhibits multicoordinated modes. Comparing compound 1 with compound 3, as they have the same metal ion Zn, it is found that the introduction of the *N*-containing ligand phen leads to more complicated framework. In these complexes, the carboxylates of btc and water molecules are involved in intermolecular hydrogen bonds to reinforce the structural stability of complexes.

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Supplementary

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center with CCDC deposition numbers (CCDC: 1008740-1008742) for complexes 1–3, respectively. Copies of this information may be obtained free of charge from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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