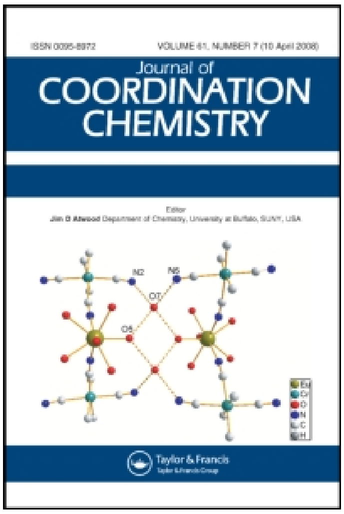

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Syntheses and structures of two copper coordination polymers with *bis* (1,2,4-triazol-1-ylmethyl)benzene and benzenedicarboxylate

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Syntheses and structures of two copper coordination polymers with *bis*(1,2,4-triazol-1-ylmethyl)benzene and benzenedicarboxylate

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Two copper coordination polymers $[Cu(obtz)(bdc)]_n$ (**1**) and $\{[Cu(obtz)(phth)]\cdot 2H_2O\}_n$ (**2**) (obtz = 1,2-*bis*(1,2,4-triazol-1-ylmethyl)benzene, bdc = 1,3-benzenedicarboxylate, phth = 1,4-benzenedicarboxylate) were synthesized and characterized. Both **1** and **2** are 2-D networks constructed via the bridging ligands bdc and phth. The obtz ligands do not extend the dimension (2-D network) but add their thickness, 10.9 Å for **1** and 11.6 Å for **2**. Complex **1** further constructs a 3-D network via $\pi-\pi$ stacking interactions between the benzene rings of obtz ligands of adjacent 2-D networks. The thermal stabilities have been investigated.

Keywords: Coordination polymer; *Bis*(1,2,4-triazol-1-ylmethyl)benzene; Benzenedicarboxylate; Copper complex; Crystal structure

1. Introduction

Crystal engineering of coordination frameworks have potential applications in magnetism, electric conductivity, molecular adsorption, molecular recognition and catalysis, and intriguing variety of architectures and topologies [1]. 1,2,4-Triazole and its derivatives combine the coordination geometry of both pyrazole and imidazole with regard to arrangement of their heteroatoms. Many transition metal complexes of 1,2,4-triazole derivatives have been synthesized [2]. However, 1,2-*bis*(1,2,4-triazol-1-methyl)benzene (obtz) (scheme 1) has not been exploited.

Metal-organic coordination polymers constructed from aromatic polycarboxylates, such as 1,3-benzenedicarboxylate (bdc) with 120° angle [3] and 1,4-benzenedicarboxylate (phth) with a 180° angle [4], between two carboxylates, have been extensively studied because of their diverse coordination modes and sensitivity to pH values of the carboxylate. However, coordination polymers with triazole and polycarboxylates are not well exploited [5].

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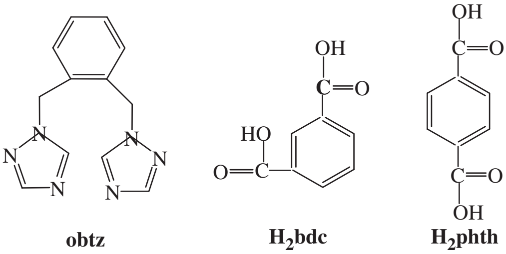

Scheme 1. Structures of obtz, H_2bdc, and H_2phth.

Recently, we synthesized a number of coordination polymers with flexible *bis*(triazole) ligands such as 1,2-*bis*(1,2,4-triazol-1-yl)ethane (bte) [6], 1,4-*bis*(1,2,4-triazol-1-methyl)benzene (bbtz) [7], 1,3-*bis*(1,2,4-triazol-1-methyl)benzene (mbtz) [8], and 1,4-*bis*(1,2,4-triazol-1-yl)butane (btb) [9]. In this article, two copper coordination polymers $[Cu(obtz)(bdc)]_n$ (**1**) and $\{[Cu(obtz)(phth)] \cdot 2H_2O\}_n$ (**2**) were synthesized with obtz, bdc, and phth. The crystal structures are presented and discussed. Thermal stabilities of both compounds have been investigated.

2. Experimental

2.1. *Materials and physical measurements*

2.1.1. Materials and general methods. All reagents were of analytical grade and used without purification. The obtz was synthesized according to the literature method [10]. Elemental analyses for C, H, and N were performed on a Perkin–Elmer 240C analyzer. IR spectra were obtained with KBr pellets on a Nicolet 170SX FT-IR spectrophotometer from 4000 to $400\,cm^{-1}$. TGA analyses were measured on a Thermal Analyst 2100 TA Instrument and a SDT 2960 Simultaneous TGA-DTA Instrument in flowing dinitrogen at a heating rate of $10°C\ min^{-1}$.

2.2. *Synthesis of $[Cu(obtz)(bdc)]_n$ (1)*

A solution of H_2bdc (0.033 g, 0.2 mmol) in 10 mL H_2O was adjusted to approximately pH 6 with dilute Et_3N solution. Then obtz (0.048 g, 0.2 mmol) in 10 mL CH_3OH was added and the mixture was placed on one side of an "H-shaped" tube. $Cu(NO_3)_2 \cdot 3H_2O$ (0.048 g, 0.2 mmol) in 20 mL of water was added to the other side of the tube. Blue crystals of **1** were obtained in 61% yield (0.057 g) after 1 month. Anal. Calcd for $C_{20}H_{16}CuN_6O_4$ (**1**) (%): C, 51.34; H, 3.44; N, 17.96. Found (%): C, 51.18; H, 3.36; N, 17.89. IR data (cm^{-1}): 1689m, 1605s, 1566s, 1405w, 1350vs, 1288m, 1242m, 1188w, 1126w, 1096w, 1003w, 794w, 725m, 694w, 671w, and 440w.

2.3. *Synthesis of $\{[Cu(obtz)(phth)] \cdot 2H_2O\}_n$ (2)*

The synthetic procedure was similar to the synthesis of **1**, except that H_2phth was used instead of H_2bdc. Blue crystals of **2** were obtained in 65% yield (0.066 g) after 1 month.

Table 1. Crystallographic data for compounds **1** and **2**.

	1	**2**
Empirical formula	$C_{20}H_{16}CuN_6O_4$	$C_{20}H_{20}CuN_6O_6$
Formula weight	467.93	503.96
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Temperature (K)	293(2)	223(2)
Unit cell dimensions (Å, °)		
a	11.2631(18)	9.128(2)
b	10.9751(17)	11.961(3)
c	15.581(3)	20.561(5)
α	90	90
β	95.302(4)	98.476(4)
γ	90	90
Volume (Å^3), Z	1917.7(5), 4	2220.3(10), 4
Calculated density (g cm^{-3})	1.621	1.508
Absorption coefficient (mm^{-1})	1.182	1.033
$F(000)$	956	1036
Reflections collected	18,130	11,346
Unique reflections	3505 [R(int) = 0.0500]	5043 [R(int) = 0.0266]
Parameters	280	307
Goodness-of-fit on F^2	1.087	1.092
R_1 [$I > 2\sigma(I)$]	0.0555	0.0674
wR_2 (all data)	0.1277	0.1977

Anal. Calcd for $C_{20}H_{20}CuN_6O_6$ (**2**) (%): C, 47.67; H, 4.00; N, 16.68. Found (%): C, 47.62; H, 3.85; N, 16.65. IR data (cm^{-1}): 3415vs, 1656s, 1628s, 1532m, 1474w, 1437w, 1345w, 1292w, 1238w, 1192w, 1167w, 1130w, 1030w, 989w, 935w, 835w, 748w, 665m, and 599w.

2.4. *X-ray crystallography*

Suitable single crystals of **1** and **2** were carefully selected under an optical microscope and glued to thin glass fibers. Diffraction data were collected on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Intensities were collected by the ω scan technique. The structures were solved by direct methods and refined with full-matrix least-squares (SHELXTL-97) [11]. The positions of the hydrogens of organic ligands were determined from calculation. No appropriate hydrogens of the disordered water molecules of **2** were obtained. The parameters of the crystal data collection and refinement of **1** and **2** are given in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structures*

3.1.1. [Cu(obtz)(bdc)]$_n$ (1). The crystal structure of **1** is a 2-D coordination network. The coordination geometry of Cu(II) in **1** is a distorted octahedron, with equatorial plane containing four oxygens (Cu(1)–O(1) 1.967(3) Å, Cu(1)–O(2) 2.703(3) Å,

Table 2. Selected bond lengths (Å) and angles (°) for compounds **1** and **2**.

1			
Cu(1)–O(1)	1.967(3)	Cu(1)–O(2)	2.703(3)
Cu(1)–O(4A)	1.938(3)	Cu(1)–O(3C)	2.372(3)
Cu(1)–N(3)	2.003(3)	Cu(1)–N(6B)	1.994(3)
O(1)–Cu(1)–O(2)	53.97(10)	O(4A)–Cu(1)–O(2)	101.45(10)
O(1)–Cu(1)–O(3C)	84.15(11)	O(4A)–Cu(1)–O(3C)	120.40(11)
N(6B)–Cu(1)–N(3)	173.23(13)	O(1)–Cu(1)–N(3)	93.05(12)
O(1)–Cu(1)–N(6B)	89.96(13)	N(3)–Cu(1)–O(2)	96.76(12)
N(6B)–Cu(1)–O(2)	89.91(12)	O(4A)–Cu(1)–N(3)	88.14(12)
O(4A)–Cu(1)–N(6B)	91.64(13)	N(3)–Cu(1)–O(3C)	84.04(13)
N(6B)–Cu(1)–O(3C)	90.24(13)		
2			
Cu(1)–O(1)	1.971(3)	Cu(1)–O(2)	2.803(4)
Cu(1)–O(3B)	2.049(3)	Cu(1)–O(4B)	2.611(5)
Cu(1)–O(4C)	2.522(5)	Cu(1)–N(3)	1.968(3)
Cu(1)–N(6A)	1.982(3)		
O(1)–Cu(1)–O(2)	51.58(11)	O(3B)–Cu(1)–O(2)	99.17(14)
O(3B)–Cu(1)–O(4B)	54.49(15)	O(4B)–Cu(1)–O(4C)	73.26(12)
O(1)–Cu(1)–O(4C)	81.80(13)	N(3)–Cu(1)–N(6A)	173.76(15)
N(3)–Cu(1)–O(1)	90.79(13)	N(3)–Cu(1)–O(2)	99.12(13)
N(3)–Cu(1)–O(3B)	90.58(14)	N(3)–Cu(1)–O(4B)	90.24(13)
N(3)–Cu(1)–O(4C)	87.01(14)	O(1)–Cu(1)–N(6A)	92.70(13)
N(6A)–Cu(1)–O(2)	87.10(13)	N(6A)–Cu(1)–O(3B)	88.92(14)
N(6A)–Cu(1)–O(4B)	84.41(13)	N(6A)–Cu(1)–O(4C)	88.38(14)

Symmetry transformations used to generate equivalent atoms: A: $x-1/2$, $-y+3/2$, $z+1/2$; B: $-x+1$, $-y+1$, $-z+1$; C: $-x+3/2$, $y-1/2$, $-z+1/2$ for **1**. A: $-x+2$, $-y+1$, $-z$; B: $x-1/2$, $-y+1/2$, $z-1/2$; C: $-x+5/2$, $y+1/2$, $-z+1/2$ for **2**.

Cu(1)–O(4A) 1.938(3) Å, and Cu(1)–O(3C) 2.372(3) Å) from three bdc ligands, and the axial positions are occupied by two nitrogens from two obtz ligands (Cu(1)–N(3) 2.003(3) Å and Cu(1)–N(6B) 1.994(3) Å) (figure 1). One COO (O(1)O(2)) of bdc exhibits bidentate chelating coordination. The other COO (O(3)O(4)) of bdc exhibits bidentate bridging. Two bridging COO groups and two obtz join two Cu(II)'s to form a $[Cu_2(obtz)_2(bdc)_2]$ dimer, with Cu···Cu distance of 4.3129(8) Å.

Each bdc connects two $[Cu_2(obtz)_2(bdc)_2]$ dimers with Cu···Cu distances of 8.5339(11) and 10.4697(15) Å. Each $[Cu_2(obtz)_2(bdc)_2]$ dimer is four-connected, linking four $[Cu_2(obtz)_2(bdc)_2]$ dimers with its four COO groups. A 2-D planar network is constructed via the bdc bridges (figure 2). The obtz ligands do not extend the 2-D network but add the thickness of 10.9 Å. The obtz ligands exhibit *gauche* conformation. The dihedral angle between two triazole ring planes of obtz is 22.9° and the centroid-to-centroid distance is 3.869 Å, showing obvious intramolecule $\pi-\pi$ stacking interaction which stabilizes its conformation.

Adjacent 2-D networks stack parallel with intersheet distance of 9.7 Å. There are obvious $\pi-\pi$ stacking interactions between benzene rings (the perpendicular distance of one centroid to the other plane is 3.350 Å and the centroid-to-centroid distance is 3.807 Å of the benzene rings) of obtz of adjacent 2-D networks. Through these $\pi-\pi$ stacking interactions, compound **1** further constructs a 3-D network (figure 3).

3.1.2. $\{[Cu(obtz)(phth)] \cdot 2H_2O\}_n$ (2). The structure of **2** is a 2-D network with Cu(II), a pentagonal bipyramid, coordinated with five oxygens from three COO groups from three phth ligands (Cu(1)–O(1) 1.971(3) Å, Cu(1)–O(2) 2.803(4) Å, Cu(1)–O(3B)

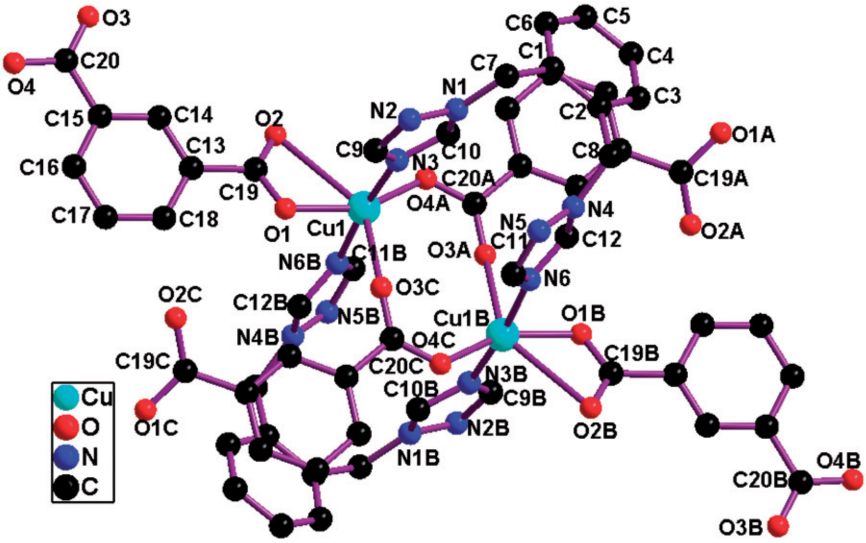

Figure 1. The coordination environment of Cu(II) of **1**, and hydrogens have been omitted for clarity.

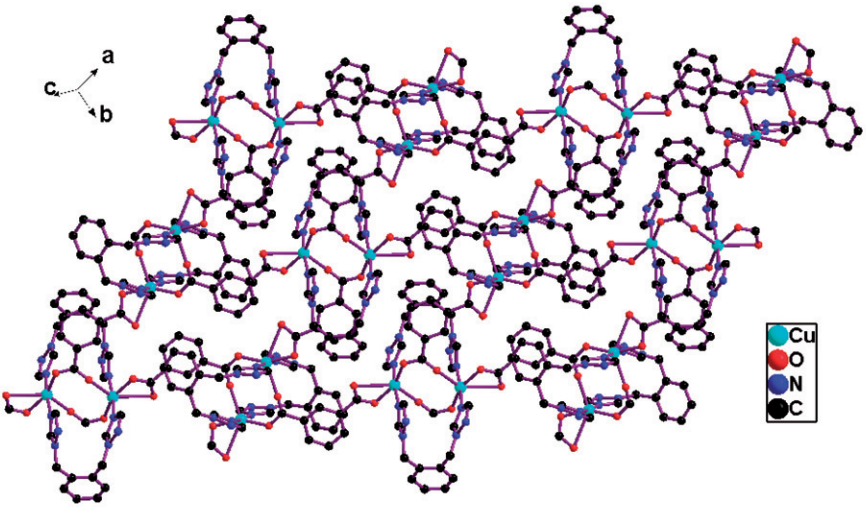

Figure 2. The 2-D network of **1**.

2.049(3) Å, Cu(1)–O(4B) 2.611(5) Å, and Cu(1)–O(4C) 2.522(5) Å) in plane, and two nitrogens from two obtz ligands (Cu(1)–N(3) 1.968(3) Å and Cu(1)–N(6A) 1.982(3) Å) in apical positions (figure 4). One COO group (O(1)O(2)) of phth exhibits bidentate chelating coordination and the other COO group (O(3)O(4)) of phth exhibits tridentate bridging. Two bridging COO groups and two obtz join two Cu(II)'s to form a $[Cu_2(obtz)_2(phth)_2]$ dimer, with Cu···Cu distance of 4.1196(11) Å.

Each phth connects two $[Cu_2(obtz)_2(phth)_2]$ dimers with Cu···Cu distances of 10.7791(18) and 10.9206(23) Å. Each $[Cu_2(obtz)_2(phth)_2]$ dimer is four-connected, linking four $[Cu_2(obtz)_2(phth)_2]$ dimers with four COO groups, and constructs a 2-D

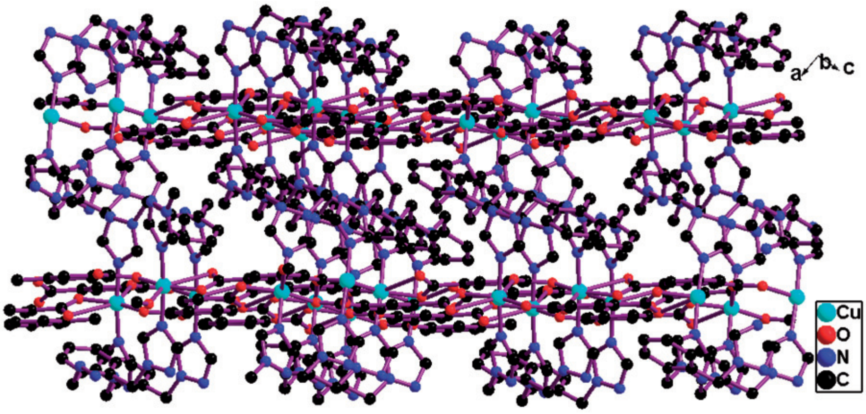

Figure 3. Packing of two adjacent 2-D networks of **1**.

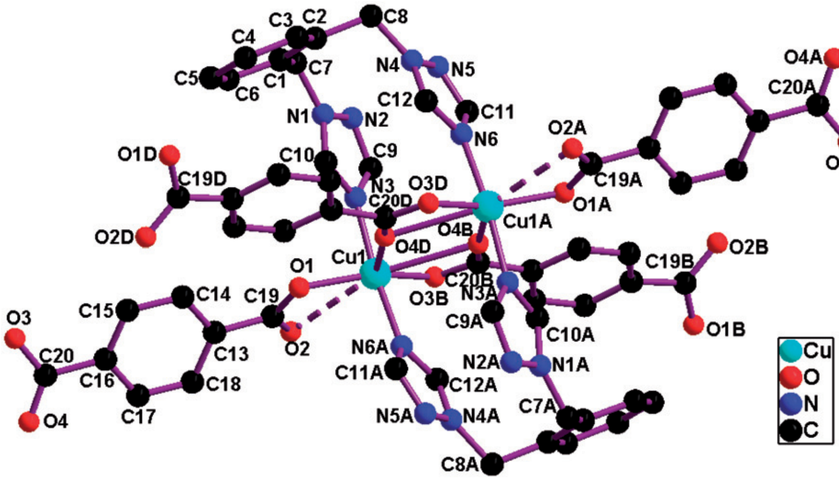

Figure 4. The coordination environment of Cu(II) of **2**, and hydrogens have been omitted for clarity.

planar network (figure 5). The obtz ligands do not extend the 2-D network but add the thickness of 11.6 Å. The obtz ligands are *gauche*. The dihedral angle between two triazole rings of obtz is 16.4° and the centroid-to-centroid distance is 3.577 Å, showing obvious intramolecule π–π stacking interaction which stabilizes its conformation.

Adjacent 2-D networks stack parallel with intersheet distance of 11.3 Å. There are not obvious π–π stacking interactions between benzene rings of obtz of adjacent 2-D networks (figure 6).

3.2. *Thermal stability*

The thermal stabilities of **1** and **2** have been investigated (Supplementary material). Compound **1** is stable to 226°C and then displays an explosive decomposition from 226 to 240°C. This may be attributed to the decomposition of bdc (observed: 30.7%;

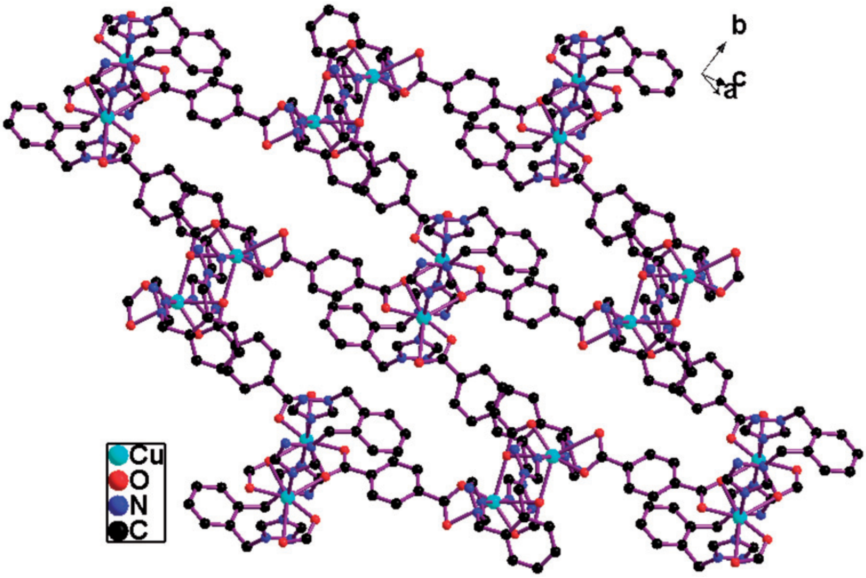

Figure 5. The 2-D network of **2**.

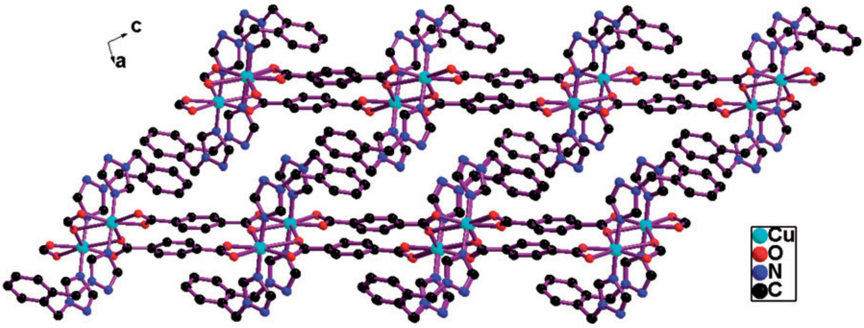

Figure 6. Packing of two adjacent 2-D networks of **2**.

Calcd: 31.63% for $C_8H_4O_4$). Weight of **1** is not lost from 240 to 286°C, but above 286°C **1** continuously rapidly lost weight. The residue may be CuO (observed: 17.69%; Calcd 16.97%) upon heating to 750°C. Compound **2** loses two lattice waters from 37 to 122°C (observed: 6.91%; Calcd 7.14%), rapidly decomposes in the range 274–420°C (observed: 49.59%), and then slowly decomposes from 420 to 750°C (observed: 11.17%). The residue is 29.81% weight upon heating to 750°C. No reasonable fragments can be assigned corresponding to the weight loss processes of **2**.

4. Conclusion

Several coordination polymers with triazole and polycarboxylate mixed-ligands have been synthesized [5]. $[Zn_2(bte)_2(obdc)_2]$ (obdc = 1,2-benzenedicarboxylate) exhibits a 2-D network through helical chains linking $Zn_2(obdc)_2$ 14-membered rings forming 50-membered macrometallacyclic rings. $[Zn(bte)(phth)] \cdot 2H_2O$ constructs a 2-D rhombic network through bridging phth ligands linking $Zn_2(bte)_2$ 18-membered rings [5a]. $[Zn_2(phth)_2(btb)_2] \cdot 2H_2O$ exhibits a three-fold interpenetrated diamondoid network [5b], but a supramolecular isomer $[Zn(phth)(btb)] \cdot 0.5H_2O$ is a special 2-D (6,3) network [5c]. $[Zn(phth)(btb)_{0.5}]$ adopts a three-fold interpenetrated α-polonium-type network based on bimetallic cores. $[Zn(oba)(btb)_{0.5}]$ (oba = 4,4′-oxybis(benzoate)) comprises a novel (3,4)-connected three-fold interpenetrated network. $[Cd_3(phth)_3(btb)_2(H_2O)_2]$ shows a self-penetrated eight-connected $4^{20}6^8$ topology [5b]. $[Cd_2(phth)_2(btb)(H_2O)_2] \cdot 7H_2O$ exhibits a distorted 3-D cubic topology that is built from dimer Cd_2 units [5c]. $[Cd_2(btec)(btb)_3] \cdot 10H_2O$ (btec = 1,2,4,5-benzenetetracarboxylate) constructs a novel 3-D network containing an "opened-cube" with an outer edge discrete water decamer. $[Cd_2(obdc)_2(btb)(H_2O)_3] \cdot 4.5H_2O$ (**2**) forms a thick 2-D network containing an undulated water chain [5d]. Habib *et al.* [5e] synthesized 3-D Ni and Zn coordination polymers using mixed-ligand 1,2-*bis*(1,2,4-triazol-4-yl)ethane (btre, a isomer of bte) and 1,3,5-benzenetricarboxylate, which exhibit solid-state crystal-to-crystal transition upon drying, antiferromagnetic coupling (Ni), and luminescence (Zn).

The coordination polymers $[Cu(obtz)(bdc)]_n$ (**1**) and $\{[Cu(obtz)(phth)] \cdot 2H_2O\}_n$ (**2**) have different structures from the structures of the reported 14 coordination polymers with the triazole and polycarboxylate mixed-ligands [5]. Two COO groups of bdc of **1** show bidentate chelating and bidentate bridging coordination while COO groups of phth of **2** show bidentate chelating and tridentate bridging coordination. Two bridging COO groups link two Cu(II)'s forming a dimer. Each dimer joins four dimers through four bdc ligands of **1** (phth of **2**) constructing a 2-D network. The obtz ligands do not extend the 2-D network but add their thickness (10.9 Å for **1** and 11.6 Å for **2**). Complex **1** further constructs a 3-D network via π–π stacking interactions between benzene rings of obtz of adjacent 2-D networks. However, there are no obvious π–π stacking interactions between the benzene rings of obtz ligands of the adjacent 2-D networks of **2**.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, with CCDC reference numbers CCDC-724345 for **1**, CCDC-724346 for **2**.

Acknowledgments

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