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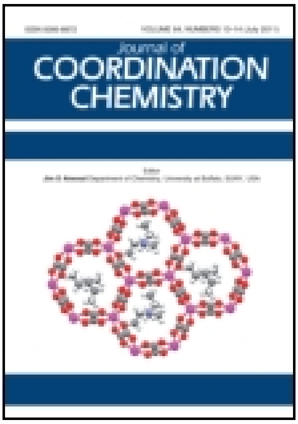

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Copper(II) coordination polymers constructed from flexible ligands with different spacer lengths: syntheses, structures, and properties

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Copper(II) coordination polymers constructed from flexible ligands with different spacer lengths: syntheses, structures, and properties

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A new family of coordination polymers, $\{[Cu(btm)_2(H_2O)_2](NO_3)_2(H_2O)_4\}_n$ (**1**, btm = bis(1,2,4-triazol-1-yl)methane), $\{[Cu(bte)_2(H_2O)_2](NO_3)_2\}_n$ (**2**, bte = 1,2-bis(1,2,4-triazol-1-yl)ethane), $[Cu(btp)_2(NO_3)_2]_n$ (**3**, btp = 1,3-bis(1,2,4-triazol-1-yl)propane), and $\{[Cu(btb)_2(H_2O)_2](NO_3)_2\}_n$ (**4**, btb = 1,4-bis(1,2,4-triazol-1-yl)butane), have been prepared under hydrothermal conditions and characterized by X-ray structural analyses. The bis(triazole) ligands with different spacer lengths exhibit conformational flexibility and lead to diverse architectures. Compound **1** shows 2-D rectangular networks with (4,4) topology, with 2-D planar nanogrid networks stacked in a step stacking fashion. Compounds **2** and **3** show 1-D double-strained chains; **4** is a 3-D *dia* diamond network with one point, $\{6^6\}$. Elemental analysis, IR, and thermal stability also characterize the compounds.

Keywords: Bis(1,2,4-triazol-1-yl)methane; 1,2-Bis(1,2,4-triazol-1-yl)ethane; 1,3-Bis(1,2,4-triazol-1-yl)propane; 1,4-Bis(1,2,4-triazol-1-yl)butane; Supramolecular structure; Hydrogen-bond interaction

1. Introduction

Coordination polymers have attracted interest as materials with potential for new electronic, optical, magnetic, and/or catalytic properties [1–7]. A key step for construction of polymeric transition metal complexes is to select appropriate multidentate bridging ligands [8–12]. Recently, new flexible bispolyazole ligands such as 1- or 4-substituted 1,2,4-triazole rings tethered by alkyl spacers have been used to obtain a variety of polynuclear molecules and linear coordination polymers [13, 14]. Mononuclear, oligonuclear, and polynuclear metal coordination compounds with bis(1,2,4-triazole) derivatives have been prepared and characterized due to interesting magnetic properties and topologies [15–25]. The characteristics of flexible bis(triazole) ligands are: (1) the flexible bis(triazole) ligands can adopt different conformations on the basis of relative orientations of CH_2 groups which allow bending and rotating to conform to the coordination environment of the metal ions, creating structural diversity

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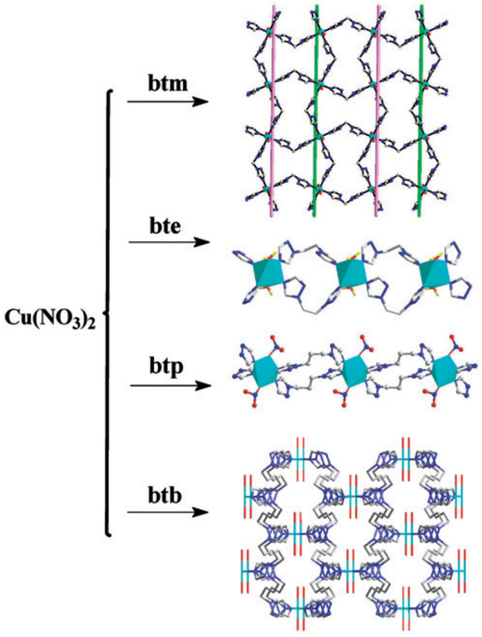
[26–28] and (2) the flexible bis(triazole) ligands possess four potential coordination sites, enhancing coordination capacity to obtain unexpected structures.

We reported crystal structures of a series of transition metal coordination polymers (Cd^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}) with flexible bis(triazole) ligands [29–32]. To extend our work, four new copper(II) coordination polymers, $\{[Cu(btm)_2(H_2O)_2](NO_3)_2(H_2O)_4\}_n$ (**1**, btm = bis(1,2,4-triazol-1-yl)methane), $\{[Cu(bte)_2(H_2O)_2](NO_3)_2\}_n$ (**2**, bte = 1,2-bis(1,2,4-triazol-1-yl)ethane), $[Cu(btp)_2(NO_3)_2]_n$ (**3**, btp = 1,3-bis(1,2,4-triazol-1-yl)propane), and $\{[Cu(btb)_2(H_2O)_2](NO_3)_2\}_n$ (**4**, btb = 1,4-bis(1,2,4-triazol-1-yl)butane), were fabricated with different flexible bis(triazole) ligands as spacers. The solids exhibit structures varying from 1-D chain to 3-D architecture with interesting supramolecular architectures (scheme 1). The role of the flexible bis(triazole) ligands on the resulting structure of the four polymers is discussed. IR spectra and thermal stabilities of these complexes are also discussed.

2. Experimental

2.1. *General remarks*

The bridging bis(triazole) ligands were synthesized according to the literature method [33]. All other reagents and solvents were commercially available and used without purification. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer elemental analyzer. TG experiments were performed on a NETZSCH TG 209 instrument with a heating rate of 10°C min^{-1} under nitrogen.



Scheme 1. Syntheses of **1**–**4**.

2.2. *Syntheses of 1–4*

All four compounds were obtained by mixing $Cu(NO_3)_2 \cdot 3H_2O$ (14 mg, 0.06 mmol), bis-triazole (0.06 mmol, btm for **1**, bte for **2**, btp for **3**, btb for **4**), H_2O (2 mL), and CH_3CN (2 mL) in a Parr Teflon-lined stainless steel vessel (15 mL), and then the vessel was sealed and heated to 90°C for 3 days. The autoclave was cooled to room temperature at $1.5^\circ C\,h^{-1}$ and blue block crystals **1**–**4** were obtained.

Anal. Calcd for $C_{10}H_{24}CuN_{14}O_{12}$ (**1**) (%): C, 20.15; H, 4.06; N, 32.91. Found (%): C, 20.57; H, 4.22; N, 32.48.

Anal. Calcd for $C_{12}H_{20}CuN_{14}O_8$ (**2**) (%): C, 26.11; H, 3.65; N, 35.54. Found (%): C, 25.97; H, 3.28; N 35.11.

Anal. Calcd for $C_{14}H_{20}CuN_{14}O_6$ (**3**) (%): C, 30.90; H, 3.71; N, 36.06. Found (%): C, 30.55; H, 3.44; N 36.39.

Anal. Calcd for $C_{16}CuH_{28}N_{14}O_8$ (**4**) (%): C, 31.60; H, 4.64; N, 32.26. Found (%): C, 31.50; H, 4.24; N 32.49.

2.3. *Crystallographic data collection and structure determination*

Single-crystal X-ray diffraction measurements of **1**–**4** were carried out with a Bruker Smart CCD diffractometer and a graphite crystal monochromator situated in the incident beam for data collection at room temperature. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXS-97 and SHELXL-97 [34, 35]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and refined isotropically. Crystallographic data for **1**–**4** are summarized in table 1. Bond distances and angles of **1**–**4** are listed in table 2.

3. Results and discussion

3.1. *Crystal structure of 1*

Compound **1** crystallizes in the space group $P2_1/n$. The asymmetric unit consists of one btm, one coordinated water molecule, one free NO_3^- and two free water molecules. As shown in figure 1(a), the Cu adopts a distorted octahedral environment, in which the apical positions are completed by two oxygen atoms (O1 and O1A) from two coordinated water molecules, and the basal plane is formed by four nitrogen atoms (N1, N1A, N6B, and N6C) from four different btm ligands. The btm exhibits *trans* conformation and the dihedral angle between the triazole rings is 113.2°. The torsion angles N3–N2–C3–N4 and N5–N4–C3–N2 are 72.1(8)° and 91.1(9)°, respectively.

As shown in figure 1(b), btm spacers bridge Cu(II) centers to afford 1-D $[Cu(btm)]_n$ motifs with 2_1 helicity along the [010] direction, in which the helical pitch is equal to the length of the *b*-axis. Neighboring helical arrays are further connected by btm spacers to generate a 2-D coordination layer (figure 1b). In **1**, one coordinated water molecule and two solvent water molecules form water trimers (table 3), which are further linked by NO_3^- to form a 2-D supramolecular layer (figure 2a). The 2-D hydrogen-bond layers

Table 1. Crystallographic data and structure refinement details for **1**–**4**.

	1	**2**	**3**	**4**
Formula	$C_{10}H_{24}CuN_{14}O_{12}$	$C_{12}H_{20}CuN_{14}O_8$	$C_{14}H_{20}CuN_{14}O_6$	$C_{16}CuH_{28}N_{14}O_8$
Formula weight	595.98	551.96	543.98	608.08
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$Fddd$
Unit cell dimensions (Å, °)				
a	7.9724(6)	8.43830(16)	7.5888(8)	16.9982(12)
b	13.7910(4)	15.9561(5)	8.7339(10)	12.8924(8)
c	10.8841(4)	16.3975(3)	9.1187(14	24.7143(16)
α	90	90.00	79.001(11)	90
β	90.968(4)	91.8688(17)	75.737(11)	90
γ	90	90.00	64.706(11)	90
Volume ($Å^3$), Z	1196.51(10), 2	2206.63(9), 4	527.07(11), 1	5416.1(6), 8
Calculated density ($Mg\,m^{-3}$)	1.654	1.661	1.714	1.491
Absorption coefficient (mm^{-1})	0.999	1.063	1.105	0.874
$F(000)$	614	1132	279	2519
θ range for data collection (°)	2.38–25.00	2.41–25.01	2.59–25.01	2.91–25.01
Limiting indices	$-9 \le h \le 7$; $-16 \le k \le 14$; $-9 \le l \le 12$	$-10 \le h \le 10$; $-17 \le k \le 18$; $-19 \le l \le 11$	$-9 \le h \le 9$; $-10 \le k \le 8$; $-8 \le l \le 10$	$-13 \le \mathrm{h} \le 20$; $-15 \le \mathrm{k} \le 6$; $-29 \le \mathrm{l} \le 19$
Reflections collected/unique	4486/2099	8982/3884	3365/2406	3428
Goodness-of-fit on F^2	1.049	1.126	1.080	1.383
R_1/wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0372$, $wR_2 = 0.0871$	$R_1 = 0.0718$, $wR_2 = 0.2088$	$R_1 = 0.0743$, $wR_2 = 0.1516$	$R_1 = 0.1032$ $wR_2 = 0.3091$
R_1/wR_2 (all data)	$R_1 = 0.0449$, $wR_2 = 0.0928$	$R_1 = 0.0943$, $wR_2 = 0.2186$	$R_1 = 0.1006$, $wR_2 = 0.1822$	$R_1 = 0.1147$ $wR_2 = 0.3226$

link the 2-D layers through N5–H6B···O6 (3.125(5) Å) to form a 3-D superframework (figure 2b).

3.2. *Crystal structure of 2*

When bte was used instead of btm, a 1-D chain (**2**) with ribbons of an 18-membered cycle was obtained. As shown in figure 3(a), the Cu(II) center in **2** lies in a distorted CuN_4O_2 octahedral environment, which is provided by four nitrogen atoms from four different bte ligands and two oxygen atoms from two water molecules. The axial Cu1–O1 (2.507(5) Å) and Cu1–O2 (2.438(5) Å) distances are a little longer than normal Cu–O distances, attributed to Jahn-Teller elongation. The two kinds of bte ligands adopt *gauche* conformations and the dihedral angles between the triazole rings are 57.0° and 122.9°, respectively (figure 3a). The torsion angles N2–N3–C3–C4, N5–N4–C4–C3, N9–N8–C9–C10, and N11–N10–C10–C9 are 74.3(8)°, 68.2(7)°, 65.2(7)°, and 65.3(9)°, respectively. The two different conformations of bte ligands give the same μ_2 coordination mode.

Every Cu(II) is linked by four bte ligands, leading to a 1-D chain along the *a*-direction with Cu···Cu separations of 8.438 Å, as depicted in figure 3(b). Between every two chains, there is a 1-D supermolecular chain from hydrogen bonds between free NO_3^- and coordinated water, which connects chains to give a 2-D layer (figure 3c). The resulting 2-D structures are cross-linked by weak hydrogen-bond interactions (C4–H4A···O1 3.239(3) Å, C4–H4A···O5 3.675(3) Å, C10–H10A···O4 3.398(3) Å,

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**4**.

1			
Cu(1)–N(1)	2.023(2)	N(1)–Cu(1)–N(6)#2	89.92(8)
Cu(1)–N(6)#2	2.043(2)	N(1)–Cu(1)–N(6)#3	90.08(8)
Cu(1)–O(1)	2.386(2)	N(1)–Cu(1)–O(1)#1	89.14(8)
N(1)–Cu(1)–N(1)#1	180.0	N(1)–Cu(1)–O(1)	90.87(8)
N(6)#2–Cu(1)–O(1)	89.90(8)	N(6)#3–Cu(1)–O(1)	90.10(8)
O(1)#1–Cu(1)–O(1)	180.00(8)		
2			
Cu(1)–N(7)	1.998(5)	N(1)–Cu(1)–N(6)#1	89.67(18)
Cu(1)–N(1)	2.009(5)	N(7)–Cu(1)–N(12)#2	89.76(19)
Cu(1)–N(6)#1	2.010(4)	N(1)–Cu(1)–N(12)#2	90.64(19)
Cu(1)–N(12)#2	2.019(5)	N(6)#1–Cu(1)–N(12)#2	90.53(19)
Cu(1)–O(2)	2.438(5)	N(7)–Cu(1)–O(2)	83.29(11)
Cu(1)–O(1)	2.507(5)	N(1)–Cu(1)–O(2)	89.20(19)
N(7)–Cu(1)–N(1)	179.5(2)	N(6)#1–Cu(1)–O(2)	87.12(18)
N(7)–Cu(1)–N(6)#1	89.95(18)	N(12)#2–Cu(1)–O(2)	96.49(19)
O(2)–Cu(1)–O(1)	174.84(16)	N(1)–Cu(1)–O(1)	88.62(18)
3			
Cu(1)–N(12)#1	2.004(18)	N(12)#1–Cu(1)–N(7)	93.7(6)
Cu(1)–N(6)#2	2.021(16)	N(6)#2–Cu(1)–N(7)	87.9(6)
Cu(1)–N(1)	2.024(15)	N(1)–Cu(1)–N(7)	176.7(9)
Cu(1)–N(7)	2.025(15)	N(12)#1–Cu(1)–O(4)	90.5(6)
Cu(1)–O(4)	2.373(15)	N(6)#2–Cu(1)–O(4)	91.3(6)
Cu(1)–O(1)	2.380(16)	N(1)–Cu(1)–O(4)	85.8(5)
N(12)#1–Cu(1)–N(6)#2	177.4(9)	N(7)–Cu(1)–O(4)	97.3(6)
N(12)#1–Cu(1)–N(1)	87.5(6)	N(12)#1–Cu(1)–O(1)	92.9(6)
N(6)#2–Cu(1)–N(1)	90.9(6)	N(1)–Cu(1)–O(1)	84.7(6)
N(6)#2–Cu(1)–O(1)	85.0(6)	N(7)–Cu(1)–O(1)	92.1(6)
O(4)–Cu(1)–O(1)	169.8(5)		
4			
Cu(1)–N(1)	2.007(5)	N(1)#2–Cu(1)–N(1)	178.9(3)
Cu(1)–O(1)	2.409(6)	N(1)#3–Cu(1)–N(1)	89.7(3)
N(1)#1–Cu(1)–N(1)	90.3(3)	N(1)#1–Cu(1)–O(1)#3	89.46(14)
N(1)#2–Cu(1)–O(1)#3	90.54(14)	O(1)#3–Cu(1)–O(1)	179.999(1)

Symmetry transformations used to generate equivalent atoms: for **1** #1 $-x, -y+1, -z+1$; #2 $-x+1/2, y+1/2, -z+1/2$; #3 $x-1/2, -y+1/2, z+1/2$; for **2** #1 $x+1, y, z$; #2 $x-1, y, z$; for **3** #1 $x-1, y, z+1$; #2 $x+1, y, z-1$; for **4** #1 $-x+7/4, y, -z+7/4$; #2 $x, -y+3/4, -z+7/4$; #3 $-x+7/4, -y+3/4, z$.

and C9–H9A···O4 3.169(3) Å) (table 3) between C–H groups in bte and oxygen atoms in free NO_3^-, leading to a 3-D supramolecular architecture, as shown in figure 3(d).

3.3. *Crystal structure of 3*

Compound **3** also features a double-stranded chain which is composed of ribbons of a 20-membered cycle. Both **2** and **3** have the same CuN_4O_2 polyhedra as fundamental units. However, there are some differences about the basic structural units in **2** and **3**. In **3**, copper(II) lies in the general position and comprises two nitrates in comparison to water molecules in **2**. Both btp ligands in **3** exhibit *trans* and *gauche* conformations and the dihedral angles between the triazole rings are 108.9° and 109.4°, respectively (figure 4a).

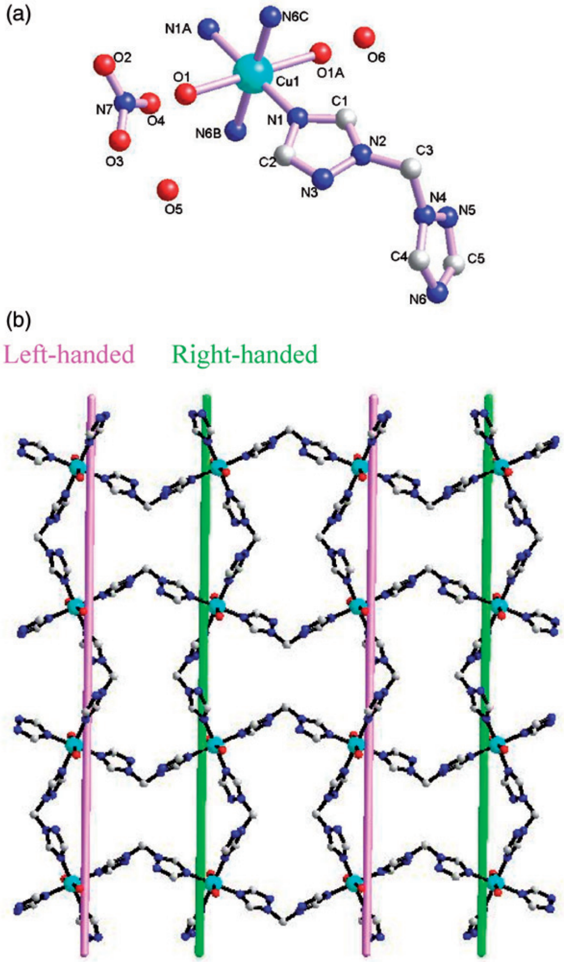


Figure 1. (a) Molecular structure of **1** showing the coordination environments of Cu^{2+} and btm. Symmetry operator: $A = -x,\ 1-y,\ 1-z$; $B = -0.5+x,\ 0.5-y,\ 0.5+z$; $C = 0.5-x,\ 0.5+y,\ 0.5-z$. (b) The 2-D coordination layer of **1** highlighting the left- and right-handed helical arrays.

All btp ligands have the same μ_2 coordination. Every Cu(II) is linked by four btp ligands, leading to a 1-D chain along the *c*-direction with Cu···Cu separations of 10.327 Å, *ca* 1.9 Å longer than that in **2** (figure 4b). In addition, C–H···O hydrogen-bonding interactions between C–H groups in btp and oxygen atoms in free NO_3^- connect the chains to give a 3-D supramolecular framework (figure 4c and table 3).

3.4. *Crystal structure of 4*

Compound **4** is isomorphous to our recently reported Cu(II) complex $\{[Cu(btb)_2(H_2O)_2](ClO_4)_2\}_n$ [36]. The coordination environment of **4** is like **2**. All btb ligands adopt *gauche trans gauche* conformations and the two triazole rings are exactly

Table 3. Selected hydrogen-bond data for **1**–**4**.

Interaction	H···A (Å)	D···A (Å)	D–H···A (°)	Symmetry operation
1				
O1–H1A···O4	1.997	2.829	167.44	$-x+3/2,\ y-1/2,\ -z+3/2$
O1–H1A···O2	2.618	3.275	135.30	$-x+3/2,\ y-1/2,\ -z+3/2$
O1–H1B···O5	1.877	2.805	178.92	
O5–H5A···O6	1.944	2.778	162.63	$x,\ y,\ z+1$
O5–H5B···O4	1.926	2.772	169.67	$x-1,\ y,\ z$
O6–H6A···O3	2.128	2.975	172.53	$x-1/2,\ -y+3/2,\ z-1/2$
O6–H6B···N5	2.351	3.125	152.05	$-x,\ -y+1,\ -z$
2				
O1–H1A···O5	2.026	2.835	158.73	$-x+1,\ -y,\ -z+1$
O1–H1B···O6	2.076	2.895	161.31	$x,\ y-1,\ z$
O2–H2A···O7	2.062	2.901	170.13	$-x+1,\ y-1/2,\ -z+1/2$
O2–H2B···O3	2.138	2.978	172.21	$1+x,\ -y+1/2,\ z-1/2$
C4–H4A···O1	2.865	3.239	104.00	$1-x,\ -y,\ -z$
C4–H4A···O5	2.821	3.675	147.37	$1-x,\ -y,\ -z$
C10–H10A···O4	2.740	3.398	125.67	$x+1,\ y,\ z$
C9–H9A···O4	2.801	3.169	103.36	$x+1,\ y,\ z$
3				
C3–H3A···O2	2.405	2.951	115.12	$-1+x,\ y,\ z$
C3–H3B···O5	2.494	3.421	160.06	$x,\ y,\ 1+z$
C4–H4A···O3	2.529	3.465	162.09	$x,\ -1+y,\ z$
C10–H10B···O2	2.539	3.432	153.01	$x,\ y,\ -1+z$
C10–H10A···O5	2.659	3.114	109.07	$-1+x,\ y,\ z$
C11–H11B···O6	2.531	3.479	165.46	$x,\ y+1,\ z$
4				
O1–H1···O2	1.959	2.762	156.65	$-x+5/4,\ -y+1/4,\ z$
O1–H1A···O3′	2.090	2.916	163.29	$x+1,\ y,\ z$
O1–H1B···N1	2.509	3.151	132.58	$-x+7/4,\ -y+3/4,\ z$

parallel. The btb bridge two adjacent coppers with Cu···Cu separations (12.236 Å) and simultaneously, every copper is coordinated with four ligands acting as a square-planar node, leading to a 3-D diamond network with one single point, $\{6^6\}$ (figure 5).

3.5. *IR spectra*

In IR spectra of **1**–**4** (“Supplementary material” section), broad peaks centered at *ca* 3400 $\mathrm{cm^{-1}}$ (for **1**, **2**, and **4**) indicate O–H stretch of water. Sharp peaks at 3100–3200 $\mathrm{cm^{-1}}$ are characteristic for 1-triazole ligands, attributed to aromatic C–H stretches (3111 $\mathrm{cm^{-1}}$ for **1**, 3140 $\mathrm{cm^{-1}}$ for **2**, 3142 $\mathrm{cm^{-1}}$ for **3** and 3127 $\mathrm{cm^{-1}}$ for **4**).

3.6. *Thermal analyses*

Thermal behaviors of these new crystalline materials were studied by thermogravimetric analysis (TGA) under nitrogen and their thermogravimetric curves are shown in “Supplementary material” section. TGA results of **1** and **2** display two weight losses. For **1**, the first weight loss of 18.00% from 50°C to 162°C (Calcd 18.15%) should be attributed to the loss of free and coordinated water, and the second weight loss is ascribed to loss of btm above 300°C. The TGA of **2** and **4** is similar to that of **1**, also

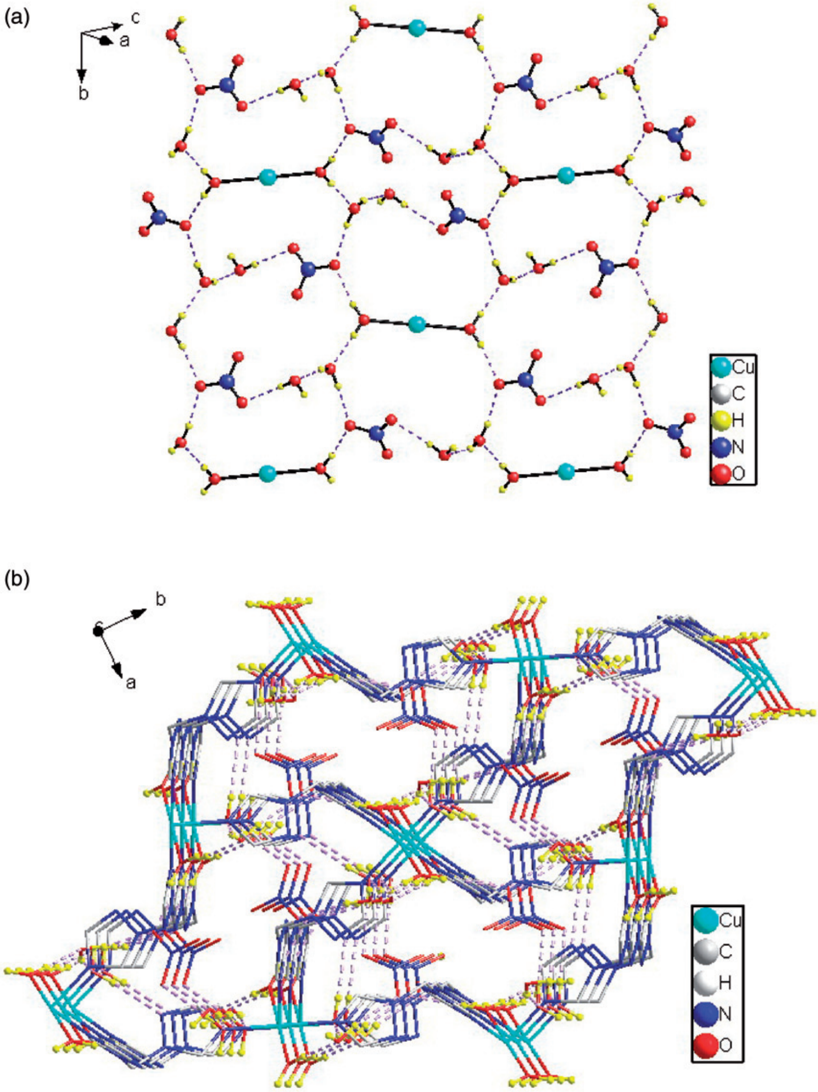


Figure 2. (a) The 2-D supramolecular network in **1** (dotted line, hydrogen-bonding). (b) The 3-D supramolecular framework of **1** viewed from the *c*-direction.

showing two weight losses. For **3**, a very rapid weight loss occurs at 230°C, as the only weight loss.

4. Conclusion

Many flexible triazole copper coordination polymers have been synthesized [24–26]. The Li group synthesized two copper coordination polymers (**1r** and **2r**) with 1,2-bis(1,2,4-triazol-1-yl)ethane (bte) with different anions [24]. Both showed 1-D

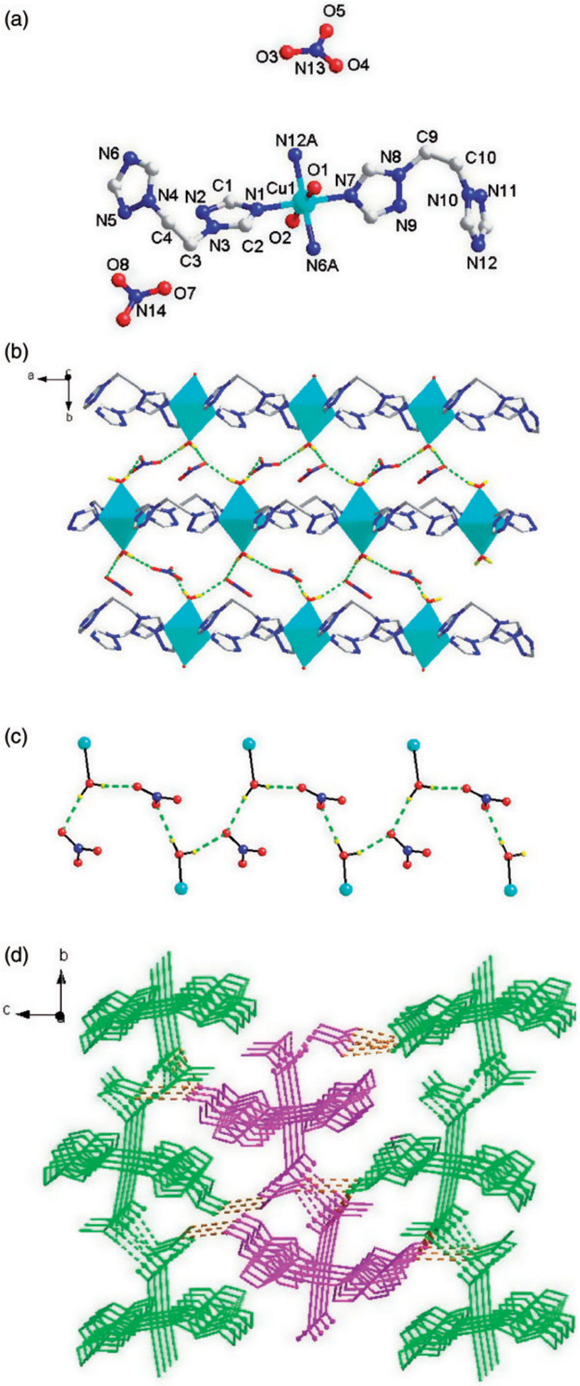


Figure 3. (a) Molecular structure of **2** showing the coordination environments of Cu^{2+} and bte. Symmetry operator: $A = 1 + x, y, z$. (b) The 2-D supermolecular layers of **2** (dotted line, hydrogen-bonding). (c) The 1-D hydrogen-bond chain of **2** along the *a*-direction (dotted line, hydrogen-bonding). (d) The 3-D supramolecular structure of **2** viewed from the *a*-direction.

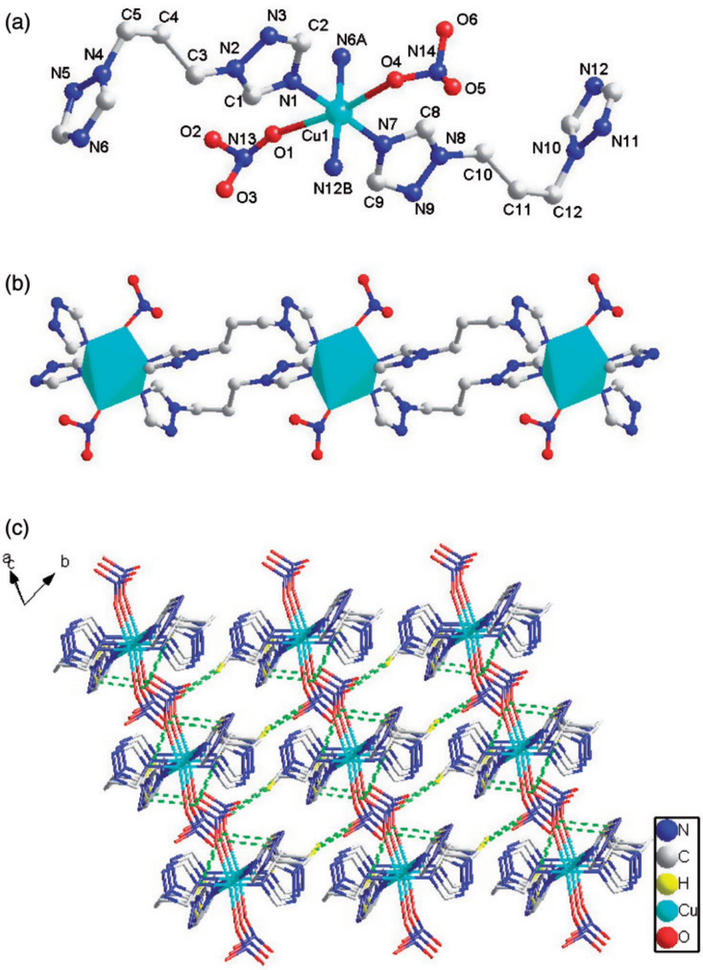


Figure 4. (a) Molecular structure of **3** showing the coordination environments of Cu^{2+} and btp. Symmetry operator: $A = 1 + x, y, -1 + z$; $B = -1 + x, y, 1 + z$. (b) The 1-D ribbons of **3**. (c) The 3-D supramolecular structure of **3** viewed from the *c*-direction (C3–H3A···O2, C3–H3B···O5, C4–H4A···O3, C10–H10B···O2, C10–H10A···O5, or C11–H11B···O6).

chains, one a single-stranded chain, the other a double-stranded chain. The double-stranded chain is like the structure of **2** and **3**, but they belong to different space groups. Our group also reported polymers [36] based on btm, bte, btp, and btb. In the compounds, all triazole ligands are bis-connected; the structures of the compounds are different because of the flexibility of the bis-triazole ligands.

The diverse architectures for **1–4** mainly result from bis(triazole) ligands with different spacer lengths and conformational flexibility (scheme 1). The flexible btm employs the *trans* conformation to generate a 2-D rectangular network with (4,4) topology in **1**. The bte ligand adopts *gauche* conformation, which gives **2** as a 1-D double-stranded chain. The btp ligand in **3** employs *gauche trans* conformation, which also assembles in a 1-D chain. *Gauche trans gauche* conformations in **4** give a 3-D framework. Extended supramolecular architectures are constructed for these complexes

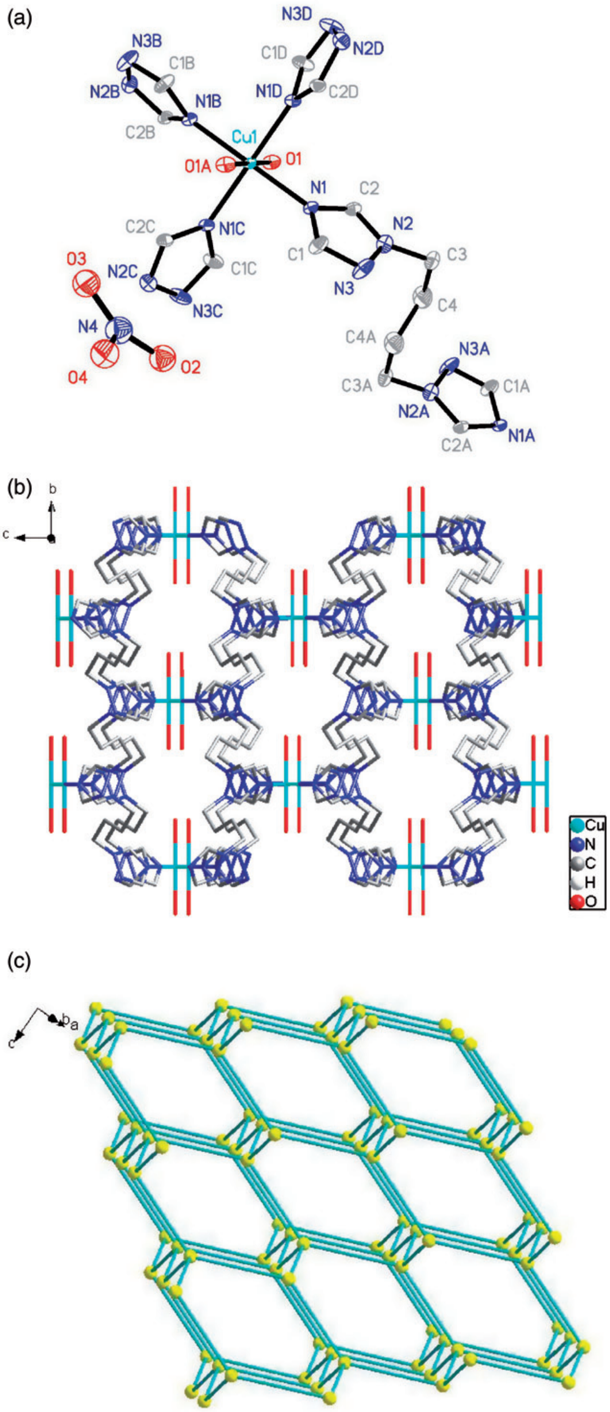


Figure 5. (a) Molecular structure of **4** showing the coordination environments of Cu^{2+} and btb. Symmetry operator: A = $0.25-x$, $1.25-y$, z; B = $0.25-x$, y, $0.25-z$; C = x, $1.25-y$, $0.25-z$; D = $-x$, $0.5-y$, $0.5-z$.(b) The 3-D framework of **4** viewed along the *c*-direction linked by btb. (c) The 3-D topological structure of **4**.

via predictable secondary interactions such as hydrogen-bonding. This work emphasizes that tuning the organic spacer length is an effective strategy in crystal engineering of inorganic–organic hybrid coordination polymers.

Supplementary material

CCDC-**1** 840174, CCDC-**2** 840173, CCDC-**3** 840175, and CCDC 800365 contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; or Email: deposit@ccdc.cam.ac.uk).

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