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Cu(II) coordination architectures with two positionally isomeric triazole–bipyridine ligands

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The Cu(II) coordination polymer, {[Cu(*p*-bdc)(4,4′-bpt)]}$_n$ shows a 2D layer structure bridged by a *p*-bdc anion and the polymer {[Cu(H_2btc)(3,3′-bpt)$_2$(H_2O)$_2$]·2H_2O}$_n$, whose thermal stability has been briefly investigated, shows a 1D chain structure bridged by an H_2btc anion. [*p*-H_2bdc = 1,4-benzenedicarboxylate acid, H_4btc = 1,2,4,5-benzenetetracarboxylic acid, 4,4′-bpt = 1H-3,5-bis(4-pyridyl)-1,2,4-triazole, 3,3′-bpt = 1H-3,5-bis(3-pyridyl)-1,2,4-triazole] Both complexes have been prepared by the reaction of the relevant carboxylate acid and positional isomeric triazole–bipyridine ligand with Cu(II) salts under hydrothermal conditions. Both structures are further extended through intermolecular interaction to form 3D supramolecular frameworks.

Keywords: Cu(II) coordination polymers, crystal structure, positional isomer, triazole–bipyridine ligands

The design and construction of coordination polymers has given rise to many architectures and topologies of potential applications in luminescence, catalysis, nonlinear optics, gas adsorption, magnetism, medicine and crystal engineering.[1–6] Since several factors influence the structures of the final products, for example solvent systems, temperature, ligand structure and pH value, it is a challenge to predict and prepare their exact structures.[7–13] A helpful tool in the design of such structures and controllable synthesis of the molecular architecture, is the use of well-designed organic ligands that can bridge or act as terminal groups to metal ions, and many have been developed.[14–17] Such organic ligands can affect the final structural topologies of coordination solids.[18–21]

We have designed and synthesised two positionally isomeric N,N′-donor ligands, 1H-3,5-bis(4-pyridyl)-1,2,4-triazole (4,4′-bpt) and 1H-3,5-bis(3-pyridyl)- 1,2,4-triazole (3,3′-bpt) (Fig. 1), *via* introducing the 1H-1,2,4-triazole moiety between two 4-pyridyl or 3-pyridyl groups. These ligands give interesting coordination polymers.[22] In addition, the different positions of the pyridyl-N atoms in the positionally isomeric ligands may allow the formation of different topological structures, which may be useful in crystal engineering and supramolecular chemistry.[23] With this in mind, we have selected two carboxylic acid and positionally isomeric N,N′-donor ligands and obtained two Cu(II) complexes: {[Cu(*p*-bdc)(4,4′-bpt)]}$_n$ (**1**), and {[Cu(H_2btc)(3,3′-bpt)$_2$(H_2O)$_2$]·2H_2O}$_n$ (**2**). [*p*-H_2bdc = 1,4-benzenedicarboxylate acid, H_4btc = 1,2,4,5-benzenetetracarboxylic acid, 4,4′-bpt = 1H-3,5-bis(4-pyridyl)-1,2,4-triazole, 3,3′-bpt = 1H-3,5-bis(3-pyridyl)-1,2,4-triazole]. Structural analysis reveals that **1** is bridged by *p*-bdc anions giving a 2-D layer, and **2** is bridged by H_2btc anions giving a 1-D chain, respectively. The structures of both complexes are further extended through intermolecular interaction to form 3-D supramolecular frameworks. In addition, the thermal stability of **2** has been briefly investigated.

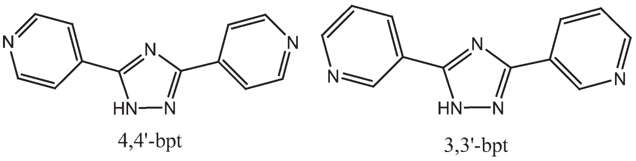
4,4'-bpt 3,3'-bpt

Fig. 1 The positional isomeric triazole–bipyridine ligands.

Experimental

The ligands 4,4′-bpt and 3,3′-bpt were prepared according to the literature,[24] other reagents and solvents for synthesis and analysis were commercially available and used as received. IR spectra were taken on a Perkin-Elmer Spectrum One FT-IR spectrometer in the 4000–400 cm^{-1} region as KBr pellets. Elemental analyses for C, H and N were carried out on a Model 2400 II, Perkin-Elmer elemental analyser. TG-DTA tests were performed on a Perkin-Elmer thermal analyser from room temperature to 1000 °C under an N_2 atmosphere at a heating rate of 5 °C min^{-1}.

{[Cu(p-bdc)(4,4′-bpt)]}$_n$ (**1**): A mixture containing Cu(NO_3)$_2$·3H_2O (120 mg, 0.5 mmol), 4,4′-bpt (112 mg, 0.5 mmol), *p*-H_2BDC (83 mg, 0.5 mmol), NaOH (40 mg, 1 mmol), water (12 mL) and ethanol (3 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL), heated at 140 °C for 72 h then slowly cooled to room temperature at 5 °C h^{-1}. Blue crystals of **1** were obtained, washed with distilled water then dried in air. Yield: 48% [based on Cu(II)]. Anal. Calcd for $C_{20}H_{13}CuN_5O_4$: C, 53.22; H, 2.88; N, 15.52. Found: C, 53.34; H, 2.96; N, 15.36%. IR (KBr, cm^{-1}): 3611m, 3407w, 3199w, 1717m, 1613m, 1580s, 1500 m, 1410s, 1283m, 1011w, 930s, 831m, 735s, 563m, 469w.

{[Cu(H_2btc)(3,3′-bpt)$_2$(H_2O)$_2$]·2H_2O}$_n$ (**2**): A mixture containing Cu(NO_3)$_2$·3H_2O (120 mg, 0.5 mmol), 3,3′-bpt (112 mg, 0.5 mmol), H_4btc (127 mg, 0.5 mmol), NaOH (40 mg, 1 mmol) and water (10 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL), heated at 110 °C for 72 h then slowly cooled to room temperature at 5 °C h^{-1}. Green crystals of **2** were obtained, washed with distilled water then dried in air. Yield: 46% (based on Cu(II)). Anal. Calcd for $C_{34}H_{30}CuN_{10}O_{12}$: C, 48.91; H, 3.60; N, 16.78. Found: C, 48.86; H, 3.52; N, 16.87%. IR (KBr, cm^{-1}): 3533s, 3412s, 3120w, 3055m, 1698m, 1579s, 1405 m, 1333w, 1053w, 988w, 790w, 749w, 700w, 656w.

X-ray crystallography

X-ray single-crystal diffraction data for **1** and **2** were recorded at room temperature on a Bruker Smart CCD apparatus using graphite-monochromated MoKα radiation (λ = 0.71073 Å). Absorption effects were corrected by semi-empirical methods. The structure was solved by direct methods, successive Fourier difference synthesis and refined by the full matrix least squares based on F^2.[25] The non-hydrogen atoms were refined anisotropically. The H atoms of the water molecules were located in a difference Fourier map. The C-bound H atoms were positioned geometrically with C–H = 0.93 Å. Crystal data and details of the structure are summarised in Table 1. Selected bond lengths and angles are listed in Table 2.

Results and discussion

Crystal structure of **1**: Complex **1** has a 2D polymeric coordination layer structure. The Cu1(II) atom is coordinated by four carboxylic O atoms from four *p*-bdc ions [O1, O3A, O2B, and O4, Cu1–O = 1.958(4)–1.9887(4) Å] and one N atom from one 4,4′-bpt ligand [Cu1–N1 = 2.188 (4) Å] [Fig. 2(a)]. The geometry around the metal centre is a slightly distorted

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Table 1 Crystal data and structure refinement for **1** and **2**

Complex	1	2
Empirical formula	$C_{20}H_{13}CuN_5O_4$	$C_{34}H_{30}CuN_{10}O_{12}$
Formula weight (M)	450.9	834.23
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
a (Å)	22.454 (4)	8.2740 (17)
b (Å)	10.911 (2)	9.875 (2
c (Å)	18.135 (4)	11.255 (2)
α (°)	90.00	69.93 (3)
β (°)	117.25 (3)	89.37 (3)
γ (°)	90.00	83.59 (3)
V/($Å^3$)	3949.9 (17)	858.0 (3)
Z	8	1
D_c (g m^{-3})	1.516	1.615
θ range for data collection (°)	25.00	25.25
Reflections collected / unique	15316/3474 [*R*(int) = 0.100]	4987/3063 [*R*(int) = 0.078]
Goodness-of-fit on F^2	1.006	1.002
Final R indices [I > 2σ(I)]	$R^1 = 0.0782$ $\omega R^2 = 0.2236$	$R^1 = 0.0956$ $\omega R^2 = 0.2217$
R indices (all data)	$R^1 = 0.1095$ $\omega R^2 = 0.2022$	$R^1 = 0.1248$ $\omega R^2 = 0.2494$

Table 2 Selected atomic distances (Å) and bond angles (deg) for complex **1–2**

	1		
Atomic distances/Å			
Cu1—O1	1.958 (4)	Cu1—O4	1.988 (4)
Cu1—O3A	1.980 (4)	Cu1—N1	2.188 (4)
Cu1—O2B	1.987 (4)		
Bond Angles [°]			
O1—Cu1—O3A	91.02 (17)	O2B—Cu1—O4	87.87 (17)
O1—Cu1—O2B	167.29 (15)	O1—Cu1—N1	98.76 (17)
O3A—Cu1—O2B	88.12 (17)	O3A—Cu1—N1	94.21 (17)
O1—Cu1—O4	90.27 (17)	O2B—Cu1—N1	93.95 (17)
O3A—Cu1—O4	167.37 (15)	O4—Cu1—N1	98.01 (16)
Symmetry codes: A −*x*, *y*, −*z*+1/2; B −*x*, *y*+1, −*z*+1/2			
	2		
Atomic distances/Å			
Cu1—O1	1.995 (4)	Cu1—O5	2.436 (6)
Cu1—N1	2.009 (5)		
Bond angles/°			
O1A—Cu1—N1	87.8 (2)	N1—Cu1—O5	88.2 (2)
O1—Cu1—N1	92.2 (2)	N1A—Cu1—O5	91.8 (2)
O1A—Cu1—N1A	92.2 (2)	O1A—Cu1—O5A	82.6 (2)
O1—Cu1—N1A	87.8 (2)	O1—Cu1—O5A	97.4 (2)
O1A—Cu1—O5	97.4 (2)	N1—Cu1—O5A	91.8 (2)
O1—Cu1—O5	82.6 (2)	N1A—Cu1—O5A	88.2 (2)
Symmetry codes: −*x*,−*y*+2, −*z*+1			

Table 3 Selected hydrogen-bond geometry/Å for **1** and **2**

D—H···*A*	*D*—*H*	*H*···*A*	*D*···*A*	*D*—H···*A*
		1		
N3—H3A···N5 #1	0.87	2.08	2.943 (10)	172
Symmetry code: #1 *x*, −*y*−1, *z*−3/2				
		2		
N3—H3···O2#1	0.87	1.87	2.742 (7)	180
O5—H5A···N4#2	0.86	2.36	3.116 (9)	147
O5—H5B···O6	0.84	2.04	2.856 (9)	163
N5—H5C···O4#3	0.87	1.73	2.598 (8)	179
O6—H6A···O3#4	0.86	2.05	2.845 (9)	154
O6—H6B···N2	0.85	2.50	3.021 (9)	120
Symmetry codes: #1 −*x*+1, −*y*+1, −*z*+1; #2 *x*, *y*+1, *z*; #3 *x*−1, *y*−1, *z*; #4 *x*−1, *y*, *z*.				

tetragonal-pyramid. The carboxylic groups of the *p*-bdc ligands adopt *syn-syn* modes to connect with four Cu(II) atoms. Based on these connection modes, two Cu(II) ions are coordinated by four carboxylic groups of *p*-bdc ligands to give a $[Cu_2(CO_2)_4]_n$ unit. These $[Cu_2(CO_2)_4]_n$ units are further interlinked through *p*-bdc spacers to generate a 2D layer structure. From a topological perspective, the $[Cu_2(CO_2)_4]_n$ unit connecting four ligands acts as the four-connected node and the *p*-bdc ligand can be viewed as the linker. In this way, this framework can be simplified to be a four-connected 2D (4,4)-sql layer architecture [Fig. 2(b)]. The intermolecular packing is further controlled by hydrogen bonds (N3—H3A···N5 #1, symmetry code: #1 *x*, −*y*−1, *z*−3/2, Table 3) between the triazole N atoms and pyridine N atoms to generate a 3D supramolecular architecture [Fig. 2(c)].

Crystal structure of **2**: Complex **2** has a 1D polymeric coordination layer structure. The Cu(II) atoms lie on inversion centres and are coordinated by four O atoms from two H_2btc ions [O1 and O1A, Cu1–O1 = 1.955(4) Å], two water molecules [O5 and O5A, Cu1–O5 = 2.436(6) Å] and two N atoms from two 3,3′-bpt ligands [N1 and N1A, Cu1–N1 = 2.009(5) Å), Fig. 3(a)]. The geometry around the metal centre is a slightly distorted octahedron. The H_2btc spacers bridge adjacent Cu(II) atoms with the Cu···Cu separation of 11.255(2) Å, leading to a 1-D chain along the crystallographic *c* axis [Fig. 3(b)]. Both the carboxylic groups in the H_2btc ligand in **2** adopt monodentate modes to connect with two Cu atoms, and the 3,3′-bpt ligands are in the monodentate coordination fashion. Furthermore, the complex is assembled in a 3-D supramolecular framework *via* intermolecular hydrogen bonding (N3—H3···O2#1, O5—H5A···N4#2, O5—H5B···O6, N5—H5C···O4#3, O6—H6A···O3#4 and O6—H6B···N2; symmetry codes: #1 −*x*+1, −*y*+1, −*z*+1; #2 *x*, *y*+1, *z*; #3 *x*−1, *y*−1, *z*; #4 *x*−1, *y*, *z*, Table 3) among the uncoordinated triazole N atoms, uncoordinated pyridine N atoms, uncoordinated carboxyl O atoms and coordinated water molecules [Fig. 3(c)].

Both the 4,4′-bpt and 3,3′-bpt ligands coordinated to the metal atoms in **1** and **2** are monodentate, but the 4,4′-bpt and 3,3′-bpt ligands have the ability to adopt versatile coordination modes to arrange the metal ions in a variety of structures.[26–32] In addition, the complexes can further extend to 3-D supramolecular frameworks *via* intermolecular hydrogen bonding of 4,4′-bpt and 3,3′-bpt ligands.[33–35]

Thermal stability of complex **2**: In order to estimate the thermal stability of complex **2**, its thermal behaviour was studied by thermogravimetric analyses (TGA) (see Fig. 4). There are several mass loss steps, although without a clear plateau. The first observed weight loss of 9.1% in the region of 29–202 °C (peak at 161 °C) corresponds to the dehydration process (calculated 8.63%). The residual framework starts to decompose owing to the expulsion of the lattice water and the coordinated water molecules beyond 202 °C with a series of complicated weight losses (peaks at 280 and 391 °C) and does not stop until heating ends at 971 °C.

Conclusions

In this study, we have synthesised and characterised two new Cu(II) coordination polymers based on two isomeric ligands 4,4′-bpt and 3,3′-bpt in combination with two carboxylic acids. The 4,4′-bpt and 3,3′-bpt are not bridging ligands, but the work shows that the isomers of bpt and carboxylic acid ligands have versatile coordination modes to form diverse network structures.[27,35] We will further study the effect of mixed bpt isomers and carboxylic acid as bridging ligands on the molecular architecture of coordination structures.

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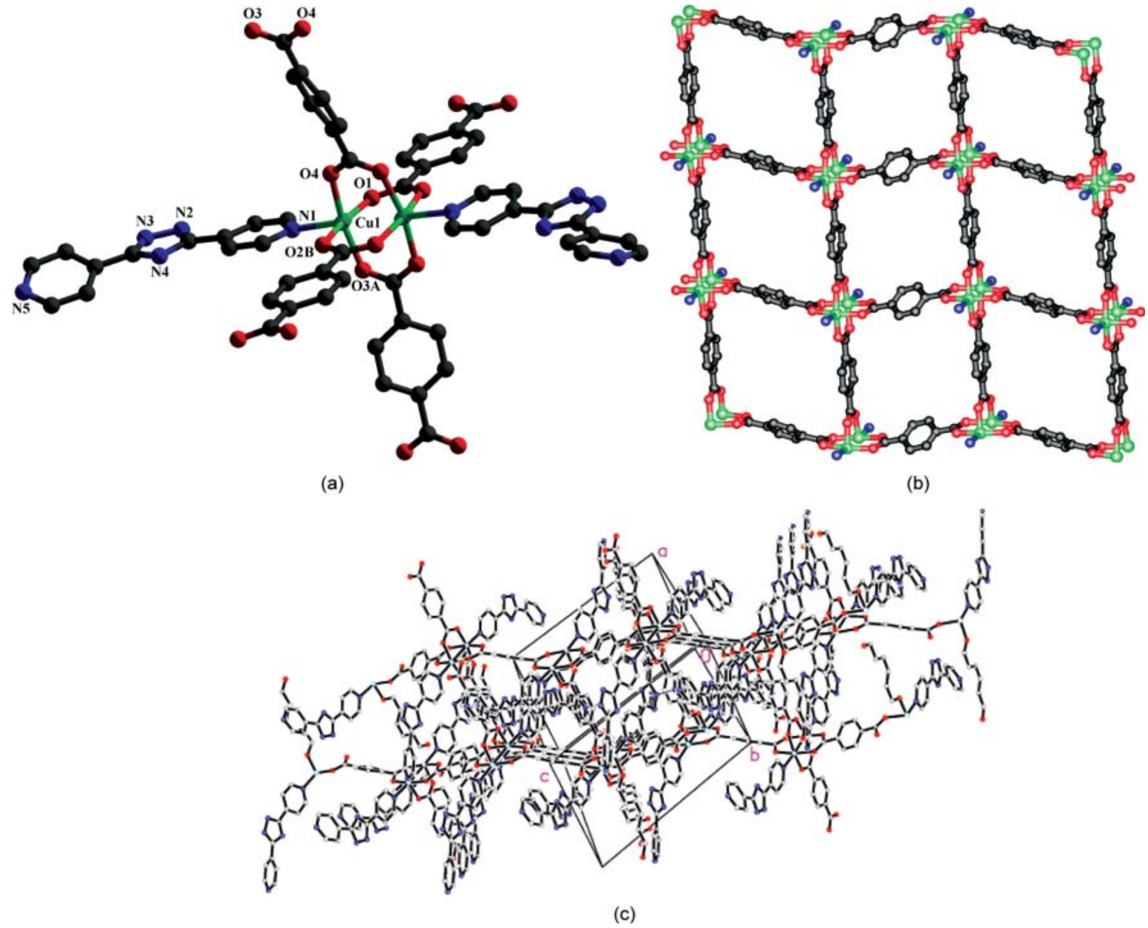

Fig. 2 (a) structure of **1** showing the local coordination environments of the Cu(II) atom; (b) the 2D layer of **1**; (c) the 3D-dimensional packing drawing of **1**.

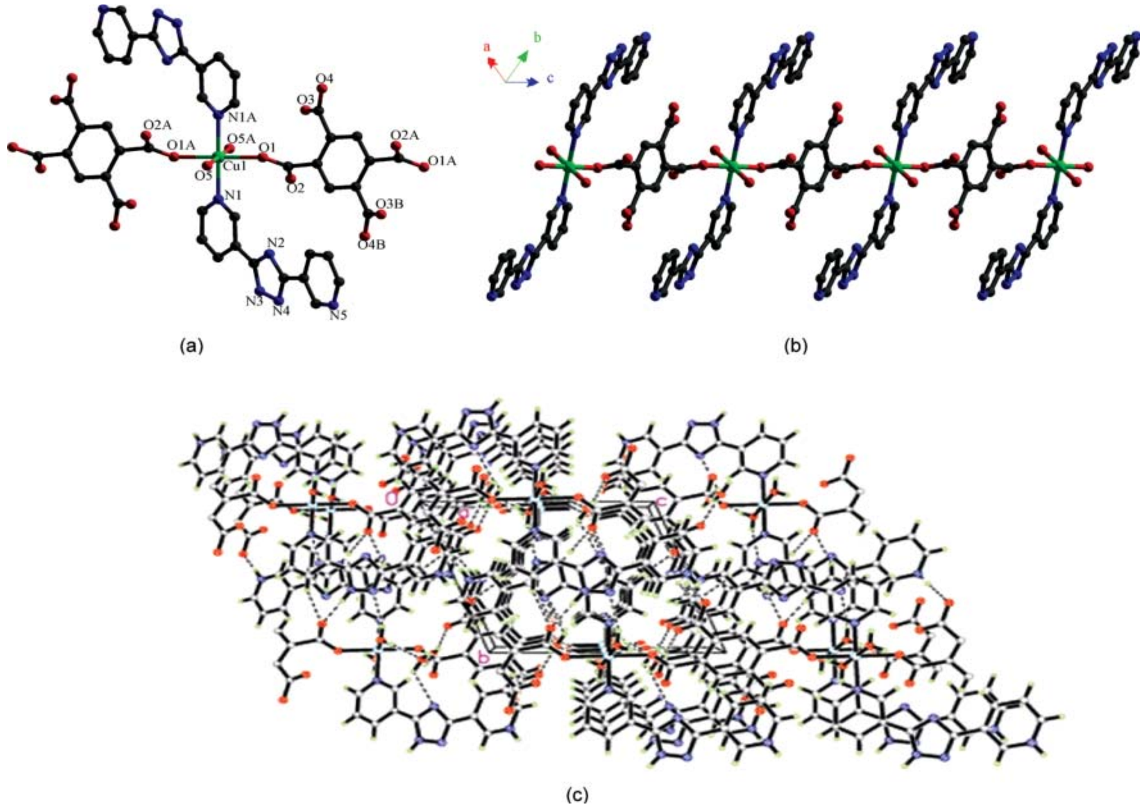

Fig. 3 (a) structure of **2** showing the local coordination environments of the Cu(II) atoms; (b) the 1-D chain of **2**; (c) 3D-dimensional packing drawing of **2**.

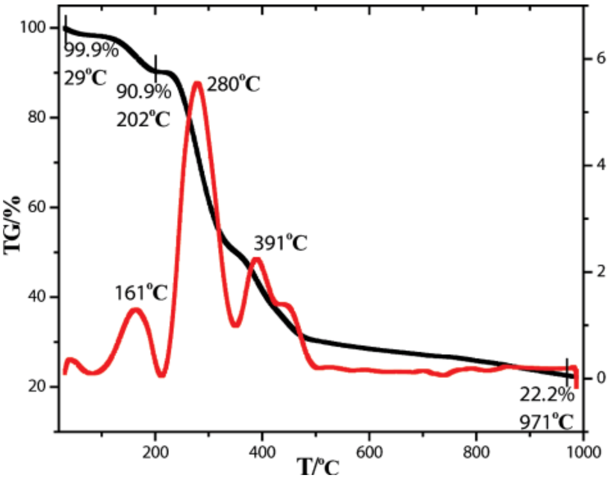

Fig. 4 The TG (black)-DTG (red) curve of complex **2**.

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