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Two-dimensional metal-organic framework constructed from 4,4′-bipydine and 1,2,4-benzenetricarboxylate: Synthesis, structure and magnetic properties

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Abstract

Two new copper coordination polymers generated from mixed organic ligands 4,4′-bipydine and 1,2,4-benzenetricarboxylate $[Cu_3(1,2,4\text{-BTC})_2(4,4'\text{-bipy})(H_2O)_4]$ **1** and $[Cu(1,2,4\text{-HBTC})(4,4'\text{-bipy})]$ **2** (1,2,4-BTC = 1,2,4-benzenetricarboxylate) have been prepared hydrothermally and characterized by single crystal X-ray diffraction. Compound **1** crystallizes in the noncentrosymmetric space group $Fdd2$, with $a = 19.004(3)$ Å, $b = 26.711(4)$ Å, $c = 11.0770(15)$ Å, $V = 5622.8(14)$ Å^3, and $Z = 8$. Its structure contains two different one-dimensional (1-D) chains for the Cu ions, namely $[Cu_2(1,2,4-BTC)_2]_n^{2n-}$ and $[Cu(4,4'-bipy)]_n^{2n+}$; the carboxylate of 1,2,4-BTC ligands links the two different 1-D chains into an interesting steplike neutral framework. Compound **2** crystallizes in the monoclinic space group $P2_1/n$, with $a = 9.9806(8)$, $b = 16.5512(16)$, $c = 11.3109(7)$ Å, $\beta = 99.375(5)°$, $V = 1843.5(3)$ Å^3, $Z = 4$. Its structure contains novel paddle-wheel clusters $Cu_2(CO_2)_4(4,4'\text{-bipy})_2$ as SBUs which are further linked by monoprotonated 1,2,4-BTC ligands into a 2-D neutral framework. The magnetic behaviors of both compounds have been studied.

Keywords: Neutral framework; Hydrothermal synthesis; Coordination polymer; Crystal structure

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1. Introduction

Studies of the synthesis of metal-organic frameworks by copolymerization of organic molecules with metal ions are of great interest, mostly owing to their intriguing structural features and enormous range of applications in catalysis, absorbent, non-linear optics and molecular recognition [1–4]. Ligands with pyridyl or carboxylate groups are employed the most often in the design and synthesis of these frameworks [5–8]. With an aim to search for novel materials and rational design and synthesis of these compounds, we and others in this field have focused largely on the combination of pyridyl and carboxylate ligands, and find it has a great ability to form neutral porous networks [9–11]. Williams et al. [12] reported a stable metal-organic framework with mixed-valence $[Cu_2]^{3+}$ dimer subunits formulated as $[Cu_4\{(1,4\text{-}C_6H_4(COO)_2)\}_3(4,4'\text{-bipy})_2]_n$. Chen et al. [13–15] reported a series of transition metal (II)-based neutral frameworks, such as $[Zn_4O(ip)_3(4,4'\text{-bipy})]$ and $[Ni(ip)(4,4'\text{-bipy})]$, etc., which were constructed by mixed ligands of 4,4′-bipy and 1,3-benzenedicarboxylate.

In our previous studies, we obtained several novel coordination polymers, such as $[Mn(maleate)(4,4'\text{-bipy})]\cdot 0.5H_2O$ and $[Mn(fumareate)(4,4'\text{-bipy})]\cdot 0.5H_2O(4,4'\text{-bipy})$, in which a structural transformation from 2D to 3D through conformation change of carboxylate ligands was observed [16]. A study of the literature about metal-organic frameworks shows that 1,2,4-benzenetricarboxylate (1,2,4-BTC) is a good candidate for assembly of these compounds. Scheme 1 illustrates the versatile coordination abilities of the organic ligand; therefore we extended our research into the metal-4,4′-bipy-1,2,4-BTC system [17–25]. As the results in this system, in this paper we report the synthesis, structure and magnetic properties of two new copper coordination polymers $[Cu_3(1,2,4\text{-BTC})_2(4,4'\text{-bipy})(H_2O)_4]$ **1** and $[Cu(1,2,4\text{-HBTC})(4,4'\text{-bipy})]$ **2**.

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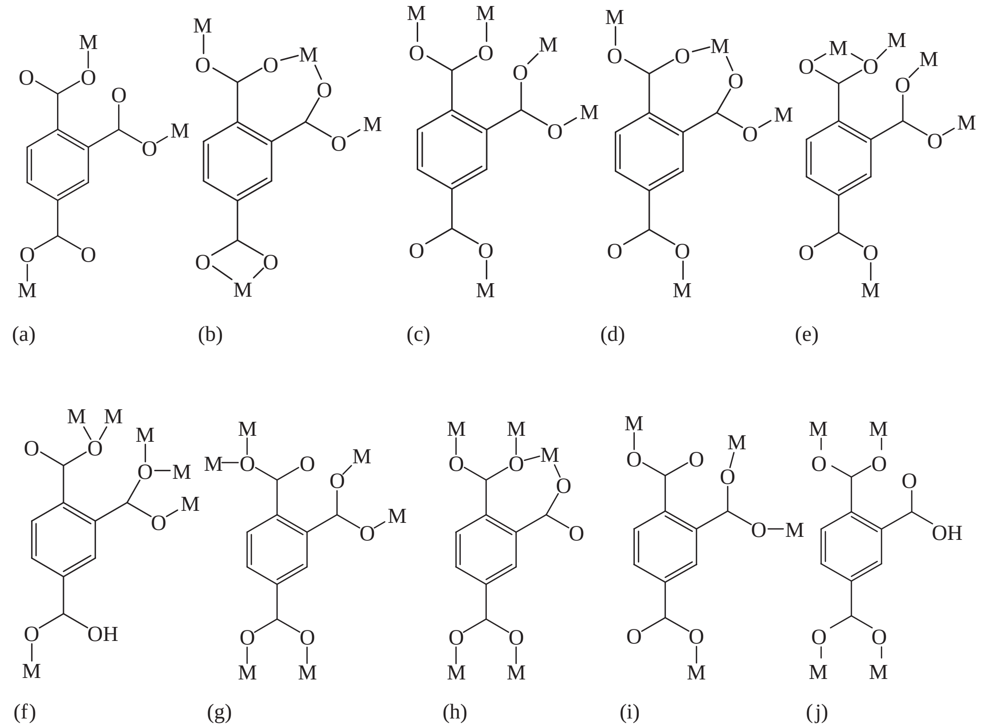

Scheme 1. Coordination modes of 1,2,4-BTC in the compounds reported in the literature: a, [17]; b, [18]; c, [19]; d, [20]; e, [21]; f, [22]; g and h, [23]; i, (see compound **1**); j, (see compound **2**).

2. Experimental

2.1. General methods

The elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. The inductively coupled plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300DV ICP instrument. The infrared (IR) spectrum was recorded within the 400–4000 cm^{-1} region on a Nicolet Impact 410FTIR spectrometer using KBr pellets. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA 7 thermogravimetric analyzer in air with a heating rate of 10 °C min^{-1}. Magnetic susceptibility data were collected over the temperature range 2–300 K at a magnetic field of 5 KG on a Quantum Design MPMS-7 SQUID magnetometer.

2.2. Synthesis and characterization of **1**

All chemicals and solvents used in the syntheses were of reagent grade and used as purchased without further purification. Compound **1** were prepared from a mixture of Cu(NO$_3$)$_2$ (0.242 g, 1.5 mmol), 1,2,4-BTC (0.210 g, 1 mmol), 4,4′-bipy (0.096 g, 0.5 mmol), NaOH (0.080 g, 2 mmol) and distilled water (10 mL) with a molar composition of 3:2:1:2:1100. The mixture was sealed in a 23 mL capacity of Teflon-lined stainless-steel autoclave under autogenous pressure, and heated at 160 °C for 120 h. After cooling blueness crystals for single-crystal X-ray diffraction were obtained. The yield was 63%, based on Cu.

The ICP analysis and elemental analyses were consistent with the theoretical values. Calcd for **1**: Cu, 22.88; C, 40.33; H, 2.64; N, 3.36%. Found: Cu, 22.17; C, 40.44; H, 2.51; N, 3.29%. The absence of the expected characteristic bands at 1730–1690 cm^{-1} atributed to the protonated carboxylate groups indicates the complete deprotonation of 1,2,4-BTC on the reactions with copper ion. The TGA curve of **1** exhibits two continuous weight loss stages in the temperature ranges 120–230 and 250–340 °C, corresponding to the concomitant release of composed water and 4,4′-bipy and 1,2,4-BTC groups. The residue was CuO. The whole weight loss (71.74%) is in good agreement with the calculated (71.36%).

2.3. Synthesis and characterization of **2**

In a typical synthetic procedure, compound **2** were prepared from a mixture of Cu(NO$_3$)$_2$ (0.242 g, 1.5 mmol), 1,2,4-BTC (0.210 g, 1 mmol), 4,4′-bipy (0.192 g, 1 mmol), 1-butanol (4 mL) and distilled water (6 mL) with a molar composition of 3:2:3:88:666. The mixture was sealed in a 23 mL capacity of Teflon-lined stainless-steel autoclave under autogenous pressure, and heated at 160 °C for 120 h. After cooling blueness crystals for single-crystal X-ray diffraction were obtained. The yield was 72%, based on Cu.

The ICP analysis and elemental analyses were consistent with the theoretical values. Calcd for **2**: Cu, 14.84; C, 53.29; H, 2.80; N, 6.54%. Found: Cu, 15.12; C, 52.82; H, 2.39; N, 6.13%. Despite their synthesis from a mixed solvothermal condition, samples of this material are stable in air and

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

Empirical formula	$C_{28}H_{22}N_2O_{16}Cu_3$	$C_{19}H_{12}N_2O_6Cu$
Formula weight	833.10	427.85
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic
Space group	*Fdd*2	*P*21/*n*
a (Å)	19.004(3)	9.9806(8)
b (Å)	26.711(4)	16.5512(16)
c (Å)	11.0770(15)	11.3109(7)
β (deg)	90	99.375(5)
Volume (Å^3)	5622.8(14)	1843.5(3)
Z	8	4
Calculated density (g/cm^3)	1.968	1.542
Absorption coefficient (mm^{-1})	2.338	1.224
F(0 0 0)	3352	868
Crystal size (mm)	0.35 × 0.26 × 0.23	0.32 × 0.27 × 0.25
θ range (deg)	2.26–30.02	2.20–24.99
Limiting indices	$-26 \leqslant h \leqslant 26$, $-37 \leqslant k \leqslant 24$, $-15 \leqslant l \leqslant 15$	$-11 \leqslant h \leqslant 11$, $-19 \leqslant k \leqslant 10$, $-12 \leqslant l \leqslant 13$
Reflections collected/unique	9655/3833 [*R*(*int*) = 0.0451]	9991/3230 [*R*(*int*) = 0.0715]
Completeness to $\theta = 30.02$	99.9%	99.6%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3833/5/240	3230/12/253
Goodness-of-fit on F^2	0.912	0.979
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0357$, w$R_2 = 0.0687$	$R_1 = 0.0543$, w$R_2 = 0.1380$
R indices (all data)	$R_1 = 0.0529$, w$R_2 = 0.0730$	$R_1 = 0.1034$, w$R_2 = 0.1580$
Largest diff. peak and hole (e. Å^{-3})	0.410 and −0.454	0.851 and −0.700

insoluble in water and common organic solvents such as alcohol, toluene, THF, DMF and DMSO. The presence of the expected characteristic bands at 1711 cm^{-1} (IR) attributed to the protonated carboxylate groups indicates that the carboxylates of the1,2,4-BTC ligand are not completely deprotonated. The TGA curve of **2** exhibits one continuous weight loss stage in the temperature ranges 210−420 °C, corresponding to the concomitant release of composed 4,4′-bipy and 1,2,4-BTC groups. The residue was also CuO. The whole weight loss (81.67%) is in good agreement with the calculated (81.40%).

2.4. Structure determination

A suitable blueness single crystal with dimensions 0.35 × 0.27 × 0.23 mm for **1** and 0.50 × 0.30 × 0.25 mm for **2** was glued to a thin glass fiber and mounted on a Siemens Smart CCD diffractometer equipped with a normal-focus, 2.4-kW sealed-tube X-ray source (graphite-monochromatic Mo*Kα* radiation ($\lambda = 1.5418$ Å) operating at 50 kV and 40 mA. The experiment was collected at room temperature. Date processing was performed using the SAINT processing program [26]. The total number of measured reflections and observed unique reflections were 9655 and 3833 for **1**, for **2** were 9991 and 3230, respectively. For compound **1**, intensity data of 3833 independent reflections ($-26 \leqslant h \leqslant 26$, $-37 \leqslant k \leqslant 24$, $-15 \leqslant l \leqslant 15$) were collected in the *ω* scan mode. For compound **2**, intensity data of 3230 independent reflections ($-11 \leqslant h \leqslant 11$, $-19 \leqslant k \leqslant 10$, $-12 \leqslant l \leqslant 13$) were collected in the *ω* scan mode. The structure was solved in the space group *Fdd*2 for compound **1** and and *P*21/*n* for compound **2** by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL97 [27]. All non-hydrogen atoms were easily found from the difference Fourier map and refined anisotropically. The hydrogen atoms on the ligand were placed geometrically. The crystallographic data and details on the refinements for compounds **1** and **2** are summarized in Table 1. Selected bond distances and angles are listed in Table 2.

3. Results and discussion

3.1. Crystal structure of [Cu_3(1,2,4-BTC)$_2$(4,4′-bipy)(H_2O)$_4$] **1**

Single-crystal X-ray diffraction study performed on **1** revealed an extended 2-D coordination network that crystallizes in the noncentrosymmetric space group *Fdd*2. The asymmetric unit of **1** (Fig. 1) consists of two copper centers, one 1,2,4-BTC anions, one 4,4′-bipy molecule, and two coordinated water molecules. The Cu1 center coordinates to two carboxylate oxygen atoms of two separated 1,2,4-BTC ligands (Cu1-O3 1.975(2) Å) and two nitrogen atoms of two 4,4′-bipy (Cu(1)–N(1) 2.001(5), Cu(1)–N(2) 1.986(5) Å) to furnish a distorted square geometry; while the Cu2 center coordinates to three carboxylate oxygen atoms of three separated 1,2,4-BTC ligands (Cu(2)–O(1) 1.941(3), Cu(2)–O(4) 2.234(2), Cu(2)–O(5) 1.960(3) Å), and two water molecules (Cu(2)–O(7) 1.950(3), Cu(2)–O(8) 1.982(2) Å) , exhibits a distorted trigonal bipyramidal geometry with the O–Cu–O angles in the range from

Table 2
Selected bond lengths (Å) and angles (deg) for **1**

Compound **1**			
Cu(1)–O(3)#1	1.975(2)	O(3)–Cu(1)–N(1)	91.27(8)
Cu(1)–O(3)	1.975(2)	N(2)–Cu(1)–N(1)	180.000(4)
Cu(1)–N(2)	1.986(5)	O(1)–Cu(2)–O(7)	83.81(12)
Cu(1)–N(1)	2.001(5)	O(1)–Cu(2)–O(5)	168.44(14)
Cu(2)–O(1)	1.941(3)	O(7)–Cu(2)–O(5)	94.04(12)
Cu(2)–O(7)	1.950(3)	O(1)–Cu(2)–O(8)	93.71(12)
Cu(2)–O(5)	1.960(3)	O(7)–Cu(2)–O(8)	167.67(12)
Cu(2)–O(8)	1.982(2)	O(5)–Cu(2)–O(8)	85.97(12)
Cu(2)–O(4)	2.234(2)	O(1)–Cu(2)–O(4)	97.48(11)
O(3)#1–Cu(1)–O(3)	177.46(15)	O(7)–Cu(2)–O(4)	86.59(10)
O(3)#1–Cu(1)–N(2)	88.73(8)	O(5)–Cu(2)–O(4)	93.73(11)
O(3)–Cu(1)–N(2)	88.73(8)	O(8)–Cu(2)–O(4)	105.73(9)
O(3)#1–Cu(1)–N(1)	91.27(8)		
Compound **2**			
Cu(1)–O(2)	1.955(4)	O(2)–Cu(1)–O(6)	90.98(19)
Cu(1)–O(1)	1.976(4)	O(5)–Cu(1)–O(6)	166.56(16)
Cu(1)–O(5)	1.961(4)	O(1)–Cu(1)–O(6)	88.88(19)
Cu(1)–O(6)	1.979(4)	O(2)–Cu(1)–N(1)	100.08(18)
Cu(1)–N(1)	2.154(5)	O(5)–Cu(1)–N(1)	99.13(17)
O(2)–Cu(1)–O(5)	88.43(19)	O(1)–Cu(1)–N(1)	93.63(17)
O(2)–Cu(1)–O(1)	166.26(16)	O(6)–Cu(1)–N(1)	94.19(17)
O(5)–Cu(1)–O(1)	88.53(19)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, z$.

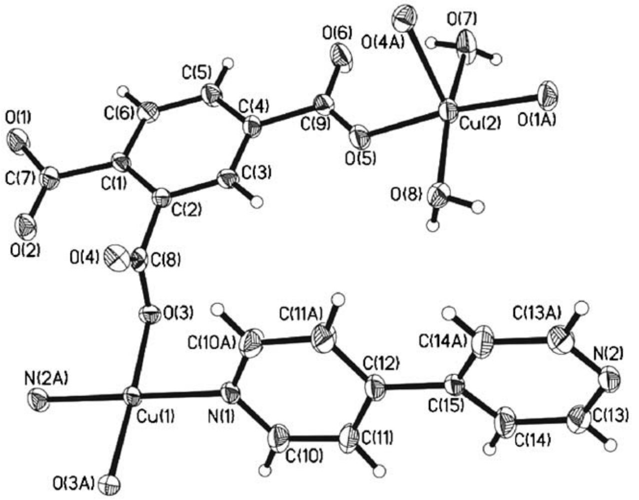

Fig. 1. The building block unit including the asymmetric unit present in crystalline **1** (50% thermal ellipsoids).

83.81(12)° to 168.44(14)°. The carboxylic O–Cu bond distances range from 1.941(3) to 2.234(2) Å for Cu1 and Cu2, where O1, O3, and O5 are tightly bonded, while O4 is weakly bonded. The 1,2,4-BTC ligand shows a new coordination mode connecting four coppers through its three asymmetry $-COO^-$ groups, two of which in a monodentate mode, while the third in a bridging mode; this simple coordination mode is not seen in other metal 1,2,4-BTC compounds (Scheme 1i). The dihedral angles between benzene rings (C1/C2/C3) and the three different carboxylate moieties are 4.9° (C7/O1/O2), 89.5° (C8/O3/O4), and 4.6° (C9/O5/O6), respectively.

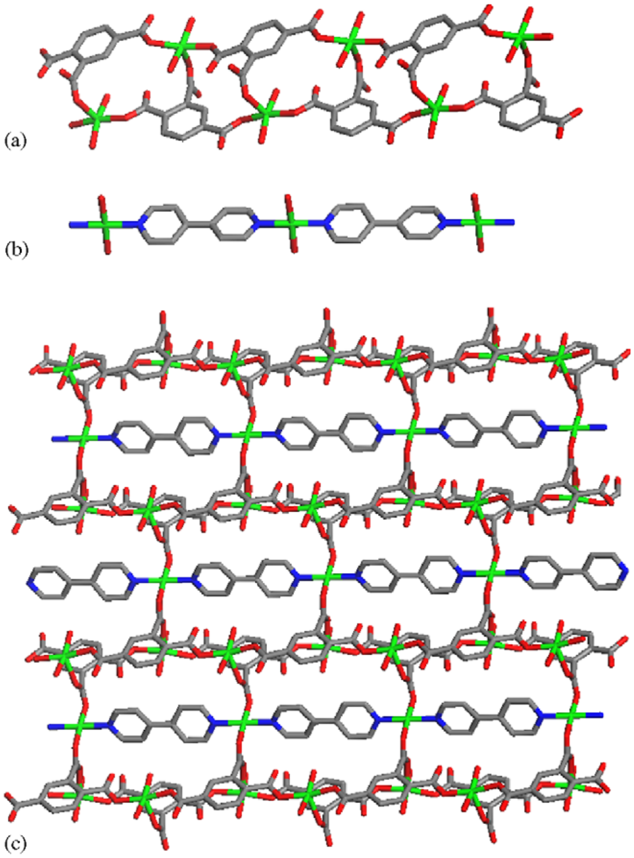

Fig. 2. (a) A view of the infinite double $[Cu_2(1,2,4-BTC)_2]_n^{2n-}$ chain and (b) the infinite $[Cu(4,4'-bipy)]_n^{2n+}$ chain; (c) the two-dimensional neutral framework along the *b*-axis. Hydrogen atoms are omitted for clarity.

The most interesting structure feature of **1** is that it exhibits two different 1-D chains along the *b*-axis, as shown in Fig. 2: the 4,4′-bipy molecule links the Cu1 center to form an infinite $[Cu(4,4'-bipy)]_n^{2n+}$ chain, while the 1,2,4-BTC ligand links the Cu2 center to form an infinite double $[Cu_2(1,2,4-BTC)_2]_n^{2n-}$ chain. Thus, the 2-D neutral framework can be viewed as constructed by the later $[Cu_2(1,2,4-BTC)_2]_n^{2n-}$ chain connecting the $[Cu(4,4'-bipy)]_n^{2n+}$ chain through the carboxylate (C8/O3/O4) of 1,2,4-BTC linkers. The adjacent 2-D steplike layers are parallel with each other and construct a 3-D noncentrysymmetric framework via hydrogen bonding interactions between the two coordinated water molecules and the carboxyl groups of 1,2,4-BTC. The typical hydrogen bonds are $O(7)-H(7A)\cdots O(3)$ 2.842(3) Å, $O(7)-H(7B)\cdots O(6)$ 2.675(4) Å, $O(8)-H(8A)\cdots O(6)$ 2.725(4) Å, and $O(8)-H(8B)\cdots O(2)$ 2.600(4) Å.

3.2. Crystal structure of [Cu(1,2,4-HBTC)(4,4′-bipy)] **2**

Single-crystal X-ray diffraction study performed on **2** reveals an extended 2-D coordination network. The fundamental unit is shown in Fig. 3. There is only one

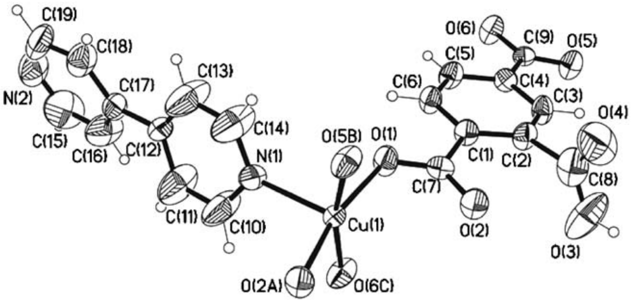

Fig. 3. The building block unit including the asymmetric unit present in crystalline **2** (50% thermal ellipsoids).

crystallographically unique Cu center in the crystal structure. The Cu center coordinates to four carboxylate oxygen atoms of four separated 1,2,4-BTC ligands and one nitrogen atoms of 4,4′-bipy to furnish a pseudo-octahedral geometry. The O–Cu–O angles are in the range from 83.81(12)° to 168.44(14)° and the O–Cu–N angels are in the range from 93.63(17)° to 100.08(18)°, respectively. The average O–Cu bond lengths is 1.967 Å and the N–Cu bond length is 2.154(5) Å. The 1,2,4-BTC ligand shows a new coordination mode (Scheme 1j) connecting four coppers through its three asymmetry carboxylate groups, two of which in a di-monodentate mode; while the third group, C(8)/O(3)/O(4), is a carboxylic complex in which the O(3) atom is the acidic oxygen, in agreement with the IR spectrum (1711 cm^{-1}) and the observed C(8)–O(3) bond length (1.284 Å). The 4,4′-bipy molecule here as a monodentate ligand is little seen in coordination polymers, but can be seen in some hybrid metal phosphates reported by Lii [28–30].

As shown in Fig. 4, the 2-D framework can be viewed as constructed form paddle-wheel clusters $Cu_2(CO_2)_4$(4,4′-bipy)$_2$ as SBUs bridged by 1,2,4-BTC linkers. The distance between the dimeric cupper centers is 2.689 Å. The SBU paddle-wheel cluster $M_2(CO_2)_4(L)_2$ (where $M =$ Cu or Zn, $L = H_2O$ or pyridine) is known in many compounds, such as interesting Zn(1,4-BDC)(DMF)(H_2O), [Cu_3(TMA)$_2$ (pyridine)$_3$], etc., but to our knowledge this is the first instance of a SBU where $L =$ 4,4′-bipy is reported [31–35]. In the packing arrangement of **2**, the adjacent 2-D supramolecurlar layers are parallel with each other and construct a 3-D supramolecular framework via the weak π–π interactions between the aromatic groups of 4,4′-bipy and 1,2.4-BTC ligands. The average distance of the aromatic is about 11.176 Å between the 1,2.4-BTC ligands and 11.390 Å between the 4,4′-bipy groups.

One intriguing feature of the compound is its close structural relation to the known 2-D MOF Zn(1,4-BDC)(DMF)(H_2O) [35]. The main difference of the two structures is that, in the case of Zn(1,4-BDC)(DMF)(H_2O), the axial positions on Zn are occupied by water ligands which serve to hold together the sheets by mutual hydrogen bonding to the carboxylate oxygen on an adjacent sheet. The sheets stack in registry to allow the formation of 1-D channels where DMF guests reside. But in the instance of compound **2**, the axial positions on Cu are occupied by 4,4′-bipy ligands which serve to hold together via the π–π interactions, and no water or solvent guests reside in the 1-D channels but the organic ligand itself.

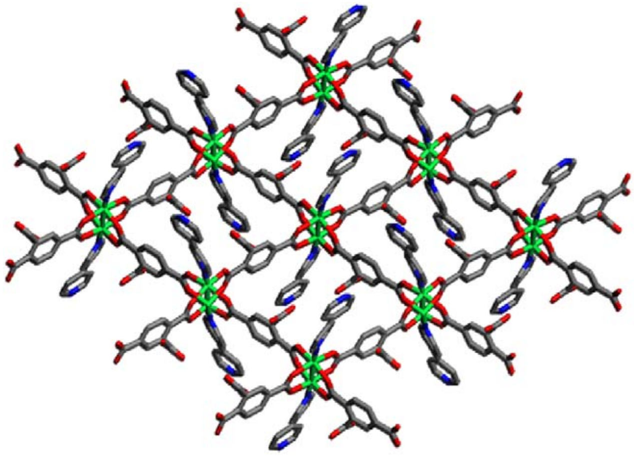

Fig. 4. Crystal structure of **2** viewed along the *c*-axis. Hydrogen atoms are omitted for clarity.

3.3. Magnetic studies

Temperature dependence of the magnetic susceptibility of **1** was investigated in the temperature range 2–300 K at 5 kOe (Fig. 5). The effective magnetic moment at 300 K, calculated from $\mu_{\rm eff} = 2.828(X_{\rm M}T)^{1/2}$, is 1.90 $\mu_{\rm B}$ per Cu, which is in the range of the experimentally observed value (1.70–2.20 $\mu_{\rm B}$) for Cu(II) ions. The susceptibility data above 8 K can be fitted by Curie–Weiss law, $X_{\rm M} = C/(T-\theta)$, where C is the Currie constant, and θ the Weiss constant, resulting in parameters $C = 0.44\,\mathrm{cm^3\,kmol^{-1}}$ and $\theta = +6.6$ K. The positive Weiss constant indicates a predominantly ferromagnetic interaction between the copper centers. This is confirmed by the continuous increases of $\chi_{\rm M}T$ value upon cooling. According to the structural data, the shorter Cu1 ··· Cu2 distance between the two different 1-D chains (4.846 Å) bridged by the carboxylate can contribute to the ferromagnetic interaction.

The magnetic behavior of compound **2** is shown in Fig. 6. The effective magnetic moment at 300 K, calculated from $\mu_{\rm eff} = 2.828(X_{\rm M}T)^{1/2}$, is 1.99 $\mu_{\rm B}$ per Cu, which is in the range of the experimentally observed value (1.70–2.20 $\mu_{\rm B}$) for Cu(II) ions. The $\chi_{\rm M}T$ versus T exhibits a value of 0.99 emu kOe^{-1} mol^{-1} at 300 K and continuously increases on cooling to a value of 1.36 emu kOe^{-1} mol^{-1} at 21 K. This behavior of the $\chi_{\rm M}T$ curve shows that there exist ferromagnetic interactions in **2**. However, the curve drops abruptly below 15 K, indicating that an antiferromagnetic interaction exists in **2** at lower temperatures. The Weiss constant, determined in the temperature range 80–300 K, is + 30.15 K, suggesting a strong predominantly ferromagnetic interaction between the copper centers. According to the structural data, compound **2** contains interesting paddle-wheel clusters as SBUs which are further linked

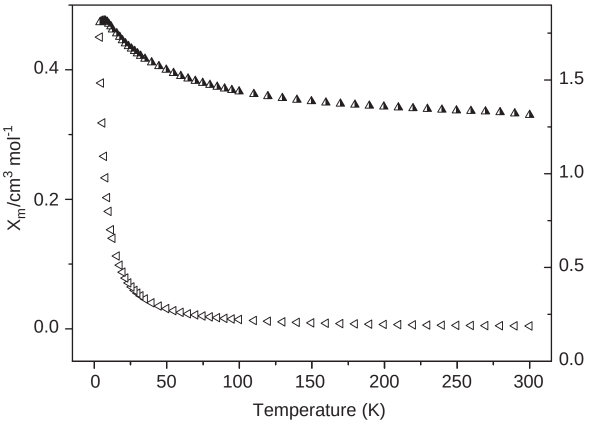

Fig. 5. Temperature dependence of magnetic susceptibility of **1**.

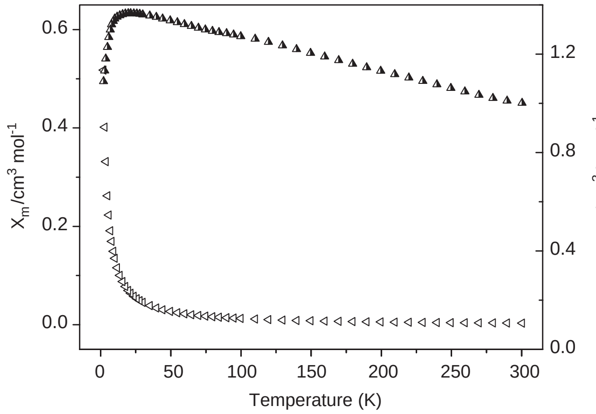

Fig. 6. Temperature dependence of magnetic susceptibility of **2**.

by 1,2,4-BTC ligands into a 2-D framework; the ferromagnetic interactions may be facilitated by the planar aromatic bridges between the $[Cu]_2$ units. But within the paddle-wheel cluster, the carboxylate bridge adopts a *syn–syn* conformation; according to the literatures reported [36], these *syn–syn* carboxylate groups interact effectively with the unpaired electrons in the $d_{x^2-y^2}$ orbitals of the Cu(II) ions and can lead to efficient antiferromagnetic superexchange at lower temperatures.

4. Conclusions

In summary, two new copper coordination polymers constructed from 4,4′-bipydine and 1,2,4-benzenetricarboxylate $[Cu_3(1,2,4\text{-BTC})_2(4,4'\text{-bipy})(H_2O)_4]$ **1** and $[Cu(1,2,4\text{-HBTC})(4,4'\text{-bipy})]$ **2** have been prepared under hydrothermal (solvothermal) conditions. Both compounds show interesting 2-D neutral framework. In compound **1**, the 2-D layers are further linked by hydrogen bonding between the water molecules and the carboxylate into a 3-D supramolecular framework. But in compound **2,** the adjacent 2-D layers are parallel with each other and construct a 3-D supramolecular framework via the weak $\pi-\pi$ interactions. The magnetic studies for both compounds show a dominant ferromagnetic exchange between the Cu(II) ions. Further research of this system may focus on the replacement of copper and 4,4′-bipy with other transition metals and multidentate pyridyl ligands to prepare novel polymeric compounds and explore their valuable properties.

Acknowledgments

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