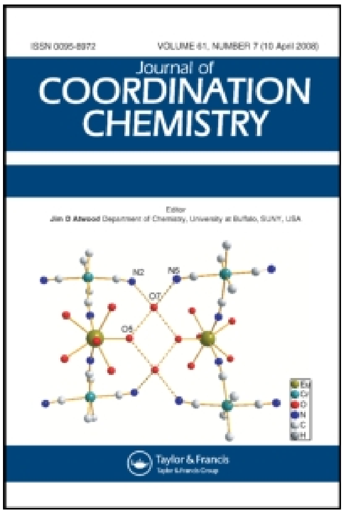

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Synthesis, X-ray crystal structure, and magnetic property of a 3-D self-assembled supermolecule

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The reaction of 2,2′-bipyrazine (bpz) and $Cu(NO_3)_2$ with addition of HCl gave a new complex $[Cu_5(bpz)_2Cl_{10}(H_2O)]_n \cdot nH_2O$, with bpz serving as a μ_3-ligand to link three different copper centers. X-ray crystallography shows a self-assembled supermolecule formed by $[Cu_5(bpz)_2]$ repeating unit further bridged through Cl^-. This is the first Cu(bpz) complex which possesses extended topology instead of closure. Magnetic susceptibility measurements for this complex from 2 to 300 K reveal weak antiferromagnetic interactions between copper(II) in agreement with out-of-plane exchange pathways and large Cu–Cu separation.

Keywords: 2,2′-bpz; Self-assembly; Extending topology; Magnetism

1. Introduction

Adapting multi-modal bridging ligands as building units has gained interest in crystal engineering since they are capable of binding various metal centers in a predictable way to compose "preprogrammed" structural information and functionality [1–4]. 2,2′-Bipyrazine (bpz) is of particular interest among these ligands due to its versatile binding capabilities from four potential N coordinating sites and its structural flexibility about the central C–C bond resulting in further control of network formation [5, 6] (scheme 1). It is a special multimodal ligand because it has an angle of nearly 60° to construct molecular architectures. There are many investigations relating to this ligand, e.g. Navarro and Lippert [7] reported molecular triangles, squares, and infinite loops based on the bpz; Blake *et al.* [8, 9] demonstrated chiral adamantoid networks $\{[Ag(bpyz)]X\}_n$ ($X = BF_4^-$, PF_6^-); Yeh *et al.* [5] afforded a luminescent coordination polymer $[Ag_2(bpyz)(NO_3)_2]_n$ with an unusual μ_4-bridging bonding mode

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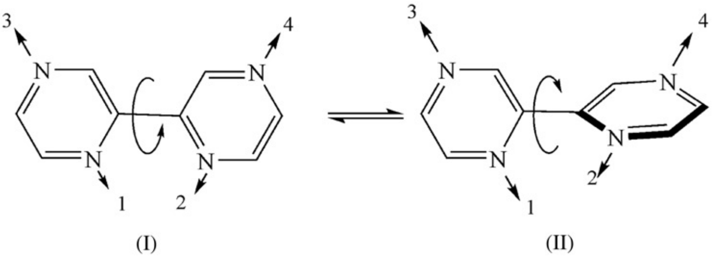

Scheme 1. Four potential N binding sites of 2,2′-bpz and its structural flexibility about the central C–C bond.

of 2,2′-bipyrazine. However, these reports focus exclusively on the noble ions of Ag^+, Pd^{2+}, and Pt^{2+} instead of other transition and main group metal ions to build metal frameworks.

Herein, we widen the research of bpz to explore its ability to create extended networks. As $[M_n(bpz)_n]$ is a cationic framework, the role of anion may be crucial in the reaction system to balance charge and satisfy the coordination of the central ions. In this work Cl^- was introduced into the reaction system of Cu^{2+} and bpz to synthesize a new complex $[Cu_5(bpz)_2Cl_{10}(H_2O)]_n \cdot nH_2O$ (**1**). Our investigations show that bpz provides the chelating bidentate site and the two monodentate N donor sites to bind three different metal ions. Moreover, apart from strong covalent coordination bonds, weaker Cu···Cl interaction and H-bonding play key roles in the increased dimensionalities of the desired product. Neighboring metal ions are bridged by bi-μ_2-Cl to form infinite Cu–2Cl–Cu chains in a self-assembled supermolecule. The magnetic measurement is also presented.

2. Results and discussion

2.1. *Structure of 1*

Single-crystal X-ray diffraction reveals that **1** crystallizes in triclinic crystal system with space group $P\bar{1}$. The asymmetric unit contains two and a half crystallographically unique Cu's, one bpz group, five Cl^- ligands, and two waters (figure 1). The bpz is a μ_3-bridge with chelating and monodentate modes to ligate three different copper ions. The central C(1)–C(5) bond between two pyrazine rings of bpz rotates to allow coordination to three coppers, giving a slight twist of two halfs of bpz rings with torsional angle *ca* 10.7°. The Cu(1)···Cu(3) and Cu(2)···Cu(3) distances through bpz are about 6.8 Å.

Cu(1) is in a slightly distorted trigonal bipyramidal geometry. The basic trigonal plane is defined by three Cl^-, while one N from bpz and one water occupy axial positions. Cu(2) is located at the symmetry center and has an occupancy of 0.5. Taking into account all Cu–Cl interactions, Cu(2) may be described as elongated octahedral, two nitrogens from different bpz ligands and two Cl^- ligands form the equatorial plane, and two symmetrically related Cl^-'s occupy the apical positions with long Cu···Cl bond lengths of [Cu(2)···Cl(2A) = Cu(2)···Cl(2B) = 2.948 Å]. Cu(3) is in a seriously

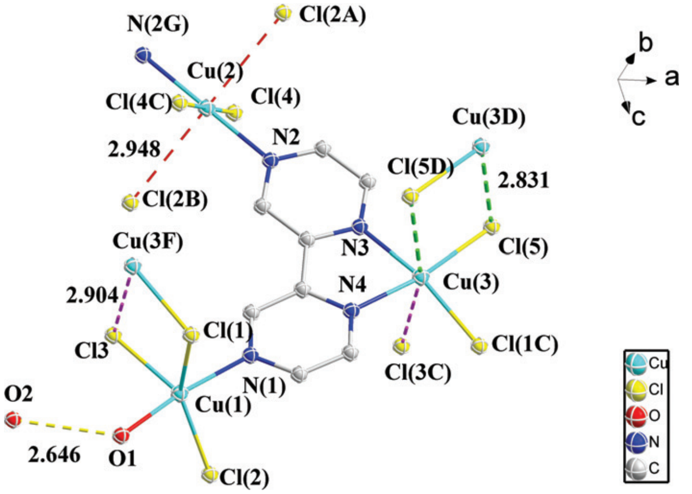

Figure 1. Atom labeling scheme for **1** (H atoms omitted for clarity) (symmetry code: A x, $y+1$, $z-1$; B $-x+1$, $-y$, $-z$; C $x+1$, y, z; D $-x+2$, $-y+1$, $-z$; F $x-1$, y, z; G $-x+1$, $-y+1$, $-z-1$).

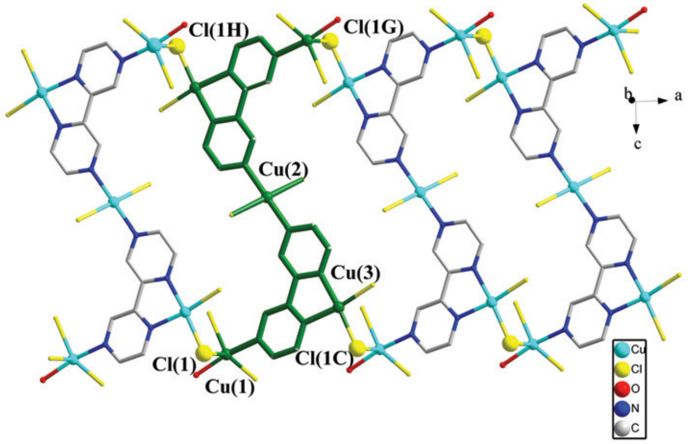

Figure 2. Ribbon-like chain of $[Cu_5(bpz)_2Cl_{10}]$ showing Cl-bridged units (symmetry code: C $1+x$, y, z; G $1-x$, $1-y$, $-z-1$; H $-x$, $1-y$, $-z-1$).

distorted octahedral geometry, chelated by bpz via N(3) and N(4), and two Cl^- in the equatorial plane; two other Cl^- ligands complete the octahedral geometry with long metal-chloride separation Cu(3) $\cdots$ Cl(5D) = 2.831 and Cu(3) $\cdots$ Cl(3C) = 2.904 Å. These Cu $\cdots$ Cl bond lengths are comparable to those of reported Cu–Cl complexes [10–13].

The basic building block of **1** is $[Cu_5(bpz)_2Cl_8]$, generated with symmetry center operation from the asymmetric unit. The coppers and bpz ligands in $[Cu_5(bpz)_2]$ are almost coplanar. As shown in figure 2, such entities are linked by the out-of-plane bridge provided by Cl(1) to afford a ribbon-like chain, with Cu(1)–Cl(1) = Cu(3)–Cl(1C) = 2.487 Å (symmetry code: C $1+x$, y, z; G $1-x$, $1-y$, $-z-1$; H $-x$, $1-y$, $-z-1$). The width of the ribbon is 15.9 Å [based on the distance of Cu(3) $\cdots$ Cl(1H)].

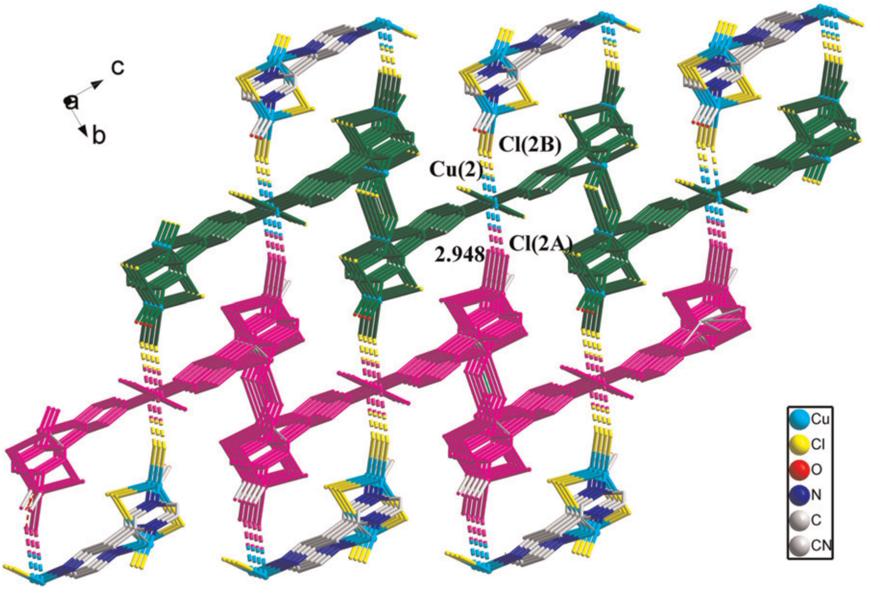

Figure 3. View along *a*-axis of 3-D network in **1** showing the 2-D layer and Cl2-bridged units (symmetry code: A x, $y+1$, $z-1$; B $-x+1$, $-y$, $-z$).

2.2. *Structural modulation by weaker interactions*

Neighboring ribbons are further connected through weaker interactions [$Cu(3)\cdots Cl(5D) = 2.831$ Å; D $2-x$, $1-y$, $-z$] creating sheets with a staircase-like appearance (figure S1). These layers cross-link to form a 3-D network through even weaker copper-chloride interactions [$Cu(2)\cdots Cl(2A) = Cu(2)\cdots Cl(2B) = 2.948$ Å; symmetry code: A x, $1+y$, $z-1$; B $1-x$, $-y$, $-z$] (figure 3). With connection of the copper ions via Cl-bridges, an inorganic Cu–Cl chain exists as shown in figure 4(a). Thus, the structure can be viewed as a 3-D organic–inorganic network [figure 4(b)] by the combination of Cu–Cl chains via organic spacer bpz. The $Cu\cdots Cu$ spaces are 3.465 and 3.611 Å via di-μ-Cl bridges and 4.592 Å via mono-μ-Cl bridge.

With Cl^- and H_2O in this structure, there are abundant hydrogen bonds (table 1). As shown in figure S2, the H-bonds interweave the 3-D super network and consolidate the structure.

2.3. *Magnetism property*

The molar magnetic susceptibility χ_M of **1** is measured in the range 300.8–2.0 K in a field of 10 kOe; plots of χ_M *versus* T and μ_{eff} *versus* T are shown in figure 5. The μ_{eff} for **1** at room temperature is $1.688\mu_B$, smaller than the spin-only value for an uncoupled Cu(II) ion (g 2.0; $1.73\mu_B$). From 300.8 to 56.8 K, the value of $\chi_M T$ remains constant upon cooling, but it sharply decreases to $1.042\,cm^3\,mol^{-1}$ at 2.2 K. The shape of this plot indicates a weak antiferromagnetic interaction between adjacent copper ions. The data fit the Curie–Weiss law with $\theta = -1.07$ K and $C = 0.351\,cm^3\,mol^{-1}\,K$.

According to the structure, the copper(II) separation via μ_3-bridging bpz ligand is *ca* 6.8 Å, so the corresponding magnetic interactions between them are very weak and

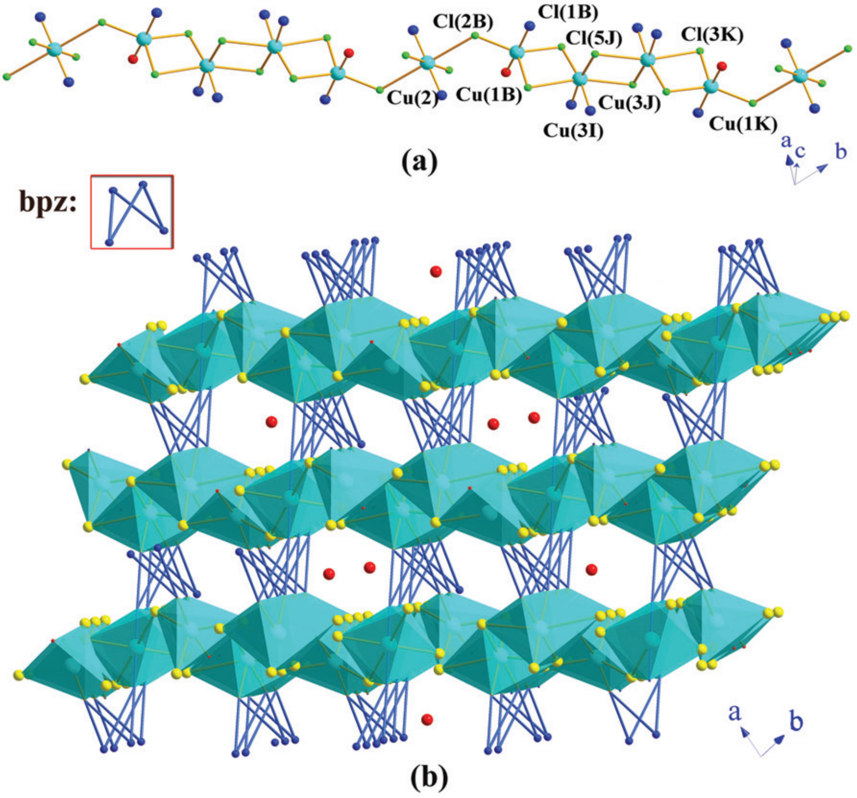

Figure 4. (a) Section of the Cu–Cl chain in **1**; (b) Schematic showing Cu–Cl chain combined by the triangle ligand (bpz: in the inset) to construct the 3-D network, with lattice water in the channel (symmetry code: B $1-x, -y, -z$; I $2-x, -y, -z$; J $x, y-1, z$; K $1+x, y-1, z$).

antiferromagnetic in nature, comparable to hat-bridged copper complexes [14]. Magnetic coupling might occur with the presence of Cl-bridges between the copper ions, but they contribute little to the magnetic exchange pathway. The magnetic orbital on Cu(3)/Cu(1C) via μ-Cl(1) bridge (2.3–2.487 Å) is mainly located in the equatorial plane, and the spin density on its axial position is expected to be very small. The Cu(2)$\cdots$Cu(2A) distance is even longer via Cl(2A), 2.948 Å, neither do their magnetic orbits overlap well. So the poor overlap between the parallel magnetic orbits centered on Cu(3)/Cu(1C) or Cu(2)$\cdots$Cu(2A) lead to no significant contributions to the magnetic coupling of this complex, in agreement with other μ-Cl bridged copper(II) dimeric and chain compounds [15].

3. Experimental

3.1. *Materials and measurements*

All reagents and solvents were commercially available and used as received except that 2,2′-bpz was prepared as reported [16]. IR spectra as KBr disks were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer (4000–400 cm^{-1}). Elemental analyses

Table 1. Summary of crystallographic data and structure refinement for **1**.

Formula	$C_{16}H_{20}Cl_{10}Cu_5N_8O_4$
M	1060.60
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	7.742(2)
b	10.879(3)
c	11.202(3)
α	62.941(6)
β	89.02(1)
γ	75.403(9)
U (Å^3)	807.9(4)
Z	1
ρ (Mg m^{-3})	2.180
μ (mm^{-1})	4.105
F(000)	519
θ range for data collection	2.19–27.48°
Limiting indices	$-10 \le h \le 8$, $-13 \le k \le 14$, $-14 \le l \le 14$
Reflections collected/unique	6169/3614 [$R_{(int)} = 0.0217$]
Completeness to $\theta = 27.48$	97.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3614/0/196
Goodness-of-fit on F^2	1.000
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0343$, $wR_2 = 0.0897$
R indices (all data)	$R_1 = 0.0400$, $wR_2 = 0.0934$
Largest different peak and hole	0.828 and −1.103 (e Å^{-3})

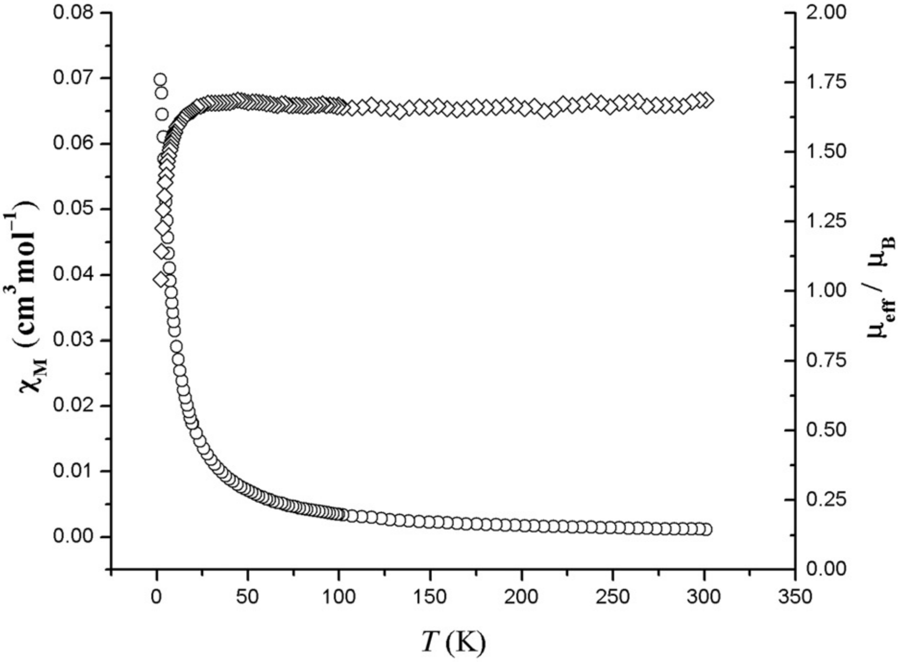

Figure 5. Temperature dependence of χ_M and μ_{eff} *vs.* T for **1**.

for C, H, and N were determined on an Elementary Vario ELIII analyzer. Variable-temperature (2.0–300.8 K) magnetic susceptibility measurements were carried out on a MPMS/C magnetometer at 10 kOe magnetic field using the SQUID method. Diamagnetic corrections were evaluated from Pascal's constants.

3.2. *Synthesis*

A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (85 mg, 0.35 mmol) and bpz (27 mg, 0.17 mmol) was dissolved in 15 mL aqueous methanol solution (v/v = 1/1). Then the pH was adjusted to about 5–6 by slow addition of 0.1 M HCl solution. The pale green solution was heated to 70°C for about 30 min with continuous stirring and then filtered. Green crystals suitable for X-ray determination were grown by slow evaporation of the solvents at room temperature for 1 month. Yield: 56% (based on bpz). Elemental analysis (%) Calcd for $Cu_5C_{16}H_{20}Cl_{10}N_8O_4$(1060.65): C, 18.12; H, 1.90; N, 10.56. Found: C, 18.09; H, 1.96; N, 10.54%. IR (KBr disc, cm^{-1}): 3443(ab), 3360.2(s), 3064(w), 3024(w), 1637.7(m), 1403.37(s), 1384.66(s), 1306.08(m), 1147.55(s), 1102.69(m), 1044.90(s), 859(s).

3.3. *X-ray structure determination*

Single crystal of **1** with approximate dimension 0.15 mm × 0.22 mm × 0.18 mm was coated with epoxy glue and mounted on a glass fiber for data collection. The intensity data were collected on a Mercury CCD diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at room temperature in the $\omega - 2\theta$ scan mode. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares with the SHELXTL-97 program package [17]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated

Table 2. Selected bond lengths (Å) and angles (°) for **1**, with e.s.d. in parentheses.

Bond length		Bond angle	
Cu(1)–O(1)	1.956(2)	O(1)–Cu(1)–N(1)	168.1(1)
Cu(1)–N(1)	2.016(2)	O(1)–Cu(1)–Cl(2)	89.82(7)
Cu(1)–Cl(2)	2.290(1)	N(1)–Cu(1)–Cl(3)	98.06(7)
Cu(1)–Cl(3)	2.380(1)	Cl(2)–Cu(1)–Cl(3)	119.96(4)
Cu(1)–Cl(1)	2.488(1)	Cl(2)–Cu(1)–Cl(1)	142.61(4)
Cu(2)–N(2)	2.040(2)	N(2)–Cu(2)–N(2G)	180.0
Cu(2)–N(2G)	2.040(2)	Cl(4G)–Cu(2)–Cl(4)	180.00(4)
Cu(2)–Cl(4G)	2.2654(8)	Cl(2B)–Cu(2)–Cl(2A)	180.00(4)
Cu(2)–Cl(4)	2.2654(8)	N(2)–Cu(2)–Cl(4G)	89.85(7)
Cu(2) ··· Cl(2B)	2.949(1)	N(2)–Cu(2)–Cl(2B)	91.67(7)
Cu(2) ··· Cl(2A)	2.949(1)	N(4)–Cu(3)–N(3)	79.62(9)
Cu(3)–N(4)	2.038(2)	Cl(5)–Cu(3)–Cl(1C)	93.92(3)
Cu(3)–N(3)	2.042(2)	Cl(5D)–Cu(3)–Cl(3C)	163.83(3)
Cu(3)–Cl(5)	2.251(1)	Cl(5)–Cu(3)–Cl(5D)	90.18(3)
Cu(3)–Cl(1C)	2.300(1)		
Cu(3) ··· Cl(5D)	2.832(1)		
Cu(3) ··· Cl(3C)	2.907(1)		

Symmetry code: A $x, y+1, z-1$; B $-x+1, -y, -z$; C $x+1, y, z$; D $-x+2, -y+1, -z$; F $x-1, y, z$; G $-x+1, -y+1, -z-1$.

Table 3. Hydrogen bonds for **1**.

D–H ··· A	*d*(D–H) (Å)	*d*(H ··· A) (Å)	*d*(D ··· A) (Å)	∠(DHA) (°)
O(2)–H(2a) ··· Cl(3 E)	0.83	2.42	3.220(3)	163.6
O(2)–H(2b) ··· Cl(2F)	0.83	2.44	3.255(3)	167.5
O(1)–H(1b) ··· Cl(4B)	0.84	2.30	3.105(2)	159.4
O(1)–H(1a) ··· (2)	0.87	1.81	2.645(4)	161.7

Symmetry transformations used to generate equivalent atoms: B $-x+1$, $-y$, $-z$; F $x-1$, y, z; E $-x$, $-y$, $-z$.

positions and refined with isotropic displacement parameters according to the riding model, except for two water protons, which could be located with difference Fourier synthesis. Crystal data and structure refinement parameters are summarized in table 2. Selected bond lengths and angles are listed in table 3 and hydrogen bonds are listed in table 1. CCDC number is 690608.

4. Conclusions

A magnetic extended supramolecular network composed of Cu^{II} and bpz has been prepared and characterized in the solid state. Copper(II) ions are linked through both mono-/di- μ-chloro-bridges and bpz to afford weak antiferromagnetism. This work explored the multi-modal 2,2′-bpz bridging ligand. Efforts to use bpz to produce new clusters as well as polymeric structures with paramagnetic metal centers are in progress.

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