Extended Network via π···π Interaction and Hydrogen Bond Linkages of 1D Copper(II) Coordination Polymer: Synthesis, Crystal Structure and Characterization of [Cu(4,4′-bpy)(2-pzc)-(H_2O)]$ClO_4 \cdot H_2O$ (2-pzc = 2-pyrazine-5-carboxylate; 4,4′-bpy = 4,4′-bipyridine)

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A penta-coordinated Cu(II) complex with mixed ligands 4,4′-bipyridine (4,4′-bpy) and 2-pyrazine-5-carboxylate anion (2-pzc), [Cu(4,4′-bpy)(2-pzc)(H_2O)]$ClO_4 \cdot H_2O$ (1), has been solvothermally synthesized and characterized. Complex 1 crystallizes in the monoclinic space group $P2_1/n$ with a = 0.82996(2) nm, b = 1.58156(5) nm, c = 1.53837(1) nm, β = 103.536(2)°, V = 1.96322(8) nm^3, M_r = 478.30, Z = 4, D_c = 1.618 g/cm^3, final R = 0.0544 and wR = 0.1487. The Structure of 1 indicates that the central Cu(II) atom is penta-coordinated by two N atoms from two 4,4′-bpy ligands, and one N atom and one oxygen atom of the 2-pzc ligand in the equatorial plane, and one oxygen atom of the coordinated water molecule at the axial position. The coordination geometry of Cu(II) atom could be considered as a slightly distorted square-pyramidal environment. The 4,4′-bpy ligands bridge the Cu(II) centers to form a one-dimensional chain, and 2-pzc acts as a terminal chelated ligand, and π···π interaction between the pyrazine rings of 2-pzc ligands of adjacent chains links the chains into a 2D sheet. Furthermore, the hydrogen bonds among the oxygen atoms of the uncoordinated water molecules and the N atoms and O atoms of 2-pzc ligands and the oxygen atoms of the coordinated water molecules link the sheets into the ultimate 3D network of complex 1.

Keywords crystal structure, 4,4′-bipyridine, 2-pyrazine-5-carboxylic, copper(II) polymer, π···π interaction and hydrogen bonding

Introduction

Functional coordination polymers are of great interest due to their potential applications in many areas, such as microporosity, electrical conductivity, molecular magnetism, linear optical behavior or catalysis.[1-6] Considerable effort has been focused on the supramolecular networks assembled by covalent, hydrogen bonds, π···π interaction or other weak interactions owing to their fascinating structural diversity and potential application in design of porous materials with novel inclusion or reactivity properties and supramolecular devices such as sensor and indicator.[7-16] Many promising supramolecular architectures in crystal engineering have been designed and constructed from mono- or poly-nuclear complexes,[8-13] low-dimensional coordination polymers[13-17] through using π···π interactions and hydrogen bonds as tools.

Some control over the supramolecular feactures can be exercised by the choice of suitable reaction conditions and building blocks. Recent investigations have addressed the use of molecules having an inherently rigid spacer such as the bipyridines (bpy), the 2,4′- and 4,4′-isomers being used as connector.[18] The 2,4′- and 4,4′-bipyridines, which can rotate around the single bond, template the reactions to afford self-assembled metal-organic complexes.[19] A number of one to three dimensional meta-bridging building blocks containing the rod-like type 2-connector, 4,4′-bpy, have been reported.[20-22] Herein, we report a three-dimensional copper(II) polymer [Cu(4,4′-bpy)(2-pzc)(H_2O)]$ClO_4 \cdot H_2O$ (**1**), constructed from one-dimensional polymer chain building blocks through inter-chain π···π interaction and hydrogen bond linkages.

Experimental

Materials and measurements

4,4′-Bipyridine and 2-pyrazinecarboxylic acid are pur-

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chased from Acros Organics, and other reagents were purchased from Shaihai Reagent Co. All reagents were of analytical grade and used without further purification. The IR spectrum (KBr pellets) was recorded on a Magna 750 FT-IR spectrophotometer. C, H and N elemental analyses were determined on an Elementar Vario ELIII elemental analyzer. Thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyser under N_2(26—700 ℃) at a heating rate of 10 ℃/min. EPR spectra were recorded on powdered samples at an X-band frequency of *ca*. 9.77 GHz with a Bruker ER420 automatic spectrometer.

Synthesis of [Cu(4,4′-bpy)(2-pzc)(H_2O)]ClO_4·H_2O (**1**)

A mixture of 4,4-bipyridine (0.08 g, 0.5 mmol), $CuCl_2$·$4H_2O$ (0.085 g, 0.50 mmol), 2-pyrazine-5-carboxylic acid (0.06 g, 0.50 mmol) in CH_3OH/H_2O mixed solvent (V_{CH_3OH}/V_{H_2O} = 2/5, 20 mL) (the pH value of the mixture was pre-adjusted to *ca*. 6 using NaOH/$HClO_4$ aqueous solution) was placed in a Parr Teflon-lined stainless steel vessel and heated to 150 ℃ for 72 h, then cooled to room temperature during 14 h. Blue crystals were obtained and collected by filtration and washed with water. Yield 72%, based on 4,4′-bpy. IR ν: 3421 (br), 3080 (w), 3018 (w), 1674 (s), 1653 (s), 1612 (m), 1595 (m), 1417 (m), 1352 (m), 1223 (w), 1149 (m), 1092 (s), 1051 (m), 812 (m), 638 (w), 672 (m), 459 (w), 418 (w) cm^{-1}. Anal. calcd for $C_{15}H_{15}N_4CuClO_8$: C 37.63, H 3.14, N 11.71; found C 37.58, H 3.06, N 11.58.

X-*Ray crystallography*

Intensity data were measured on a Siemens Smart CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.071073 nm) at 298 K. Empirical absorption corrections were applied by using the SADABS program. The structure was solved by direct methods and all calculations were performed using the SHELXL PC program. The positions of H atoms were generated geometrically (C—H bond lengths were fixed at 0.096 nm), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. The structure was refined by full-matrix least-squares analysis with anisotropic thermal parameters for all atoms except the H atoms. The crystal data and structure determination summary is given in Table 1. Additional crystallographic details, complete listings of the complex have been deposited at the Cambridge Crystallographic Data Center (CCDC) as supplementary publications reference number 175521.

Table 1 Crystal data and structure refinement for [Cu(4,4′-bpy)(2-pzc)(H_2O)]ClO_4·H_2O

Empirical formula	$C_{15}H_{15}ClCuN_4O_8$
Formula weight	478.30
Temperature (K)	293(2)
Wavelength (nm)	0.071073
Crystal system	Monoclinic
Space group	$P2(1)/n$
Unit cell dimensions	a = 0.82996(2) nm;
	b = 1.58156(5) nm;
	c = 1.53837(1) nm;
	β = 103.536(2)°
Volume (nm^3)	1.96322(8)
Z	4
Calculated density ($g·cm^{-3}$)	1.618
Absorption coefficient (cm^{-1})	13.00
F(000)	972
Crystal size (nm)	0.26×0.31×0.28
2θ range for data collection (°)	1.87 to 25.04
Limiting indices	$-4 \leqslant h \leqslant 6$,
	$-11 \leqslant k \leqslant 8$,
	$-11 \leqslant l \leqslant 10$
Reflections collected/unique	1931/1083 [R_{int} = 0.0328]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1083/0/263
Goodness-of-fit on F^2	1.101
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0544, wR_2 = 0.1487
Largest diff. peak and hole ($e·nm^{-3}$)	569 and −327

Results and discussion

Synthesis and characterization

In the reaction of metal halide with 4,4′-bpy, the products are normally obtained as powdered materials through conventional synthetic methods and typically insoluble in all organic solvents, so their structure are difficult to characterize. By improving the synthetic methods, many coordination polymers in the crystalline form have been obtained, such as [MCl_2(4,4′-bpy)]$_n$(M = Fe, Co, Ni, Co/Ni),[23][CuX_2(4,4′-bpy)]$_n$(X = Cl, Br) and [CuBr(4,4′-bpy)]$_n$.[24] In this paper, $CuCl_2$·$4H_2O$ was reacted with mixed ligands 4,4′-bpy and 2-Hpzc under solvothermal conditions, affording complex **1**, [Cu(4,4′-bpy)(2-pzc)(H_2O)]ClO_4·H_2O, which is stable at room temperature. IR spectrum of the complex shows a broad band centered at 3421 cm^{-1}, mainly attributed to H—O—H stretching vibrations, suggesting the existence of hydrogen bonding interactions,[25] which is in agreement with the X-ray analyses results. The difference between the antisymmetric (1674 cm^{-1}) and symmetric (1352 cm^{-1}) stretching bands of the carboxylate group ($\Delta\nu$ = 322 cm^{-1}) suggests[26] a monodentate bonding mode. The 418 cm^{-1} peak is assigned to the stretching vibration of Cu—N bond and the peak at 459 cm^{-1} to the Cu—O bond.

The UV-Vis spectrum of the complex in DMF solution exhibits two intense bands, at 254 and 273 nm, attributed to the π-π^* and n-π^* transitions, espectively, in 4,4′-bpy or 2-pzc ligands. The broad band centered at 628 nm corre-

sponds to the d-d transition of the copper(II) ion. The power X-band EPR spectrum at room temperature is anisotropic having a $g_{\perp}$ parameter value of 2.065 and a $g_{\parallel}$ value of 2.228 with $g_{av} = 2.119$, where $g_{av} = (g_{\parallel} + 2g_{\perp})/3$. No half-field transition was observed.

Thermal analyses under N_2 (from RT to 700 ℃) shows that the decomposition of complex **1** begins when it is heated above 90 ℃ and stops at above 574 ℃. The TGA data indicate that the total weight loss (7.53% at 90—125 ℃) is consistent with the loss of one coordinated water molecule and one molecule of free water (calcd 28.32%).

Description of the crystal structure

Atomic coordinates and equivalent isotropic displacement parameters are given in Table 2 and the selected bond lengths and angles are listed in Table 3.

The X-ray analysis reveals that the copper(II) centers in **1** are bridged by 4,4′-bipy with occurrence of 1D coordination polymeric zig-zag chain along *a*-axis as shown in Fig. 1 (a). An ORTEP drawing for the molecular structure of **1** with atom number labeling is schemed in Fig. 1(b), showing that each copper(II) atom has five-coordinated, slightly distorted square-pyramidal geometry, with two N atoms from two 4,4′-bpy ligands, and one O atom and one N atom from the 2-pzc ligand in the equatorial plane, and one O atom of the water molecular at the apical position. The central Cu(II) ion is 0.00655 nm above the basal square plane defined by N(1), N(2), N(3) and O(1), toward the apical O(7) atom. The 2-pzc ligand chelated the Cu(II) center to form a five-membered ring through one O atom of the carboxylate group and the N atom beside the carboxylate group. The Cu—N(2-pzc) bond length is 0.2005(17) nm, and the Cu—O(2-pzc) bond length is 0.1955(15) nm, which are both comparable to those of the other reported Cu-(2-pzc) complexes.[27] The bond

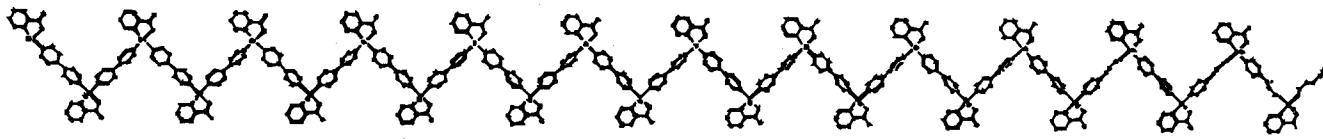
Table 2 Atomic coordinates $\pi\cdots\pi$ ($\times 10^4$) and equivalent isotropic displacement parameters ($nm^2 \times 10$) for $[Cu(4,4'\text{-bpy})(2\text{-pzc})(H_2O)]ClO_4 \cdot H_2O$

Atom	*x*	*y*	*z*	U_{eq}[a]
Cl(1)	3595(10)	4644(5)	6519(5)	99(3)
Cu(1)	208(2)	5022(1)	7783(1)	43(2)
N(1)	1210(40)	5897(13)	8667(10)	24(4)
N(2)	4470(40)	9068(11)	11856(9)	39(7)
N(3)	-520(20)	4033(14)	6970(20)	26(4)
N(4)	-1250(30)	2474(12)	6180(20)	62(7)
O(1)	1272(18)	4171(9)	8650(10)	58(6)
O(2)	1399(14)	2745(9)	8786(9)	57(5)
O(3)	3700(30)	5402(18)	6000(20)	117(13)
O(4)	3200(20)	4970(8)	7275(11)	125(6)
O(5)	2390(20)	4126(14)	6064(14)	112(13)
O(6)	5120(20)	4279(8)	6631(10)	129(6)
O(7)	-2261(13)	4869(5)	8243(6)	59(4)
O(8)	-2922(12)	5823(5)	9592(6)	56(4)
C(1)	340(30)	6570(30)	8790(20)	56(7)
C(2)	860(50)	7200(20)	9390(30)	55(6)
C(3)	2430(60)	7100(20)	9957(18)	32(6)
C(4)	3010(40)	7778(18)	10631(17)	37(9)
C(5)	2060(30)	8380(20)	10984(19)	46(7)
C(6)	2830(50)	9001(15)	11574(17)	47(7)
C(7)	5390(30)	8490(20)	11543(19)	50(9)
C(8)	4710(50)	7869(15)	10956(18)	51(8)
C(9)	3370(30)	6410(30)	9860(20)	39(6)
C(10)	2690(40)	5843(17)	9210(30)	32(5)
C(11)	20(30)	3320(30)	7480(30)	64(13)
C(12)	-400(30)	2590(30)	7030(20)	56(8)
C(13)	-1770(20)	3160(30)	5722(14)	46(6)
C(14)	-1390(30)	3950(20)	6120(30)	38(5)
C(15)	980(20)	3480(30)	8400(16)	55(10)

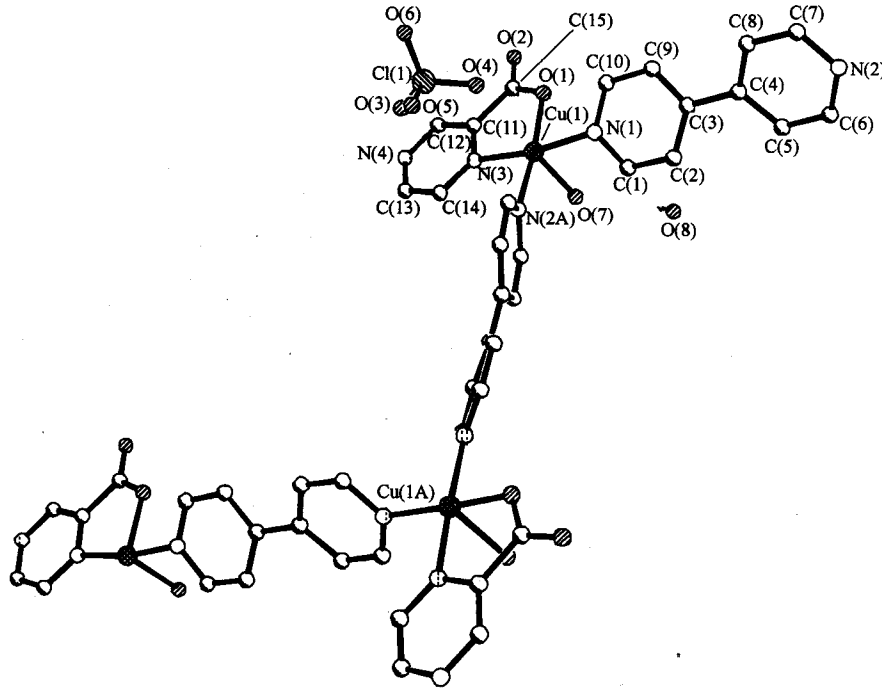
[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Selected bond lengths (nm) and angles (°) for $[Cu(4,4'\text{-bpy})(2\text{-pzc})(H_2O)]ClO_4 \cdot H_2O$

Cu(1)—O(1)	0.1955(15)	Cu(1)—N(3)	0.2005(17)
Cu(1)—N(1)	0.1981(14)	Cu(1)—N(2A)	0.2017(17)
Cu(1)—O(7)	0.2332(10)	Cl(1)—O(5)	0.1355(18)
Cl(1)—O(4)	0.1380(14)	Cl(1)—O(6)	0.1367(13)
Cl(1)—O(3)	0.145(3)		
O(1)-Cu(1)-N(3)	84.8(12)	N(1)-Cu(1)-N(2A)	89.8(9)
N(1)-Cu(1)-N(3)	171.7(13)	N(3)-Cu(1)-N(2A)	96.8(12)
O(1)-Cu(1)-N(2A)	171.0(10)	O(1)-Cu(1)-O(7)	90.6(4)
N(1)-Cu(1)-O(7)	97.0(8)	N(2A)-Cu(1)-O(7)	98.4(9)
N(3)-Cu(1)-O(7)	87.0(4)	O(1)-Cu(1)-N(1)	87.9(10)
O(5)-Cl(1)-O(6)	111.2(11)	O(6)-Cl(1)-O(4)	116.7(10)
O(5)-Cl(1)-O(4)	111.6(11)	O(5)-Cl(1)-O(3)	110.2(15)
O(6)-Cl(1)-O(3)	104.2(12)	O(4)-Cl(1)-O(3)	102.2(13)



(a)



(b)

Fig. 1 View of (a) the one-dimensional chain in complex **1** and (b) the molecular structure of complex **1** with atomic numberings.

length of apical Cu—O (water) is 0.2332(10) nm, which is significantly longer than that of Cu—O(2-pzc). The 4,4'-bpy bridge the Cu (II) centers with Cu—N bond lengths of 0.2017(17) nm for Cu—N(2A) and 0.1981(14) nm for Cu—N(1), which are comparable with the Cu—N distances found in other copper(II)-(4,4'-bpy) compounds.[28] The two

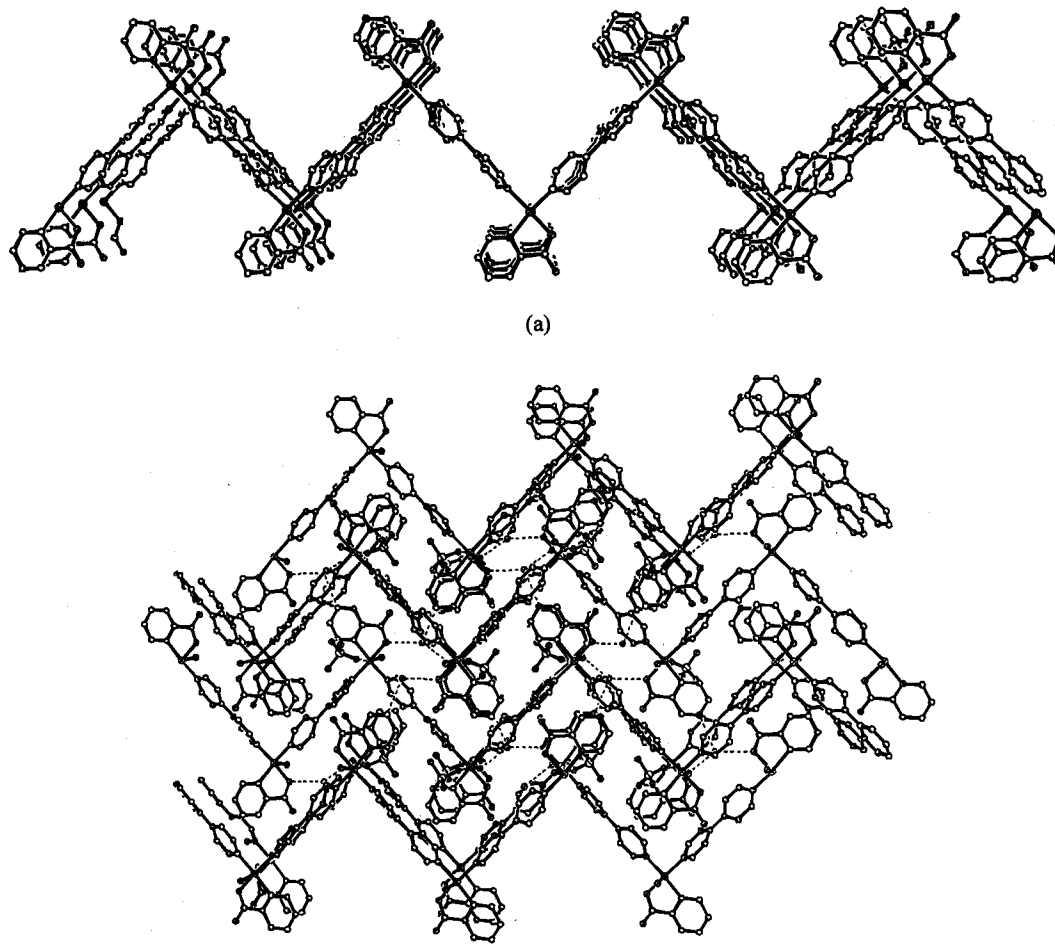


Fig. 2 View of (a) the 2D sheet in complex **1** via $\pi\cdots\pi$ interaction and (b) the ultimate three-dimensional network structure of complex **1** along *a*-axis.

pyridine rings of the 4,4′-bpy ligand are not co-planar with dihedral angle of 21.8° and the dihedral angle of the two pyridine rings which coordinated the same copper(II) atom is 71.2°. The pyrazine ring of 2-pzc ligand is almost coplanar with the basal square plane of the coordinated geometry of the penta-coordinated copper(II) atom with dihedral angle of 0.7°. The Cu⋯Cu seperation is 1.1085 nm through the bridge ligand 4,4′-bpy.

It must be noted that $\pi\cdots\pi$ interactions are evident, with the shortest distance of 0.345 nm between the pyrazine rings of 2-pzc ligands of adjacent chains, thus linking the $[Cu(4,4'\text{-bpy})(2\text{-pzc})(H_2O)]_n^{n+}$ chains into a 2D sheet. Furthermore, the hydrogen bonds among the oxygen atoms of the uncoordinated water molecules and the N atoms and O atoms of 2-pzc ligands and the oxygen atoms of the coordinated water olecules link the sheets into the ultimate 3D network of complex **1**. [O(8)—O(1)^{i} 0.2780 nm, O(8)—N(4)^{ii} 0.2870 nm, O(8)—O(7) 0.2714 nm; symmetry code: (i) $-x$, $-y+1$, $-z+2$; (ii) $-x$, $-1/2$, $y+1/2$, $-z+3/2$]. The ClO_4^- anions are situated in the pores of the ultimated 3D network of complex **1** and one oxygen atom of the ClO_4^- anion is weakly-coordinated to the Cu(II) center with Cu—O(3) bond distance of 0.2772 nm.

Conclusion

Solvothermal reaction of 4.4′-bipyridine and 2-pyrazine-5-carboxylic acid with $CuCl_2\cdot 4H_2O$ in CH_3OH/H_2O solution gave a three-dimensional complex constructed from one-dimensional polymeric chains via $\pi\cdots\pi$ interactions and hydrogen bonds, consisting of one independent bridging ligand 4,4′-bpy, one terminally chelated ligand 2-pzc, one coordinated water molecule, one free water molecule and the penta-coordinated Cu(II) center. This work exhibits that the combination of coordination covalent bonds and hydrogen bonds, $\pi\cdots\pi$ interactions is an useful tool to construct promising supramolecular architectures by using one-dimensional polymeric chains as building blocks.

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