

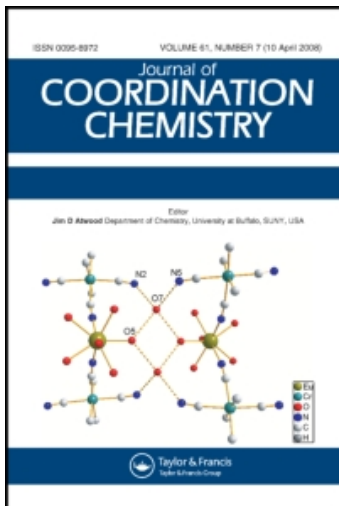
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1-D zigzag copper(II) complex with pyrazine-2,3,5,6-tetracarboxylate and oxalate

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1-D zigzag copper(II) complex with pyrazine-2,3,5,6-tetracarboxylate and oxalate

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A 1-D zigzag coordination polymer, $\{[\text{Cu}_2(\text{H}_2\text{pztc})(\text{ox})(\text{bpy})_2] \cdot 8\text{H}_2\text{O}\}_n$ (**1**) (H_4pztc = pyrazine-2,3,5,6-tetracarboxylic acid, ox = oxalate, bpy = 2,2'-bipyridine), has been synthesized under hydrothermal conditions. X-ray single crystal diffraction analysis indicates that the structure of the complex belongs to triclinic system, $P\bar{1}$ space group with $a = 9.6085(19) \text{ \AA}$, $b = 10.111(2) \text{ \AA}$, $c = 11.009(2) \text{ \AA}$, $\alpha = 99.41(3)^\circ$, $\beta = 102.87(3)^\circ$, $\gamma = 114.55(3)^\circ$, $V = 907.9(3) \text{ \AA}^3$, $Z = 1$. Cu(II) is six coordinate by $\text{H}_2\text{pztc}^{2-}$, bpy, and ox^{2-} , the oxalate produced from decarboxylation of H_4pztc . $[\text{Cu}_2(\text{ox})(\text{bpy})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]$ (**2**) was also obtained from filtrate after **1** separated.

Keywords: Cu(II) complex; Hydrothermal synthesis; Pyrazine-2,3,5,6-tetracarboxylic acid; Decarboxylation; Oxalate

1. Introduction

Pyrazine-2,3,5,6-tetracarboxylic acid (H_4pztc) has rich coordination groups with N and O donors, high symmetry, and use in metal-organic frameworks (MOFs) [1–6]. However, complexes with H_4pztc were all synthesized at room temperature; in 2006, Yigit *et al.* [7] wanted to obtain Cu(II) complex with H_4pztc under hydrothermal conditions, but decarboxylation of H_4pztc occurred, giving a pyrazine-2,6-dicarboxylate complex. Decarboxylation is common under hydro(solvo)thermal conditions with metal ion, temperature and pH affecting decarboxylation of H_4pztc . Higher reaction temperature favors decarboxylation of the aromatic carboxyl groups under hydrothermal conditions [8, 9]. Cu(II) [8, 10–12] and other transition metal ions such as Zn(II), Co(II), and Mn(II) play a catalytic role in decarboxylation [9, 13, 14].

Decarboxylation occurs easily for H_4pztc and must be avoided for constructing coordination polymers. Co(II) [15], Ni(II) [16], and Mn(II) [17] complexes with

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H₄pztc were synthesized by our team without decarboxylation under hydrothermal conditions.

In this article, a new 1-D coordination polymer, {[Cu₂(H₂pztc)(ox)(bpy)₂]·8H₂O}_n (**1**) (ox = oxalate, bpy = 2,2'-bipyridine), has been synthesized under hydrothermal conditions. Oxalate was produced from decarboxylation of H₄pztc; both oxalate and H₄pztc bridged Cu(II) alternately to form a 1-D chain. When the filtrate was allowed to continue standing at room for 2 weeks, blue plate crystals of **2** ([Cu₂(ox)(bpy)₂(H₂O)₂(NO₃)₂]) were obtained, which had been reported by Tang *et al.* [18], from stirring mixture of oxalate, bpy, and Cu(II) at room temperature. Crystal data of **2** were measured as follows: C₂₂H₂₀Cu₂N₆O₁₂, *Mr* = 687.52, Monoclinic, *P2(1)/n*, *a* = 7.6566(15) Å, *b* = 10.223(2) Å, *c* = 16.168(3) Å, β = 99.67(3)°, *V* = 1247.6(4) Å³, *Z* = 2, ρ_{Calcd} = 1.830 Mg/m³, *F*(000) = 696, *GOF* = 1.050, *R1* = 0.0343, *wR2* = 0.0822 [*I* > 2σ(*I*)].

2. Experimental

2.1. General

H₄pztc was synthesized by Wolff's synthesis [19]. Other chemicals purchased were reagent grade and used without purification. Elemental analysis (C, H, and N) was performed on a Perkin-Elmer 240 CHN elemental analyzer. IR spectrum was recorded from 400 to 4000 cm⁻¹ with a Bruker TENOR 27 spectrophotometer using a KBr pellet. Thermal gravimetric analysis (TGA) was performed on a NETZSCH TG 209 instrument with a heating rate of 10°C min⁻¹. Ultraviolet spectrum was measured by a Hewlett Packard 8453 ultraviolet spectrometer.

2.2. Preparation of the complexes

Complex **1** was synthesized in a mixture of Cu(NO₃)₂·3H₂O (0.0363 g, 0.15 mmol), H₄pztc (0.0390 g, 0.15 mmol), bpy (0.0234 g, 0.15 mmol), and H₂O (12 mL) under hydrothermal conditions at 120°C for 27 h, and then cooling to room temperature at a rate of 1°C h⁻¹. Blue needle crystals of **1** were obtained, yield 31%. Anal. Calcd for C₃₀H₃₄Cu₂N₆O₂₀ (*f_w* = 925.71) C, 38.92; H, 3.70; N, 9.08%. Found: C, 38.90; H, 3.85; N, 9.12%. The filtrate was allowed to continue standing at room temperature for 2 weeks; blue plate crystals of **2** were obtained.

2.3. X-ray crystallography

A single crystal of **1** with dimensions 0.08 × 0.02 × 0.02 mm³ was selected for crystal structure analysis. X-ray diffraction data were collected on a computer-controlled Rigaku Saturn diffractometer. The detector was equipped with graphite-monochromated Mo-Kα radiation (0.71073 Å) by using the ω-scan technique. The structure was solved by direct methods and refined with full-matrix least-squares on *F*² using SHELXS-97 and SHELXL-97 [20]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were located and refined isotropically. Crystallographic data

Table 1. Crystal data and structure refinement details for **1**.

Empirical formula	C ₃₀ H ₃₄ Cu ₂ N ₆ O ₂₀
Formula weight	925.71
Temperature (K)	113(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Unit cell dimensions (Å, °)	
<i>a</i>	9.6085(19)
<i>b</i>	10.111(2)
<i>c</i>	11.009(2)
α	99.41(3)
β	102.87(3)
γ	114.55(3)
Volume (Å ³), <i>Z</i>	907.9(3), 1
Calculated density (mg m ⁻³)	1.693
Absorption coefficient (mm ⁻¹)	1.266
<i>F</i> (000)	474
θ range for data collection (°)	1.98–27.89
Reflections collected	7069
Independent reflection	4274 [<i>R</i> _{int} = 0.0264]
Max. and min. transmission	0.9751 and 0.9055
Data/restraints/parameters	4274/0/284
Goodness-of-fit on <i>F</i> ²	1.050
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0353, <i>wR</i> ₂ = 0.0873
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0443, <i>wR</i> ₂ = 0.0916
Largest difference peak and hole (e Å ⁻³)	0.835 and -0.457

for **1** are listed in table 1. The crystal structure of **2** was also solved and consistent with the structure of [Cu₂(ox)(bpy)₂(H₂O)₂(NO₃)₂] reported by Tang *et al.* [18].

3. Results and discussion

3.1. Crystal structure

X-ray single crystal diffraction for **1** reveals that it contains infinite 1-D zigzag chains running along the *c*-axis. In the chain structure, every symmetric unit consists of two Cu(II) ions, one H₂pztc²⁻, one ox²⁻, two bpy, and eight uncoordinated water molecules (figure 1). Cu(II) ions were alternately bridged by H₂pztc²⁻ and ox²⁻ in a bisbidentate chelate mode. Oxalate formed from decarboxylation of H₄pztc. The bpy acts as blocking ligand to avoid further growth in 2-D space.

Cu(II) ion is six coordinate in a distorted octahedron coordination environment. The equatorial plane is formed by one oxygen (O1) of H₂pztc²⁻, one oxygen (O6A) of ox²⁻, and two nitrogens (N2, N3) of bpy. The axial sites are occupied by one nitrogen (N1) of H₂pztc²⁻ and one carboxylate oxygen (O5) from ox²⁻. The bond lengths in axial sites, Cu1–O5 = 2.2957(16) Å and Cu1–N1 = 2.4427(19) Å, are longer than those in the equatorial plane. Selected bond lengths and angles are shown in table 2.

In the crystal structure of **1**, planes of H₂pztc²⁻ or bpy are parallel to each other. The bpy plane is almost perpendicular to the mean plane of the pyrazine ring, with dihedral angle of 91.4°. The complex has rich hydrogen bonding and face-to-face $\pi \cdots \pi$ interactions between adjacent pyridyl rings (centroid–centroid distance of 3.762 Å) giving a 2-D corrugated layer (figure 2) and 3-D network (figure 3).

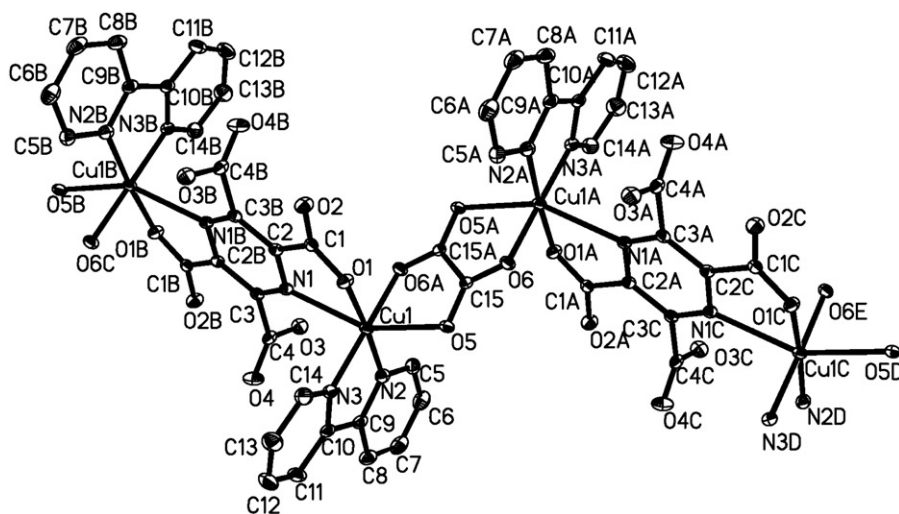


Figure 1. ORTEP representation of **1** showing the molecular structure with 50% probability thermal ellipsoids. The uncoordinated water molecules and hydrogens are not shown for clarity.

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

Cu(1)–O(1)	1.9783(18)	Cu(1)–O(6) ⁱ	1.9925(15)
Cu(1)–N(2)	1.983(2)	Cu(1)–O(5)	2.2957(16)
Cu(1)–N(3)	1.9891(19)	Cu(1)–N(1)	2.4427(19)
O(1)–Cu(1)–N(2)	175.81(7)	N(3)–Cu(1)–O(5)	104.75(7)
O(1)–Cu(1)–N(3)	94.38(7)	O(6) ⁱ –Cu(1)–O(5)	78.37(6)
N(2)–Cu(1)–N(3)	81.71(8)	O(1)–Cu(1)–N(1)	74.46(7)
O(1)–Cu(1)–O(6) ⁱ	89.14(7)	N(2)–Cu(1)–N(1)	104.11(8)
N(2)–Cu(1)–O(6) ⁱ	94.70(8)	N(3)–Cu(1)–N(1)	92.51(7)
N(3)–Cu(1)–O(6) ⁱ	175.55(6)	O(6) ⁱ –Cu(1)–N(1)	85.81(6)
O(1)–Cu(1)–O(5)	82.67(7)	O(5)–Cu(1)–N(1)	152.33(5)
N(2)–Cu(1)–O(5)	99.72(7)	O(1)–Cu(1)–N(1)	74.46(7)

Symmetry code: (i) $-x+1, -y+2, -z+1$.

Hydrogen-bonding interactions involve carboxylate from $\text{H}_2\text{pztc}^{2-}$ and ox^{2-} , carboxyl oxygen, and waters. Four lattice waters (O7, O8, O9, O10) link by O–H \cdots O hydrogen bonds to form U-shaped $(\text{H}_2\text{O})_4$ clusters, every two $(\text{H}_2\text{O})_4$ clusters stand together by back-to-back arrangement (figure 4).

Nonbonded O \cdots O distances and O–H \cdots O angles for the $(\text{H}_2\text{O})_4$ cluster are presented in table 3. The O \cdots O distances range from 2.674 to 2.803 Å, resulting in an average O \cdots O distance of 2.741 Å, and the average O–H \cdots O angle is 174.9°. The average distance is shorter than that observed in four-membered water rings (2.810 Å) [21] and the average O–H \cdots O angle is also large, probably because of the reduced tensile force in this chain-water tetramer than ring-water tetramer. Hydrogen bond data in $(\text{H}_2\text{O})_4$ cluster are shown in bold in table 3.

The decarboxylation mechanism of **1** and **2** may be similar to the report of Min *et al.* [22], who gained insight into the mechanism for formation of the oxalate experimentally, consisting of anionic $\bullet\text{CO}_2^-$ radical formation and the subsequent radical coupling. In addition, Ghosh *et al.* also obtained oxalate complex from the decarboxylation of pyridine-2,4,6-tricarboxylic acid [23].

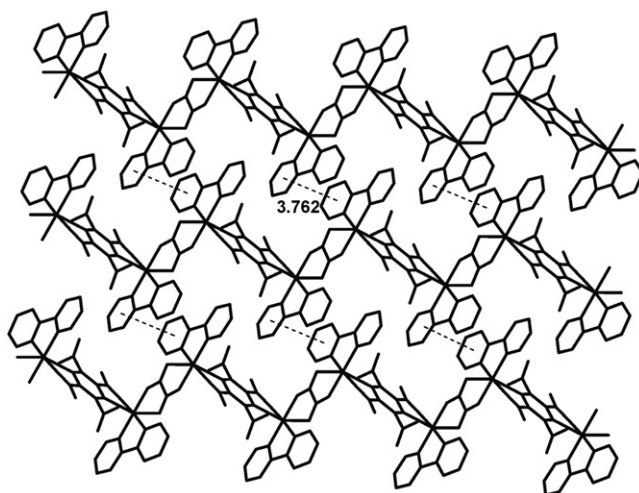


Figure 2. 2-D corrugated layers of **1** connected by $\pi \cdots \pi$ interactions.

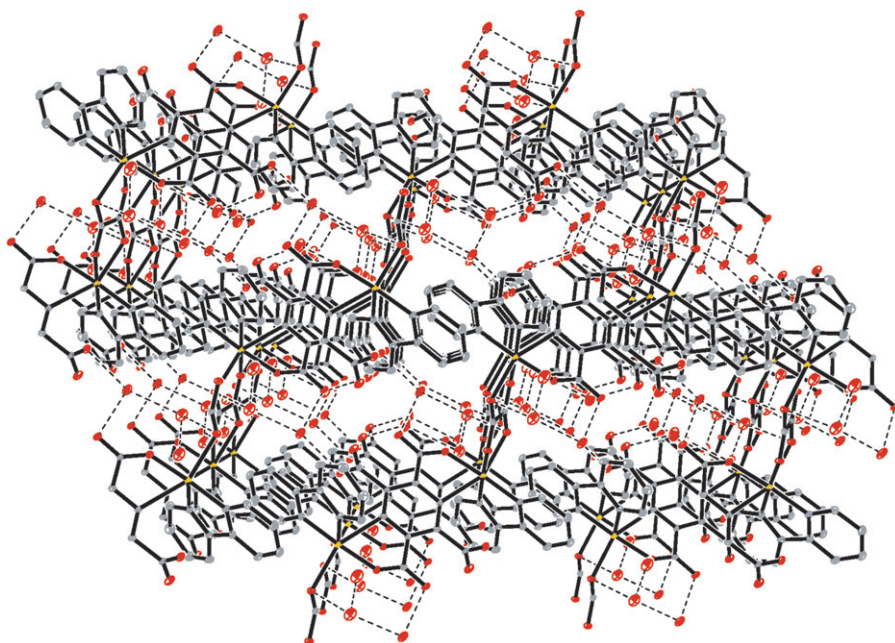
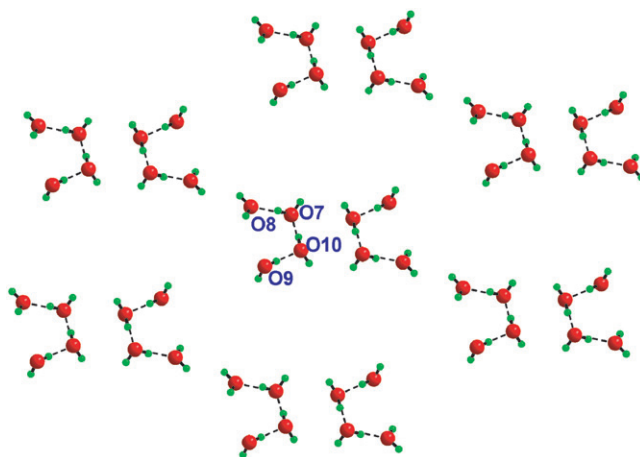


Figure 3. The crystal packing of **1** connected by $\pi \cdots \pi$ interactions and hydrogen bonds.

3.2. IR result

The IR spectrum of **1** shows an absorption at 1702 cm^{-1} indicating incomplete deprotonation of H_4pztc . The asymmetric and symmetric stretching vibrations of carboxylate are observed at 1652 , 1448 , and 1417 cm^{-1} ; the separations (Δ) between $\nu_{\text{asym}}(\text{CO}_2)$ and $\nu_{\text{sym}}(\text{CO}_2)$ of 204 and 235 cm^{-1} indicate monodentate mode in **1** [24]. These results are in agreement with the X-ray results. Lattice water absorption bands

Figure 4. The (H₂O)₄ clusters in **1**.Table 3. Hydrogen-bonding data (Å, °) in **1**.

D–H...A ^a	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
O7–H7A...O6 ⁱ	0.853	2.139	2.987	172.51
O7–H7B...O8ⁱ	0.880	1.873	2.744	170.10
O8–H8A...O4 ⁱⁱ	0.849	1.924	2.773	179.84
O8–H8B...O4 ⁱⁱ	0.900	2.149	2.944	146.96
O9–H9A...O10	0.850	1.823	2.674	179.59
O9–H9B...O2 ⁱⁱⁱ	0.866	1.944	2.801	170.08
O9–H9B...O1 ⁱⁱⁱ	0.866	2.473	3.103	130.11
O10–H10A...O7^{iv}	0.999	1.806	2.803	174.99
O10–H10B...O5 ⁱⁱⁱ	0.885	2.043	2.904	164.03
O3–H3...O9 ^v	0.840	1.644	2.467	165.88

^aD = donor; A = acceptor.Symmetry code: (i) $-x+1, -y+1, -z+1$; (ii) $x, y, z-1$; (iii) $x, y-1, z$; (iv) $x+1, y, z$; (v) $x-1, y, z$.

appear near 3430 cm^{-1} and may be attributed to asymmetric and symmetric OH stretching modes. The characteristic band of bpy appeared at 774 cm^{-1} .

3.3. Thermal gravimetric analysis

TGA was carried out for **1** from 23 to 700°C (Supplementary material). All water molecules in **1** are uncoordinated, and easily lost; partial water loss of the complex takes place when placed in the air. TGA shows weight loss of 5.2% within 109°C corresponding to complete loss of residual water. From 109 to 260°C , there is almost no mass change. Above 260°C , the complex continued to decompose.

3.4. UV/Vis spectrum

The ultraviolet spectrum of **1** in aqueous solution shows four strong absorption bands (namely at 196, 245, 300, and 310 nm) and a very weak band at 500–550 nm. The four strong absorptions are due to the E1-, K-, B-, and R-bands, E1-, K-, B- most likely

correspond to π - π^* transitions, while the R-band is due to the n - π^* transition. These absorption bands of **1** are all red-shifted, caused by partial overlap of π electrons of bpy and $\text{H}_2\text{pztc}^{2-}$ in **1**, so the π - π^* and n - π^* transitions are intensified by each other, resulting in red-shift and enhancement of absorbance. The very weak absorption band at 500–550 nm is assigned to d-d transitions of Cu(II).

4. Conclusion

A 1-D zigzag coordination polymer, $\{[\text{Cu}_2(\text{H}_2\text{pztc})(\text{ox})(\text{bpy})_2] \cdot 8\text{H}_2\text{O}\}_n$, was synthesized and structurally characterized. It contains three ligands, $\text{H}_2\text{pztc}^{2-}$, ox^{2-} , and bpy, in which the ox^{2-} was from decarboxylation of H_4pztc . Cu(II) is alternately bridged by $\text{H}_2\text{pztc}^{2-}$ and ox^{2-} in a bisbidentate chelate mode. Furthermore, a U-shaped $(\text{H}_2\text{O})_4$ cluster is also observed in **1**; shorter O...O distances and larger O-H...O angles are helpful to understand water clusters of different sizes and shapes in diverse environments.

Supplementary material

CCDC: 702665 contain the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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