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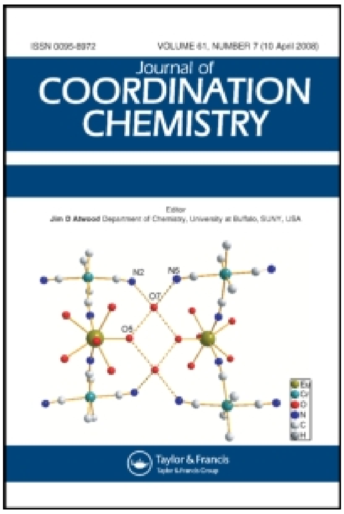

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# Synthesis and crystal structures of supramolecular compounds: $[Cu(mpca)_2(H_2O)] \cdot 3H_2O$ and $[Cu_2(mpca)_2(pyr)_4]$

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# Synthesis and crystal structures of supramolecular compounds: $[Cu(mpca)_2(H_2O)]\cdot 3H_2O$ and $[Cu_2(mpca)_2(pyr)_4]$

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A new chelate ligand, 5-methyl-1H-pyrazole-3-carboxylic acid (mpca), has been synthesized. This ligand reacts with cupric sulfate to give two supramolecular compounds $[Cu(mpca)_2(H_2O)]\cdot 3H_2O$ (**1**) and $[Cu_2(mpca)_2(pyr)_4]$ (Pyr = pyridine) (**2**), which were characterized by elemental analysis and X-ray crystal diffraction. Helical water chain and strong $\pi$–$\pi$ interaction are important for the stability of the 3-D structure of these supramolecules.

*Keywords*: Pyrazole; Water chain; Hydrogen bonds

## 1. Introduction

Crystal engineering of supramolecular metal-organic architectures assembled through covalent bonds in addition to other weak cooperative interactions such as hydrogen bonds, $\pi$–$\pi$ stacking, and electrostatic interactions has attracted considerable attention for designing and constructing new crystalline materials [1–3]. Among these secondary interactions, the hydrogen bond is more important in the molecular assembly due to its suitable strength and directionality [4]. Hydrogen-bonded water clusters have been broadly studied both theoretically and experimentally to provide useful information on the nature of cooperative association of a small collection of water molecules. Small water clusters are crucial building units for extended water morphologies including tapes [5–9].

Heterocyclic carboxylic acids such as pyrazolecarboxylic acids [10–18] are versatile ligands with multi-coordination modes by N and O donors on the heterocyclic rings and carboxyl groups. Pyrazole has two isomers, making coordination of pyrazolecarboxylic acids more complicated than pyridine-carboxylic oxygen and pyrazole nitrogens in pyrazolecarboxylic acids can coordinate to form monodentate or multidentate M–N and M–O bonds, but also form intermolecular hydrogen bonds for assembling high-dimensional networks.

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Reactions of 3-methyl-5-pyrazolecarboxylic acid (mpca) with copper(II) under hydrothermal conditions or by solvent diffusion give two new complexes, $[Cu(mpca)_2(H_2O)] \cdot 3H_2O$ and $[Cu_2(mpca)_2(pyr)_4]$, with different structural characters. Our study indicates that helical water chain and $\pi$–$\pi$ stacking interaction play important roles in the assemblies of high-dimensional architectures.

## 2. Experimental

### 2.1. *Materials and physical measurements*

All chemicals were commercial materials of analytical grade and used without purification. FT-IR spectra were recorded on a Nicolet Magna-IR 550 spectrometer in dry KBr pellets. C, H, and N analysis was measured on a MOD 1106 elemental analyzer. Thermoanalysis was performed using a TG-DTG microanalyzer of SDT 2960 and all samples were heated under a nitrogen stream of $100\,\mathrm{mL\,min^{-1}}$ with a heating rate of $10^\circ\mathrm{C\,min^{-1}}$.

### 2.2. *Synthesis of the ligand and complexes*

**2.2.1. Synthesis of mpca.** The ligand mpca was prepared by a modified literature method for the preparation of 3-isobutyl-5-pyrazolecarboxylic acid [19]. The sodium salt, $CH_3COCH{=}C(ONa)–CO_2C_2H_5$, prepared by Claisen condensation [20] was added in small portions to a 2 M KOH (aq) (31 mL) in solution at 0°C. After the reaction mixture was stirred for 1 h, hydrazine sulfate (12.8 g, 0.098 mol) was slowly added over 30 min. The precipitate was collected by filtration and dried to give the pyrazolecarboxylic acid (mpca). Yield: 50%; m.p. 56–57°C. Anal. Calcd for $C_7H_{10}N_2O_2$ (%): C, 54.45; H, 6.48; N, 18.20. Found: C, 54.54; H, 6.54; N, 18.17. IR data (KBr pellets, $\mathrm{cm^{-1}}$): 3300w (O–H), 1721s ($\nu$ C=O), 1582m ($\nu$ C=N).

**2.2.2. Synthesis of $[Cu(mpca)_2(H_2O)] \cdot 3H_2O$ (1).** A solution of mpca (0.252 g, 2 mmol) in water (10 mL) was slowly added to a solution of $CuSO_4 \cdot 5H_2O$ (0.184 g, 1 mmol) in deionized water (10 mL). The mixture was stirred for 10 min at room temperature and then placed in a 25 mL Teflon-lined autoclave and heated at 150°C for 120 h. The autoclave was cooled over a period of 12 h at $10^\circ\mathrm{C\,h^{-1}}$, and the product was collected by filtration and dried at ambient temperature to give **1** as blue crystals. Yield: 60%, based on Cu. Anal. Calcd for $C_{10}H_{16}CuN_4O_8$ (%): C, 31.29; H, 4.20; N, 14.60. Found: C, 31.30; H, 4.15; N, 14.56. IR data (KBr pellets, $\mathrm{cm^{-1}}$): 3350w ($\nu$ O–H), 1657s ($\nu$ C=O), 1557m ($\nu$ C=N).

**2.2.3. Synthesis of $[Cu_2(mpca)_2(pyr)_4]$ (2).** A solution of mpca (0.252 g, 2 mmol) in water (10 mL) was slowly added to a solution of $CuSO_4 \cdot 5H_2O$ (0.184 g, 1 mmol) in pyridine (10 mL). A blue solution formed after the resulting mixture was stirred at room temperature for 30 min. Slow evaporation of the solvent at room temperature led to formation of blue block crystals of **2**. Yield: 68%, based on Cu. Anal. Calcd for

$C_{30}H_{28}Cu_2O_4N_8$ (%): C, 52.09; H, 4.08; N, 16.20. Found: C, 52.08; H, 4.07; N, 16.23. IR data (KBr pellets, $cm^{-1}$): 1631s ($\nu$ C=O), 1565m ($\nu$ C=N).

### 2.3. *Single-crystal structure determination*

Intensity data for **1** and **2** were collected at 298 K on a Bruker SMART CCD area detector diffractometer using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) using the $\omega$–$\theta$ scan mode in the range $2.1 \le \theta \le 25$. Raw frame data were integrated with the SAINT [21] program. The structure was solved by direct methods using SHELXL-97 and refined by full-matrix least-squares on $F^2$ using SHELXL-97 [22]. An empirical absorption correction was applied with SADABS [22]. All nonhydrogen atoms were refined anisotropically. Hydrogens were set in calculated positions and refined by a riding mode, with a common thermal parameter. All calculations and graphics were performed with SHELXTL [21] and DIAMOND. The crystallographic data and experimental details for the structure analysis are summarized in table 1.

## 3. Results and discussion

### 3.1. *IR spectral studies*

Vibrations of the complexes shifted by 64–90 $cm^{-1}$ for $\nu$(C=O) and 17–28 $cm^{-1}$ for (C=N) compared to the free ligands. The shifts indicated that the ligands coordinate to

Table 1. Crystallographic data and intensity collection details for **1** and **2**.

| Complex | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{10}H_{16}CuN_4O_8$ | $C_{30}H_{28}Cu_2N_8O_4$ |
| Formula weight | 383.81 | 691.68 |
| Temperature (K) | 298(2) | 298(2) |
| Crystal system | Triclinic | Monoclinic |
| Space group | *P-1* | *P2(1)/n* |
| Color/shape | Blue, block | Blue, block |
| Unit cell dimensions (Å, °) | | |
| *a* | 7.1179(8) | 9.7842(9) |
| *b* | 9.2279(10) | 15.8246(16) |
| *c* | 13.0216(15) | 10.4551(11) |
| $\alpha$ | 81.289(2) | 90 |
| $\beta$ | 88.003(2) | 113.885(2) |
| $\gamma$ | 67.3110(10) | 90 |
| Volume (Å$^3$), *Z* | 779.75(15), 2 | 1480.1(3), 2 |
| Calculated density ($g\,cm^{-3}$) | 1.635 | 1.552 |
| Absorption coefficient ($mm^{-1}$) | 1.447 | 1.488 |
| $\theta$ range for data collection (°) | 1.58, 25.01 | 2.41, 25.00 |
| Reflections collected | 4026 | 7335 |
| Independent reflections | 2681 [$R$(int) = 0.0312] | 2604 [$R$(int) = 0.0358] |
| Final *R* indices [$I \ge 2\sigma(I)$] | $R_1 = 0.0673$ | $R_1 = 0.0339$ |
| $wR_2$ indices (all data) | $wR_2 = 0.2024$ | $wR_2 = 0.0881$ |
| Largest difference peak and hole (e Å$^{-3}$) | 0.6545, 0.6165 | 0.6638, 0.5478 |

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

| **1** | | **2** | |
|---|---|---|---|
| Cu(1)–N(1) | 1.964(5) | Cu(1)–N(2)#1 | 1.961(2) |
| Cu(1)–N(3) | 1.967(5) | Cu(1)–O(1) | 1.964(2) |
| Cu(1)–O(1) | 1.978(5) | Cu(1)–N(1) | 2.005(2) |
| Cu(1)–O(3) | 1.980(5) | Cu(1)–N(3) | 2.114(3) |
| Cu(1)–O(5) | 2.545(5) | Cu(1)–N(4) | 2.210(3) |
| N(1)–Cu(1)–N(3) | 177.7(2) | N(2)#1–Cu(1)–O(1) | 179.17(11) |
| N(1)–Cu(1)–O(1) | 82.8(2) | N(2)#1–Cu(1)–N(1) | 97.81(9) |
| N(3)–Cu(1)–O(1) | 95.4(2) | O(1)–Cu(1)–N(1) | 82.10(9) |
| N(1)–Cu(1)–O(3) | 99.8(2) | N(2)#1–Cu(1)–N(3) | 93.88(10) |
| N(3)–Cu(1)–O(3) | 81.9(2) | O(1)–Cu(1)–N(3) | 86.79(10) |
| O(1)–Cu(1)–O(3) | 172.0(2) | N(1)–Cu(1)–N(3) | 130.34(10) |
| N(1)–Cu(1)–O(5) | 93.2(2) | N(2)#1–Cu(1)–N(4) | 91.28(10) |
| N(3)–Cu(1)–O(5) | 88.5(2) | O(1)–Cu(1)–N(4) | 88.04(10) |
| O(1)–Cu(1)–O(5) | 99.44(19) | N(1)–Cu(1)–N(4) | 118.39(10) |
| O(3)–Cu(1)–O(5) | 88.08(19) | N(3)–Cu(1)–N(4) | 109.35(10) |

Symmetry code: #1 $-x+1$, $-y+1$, $-z+1$.

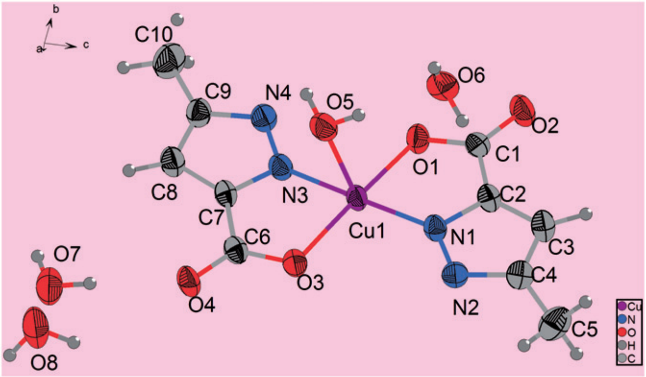

Figure 1. The Cu(II) coordination environment in the monomeric subunit in **1**.

Cu(II) via oxygen of the carboxyl group and nitrogen of the pyridine and pyrazole rings. A broad band at 3200–3500 $cm^{-1}$ for **1** can be assigned to vibration of the lattice water.

### 3.2. *Crystal structures*

Selected bond lengths and angles are listed in table 2. The molecular structure of **1** with atom numbering scheme is shown in figure 1. In **1**, the Cu(II) is a distorted square-pyramid coordinating to two nitrogens and two oxygens from two ligands and one oxygen from coordinated water. Two nitrogens (N1 and N3) and two oxygens (O1 and O3) constitute the base of the square-pyramid and water (O5) occupies the apical position with a Cu–O5 distance of 2.54(6) Å.

The uncoordinated lattice water molecules interdigitate with those in adjacent stacks giving pseudo 2-D sheets. The sheets are also connected by multiple intermolecular

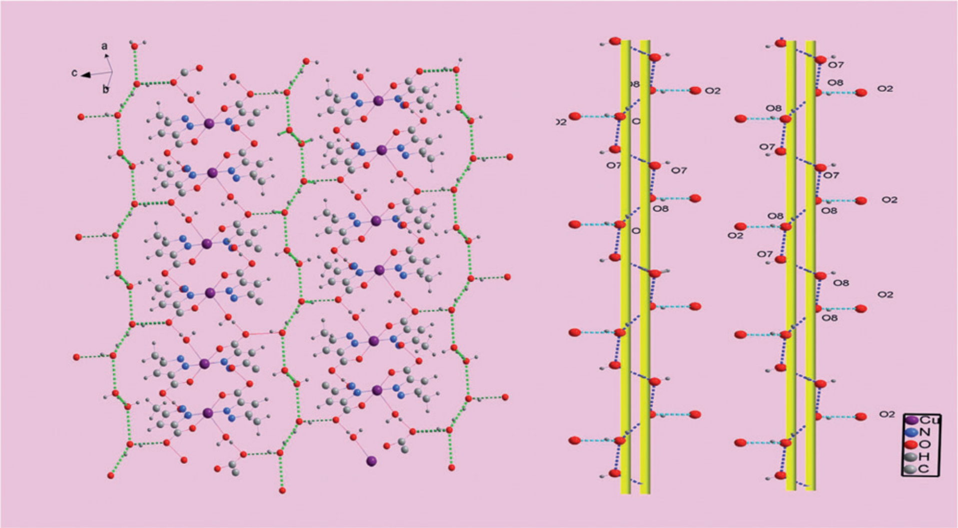

Figure 2. (a) 2-D sheet consisting of 1-D segregated water chains. (b) The entrapped 1-D helical array of water molecules.

Table 3. Hydrogen bond lengths (Å) and angles (°) for **1**.

| D–H···A | Symmetry code | D–H | H–A | D···A | ∠DHA |
|---|---|---|---|---|---|
| O5–H5D···O6 | $x, y, z+1$ | 0.850 | 2.037 | 2.887 | 179.42 |
| O5–H5E···O2 | $-x+1, -y+2, -z+3$ | 0.850 | 1.966 | 2.816 | 179.64 |
| O6–H6A···O1 | $x-1, y, z-1$ | 0.850 | 2.107 | 2.908 | 157.02 |
| O6–H6B···O4 | $-x+1, -y+1, -z+2$ | 0.850 | 2.010 | 2.810 | 156.72 |
| O6–H6B···O3 | $-x+1, -y+1, -z+2$ | 0.850 | 2.635 | 3.106 | 116.20 |
| O7–H7A···O4 | | 0.850 | 2.078 | 2.927 | 176.81 |
| O7–H7B···O7 | $-x+2, -y+1, -z+2$ | 0.850 | 1.982 | 2.831 | 176.92 |
| O8–H8A···O2 | $-x+1, -y+1, -z+3$ | 0.850 | 2.009 | 2.846 | 168.10 |
| O8–H8B···O8 | $-x+1, -y, -z+2$ | 0.850 | 1.985 | 2.823 | 168.26 |

O–H···O and O–H···N hydrogen bonds between the mononuclear subunits and the lattice water molecules (figure 2). The carboxyl O2 is a hydrogen acceptor towards O8 of the water. One H of O8 binds with the second water and hydrogens of both waters are hydrogen bond donors towards two carboxyl oxygens O2 and O4 of a neighboring complex. The H6A and H6B of the remaining water make the connection to the third complex connected by O6–H···O1 and O6–H···N4 hydrogen bonds. The carboxyl group that acts as an H bond acceptor towards both water molecules via both of its O atoms O1 and O4 exhibits a delocalized $\pi$ system with nearly identical C–O distances.

As shown in figure 2, along the *a* direction, lattice water molecules are in a shallow helical fashion O7–H7B···O8–H8B···O7 with a helical pitch of 9.228 Å, the angles O7···O8···O8#1 and O7#2···O7···O8 (#1: $2-x, -y, -z$; #2: $2-x, 1-y, -z$) in the helix are 144.17 and 110.01° (table 3), and the unit cell packing diagram shows the presence of two helical water chains located along *b*. In addition, through O8–H8A···O2#3 (carboxyl) (#3: $2-x, 1-y, 1-z$) and O7–H7A···O4 (carboxyl)

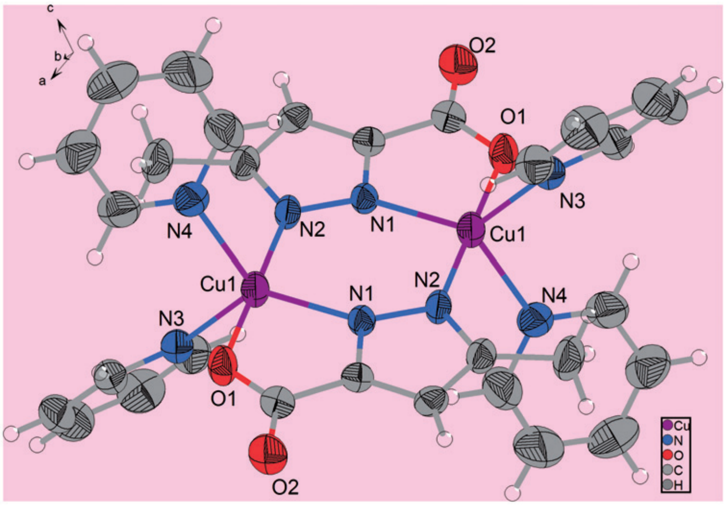

Figure 3. The Cu(II) coordination environment in the monomeric subunit in **2**.

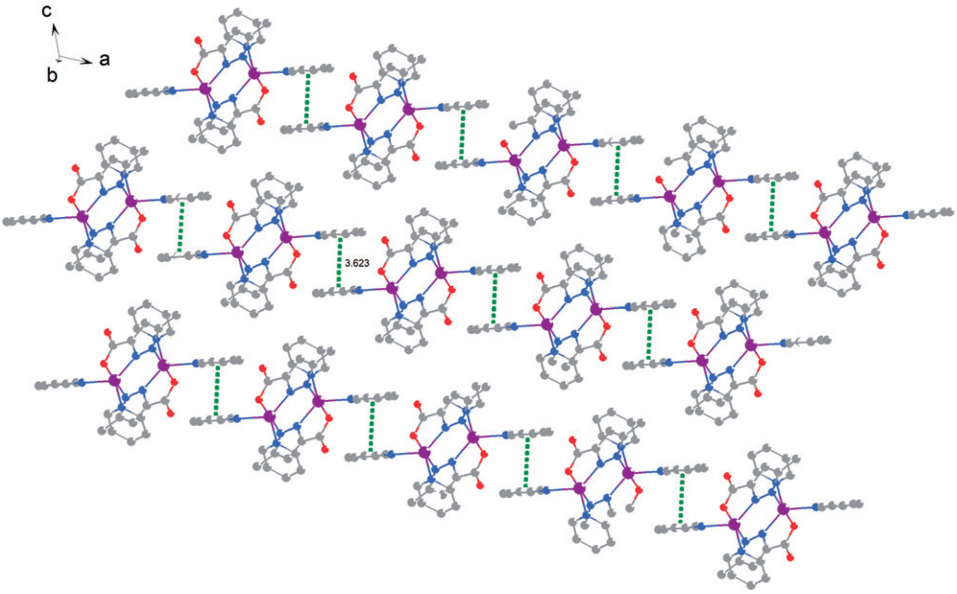

Figure 4. The $\pi$–$\pi$ interaction between pyridine rings of **2**.

hydrogen bonds, the 1-D channel as a host stabilizes the water chain. The helix water is similar with that observed recently [23].

In **2**, both Cu(II) cations adopt distorted trigonal-bipyramidal geometry (figure 3). Three nitrogens (N1, N3, and N4) constitute the base of the equatorial plane, whereas one oxygen from the carboxyl group and one nitrogen from mpca occupy the apical position with Cu–O1 and Cu1–N2 distances of 1.96(4) and 1.96(1) Å, respectively. A 2-D ladder-like supramolecule was formed by stacking (figure 4).

The centroid-to-centroid and centroid-to-plane distances between the pyridine planes (dihedral angle 0°) are 3.62(3) and 3.55(9) Å, revealing strong stacking contacts [24]. Furthermore, the short contacts extend the 2-D layers into a 3-D supermolecular framework.

In summary, we have synthesized and obtained crystal structures of two new supramolecular complexes with 5-methyl-1H-pyrazole-3-carboxylic acid, and a water chain was observed in **1**. The structures are formed via strong $\pi$–$\pi$ stacking and strong hydrogen bonding (for **1**). An unusual helix water chain was embedded in the structure via supramolecular interaction. This study demonstrates that the nature of the ligand and the geometric needs of the metal play important roles in formation of 3-D supramolecular architectures.

### 3.3. *Thermal decomposition*

In order to examine the thermal stabilities of the complexes, thermal gravimetric (TG) and differential thermal gravimetry (DTG) (Supplementary material) were carried out by heating $[Cu(mpca)_2(H_2O)] \cdot 3H_2O$ in nitrogen at the heating rate of $10°C\,min^{-1}$.

There are two main loss stages, the first starts from 50°C to 91°C with a mass loss of 18.6 wt%, corresponding to loss of four water molecules (theoretical loss 18.75 wt%), three lattice waters and one coordinated water. The second degradation stage is in the range 296–311°C with mass loss of 61.86%, corresponding to loss of two mpca molecules (theoretical loss 61.02 wt%); copper(II) was completely degraded to CuO with a total loss of 80.4 wt% (theoretical loss 80.2 wt%). The thermal decomposition of $[Cu(mpca)_2(H_2O)] \cdot 3H_2O$ can be described as follows:

$$[Cu(mpca)_2(H_2O)] \cdot 3H_2O \rightarrow Cu(mpca)_2 \rightarrow CuO$$

## Supplementary material

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 683739 and 714835 for **1** and **2**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: 44 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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