



# One-pot synthesis of two new metal–organic networks: hydrogen bonded mononuclear Cu(II) complex and mixed-valence Cu(I,II) coordination polymer with encapsulated 14-membered unique water cluster



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## ABSTRACT

{[Cu<sub>4</sub>(μ-bpe)<sub>4</sub>Cu<sub>2</sub>(μ-pydc)<sub>2</sub>(μ<sub>3</sub>-pydc)<sub>2</sub>] · 14H<sub>2</sub>O}<sub>n</sub> (**1**) and [Cu(pydcH)<sub>2</sub>(bpe)<sub>2</sub>] (**2**) have been solvothermally synthesized by 1,2-bis(4-pyridyl)ethylene (bpe) along with dianionic pyridine-2,3-dicarboxylate (pydc) ligands and characterized by elemental, FT-IR and thermal analyses techniques. In the solvothermal synthesis of complexes, **1** was isolated when the reactor was opened whereas **2** was crystallized after 3 weeks. The X-ray crystallographic studies show that complex **1** exhibits ladder-like structure involving mixed-valence Cu(I,II) which has generated a simultaneous in situ redox reaction and a unique 14-membered water cluster consisting of an eight-membered open-cube hexamer and two cyclic water trimers has been observed in hydrophilic cavities of **1**. Supramolecular network of **2**, which has proton transfer product of pydcH cations, is formed by O–H···N and aromatic interactions.

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The synthesis and design of metal organic architectures having diverse topologies and functions are one of the most significant aims in crystal engineering [1–3]. Combination of polycarboxylate anions and dipyridyl ligands is a reasonable strategy to generate extended networks. Pyridine-2,3-dicarboxylic acid (PydcH<sub>2</sub>) has proved to be interesting and versatile ligand and exhibits various coordination modes to furnish various structures [4–11]. Pydc is able to chelating and suitable for metalloligand approach [12]. Moreover, it strongly tends to form the kinetic products of 1D double-chain polymers through its coordination ability [8,9][4,5,12–16]. It is known that 1,2-bis(4-pyridyl)ethylene is multi-functional ligand largely used in the assembly of coordination polymers [17]. It acts as bridging ligand to connect metal ions to form coordination polymers. Moreover, it can serve as a template in the channel to stabilize the supramolecular networks [18]. The hydro(solvo)method has been an encouraging technique in preparing highly stable, infinite coordination polymers. It has been found that in situ reactions, such as redox process of copper, can take place under hydro(solvo)thermal condition [19]. In situ reactions represent new routes for synthesizing coordination polymers [20]. The mixedvalence Cu(I,II) coordination polymers are important due to not only their

great biological importance for their structural application in certain metallo-enzymes [21] but also to their interesting electronic properties [22]. On the other hand, control over the final product with two different oxidation states is compelling, which is reflected in the literature of mixedvalence Cu(I, II) coordination polymers [23–25].

Water clusters, groups of water molecules held together by hydrogen bonds, have been the issue of several investigations because of their importance in understanding a great number of chemical processes [26–32]. To date, various water clusters have been structurally characterized and collected information has substantially promoted the clarification of the interactions between water molecules, as well as between the water clusters and the host structures [33–40]. One encouraging way to get more information can be to dip into the water clusters encapsulated in cavities [30,41–47].

In this study, we report the syntheses and crystal structures of Cu(I,II) and Cu(II) complexes based on the pydc and 1,2-bis(4-pyridyl)ethylene ligands under solvothermal conditions. Mixed-valence complex of **1** exhibits a 1D ladder chain involving unprecedented 14-membered water cluster inside its large cavities.

Complexes were solvothermally synthesized by mixing of Cu(CH<sub>3</sub>COO)<sub>2</sub> · H<sub>2</sub>O, 1,2-bis(4-pyridyl)ethylene and pyridine-2,3-dicarboxylate ligands with solvent mixture (DMF/EtOH/H<sub>2</sub>O). The mononuclear structure of **2** containing Cu(II) center shows a different structural

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**Table 1**  
Crystal data and structure refinement parameters for complexes **1** and **2**.

Crystal data	<b>1</b>	<b>2</b>
Empirical formula	C <sub>38</sub> H <sub>40</sub> Cu <sub>3</sub> N <sub>6</sub> O <sub>15</sub>	C <sub>38</sub> H <sub>28</sub> CuN <sub>6</sub> O <sub>8</sub>
Formula weight	1011.38	760.20
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2 <sub>1</sub> /n
<i>a</i> (Å)	13.1759 (2)	13.2634 (3)
<i>b</i> (Å)	13.6060 (2)	10.2274 (2)
<i>c</i> (Å)	13.8449 (2)	14.2741 (3)
$\alpha$ (°)	95.638 (2)	90.00
$\beta$ (°)	107.7400 (9)	116.192 (2)
$\gamma$ (°)	117.224 (2)	90.00
<i>V</i> (Å <sup>3</sup> )	2017.66 (5)	1737.33 (6)
<i>Z</i>	2	2
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.665	1.453
$\mu$ (mm <sup>-1</sup> )	1.65	0.69
$\theta$ range (°)	2.6–28.3	2.5–28.4
Measured refls.	28,632	16,443
Independent refls.	7102	4296
<i>R</i> <sub>int</sub>	0.021	0.026
<i>S</i>	1.06	1.06
<i>R</i> 1/ <i>wR</i> 2	0.0301/0.089	0.044/0.132
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (eÅ <sup>-3</sup> )	0.47/–0.84	0.45/–0.35

feature compared to polynuclear **1** containing mixed-valence Cu(I,II) center, although both are taking place in the same reaction media. The brown crystals of **1** were collected in the reaction vessels while the blue crystals of **2** were collected three weeks later. It is known that Cu(II) ions can be reduced to Cu(I) by pyridine-derivative ligands under hydro(solvo)thermal reactions[48] and intriguing structures can be achieved from the reduction of copper valence states[49], therefore, solvothermal conditions are being considered to be the essential process responsible for these reductions. The appearance of brown crystals of **1** is the typical color of mixedvalence oxidation state containing Cu(I,II) ions[50]. The coexistence of Cu(I) and Cu(II) is due to the partly reduction of Cu(II) under hydrothermal conditions [51] and such reduction is the most common way for solvothermal preparations of Cu(I) and Cu(I,II)

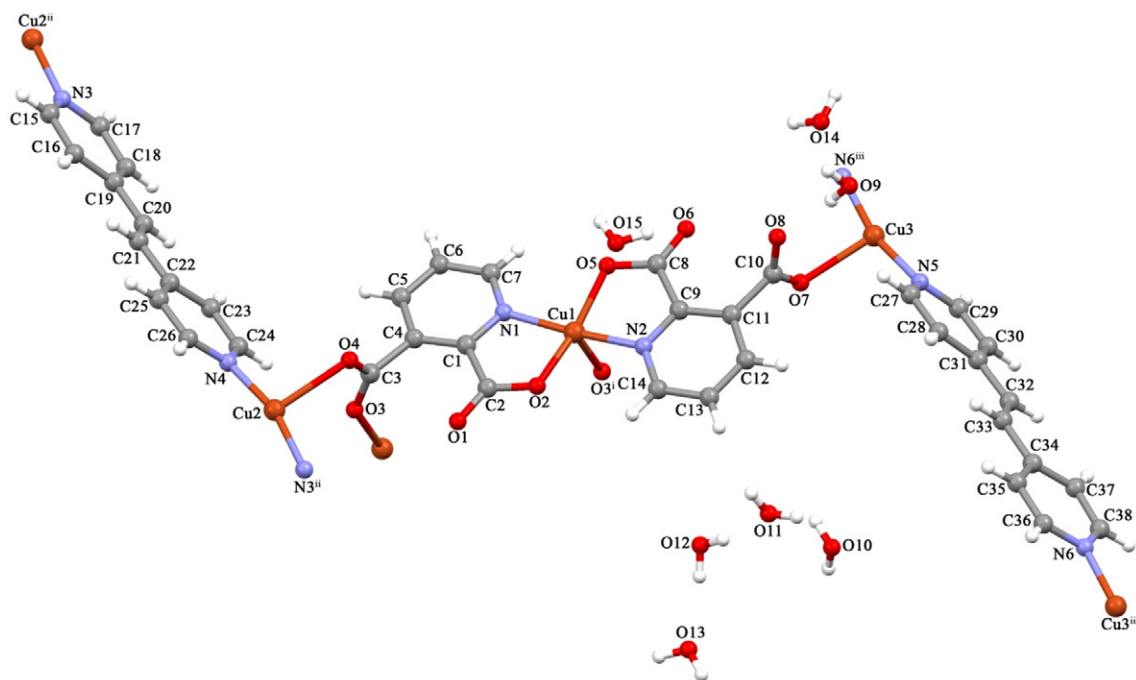
coordination polymers[48]. The results from parallel experiments, the ratios of pH 6–7, solvent mixture DMF/EtOH/H<sub>2</sub>O (1:2.5:10) and the metal salt of Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O play a key role for high quality of single crystals of **1** and **2**.

It is not easy to determine a possible mechanism because of the difficulties in determining products during the solvothermal synthesis[48]. A formation mechanism for polynuclear **1** containing mixed-valence Cu(I,II) center and mononuclear structure of **2** containing Cu(II) center is proposed as follow: Firstly, highly soluble complex **2** may be formed and catalyzed water oxidation reaction. Some of the mononuclear Cu(II) complexes with N- and O-donor atoms appeared as homogeneous water oxidation catalysts in the literature[52,53]. The liberation of electrons in the water oxidation reaction led to the formation of Cu(I) by reducing a part of Cu(II) in the reaction mixture. Cu(I) ions were stabilized via the formation of complex **1**. Because of the high solubility nature of **2**, it was crystallized three weeks later by slow evaporation after filtration from the reaction mixture.

Complexes were investigated by FT-IR spectroscopy. A broad band's observed range from 3520 to 3412 cm<sup>-1</sup> are attributed to the asymmetric and symmetric stretching modes of water molecules in **1**. The weak peaks at 3091 and 3012 cm<sup>-1</sup> are the characteristics of C–H stretching bands of the ligand groups. Strong absorption peak around 1711 cm<sup>-1</sup> indicates existence of protonation carboxylate groups in **2** as revealed by the X-ray single-crystal structure analysis. The very strong peaks range from 1664 to 1583 and 1469–1348 cm<sup>-1</sup> correspond to  $\nu_{\text{asym}}$  and  $\nu_{\text{sym}}$  of the carboxylate group, respectively.

The relevant crystal data and experimental conditions with the final parameters are summarized in Table 1. Details of these interaction distances are given in Tables S1–S3.

The asymmetric unit of the complex {[Cu<sub>4</sub>( $\mu$ -bpe)<sub>4</sub>Cu<sub>2</sub>( $\mu$ -pydc)<sub>2</sub>( $\mu_3$ -pydc)<sub>2</sub>·14H<sub>2</sub>O]<sub>n</sub> (**1**) consists of a Cu(II) ion, two Cu(I) ions, two bpe ligands, two pydc ligands and seven non-coordinated water molecules (Fig. 1). The coordination sphere of Cu1 atom is a distorted square pyramidal geometry with the  $\tau$  value of 0.178 [ $\tau = (172.17-161.48)/60 = 0.178$ ] [54]. The equatorial coordination comes from two oxygen atoms [O2 and O5] and two nitrogen atoms [N1 and N2] of two different pydc bridges, while the apical position is occupied by one oxygen atom



**Fig. 1.** The molecular structure of **1** showing the atom numbering scheme. [(i)  $-x, 1-y, -z$ ; (ii)  $-1+x, y, z$ ; (iii)  $1+x, y, z$ ].

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