

Encapsulated two distinct infinite helical water chains in a cyano-bridged copper^{II}–iron^{II} heterometal complex

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ABSTRACT

A bimetallic oligonuclear complex, [*trans*-{Cu(pmea)₂Fe(CN)₆}]·9H₂O (**1**) (pmea = bis[(2-pyridyl)methyl]-2-(2-pyridyl)ethylamine), had been synthesized and structurally characterized. **1** crystallizes in monoclinic space group *P2*(1)/*c* with *a* = 23.924(5) Å, *b* = 10.911(2) Å, *c* = 21.094(4) Å, β = 112.46(3)° and *Z* = 4, which exhibits a three dimensional (3D) framework constructed from the water rich 2D sheets. Of particular interest, two kinds of helical water chains coexist in this complex. Comparing the experimental results, it is comprehensible that hosts constructed from the hexacyanometallates plays crucial roles in the formation of the helical structures and water aggregates. Additionally, the compound was characterized by TGA, IR spectroscopy, magnetism and elemental analysis.

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Studies of water aggregates constructed by different nuclearities and structures have attracted considerable interest because of its fundamental importance in many biological and chemical processes [1–5]. The best understanding of hydrogen-bonding interactions and rearrangement dynamics of discrete water clusters, infinite water chains and sheets would be for achieving an accurate description of liquid water and its anomalous properties [1–5]. With this consideration in mind, several types of interesting water aggregates, such as water clusters (H₂O)_{*n*} [6–11], one-dimensional (1D) water chains [12–18], two-dimensional (2D) water layers [19–23], and even three-dimensional (3D) water structures [24,25], have been synthesized and documented in recent decades. Comparably, the infinite water chains attract much more attention due to the vital role of controlling proton fluxes in a large number of biomolecules, facilitating the selective permeation of water across membranes and stabilizing the native conformation of biopolymers [26–28]. Recently, much interest has been focused on the construction of helical water chains because they are very essential to understand of hydrogen bonds and other non-covalent interactions in many important biopolymers [29,30].

Despite some success has been achieved on water chains or helical water chains, it is still extremely difficult to construct thus water aggregates artificially because of the poor understanding of structural constraints required in stabilizing helical chains [29–32]. Therefore, the modulation and stabilization of thus water

chains is a long-standing challenge, despite the structural constraints originated from the environments of various crystal hosts are known to determine the water aggregates. The structures and types of water aggregates have good relationships with the synthetic achiral or chiral building block or supramolecular networks, which have provided accurate and detailed information about hydrogen bonding in diverse water clusters trapped in these host matrices [33]. But thus helical 1D water aggregate captured in achiral host is rare. The building blocks or supramolecular networks constructed by the heterobimetallic compounds derived from the hexacyanometallates [M(CN)₆]^{*n*-} (M = Fe, Cr, etc., transition metal) have been verified as an efficient host matrix to encapsulate different morphologies of water clusters by means of the uncoordinated cyano groups [34–36]. With this consideration in mind, to enrich the water chemistry and elucidate the interactions between water molecules, we set out to get new hosts constructed from the hexacyanometallates to accommodate different morphologies of waters. Herein, we present a new discrete heterobimetallic compound derived from the [Fe(CN)₆]⁴⁻, [*trans*-{Cu(pmea)₂Fe(CN)₆}]·9H₂O (**1**) (pmea = bis[(2-pyridyl)methyl]-2-(2-pyridyl)ethylamine), which interestingly stabilizes two distinct infinite helical 1D water chains in the crystal lattice.

The complex **1** was synthesized by slow evaporation at room temperature (see Supporting information). The compositions of **1** were further deduced from X-ray single crystal diffraction, elemental analyses, and IR spectrum.

Crystal data and selected bond lengths and angles are listed in Tables S1 and S2, respectively. Compound **1** crystallizes in the monoclinic space group *P2*(1)/*c*. The asymmetric unit of **1** contains

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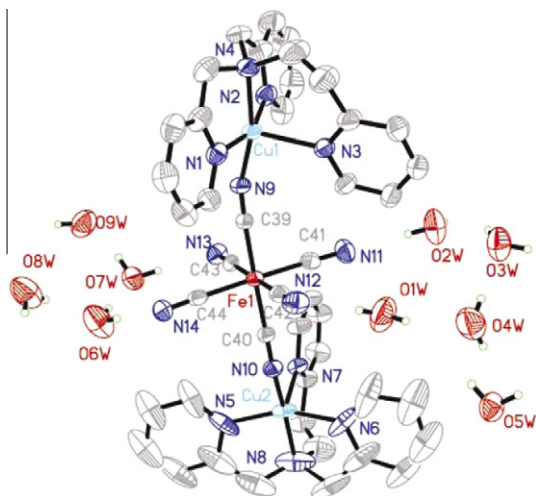


Fig. 1. ORTEP drawing (30% probability) of the crystal structure of **1** along with the atom numbering scheme. (H atoms on trinuclear center were omitted for clarity)

a complete trinuclear molecule, and nine lattice water molecules, shown in Fig. 1. The tripodal ligand pmea was selected to cap the Cu^{2+} ion because of its native coordination ability and large bulk [37], which could block the full coordination mode of hexacyanometallates and reserve cyano groups to interact with water molecules. An extension into a polymeric assembly was purposely prevented by the steric hindrance introduced by the tripodal ligand pmea. Both of the two Cu ions are coordinated by five nitrogen atoms, four from the tripodal ligand pmea and one from the bridging cyanide. The local coordination of two copper(II) ions is the same, resembling a distorted square pyramid geometry, where the basal plane is formed by one N atom from the bridging cyanide, the tri-connected aliphatic N atom and two pyridinato N atoms connected to aliphatic N atom by $-\text{CH}_2-$ group, and the axial position is occupied by the pyridinato N atom connected to aliphatic N atom by $-\text{CH}_2\text{CH}_2-$ group. As a result, for each tripodal ligand pmea in Cu1 and Cu2 moieties, two pyridinato rings connected to aliphatic N atom by $-\text{CH}_2-$ group are almost in one plane with deviated angle of $9.4(0.5)^\circ$ and $14.4(0.6)^\circ$, and the other pyridinato ring stand vertically on thus plane. The average Cu–N bond distances are $2.041(6)$ and $2.033(8)$ Å for Cu1 and Cu2, respectively, with much longer Cu1–N3 ($2.240(6)$ Å) and Cu2–N7 ($2.225(6)$ Å) bond length caused by the steric effect of six-membered ring compared to five-membered ring. The bond distances around the copper(II) atoms are very similar to those already reported [38]. Two asymmetric $[\text{Cu}(\text{pmea})]^{2+}$ moieties are capped to the central Fe atom via two *trans*-cyano bridges with the Cu–N–C angle of $158.7(6)^\circ$ and $158.2(6)^\circ$, and the dihedral angle of basal plane to basal plane of $78.8(0.2)^\circ$. The original iron(III) was reduced to iron(II) ion, and stabilized in the solid state [39,40]. The iron(II) ion in this species is

also octahedral, with Fe–C and C–N distances ranging from $1.880(7)$ to $1.928(8)$ Å and $1.149(9)$ to $1.166(9)$ Å, and the *cis*-C–Fe–C angles and the *trans*-C–Fe–C angles are close to 90° and 180° , respectively shown in Table S2. Due to the diamagnetic nature of the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ anions, the paramagnetism of the prepared trinuclear $[\text{Cu}_2\text{Fe}]$ unit is caused by the copper(II) atoms, shown in Figure S1.

The supramolecular network of **1** is shown in Fig. 2, indicating that π – π interactions play a pivotal role in assembling the discrete tri-nuclear entities towards higher dimensionality. All the tri-nuclear units are connected to adjacent ones by three types of π – π interactions with distances of $3.684(2)$, $3.744(2)$ and $3.935(3)$ Å between the Cu1 moiety in one unit and Cu2 moiety in other unit along *a* and *b* axis directions. As a result, the 3D supramolecular network with two kinds of regular 1D channels along the *b*-axis is generated by thus successive interactions. Each channel accommodates a one dimensional helical water chain, C1 for large dimensions channel and C2 for small one, as shown in Fig. 3. In C1 chain, three of lattice waters (O3W, O4W, and O5W) associated with themselves together by hydrogen bonds give rise to helical assembly, which is successively decorated by two lattice waters (O1W, O2W). While for C2 chain, helical assembly is formed by four of lattice waters (O6W, O7W, O8W, and O9W). Each water molecule in the chain forms two hydrogen bonds, one as a donor and the other as an acceptor, and all of the hydrogen bonding distances range from $2.707(10)$ to $2.851(15)$ Å ($\text{O}\cdots\text{O}$ distances), listed in Table 1. All of the 1D helical water chains are anchored onto the supramolecular host by versatile hydrogen bonding interactions of $\text{O}-\text{H}\cdots\text{N}(\text{cyanide})$ with the distances from $2.855(12)$ to $3.017(11)$ Å ($\text{O}\cdots\text{N}$ distances). And a two dimensional sheet constructed by the connection of alternating C2 water chains, discrete trinuclear units, and C1 water chains is presented in the *ab* plane, shown in Fig. 3. Each sheet is connected to adjacent ones by the versatile π – π and $\text{C}-\text{H}\cdots\pi$ interactions to form 3D supramolecular network. Here, both host–host, water–host and water–water interactions are important for the stability of the overall structure.

The solid FT-IR spectra of complex **1** shows a very intense broad band around 3400 cm^{-1} attributed to the water molecules (Figure S2) [39,40], and the split two peak at 2079 and 2046 cm^{-1} not only indicates the incomplete-coordinated cyano groups, but confirms the reduction of the iron core to Fe(II) [41,42]. We have also studied the thermal stability of the water cluster by thermogravimetric analysis (TGA), shown in Figure S3. TGA studies showed total water loses occur in two stages, and an 14.1% weight loss was observed between 25 and 113°C , which is almost equivalent to a loss of nine water molecules.

In summary, a self-assembled, two different helical 1D chains trapped within a heterometallic supramolecular host has been characterized by X-ray crystallography, TGA and IR spectra. We succeed in modulating not only the structural motifs of the metal–organic framework, but also the helical 1D water aggregates by employment of new host constructed from the hexacyanomet-

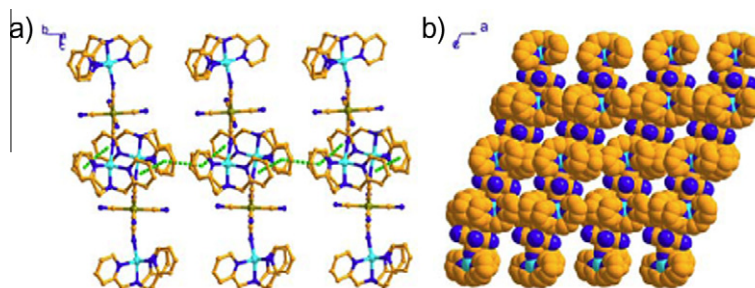


Fig. 2. (a) The perspective of the π – π and $\text{C}-\text{H}\cdots\pi$ interactions between the adjacent 2D layers, shown as dashed line and (b) the perspective of 3D crystal packing model along the crystallographic *b*-axis direction, lattice waters were omitted for clarity.

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