

# **Cu(II) coordination polymers with 4,4'-bipyridine. Synthesis and crystal structures**

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## Abstract

Extensively research has been devoted to the isolation and characterization of Cu(II) coordination poly- mers. Since many aspects can influence the final crystal structure, the effect of the solvent molecules through intermolecular interactions has been proven to be a determining factor. Herein, we elucidated the structure of two Cu(II) concomitant 1D polymers containing piperonylic acid (HPip) and 4,4'-bipyridine (4,4'-bipy), which were simultaneously crystallized and subsequently isolated changing the synthetic conditions. Complex  $\{[\text{Cu}(\text{Pip})_2(4,4' - \text{bipy})]\}_n$  (1) exhibits zig-zag polymeric chains while  $\{[\text{Cu}(\text{Pip})_2(4,4' - \text{bipy})(\text{H}_2\text{O})] \cdot \frac{1}{2}(4,4' - \text{bipy}) \cdot (\text{DMF})\}_n$  (2) displays linear polymeric chains stacked by water •••carboxylate intermolecular interactions, forming voids occupied by alternated guest 4,4' -bipy and DMF molecules.

### Keywords:

Cu(II) coordination polymers;1D chain

X-ray crystal structures

Piperonylic acid

4,4' -bipyridine

## 1. Introduction

The study of the structural arrangement and factors influencing the formation of coordination polymers is essential in materials design. An important consideration is that slight modifications of the forming conditions can lead to different arrangements which are reflected in their physical and chemical properties. To this purpose, crystal engineering aimed to be a fruitful strategy to design new structures controlling their topology through the formation of coordination bonds.

Exhaustive research has been devoted on the identification of the factor directing the preferential formation of one crystalline arrangement rather than another. Nonetheless, further studies have gathered that many factors inter alia the molar ratio [1], the structure of the ligand [2], the solvent [3], the coordination geometry of the metal atom [4] or the presence of anions [5] can have a determinant effect and are important to control the formation of the desired products. For instance, slight modifications of the forming conditions can promote the formation of cis- rather than trans-isomers. They usually possess distinct chemical and physical properties, which allows their isolation and characterization [6, 7]. In this sense, Cu(II) complexes consisting of carboxylate and N-aromatic linkers have a wide range of possibilities considering

the geometrical preferences of the Cu(II) metal node (from tetrahedral to octahedral) and the huge variety of coordination modes of the linkers, thus enabling the formation of numerous arrays [8]. Among Cu(II) compounds, their properties [9–11] can be strongly affected by the presence of water [12] since its high binding energy was associated to the water •••Cu(II) interaction [13]. The design of Cu(II) based networks is appropriate for adsorption/desorption of water, since they exhibited remarkable water uptake. Unfortunately, these materials tend to rapidly decompose after few sorption/desorption cycles [14]. Therefore, understanding of the directing effect of water molecules in the structural arrangement is to be required.

Our research group has previously reported the synthesis and characterization of numerous Cu(II) complexes containing aromatic carboxylate and N-donor aromatic ligands showing the versatility of Cu(II) as metal node, but mainly regarding discrete systems [15–18]. In them, we already noted that the presence of co-ordinated water molecules influenced the crystal packing through water •••carboxylate interaction [16]. We further extended the study of Cu(II) with the incorporation of 4,4'-bipyridine (4,4'-bipy), a ubiquitous ditopic ligand, combined with 1,3-benzodioxole-5-carboxylic acid (Piperonylic acid, HPip). Herein, we report the synthesis and characterization of two Cu(II) coordination polymers, which were initially found to be simultaneously crystallized. The elucidation of their crystal structure has enabled their identification as  $\{[\text{Cu}(\text{Pip})_2(4,4' - \text{bipy})]\}_n$  (1) and  $\{[\text{Cu}(\text{Pip})_2(4,4' - \text{bipy})(\text{H}_2\text{O})] \cdot \frac{1}{2}(4,4' - \text{bipy}) \cdot (\text{DMF})\}_n$  (2) coordination polymers having a 1D array. Besides, both products were successfully isolated by modification of the synthetic conditions (molar ratio and reaction solvent).

## 2. EXPERIMENTAL SECTION

### 2.1. Materials and methods

Cu(II) acetate monohydrate ( $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ ), 1,3-benzodioxole-5-carboxylic acid (Piperonylic acid, HPip), 4,4'-bipyridine (4,4'-bipy), methanol (MeOH), acetonitrile (ACN) and dimethylformamide (DMF) solvents were purchased from Sigma-Aldrich. All of them and Milli-Q water were used without further purification. Compound  $[\text{Cu}(\text{Pip})_2(\text{DMF})]_2 \cdot 2(\text{DMF})$  was previously reported in our group [16]. Elemental analyses (C, H, N) were carried out on a Thermo Scientific Flash 2000 CHNS Analyzer. Simultaneous TG/DTA determinations of compounds 1 and 2 were carried out in a Netzsch STA 409 instrument, with an aluminum oxide powder ( $\text{Al}_2\text{O}_3$ ) crucible and heating at  $5^\circ\text{C} \cdot \text{min}^{-1}$  from 20 to  $350^\circ\text{C}$ , under nitrogen atmosphere with a flow rate of  $80 \text{ mL} \cdot \text{min}^{-1}$ .  $\text{Al}_2\text{O}_3$  (PerkinElmer 0419-0197) was used as a standard. FTIR-ATR spectra were recorded on a Perkin Elmer spectrometer, equipped with a universal attenuated total reflectance (ATR) accessory with diamond window in the range  $4000\text{--}500 \text{ cm}^{-1}$ . The electronic spectra in DMF solution at a concentration of  $\sim 1 \cdot 10^{-4} \text{ M}$  were run on a Agilent HP 8453 UV-Vis spectrophotometer with a quartz cell having path length of 1 cm in the range of 200–1100 nm. The data obtained were corrected for dilution effects by means of Origin Pro 8.6 software.

### 2.2. Crystallization of $[\{\text{Cu}(\text{Pip})_2(4,4'\text{-bipy})\}]_n$ (1) and $[\{\text{Cu}(\text{Pip})_2(4,4'\text{-bipy})(\text{H}_2\text{O})\}] \cdot \frac{1}{2}(4,4'\text{-bipy}) \cdot (\text{DMF})_n$ (2)

Single crystals of 1 and 2 were simultaneously found layering an ACN solution (2.5 mL) of 4,4'-bipy (1.20 mg,  $7.68 \cdot 10^{-3} \text{ mmol}$ ) over a DMF (1.5 mL) solution of  $[\text{Cu}(\text{Pip})_2(\text{DMF})]_2 \cdot 2(\text{DMF})$  (7.55 mg,  $7.07 \cdot 10^{-3} \text{ mmol}$ ) for 10 days. After the elucidation of their X-ray crystal structures, we successfully isolated both products by changing the reaction conditions (different molar ratio and solvent).

### 2.3. Synthesis of $[\{\text{Cu}(\text{Pip})_2(4,4'\text{-bipy})\}]_n$ (1)

A dispersion of  $[\text{Cu}(\text{Pip})_2(\text{DMF})]_2 \cdot 2(\text{DMF})$  (100 mg, 0.0930 mmol) in 24 mL of anhydrous DMF was added to a solution of 4,4'-bipy (28.9 mg, 0.185 mmol) in 6 mL of DMF under stirring. The mixture was heated at reflux conditions and stirred for 5 h until color change from dark turquoise to dark green and the powder precipitated. The dark green solid was filtered, washed twice with 5 mL of cold MeOH and dried under vacuum.

Yield: 77.8 mg (76%). Elem. Anal. Calc. for  $\text{C}_{26}\text{H}_{18}\text{CuN}_2\text{O}_8$  (549.97 g/mol): C 56.78; H 3.30; N 5.09. Found: C 56.64; H 3.18; N 4.92. FTIR-ATR (wavenumber,  $\text{cm}^{-1}$ ): 3072(w) [ $\nu_{\text{ar}}$  (C–H)], 2904(w) [ $\nu_{\text{al}}$  (C–H)], 1635(m), 1594(s) [ $\nu_{\text{as}}$  (COO)], 1545(m) [ $\nu$  (C=C/C=N)], 1505(m), 1493(m), 1440(s) [ $\delta$  (C=C/C=N)], 1382(s) [ $\nu_{\text{s}}$  (COO)], 1253(s), 1215(m), 1167(m), 1113(m), 1077(m), 1032(s) [ $\delta_{\text{ip}}$  (C–H)], 934(m), 918(m), 882(m), 804(m), 768(s) [ $\delta_{\text{oop}}$  (C–H)], 719(m), 682(m), 633(m). UV-Vis: (DMF,  $1.4 \cdot 10^{-4} \text{ M}$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 689 nm ( $217 \text{ M}^{-1} \cdot \text{cm}^{-1}$ ).

### 2.4. Synthesis of $[\{\text{Cu}(\text{Pip})_2(4,4'\text{-bipy})(\text{H}_2\text{O})\}] \cdot \frac{1}{2}(4,4'\text{-bipy}) \cdot (\text{DMF})_n$ (2)

A dispersion of  $[\text{Cu}(\text{Pip})_2(\text{DMF})]_2 \cdot 2(\text{DMF})$  (100 mg, 0.0930 mmol) in 22 mL of DMF was added to a solution of 4,4'-bipy (43.9 mg, 0.281 mmol) in 4.5 mL of Milli-Q  $\text{H}_2\text{O}:\text{DMF}$  (1:8) solvent mixture under stirring. The mixture was heated at reflux conditions and stirred for 4 h until color changed from dark turquoise to light green and the powder precipitated. The light green solid was filtered, washed twice with 5 mL of cold MeOH and dried under vacuum. Yield: 66.3 mg (49%). Elem. Anal. Calc. for  $\text{C}_{35}\text{H}_{31}\text{CuN}_3\text{O}_{10}$  (717.17 g/mol): C 58.61; H 4.36; N 5.86. Found: C 58.35; H 4.24; N 5.72. FTIR-ATR (wavenumber,  $\text{cm}^{-1}$ ): 3356(br) [ $\nu$  (O–H)], 3077(w) [ $\nu_{\text{ar}}$  (C–H)],

2971(w) [ $\nu_{\text{al}}(\text{C-H})$ ], 2906(w) [ $\nu_{\text{al}}(\text{C-H})$ ], 1676(m) [ $\nu(\text{C=O})$ ] DMF, 1635(m), 1594(s) [ $\nu_{\text{as}}(\text{COO})$ ], 1554(m) [ $\nu(\text{C=C/C=N})$ ], 1505(m), 1489(m), 1436(s) [ $\delta(\text{C=C/C=N})$ ], 1391(s) [ $\nu_{\text{s}}(\text{COO})$ ], 1256(s), 1237(m), 1220(m), 1175(m), 1116(m), 1081(m), 1037(m) [ $\delta_{\text{ip}}(\text{C-H})$ ], 940(w), 918(m), 881(w), 839(w), 803(m), 774(s) [ $\delta_{\text{oop}}(\text{C-H})$ ], 727(w), 684(m), 628(w), 586(m). UV-Vis: (DMF,  $1.3 \cdot 10^{-4}$  M)  $\lambda_{\text{max}}(\epsilon) = 717 \text{ nm} (43 \text{ M}^{-1} \cdot \text{cm}^{-1})$ .

### 2.5. X-ray crystallographic data

Light-blue prism-like specimens (1 and 2) were used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped with a multilayer monochromator and a Mo microfocus. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. For 1, the integration of the data yielded 3654 independent reflections ( $R_{\text{sig}} = 4.23\%$ ) and 2890 (79.09%) were greater than  $2\sigma(|F|^2)$ . For 2, the integration of the data yielded 9648 independent reflections ( $R_{\text{sig}} = 9.12\%$ ) and 6079 (63.01%) were greater than  $2\sigma(|F|^2)$ .

The structures were solved and refined using the Bruker SHELXTL Software Package (version-2018/3) [19]. In compound 2, 3 DFIX constraints were used for O9 hydrogen atoms (H9OA and H9OB) which were located by different synthesis and refined with an isotropic temperature factor equal to 1.2, the equivalent temperature factor of the atom to which are linked. For 1 and 2, the final cell constants and volume, are based upon the refinement of the XYZ-centroids of reflections above  $20\sigma(I)$ . Data were corrected for absorption effects using the multi-scan method (SADABS). Crystal data and relevant details of structure refinement for compounds 1 and 2, are reported in Table 1.

Complete information about the crystal structure and molecular geometry is available in .cif format deposited in the CCDC. CCDC numbers 2,020,034 (1) and 2,020,035 (2) contain the supplementary data of this paper. Molecular graphics were generated using Mercury (version 4.3.1) [20, 21] with POV-Ray Package (version 3.7) [22]. Color codes for molecular graphics: blue (N), gray (C), white (H), orange (Cu) and red (O).

### 3. RESULTS AND DISCUSSION

#### 3.1. Synthesis and general characterization

Single crystals of 1 and 2 were simultaneously found layering an ACN solution of 4,4'-bipy over a DMF solution of  $[\text{Cu}(\text{Pip})_2(\text{DMF})]_2 \cdot 2(\text{DMF})$  for 10 days. After the elucidation of their X-ray crystal structures, we successfully isolated both products by changing the reaction conditions (different molar ratio and sol-vent). Compound 1 was synthesized using a 1:1 (Cu(II):4,4'-bipy) molar ratio in DMF as solvent under reflux conditions for 5 h. Conversely, compound 2 was achieved with a 1:2 molar ratio, using a Milli-Q  $\text{H}_2\text{O}:\text{DMF}$  (1:8) solvent mixture at reflux for 4 h (Scheme 1). Despite being scarce, there are reported case studies in which two similar Cu(II) coordination polymers composed of 4,4'-bipy linker were separately synthesized [23]. Likewise, there are limited examples where two geometrical isomers were found simultaneously crystallized [24, 25]. Remarkably, in these cases there was not a synthetic route to separately synthesize them.

Compounds 1 and 2 were characterized by elemental analysis (EA), TG/DTA determination, FTIR-ATR and UV-Vis spectroscopies and their structures were elucidated by single crystal X-ray diffraction method. EA of all the compounds is in accordance with the proposed formula. The TG/DTA determinations of 1 and 2 were carried out to establish the thermal stability of the samples (Supporting Information: Supplementary Figures S1 and S2). The measurements were performed using 67.7 mg of 1 or 55.1 mg of 2. Complex 1 is stable up to 285 °C, followed by decomposition. Complex 2 loses the coordinated water molecule between 50 °C and 112 °C (weight loss exp. 2.3%, calc. 2.5%), followed-up by thermal degradation between 112 and 231 °C until decomposition at 265 °C. FTIR-ATR spectra of compounds 1 and 2 display the characteristic bands of the Pip and 4,4'-bipy ligands. The  $\nu_{\text{as}}(\text{CO}_2)$  and  $\nu_{\text{s}}(\text{CO}_2)$  carboxylate bands appear at 1594 (1 and 2) and at 1382 (1) or 1391  $\text{cm}^{-1}$  (2) (S.I: Supplementary Figures S3–S4). In addition, their values ( $\nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2)$ ) of 206 (1) and 203  $\text{cm}^{-1}$  (2) indicate a monodentate coordination mode of the Pip linker [26]. Besides, 2 also presents bands attributable to  $\nu(\text{O}-\text{H})$  of the coordinated water molecule at 3356  $\text{cm}^{-1}$  and to  $\nu(\text{C}=\text{O})$  of the DMF at 1676  $\text{cm}^{-1}$ . Additional bands attributable to the aromatic groups  $\nu(\text{C}=\text{C})/\nu(\text{C}=\text{N})$ ,  $\delta(\text{C}=\text{C})/(\text{C}=\text{N})$ ,  $\delta(\text{C}-\text{H})_{\text{ip}}$  and  $\delta(\text{C}-\text{H})_{\text{oop}}$  are also identified [27].

UV-Vis spectra of both products show absorption bands of intra-ligand  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions from C = N and C = O groups between 250 nm and 350 nm. Located at higher wavelengths the d-d transitions [28] of the Cu(II) centers (689 nm, 1 and 717 nm, 2) are identified (S.I: Supplementary Figure S5). These d-d electronic transitions are associated to  ${}^2E_g(\text{D}) \rightarrow {}^2T_{2g}(\text{D})$  for 1 and  ${}^2e_{2g}(\text{D}) \rightarrow {}^2b_{1g}(\text{D})$  for 2. This bathochromic shift in absorption of 2 is related with the different coordination environment of the Cu(II) metal center respect to the tetrahedral 1. The additionally coordinated water molecule in 2 gives a square-pyramidal geometry which the consequent shift [29] and the bigger  $\epsilon$  value (217  $\text{M}^{-1} \cdot \text{cm}^{-1}$  for 1 and 43  $\text{M}^{-1} \cdot \text{cm}^{-1}$  for 2).

#### 3.2. Crystal and extended structure of $\{[\text{Cu}(\text{Pip})_2(4,4'\text{-bipy})]\}_n$ (1)

Compound 1 crystallizes in the monoclinic crystal system having a C2/c space group. The central Cu(II) atom is tetraordinated with a  $[\text{CuO}_2\text{N}_2]$  core composed of two monodentate Pip ligands and two 4,4'-bipy linkers in cis disposition, defining a slightly distorted tetrahedral geometry ( $\tau_4(\text{Cu}(1)) = 0.90$ ) [30]. The Cu-O and Cu-N bond lengths (Table 2) are within the range of similar reported Cu(II) coordination polymers containing 4,4'-bipy and aromatic carboxylate linkers (1.957–2.565(4) Å) [31–35].

The uncoordinated carboxylate oxygen atoms are associated with the ortho-H from the 4,4'-bipy linkers through an intramolecular interaction (C(13)-H(13)  $\cdots$  O(2)) (Table 2, Fig. 1 a). It has a 1D zigzag polymeric structure in which  $[\text{Cu}(\text{Pip})_2(4,4'\text{-bipy})]$  units are linked through  $\mu$ -4,4'-bipy- $\kappa^2\text{N}:\text{N}'$ -ligands in the ac direction (Fig. 1 b).

These linear chains are assembled through double reciprocal one-sided C–H...O interactions between the 4,4'-bipy and the Pip units. One occurs between the meta -H of each pyridyl ring and two oxygen atoms from neighboring dioxole groups, which forms layers along the  $(4\ 0\ \bar{3})$  plane (Fig. 2 a). Likewise, the other forms layers through the  $(2\ 1\ 2)$  plane by association of the ortho -H with the uncoordinated carboxylate oxygen atoms (Fig. 2 b). Both interactions hold together the zigzag polymeric chains forming a 3D net.

### 3.3. Crystal and extended structure of $\{[Cu(Pip)_2(4,4'-bipy)(H_2O)] \cdot \frac{1}{2}(4,4'-bipy) \cdot (DMF)\}_n (2)$

Compound 2 crystallize in the triclinic crystal system having a P-1 space group. The central Cu(II) atom is pentacoordinated with a  $[CuO_3 N_2]$  core composed of two monodentate Pip ligands, two 4,4'-bipy linkers in trans disposition and a H<sub>2</sub>O molecule, defining a slightly distorted square pyramidal geometry ( $\tau_5(Cu(1)) = 0.06$ ) [36] (Table 3). The Pip and 4,4'-bipy ligands are located at the basal plane, being the Cu(II) ion 0.131 Å out of this plane towards the apical position, which is occupied by a H<sub>2</sub>O molecule ( Fig. 3 a).

The Cu–O and Cu–N bond lengths ( Table 3 ) are within the range of similar reported Cu(II) coordination polymers containing 4,4'-bipy and aromatic carboxylate linkers (1.957 – 2.565(4) Å) [23, 31, 32, 34, 37]. Likewise, the Cu–O<sub>H<sub>2</sub>O</sub> bond length is slightly longer (2.149(3) Å) due to Jahn-Teller effects [38], but in range with other apical H<sub>2</sub>O molecules (2.158 Å) [24]. The  $\mu$ -4,4'-bipy- $\kappa^2$  N:N'-ligands link the  $[Cu(Pip)_2(4,4'-bipy)(H_2O)]$  units forming a linear 1D chain through the  $[\frac{1}{2}\ 0\ \frac{1}{2}]$  direction ( Fig. 3 b).

The polymeric chains are stacked along the a axis by double O–H...O interactions between the coordinated water molecules and the uncoordinated carboxylate oxygen atoms (Fig. 4 a). The Pip aromatic rings associate the parallel polymeric chains through  $\pi$ ... $\pi$ stacking interactions, thus forming a square grid void in which guest 4,4'-bipy and DMF molecules are alternately located (Fig. 4 b). These occluded molecules are associated with the polymeric chains through reciprocal weak double meta -C-H...N and single meta -C-H...O interactions. One  $\mu$ -4,4'-bipy- $\kappa^2$  N:N'-ligand interacts via C–H...N (C(18)–H(18)...N(3), 2.548 Å and C(20)–H(20)...N(3), 2.388 Å) at both sides of the pyridyl rings with two occluded 4,4'bipy molecules along the  $[3\ 1\ 0]$  direction.

Likewise, the contiguous  $\mu$ -4,4'-bipy- $\kappa^2$  N:N'-ligand interacts via C–H...O (C(23)–H(23)...O(11), 2.384 Å) with two occluded DMF molecules through b axis (Table 3) while one hydrogen atom from the dioxole group associates with one of the two coordinated carboxylate oxygen atoms (Fig. 4 b). All these set of interactions form a 3D net being the occluded 4,4'-bipy and DMF molecules disposed within the channels (solvent accessible surface of 177.77 Å<sup>3</sup>, 11.2% of unit cell volume) along the a axis (Fig. 5).

### 3.4. Structural overview

M(II) cores with square pyramidal [24 , 39] or octahedral [40–49] geometries or even higher [50] coordination numbers and having coordinated water molecules, tend to form linear polymeric chains arranged from 4,4'-bipy linkers, being trans the most common disposition. Only reduced number of Co(II) [51] , Ni(II) [52, 53] or Zn(II) [54, 55] complexes with octahedral geometry and coordinated water molecules display the cis disposition. Conversely, tetrahedral geometries without coordinated solvent molecules unavoidably form zigzag polymeric chains [56–59]

A search on the CSD database [60] has revealed a total of 44 structures containing Cu(II) ions with coordinated 4,4'-bipy and carboxylate ligands, being predominant the octahedral geometry [ 24 , 39 ] ( Table 4 ).

Focusing on the structures with coordinated water molecules, only six have a Sq geometry. In all the cases, the 4,4'-bipy linkers are in trans with the consequent formation of linear polymeric chains and the water molecules are located at the apical site, with a lengthen Cu-O bond by Jahn-Teller effect [38] ( Table 5 ). Within this frame, intermolecular interactions promoted by either intrinsic functional groups or additional molecules present in the reaction media, are identified as responsible of the final arrangement [61]. If intermolecular interactions set the chains in parallel, the formation of voids allow the incorporation of occluded solvent molecules. In this regard, use an excess of 4,4'-bipy in the synthetic procedure (molar ratios of 1:2 (Cu:4,4'-bipy) or higher) or the presence of guest solvent molecules gives support to the formation of voids [57].

Overall, the tendency of water molecules to being located at the apical site, allows the formation of strong O-H...O interactions with the uncoordinated carboxylate oxygen atoms stacking the polymeric chains in parallel, thus providing an additional stabilization through hydrogen bond interactions [6, 24, 39].



## 4. CONCLUSIONS

Two Cu(II) coordination polymers (1 and 2) were found simultaneously crystallized and their crystal structures elucidated. The modification of the synthetic conditions (molar ratio and solvent) allowed the isolation of both products. The structural analysis revealed that despite both being 1D coordination polymers, the coordination of a water molecule to the Cu(II) metal center supported the arrangement of linear chains in 2 through strong O–H...O interactions, while the absence of coordinated water molecules drove the tetrahedral geometry of the Cu(II) center and the consequent formation of zigzag chains in 1. In addition, the stacking of the linear chains by water...carboxylate interactions in 2, allowed the formation of square-shape voids, which were alternately occupied by 4,4'-bipy and DMF guest molecules. Unfortunately, TG/DTA de-termination of 2 evinced that coordinated water molecule is removed before the release of guest molecules driving the collapse of the framework. Therefore, solid-state sorption/desorption of water is not observed between 1 and 2.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### CRediT authorship contribution statement

Francisco Sánchez-Férez: Writing –original draft, Visualization, Investigation. Teresa Calvet: Resources, Funding acquisition, Validation. Mercè Font-Bardia: Data curtion, Validation. Josefina Pons: Conceptualization, Validation, Resources, Writing –review & editing, Project administration, Funding acquisition, Supervision.

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**Table 1.** Crystal structure refinement data of compounds 1 and 2 .

	1	2
Empirical formula	C <sub>26</sub> H <sub>18</sub> CuN <sub>4</sub> O <sub>8</sub>	C <sub>35</sub> H <sub>31</sub> CuN <sub>3</sub> O <sub>10</sub>
Formula weigh	549.96	717.17
<i>T</i> (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
System, space group	Monoclinic, C2/c	Triclinic, P-1
Unit cell dimensions		
<i>a</i> (Å)	19.096(2)	6.0725(7)
<i>b</i> (Å)	10.2528(10)	12.0339(15)
<i>c</i> (Å)	13.159(3)	22.334(3)
$\alpha$ (°)	90	93.026(4)
$\beta$ (°)	121.721(3)	97.0740(4)
$\gamma$ (°)	90	100.800(4)
<i>V</i> (Å <sup>3</sup> )	2191.4(5)	1583.5(3)
<i>Z</i>	4	2
<i>D</i> <sub>calc</sub> (g cm <sup>3</sup> )	1.667	1.504
$\mu$ (mm <sup>-1</sup> )	1.057	0.756
<i>F</i> (000)	1124	742
Crystal size (mm <sup>3</sup> )	0.213×0.081×0.045	0.204×0.096×0.049
<i>hkl</i> ranges	-25 ≤ <i>h</i> ≤ 28 -15 ≤ <i>k</i> ≤ 14 -19 ≤ <i>l</i> ≤ 19	-8 ≤ <i>h</i> ≤ 8 -17 ≤ <i>k</i> ≤ 17 -31 ≤ <i>l</i> ≤ 31
$\theta$ range (°)	2.349 to 31.511	2.024 to 30.524
Reflections collected/ unique/[ <i>R</i> <sub>int</sub> ]	18,195/3654 [ <i>R</i> <sub>int</sub> ] = 0.0497	49,329/9648 [ <i>R</i> <sub>int</sub> ] = 0.1000
Completeness to $\theta$ (%)	99.9	99.9
Absorption Correction	Semi-empirical	Semi-empirical
Max. and min. transmiss.	0.7462 and 0.6464	0.7461 and 0.6388
Refinement method	Full matrix least-squares on   <i>F</i>   <sup>2</sup> 3654/0/168	Full matrix least-squares on   <i>F</i>   <sup>2</sup> 9648/3/451
Data/restrains/parameters		
Goodness of fit (GOF) on   <i>F</i>   <sup>2</sup>	1.096	1.120
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0523, <i>wR</i> <sub>2</sub> = 0.1270	<i>R</i> <sub>1</sub> = 0.0681, <i>wR</i> <sub>2</sub> = 0.1224
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0756 <i>wR</i> <sub>2</sub> = 0.1471	<i>R</i> <sub>1</sub> = 0.1404, <i>wR</i> <sub>2</sub> = 0.1532
Extinction coefficient	n/a	n/a
Largest. Diff. peak and hole (e Å <sup>-3</sup> )	1.480 and -0.626	0.751 and -1.163



**Table 2.** Selected bond lengths, angles, intra- and intermolecular interactions of 1 .

Bond lengths (Å)				
Cu(1)-O(1)	1.924(2)	Cu(1)-N(1)	2.045(2)	
Bond angles (°)				
O(1)-Cu(1)-O(1)#1	108.20(15)	O(1)-Cu(1)-N(1)#1	124.70(10)	
O(1)-Cu(1)-N(1)	102.04(10)	N(1)-Cu(1)-N(1)#1	96.90(13)	
Intramolecular interactions				
	H•••A (Å)	D•••A (Å)	D-H (Å)	>D-H•••A (°)
C(13)-H(13)•••O(2)	2.236	3.085(5)	0.950	148.31
Intermolecular interactions				
	H•••A (Å)	D•••A (Å)	D-H (Å)	>D-H•••A (°)
C(9)-H(9)•••O(2)	2.494	3.328(4)	0.950	146.58
C(12)-H(12)•••O(3)	2.278	3.209(3)	0.950	166.48

#1  $-x + 1, y, -z + 1/2$ .

**Table 3.** Selected bond lengths, angles and intermolecular interactions of 2 .

Bond lengths (Å)				
Cu(1)-O(1)	1.965(3)	Cu(1)-N(2)	2.083(3)	
Cu(1)-O(5)	2.030(3)	Cu(1)-O(9)	2.149(3)	
Cu(1)-N(1)	2.080(3)			
Bond angles (°)				
O(1)-Cu(1)-O(5)	174.11(13)	N(1)-Cu(1)-N(2)	170.57(13)	
O(1)-Cu(1)-N(1)	89.47(11)	O(1)-Cu(1)-O(9)	90.39(11)	
O(5)-Cu(1)-N(1)	88.13(11)	O(5)-Cu(1)-O(9)	95.19(12)	
O(1)-Cu(1)-N(2)	87.78(12)	N(1)-Cu(1)-O(9)	95.42(12)	
O(5)-Cu(1)-N(2)	93.75(12)	N(2)-Cu(1)-O(9)	93.61(12)	
Intermolecular interactions				
	H•••A (Å)	D•••A (Å)	D-H (Å)	>D-H•••A (°)
O(9)-H(H9OA)•••O(2)	1.91(3)	2.699(4)	0.81(3)	166.11
O(9)-H(H9OB)•••O(6)	1.88(3)	2.675(4)	0.81(3)	165.37
C(18)-H(18)•••N(3)	2.548	3.477(5)	0.950	165.89
C(20)-H(20)•••N(3)	2.388	3.298(5)	0.950	160.17
C(23)-H(23)•••O(11)	2.384	3.326(6)	0.950	170.97
C(6)-H(6A)•••O(11)	2.389	3.156(5)	0.990	133.78
C(13)-H(13A)•••O(1)	2.501	3.387(5)	0.990	148.84
Cg(1)•••Cg(2)	3.636			

[Cg(1) = C10-C11-C12- C14-C15-C16; Cg(2) = C2-C3-C4-C5-C7-C8].

**Table 4.** Results from the CSD [60] search structures containing Cu(II) with coordinated 4,4'-bipy and carboxylic acids as ligands.

Cu(II) geometry	With coordinated H <sub>2</sub> O	Without coordinated H <sub>2</sub> O	Total
Oh	7	14	21
Sq	6	5	11
Bp	1	7	8
Td	0	4	4

Oh = octahedral; Sq = square-pyramidal; Bp = trigonal bipyramidal; Td = tetrahedral.

**Table 5.** Crystallographic parameters of structures containing Cu(II) with square-pyramidal geometry, coordinated 4,4'-bipy and carboxylate ligands.

Compound	Cu-O	Cu-N	Cu-OH <sub>2</sub>	O-Cu-O	N-Cu-N	H <sub>2</sub> O-Cu-O	H <sub>2</sub> O-Cu-N	τ [62]	Torsion angle	Ref.
{[Cu(Pip) <sub>2</sub> (4,4'-bipy)(H <sub>2</sub> O)]• <sup>1</sup> / <sub>2</sub> (4,4'-bipy)•(DMF) <sub>n</sub> (2)}	1.965(3)	2.080(3)	2.149(3)	174.11(13) <sup>o</sup>	170.57(13) <sup>o</sup>	90.39(11) <sup>o</sup>	93.61(12) <sup>o</sup>	0.060	0.00 <sup>o</sup>	this work [24]
	2.030(3)	2.083(3)				95.19(12) <sup>o</sup>	95.42(12) <sup>o</sup>		0.00 <sup>o</sup>	
[Cu(H <sub>2</sub> O)(bz) <sub>2</sub> (4,4'-bipy) <sub>2</sub> ]•(Hbz) <sub>2</sub> •(4,4'-bipy)	1.928	1.974	2.158	174.29 <sup>o</sup>	168.43 <sup>o</sup>	92.86 <sup>o</sup>	95.78 <sup>o</sup>	0.098	16.37 <sup>o</sup>	[24]
	1.952(1)	2.013(1)	2.216(2)	170.32(6) <sup>o</sup>	163.81(7) <sup>o</sup>	97.18(7) <sup>o</sup>	103.25(7) <sup>o</sup>	0.109	32.28 <sup>o</sup>	
[Cu <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (bz) <sub>4</sub> (4,4'-bipy) <sub>3</sub> ]•(H <sub>2</sub> O) <sub>9</sub>	1.970(1)	2.026(2)				92.39(7) <sup>o</sup>	92.89(7) <sup>o</sup>		0.00 <sup>o</sup>	[39]
	1.939(2)	1.999(3)	2.318(2)	173.3(1) <sup>o</sup>	172.7(1) <sup>o</sup>	98.62(9) <sup>o</sup>	96.3(1)	0.010	11.98 <sup>o</sup>	
[Cu <sub>3</sub> (H <sub>2</sub> O) <sub>4</sub> (bz) <sub>6</sub> (4,4'-bipy) <sub>4,5</sub> ]•(4,4'-bipy)•(H <sub>2</sub> O) <sub>5</sub>	1.941(2)	1.994(3)				87.4(1) <sup>o</sup>	93.4(7)		0.00 <sup>o</sup>	[25]
	1.958	2.054	2.180	176.35 <sup>o</sup>	172.36 <sup>o</sup>	91.83	93.82 <sup>o</sup>	0.067	9.38 <sup>o</sup>	
[Cu(cbop) <sub>2</sub> (4,4'-bipy)(H <sub>2</sub> O)] <sub>n</sub>	1.948(4)	2.029(5)	2.56(2)	173.7(2)	179.7(2) <sup>o</sup>	85.5(4) <sup>o</sup>	92.0(4) <sup>o</sup>	0.100	28.01 <sup>o</sup>	[39]
	1.931(5)	2.013(5)				100.5(4) <sup>o</sup>	87.9(4) <sup>o</sup>		-	
{[Cu <sub>2</sub> (bipy) <sub>2</sub> (L <sub>2</sub> )(H <sub>2</sub> O) <sub>2</sub> ]•(bipy)•(5H <sub>2</sub> O)} <sub>n</sub>	1.943(4)	2.027(4)	2.250(4)	176.5(2) <sup>o</sup>	176.1(2) <sup>o</sup>	93.8(2) <sup>o</sup>	88.6(2) <sup>o</sup>	0.007	22.30 <sup>o</sup>	[63]
	1.939(4)	2.038(4)				88.2(2)	90.5(2) <sup>o</sup>		20.59 <sup>o</sup>	

HBz = benzoic acid; cbop = (S)-N-(4-cyanoben-zoic)-5-oxoproline; 5-HIPA = 5-hydroxyisophthalato; L<sub>2</sub> = 5,5-(1,4-phenylenebis-(methylene))bis(oxy)diisophthalic acid.

## Figure Captions

**Scheme 1.** Outline of the crystallization and synthesis of 1 and 2.

**Fig. 1.** a) Molecular structure of the  $[\text{Cu}(\text{Pip})_2(4,4'\text{-bipy})]$  unit and (b) 1D chains through the  $ac$  direction, hydrogen atoms are omitted for clarification

**Figure 1.** View of the layers formed between a) 4,4'-bipy ( meta -H) and Pip (O-dioxole) or b) between 4,4'-bipy ( ortho -H) and Pip (O-carboxylate). In detail, reciprocal intermolecular C–H $\cdots$ O interactions.

**Figure 3.** a) Molecular structure of the  $[\text{Cu}(\text{Pip})_2(4,4'\text{-bipy})(\text{H}_2\text{O})]$  unit and (b) 1D chains through the  $[\frac{1}{2} 0 \frac{1}{2}]$  direction, hydrogen atoms are omitted for clarification.

**Figure 4.** a) Intermolecular  $\text{H}_2\text{O}\cdots\text{O}$  Pip interactions through  $a$  axis. b) Intermolecular interactions between occluded 4,4'-bipy and DMF molecules and the polymeric chains.

**Fig. 5.** View of the 3D net of compound 2 along the  $a$  axis highlighting the 4,4'- bipy and DMF occluded molecules by (a) space fill or (b) the resulting voids through solvent accessible volume representations.

**Scheme 1.**

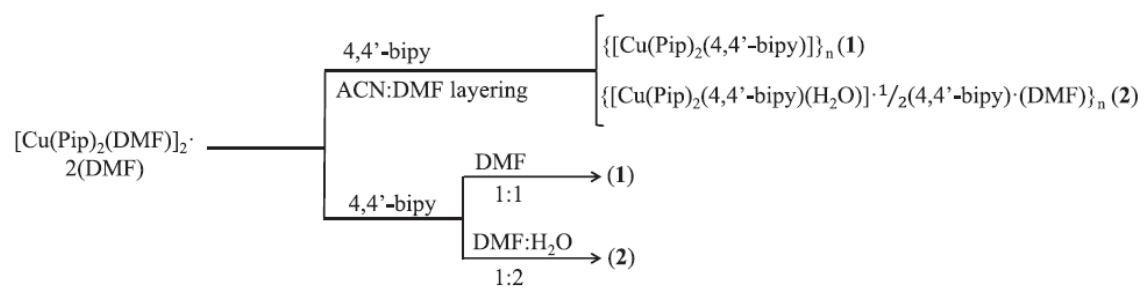


Figure 1.

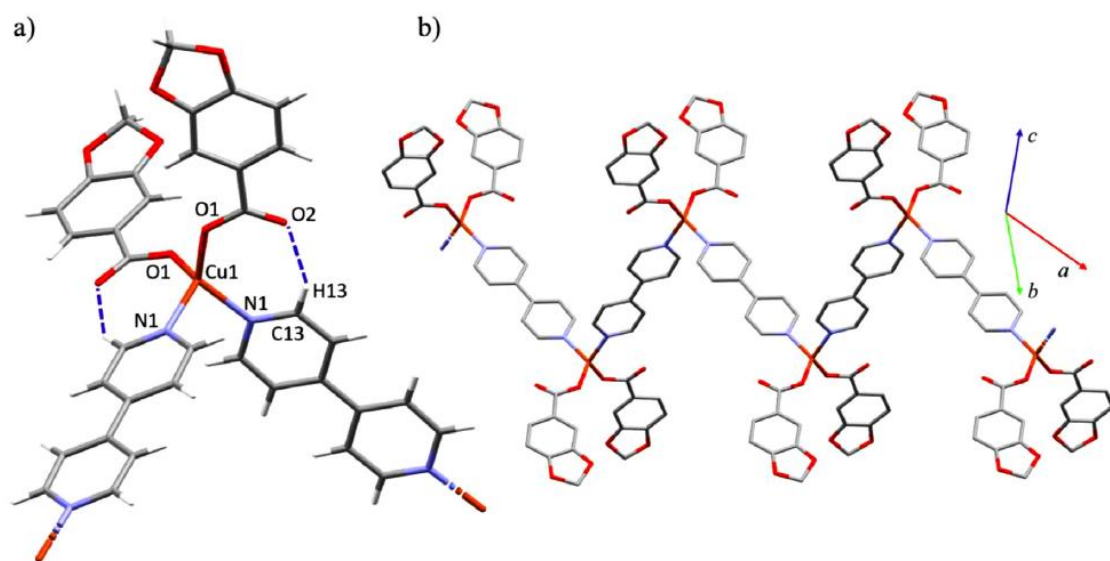


Figure 2.

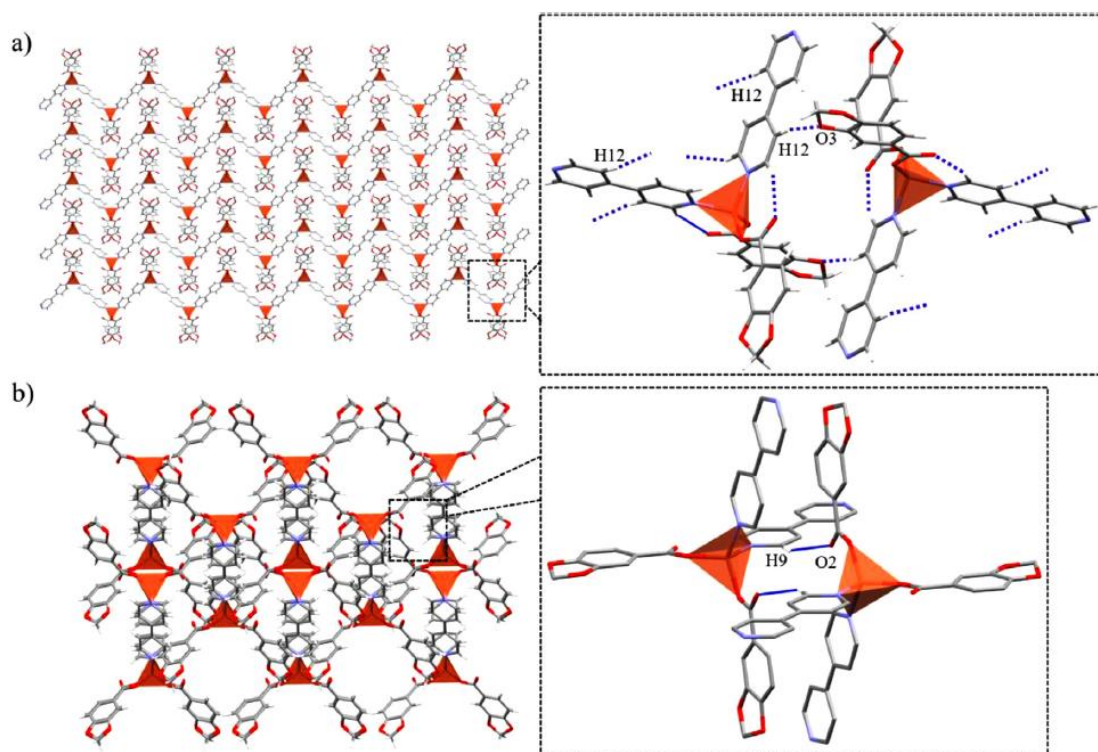




Figure 3

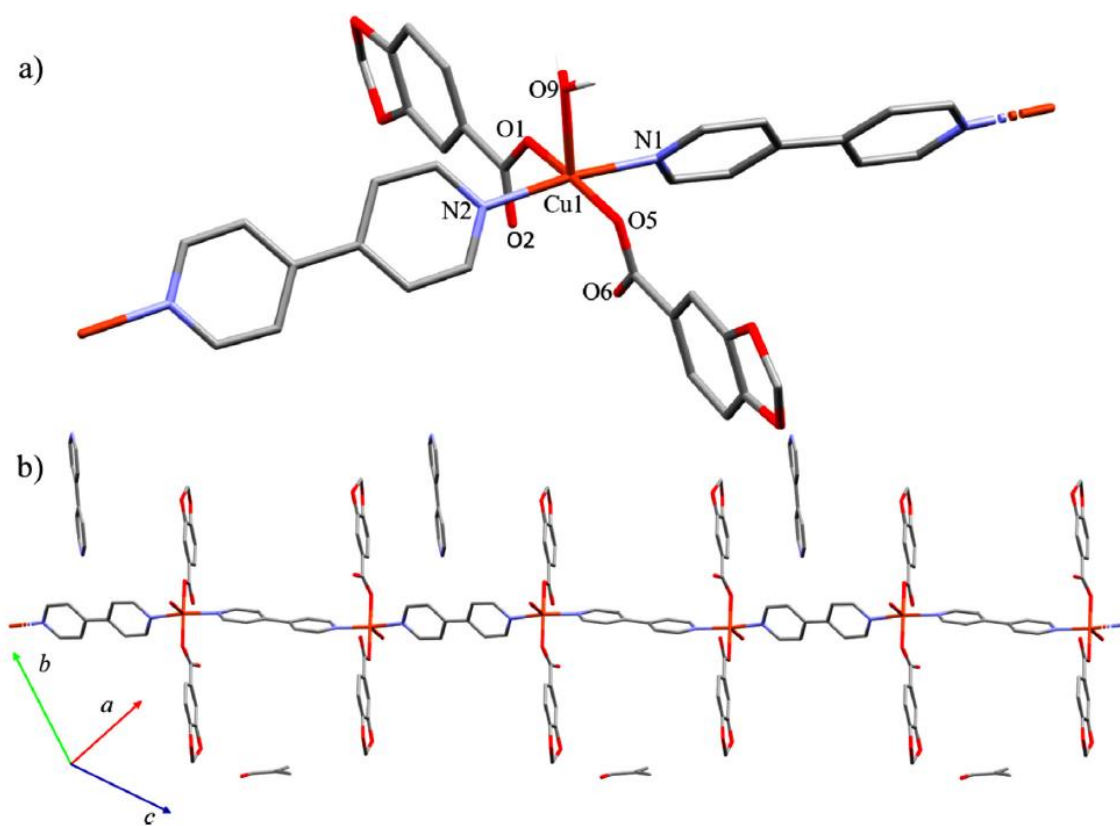


Figure 4

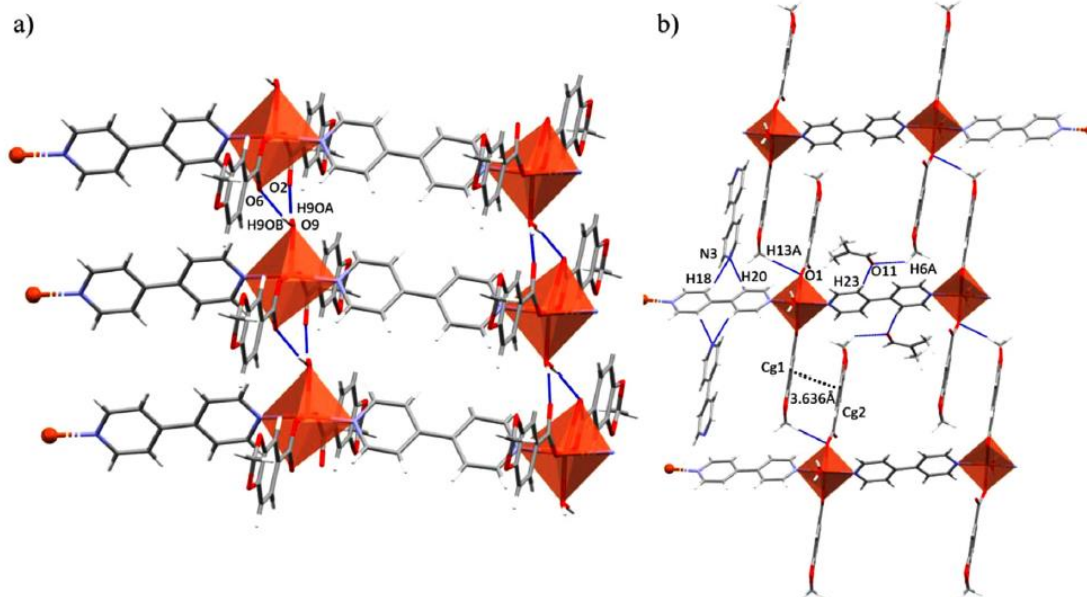


Figure 5

