

## HYDROTHERMAL SYNTHESIS AND CHARACTERIZATION OF A BINUCLEAR COMPLEX AND A COORDINATION POLYMER OF COPPER(II)

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**ABSTRACT.** Two new copper complexes [(bipy)(pydc)Cu( $\mu$ -OCO-pydc)Cu(bipy)(H<sub>2</sub>O)].3.5H<sub>2</sub>O (**1**) and  $\{[(\mu_2\text{-C}_2\text{O}_4)(2,2'\text{-bipy})\text{Cu}].2\text{H}_2\text{O}\}_n$  (**2**) (pydcH<sub>2</sub> = pyridine-2,6-dicarboxylic acid, bipy = 2,2'-bipyridine) have been hydrothermally synthesized. Both complexes were characterized by IR spectroscopy, elemental analysis and single crystal X-ray diffraction studies. Complex **1** consists of two independent neutral molecules. In every moiety, metal ion center is in a distorted octahedral geometry. Coordination polymer (**2**) has been prepared from the reaction of bis-(cyclohexanone)-oxal-dihydrazone, 2,2'-bipyridine and Cu(NO<sub>3</sub>)<sub>2</sub> in basic solution and under hydrothermal condition. The results showed that the bis-(cyclohexanone)-oxal-dihydrazone was converted to oxalate ion under heating and basic pH. Each metal ion center in **2** is in a distorted octahedral geometry and is coordinated by four oxygen atoms of two bridged oxalate ions and two nitrogen atoms of 2,2'-bipyridine molecules. In the crystal structure of **2**, some H-bonds and  $\pi$ - $\pi$  interaction cause formation of a 3D network.

**KEY WORDS:** Hydrothermal synthesis, Cu complex, Coordination polymer, Crystal structure

### INTRODUCTION

Hydrothermal synthesis refers to the synthesis by chemical reaction of substances in a sealed heated solution above ambient temperature and pressure. This technique provides a powerful tool for the construction of materials containing unique structures and special properties [1]. This method with an aqueous solvent as a reaction medium is environmentally friendly since the reactions are carried out in a closed system [2, 3]. Hydrothermal synthesis has been successful for the preparation of some solids such as microporous crystals [4], super ionic conductors [5], chemical sensors [6], complex oxide ceramics and fluorides [7, 8], materials including nanometer particles [2, 9] and transition metal complexes [10-13]. The molecular structures of complexes obtained by this method are unexpected compared to those obtained by the common solution methods [13, 14].

Polycarboxylate ligands have attracted interest as a potential bridging ligand with a variety of connection modes with transition metal centers and abundant structural motifs [13, 15-18].

Recently, we reported hydrothermal synthesis of binuclear Co(II) complex [19] and a new complex of La<sup>III</sup>-ion with bridged benzene-1,2,4,5-tetracarboxylate ligand [20]. In continuation of our research on synthesis of transition metals complexes containing polycarboxylate ligands [21, 22], in the present work, herein we report the syntheses and crystal structures of two new complexes of Cu(II) with bridged carboxylate groups, [(bipy)(pydc)Cu( $\mu$ -OCO-pydc)Cu(bipy)(H<sub>2</sub>O)].3.5H<sub>2</sub>O (**1**) and  $\{[(\mu_2\text{-C}_2\text{O}_4)(2,2'\text{-bipy})\text{Cu}].2\text{H}_2\text{O}\}_n$  (**2**).

### EXPERIMENTAL

All the purchased chemicals were of reagent grade and used without further purification. IR spectra were recorded using FTIR Spectra Bruker Tensor 27 spectrometer (Germany) (KBr pellets, nujol mulls, 4000-400 cm<sup>-1</sup>). Elemental analyses were performed using a Costech ECS 4010 CHNS-O analyzer (Italy).

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*Preparation of [(bipy)(pydc)Cu( $\mu$ -OCO-pydc)Cu(bipy)(H<sub>2</sub>O)].3.5H<sub>2</sub>O (1)*

Pyridine-2,6-dicarboxylic acid (0.167 g, 1 mmol) was dissolved in methanol (5 mL) and a solution of NaOH (0.04 g, 1 mmol) in deionized water (15 mL) was added and stirred for 30 min at room temperature. Then an aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.241 g, 1 mmol) and 2,2'-bipyridine (0.156 g, 1 mmol) was added above-mentioned solution. Reaction mixture was placed in a Parr-Teflon lined stainless steel vessel. It was sealed and heated to 110 °C for 24 h. The reaction mixture was gradually cooled by slow cooling to room temperature. The mother liquid was kept at 4 °C until the blue crystals of **1** suitable for X-ray diffraction were obtained.

IR (KBr) ( $\nu$ , cm<sup>-1</sup>): 3454 (O–H, water), 3030 (C–H, Ar), 1662 and 1630 (C=O, carboxylate), 1381 (C=O, carboxylate), 775–771 (2,2'-bipyridine). Anal. calcd. for C<sub>34</sub>H<sub>31</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>12.5</sub>: C, 47.93, H, 3.64, N, 9.87. Found: C, 47.88, H, 3.59, N, 9.82.

*Preparation of [[( $\mu_2$ -C<sub>2</sub>O<sub>4</sub>)(2,2'-bipy)Cu] .2H<sub>2</sub>O]<sub>n</sub> (2)*

bis(1,5-Cyclohexanone) oxal dihydrazone (0.139 g, 0.5 mmol) was dissolved in mixture of water/ethanol (1:1, 25 mL). Then NaOH (0.01 g, 0.25 mmol) was added and stirred for 30 min at room temperature. In next stage, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.12 g, 0.5 mmol) and 2,2'-bipyridine (0.04 g) were added. Reaction mixture was placed in a Parr-Teflon lined stainless steel vessel. It was sealed and heated to 120 °C for 17 h, then cooled by slow cooling to room temperature. The resultant solution was kept at 4 °C. Blue crystals of **2** were obtained after two weeks. IR (KBr) ( $\nu$ , cm<sup>-1</sup>): 3422 (O–H, water), 3066 (C–H, Ar), 1658, 1310–1298 and 830 (bridging oxalate), 730–724 (2,2'-bipyridine). Anal. calcd. for C<sub>12</sub>H<sub>12</sub>Cu N<sub>2</sub>O<sub>6</sub>: C, 41.89, H, 3.49, N, 8.14. Found: C, 41.80, H, 3.41, N, 8.09.

*X-ray crystallography*

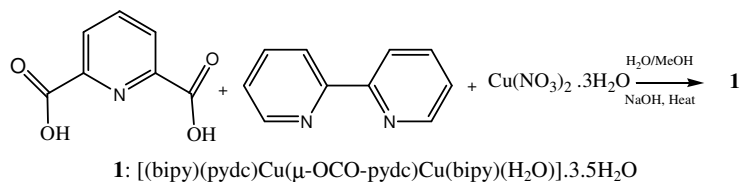
The selected crystals of **1** and **2** were covered with a per fluorinated oil and mounted on the tip of a glass capillary under a flow of cold gaseous nitrogen. The orientation matrix and unit cell dimensions were determined from 8000 (Stoe IPDS II (**1**), (graphite-monochromated Mo- $K_{\alpha}$  radiation in all cases;  $\lambda$  = 71.073 pm). In addition, absorption corrections were applied for **1** and **2** (numerical). The structures were solved by the direct methods (SHELXS-97 [23]) and refined against  $F^2$  by full-matrix least-squares using the program SHELXL-97 [24], ORTEP-3 (Farrugia, 1997) [25], software used to prepare material for publication: WinGX (Farrugia, 1999) [26].

Further details can be obtained free of charge on application to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223 336033; E-mail: deposit@ccdc.cam.ac.uk] quoting the depository number CCDC 685271 for **1** and 685272 for **2**.

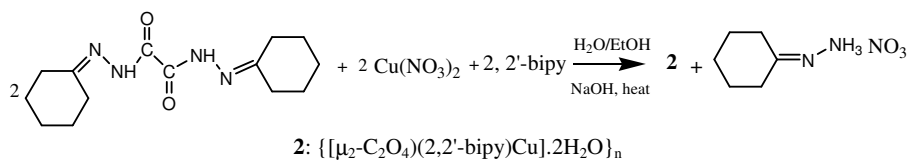
**RESULTS AND DISCUSSION**

Complex **1** can be obtained from the reaction of Cu(NO<sub>3</sub>)<sub>2</sub> with pyridine-2,6-dicarboxylic acid and 2,2'-bipyridine in the molar ratio 1:1:1 in basic solution and under hydrothermal condition (Scheme 1). Treatment of Cu(NO<sub>3</sub>)<sub>2</sub> with bis-(cyclohexanone)-oxal-dihydrazone and 2,2'-bipyridine in the molar ratio 2:2:1 and under hydrothermal condition gave complex **2**.

bis-(Cyclohexanone)-oxal-dihydrazone was changed to oxalate ions during the reaction and oxalate ions were coordinated to Cu cations (Scheme 2). The complexes **1** and **2** are blue crystalline solids and are air-stable.



Scheme 1



Scheme 2

The IR spectrum of **1** exhibits two strong bands at 1662 and 1630 cm<sup>-1</sup> due to the vibrations of two kinds of carboxylate groups. The characteristic strong bands of bridged carboxylate group appeared at 1630 cm<sup>-1</sup> (for asymmetric stretching) and 1381 cm<sup>-1</sup> (for symmetric stretching). The difference ( $\Delta\nu = 259$  cm<sup>-1</sup>) between  $\nu_{\text{asym}}(\text{COO}^-)$  and  $\nu_{\text{sym}}(\text{COO}^-)$  bands can be assigned to chelating acetate group [10, 12, 27], which was confirmed by the crystal structure of the compound. The IR spectrum of **2** shows three characteristic bands of the bridging oxalate group (1650 cm<sup>-1</sup>, 1310–1298 cm<sup>-1</sup> (doublet band) and 830 cm<sup>-1</sup>). These bands can be assigned to  $\nu_{\text{as}}(\text{CO})$ ,  $\nu_{\text{s}}(\text{CO})$  and  $\delta(\text{OCO})$  [10]. In addition, the IR spectra of two complexes show broad, strong bands near 3440 cm<sup>-1</sup> is assigned to the O–H stretching vibration of H<sub>2</sub>O and absorptions typical for coordinated 2,2'-bipyridine can be observed at 775–771 cm<sup>-1</sup> and 730–724 cm<sup>-1</sup> [28, 29].

#### Description of the structures

Table 1 shows the crystallographic data of **1** and **2**. Selected bond lengths and angles are given in Table 2. Figure 1 illustrates the principal structural features of complex **1**, selected bond lengths and bond angles are listed in Table 1. Complex **1** is a binuclear complex of Cu(II). As shown in Figure 1, the asymmetric structure unit of **1** consists of two crystallographically independent neutral binuclear Cu<sup>II</sup>-complexes, {[ (bipy)(pydc)Cu( $\mu$ -OCO-pydc)Cu(bipy) (H<sub>2</sub>O)]. 3.5H<sub>2</sub>O}. Here, we just describe one of them at length.

The crystal structure of **1** contains two types of Cu centers. Each metal ion center is in a distorted octahedral geometry. The basal plane around Cu1 is formed by two nitrogen atoms of 2,2'-bipyridine, one nitrogen atom of pyridine-2,6-dicarboxylate and one oxygen atom of water with the distances Cu(1)–N(1), 2.026(5) Å; Cu(1)–N(2), 2.008(5) Å; Cu(1)–N(3), 2.006(5) Å and Cu(1)–O(1), 2.005(5) Å, respectively and axial positions are occupied by two oxygen atoms of carboxylate groups with the distances Cu(1)–O(2), 2.260(4) Å and Cu(1)–O(4), 2.377(4) Å. The Cu(2) coordinated with two N atoms of 2,2'-bipyridine, one oxygen of bridged pyridine-2,6-dicarboxylate, one nitrogen and two oxygen atoms of another pyridine-2,6-dicarboxylate acid. Cu(2)–O(6) (2.261(4) Å) and Cu(2)–O(8) (2.393(6) Å) distances are longer than Cu(2)–O(5) (2.018(4) Å) and they filled axial positions. All Cu–N and Cu–O distances are in the range of mononuclear Cu(II) complex containing pyridine-2,6-dicarboxylate ion [30, 31].

Table 1. Crystallographic data for **1** and **2**.

Compound	<b>1</b>	<b>2</b>
Empirical formula	C <sub>34</sub> H <sub>31</sub> Cu <sub>2</sub> N <sub>6</sub> O <sub>12.5</sub>	C <sub>12</sub> H <sub>12</sub> Cu N <sub>2</sub> O <sub>6</sub>
Color	Blue	Blue
Formula mass	851.25	343.79
Crystal size (mm)	0.35 x 0.35 x 0.23	0.35 x 0.21 x 0.12
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> [pm]	10.3600(1)	8.9298(2)
<i>b</i> [pm]	19.738(2)	9.1011(2)
<i>c</i> [pm]	19.700(2)	9.7112(2)
$\alpha$ [°]	76.573(8)	110.46(3)
$\beta$ [°]	87.280(8)	97.61(3)
$\gamma$ [°]	86.601(8)	105.80(3)
Volume Å <sup>3</sup>	3909.0(7)	688.5(2)
<i>Z</i>	4	2
<i>D</i> <sub>calcd.</sub> [g.cm <sup>-3</sup> ]	1.446	1.658
Absorption correction	Numerical	Numerical
<i>F</i> (000)	1742	350
Temperature [k]	293	293
Index range		
<i>h</i>	-11→13	-12→12
<i>k</i>	-26→24	-12→11
<i>l</i>	-25→26	0→13
Reflections collected	41471	3711
Unique reflections ( <i>R</i> <sub>int</sub> )	18593 (0.0991)	3711 (0.1888)
Reflections with <i>F</i> <sub>o</sub> >4σ( <i>F</i> <sub>o</sub> )	9117	2490
Parameters	1183	206
<i>R</i> <sub>1</sub>	0.1427	0.2033
<i>wR</i> <sub>2</sub> (all data)	0.2295 <sup>a</sup>	0.02590 <sup>b</sup>

<sup>a</sup>*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.01617*P*)<sup>2</sup> + 9.4004], *P* = [max(*F*<sub>o</sub><sup>2</sup>, 0) + 2 *F*<sub>c</sub><sup>2</sup>]/3; <sup>b</sup>*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.0824 *P*)<sup>2</sup>]; *P* = [max(*F*<sub>o</sub><sup>2</sup>, 0) + 2 *F*<sub>c</sub><sup>2</sup>]/3.

Uncoordinated water molecules occupy general positions in the cell. These water molecules act as bridging agent and link adjacent molecules *via* hydrogen bonds. Hydrogen bonding interactions between uncoordinated and coordinated water molecules and carboxylate groups (Table 2) lead to the formation of the one-dimensional chain motif (Figure 2).

The structural features of complex **2** are shown in Figure 3, and bond parameters are given in Table 3. The complex **2** crystallizes in the triclinic space group  $P\bar{1}$  and consists of a coordination polymer with bridged oxalate ions. As shown in Figure 4, each metal is connected to two neighboring ones, through four μ<sub>2</sub>-oxo bridges, to form infinite metal–metal chain running in a zigzag fashion along the *a* axis. Each metal ion centers in **2** is in a distorted octahedral geometry and coordinated by four oxygen atoms from two bridged oxalate ions and two nitrogen atoms of 2,2'-bipyridine. Atoms N(1), N(2), O(1) and O(3) occupy the equatorial positions with an average bond length of 2.050 Å for Cu–N and 1.984 Å for Cu–O, while two oxygen atoms of carboxylic groups ((Cu(1)–O(2a), 2.319(9) Å and Cu(1)–O(4), 2.317(10) Å)) occupy the axial positions. Cu–O distances are in the range of other Cu(II) μ<sub>2</sub>-oxalate complexes [10, 32].

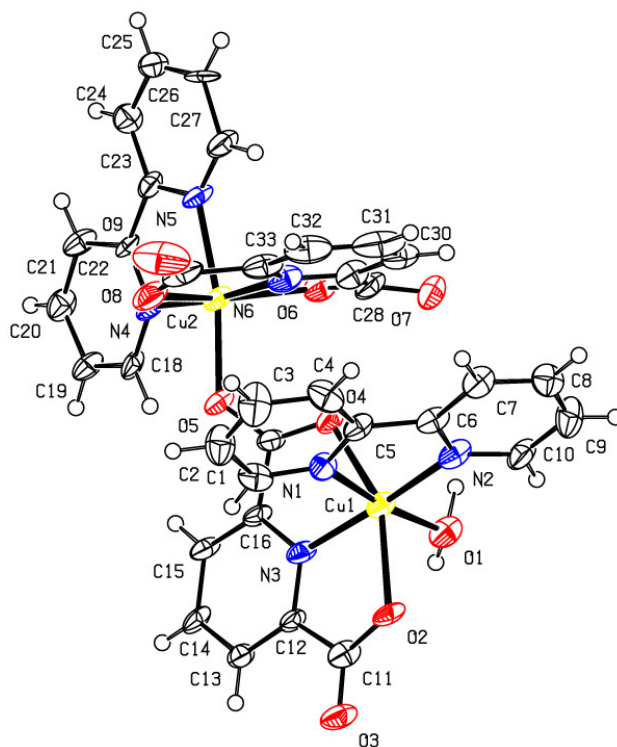


Figure 1. Asymmetric unit of **1** showing two kinds of pydc coordination modes; uncoordinated water molecules have been omitted for clarity (thermal ellipsoide at the 50% probability level).

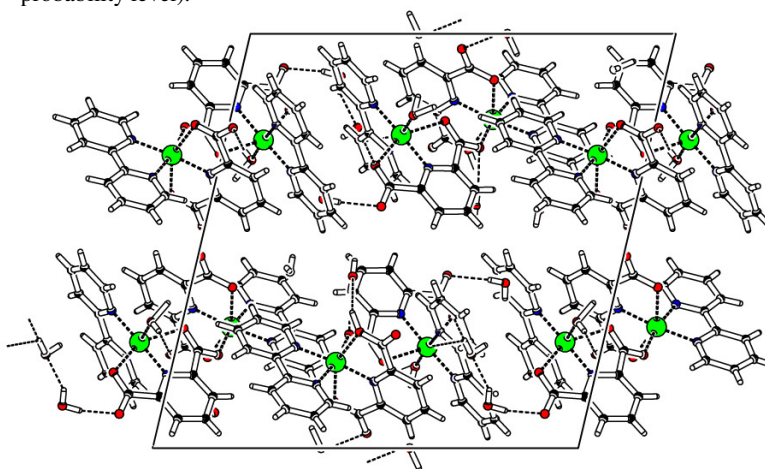


Figure 2. The fragment of crystal packing of  $[(\text{bipy})(\text{pydc})\text{Cu}(\mu\text{-OCO-pydc})\text{Cu}(\text{bipy})(\text{H}_2\text{O})] \cdot 3.5\text{H}_2\text{O}$  (**1**). Hydrogen bonds are shown with dashed lines.

Table 2. Selected bond lengths [Å] and bond angles [°] in **1** and **2**.

<b>1</b>			
O(1)-Cu(1)	2.005(5)	O(1)-Cu(1)-N(3)	92.0(2)
O(2)-Cu(1)	2.260(4)	N(3)-Cu(1)-N(2)	175.2(2)
O(4)-Cu(1)	2.377(4)	O(1)-Cu(1)-N(1)	172.8(2)
N(1)-Cu(1)	2.026(5)	N(2)-Cu(1)-N(1)	81.1(2)
N(2)-Cu(1)	2.008(5)	O(1)-Cu(1)-O(2)	87.4(2)
N(3)-Cu(1)	2.006(5)	N(1)-Cu(1)-O(4)	87.26(2)
O(5)-Cu(2)	2.018(4)	O(2)-Cu(1)-O(4)	151.12(2)
O(6)-Cu(2)	2.261(5)	N(6)-Cu(2)-N(4)	173.4(2)
O(8)-Cu(2)	2.393(6)	N(4)-Cu(2)-N(5)	80.9(2)
N(4)-Cu(2)	2.018(5)	N(6)-Cu(2)-O(6)	76.8(2)
N(5)-Cu(2)	2.049(5)	N(5)-Cu(2)-O(6)	90.6(2)
N(6)-Cu(2)	2.011(5)	N(5)-Cu(2)-O(8)	88.02(2)
O(10)-Cu(3)	2.276(5)	O(6)-Cu(2)-O(8)	151.40(2)
O(12)-Cu(3)	2.407(6)	N(9)-Cu(3)-N(7)	173.1(2)
O(14)-Cu(3)	2.017(4)	N(7)-Cu(3)-N(8)	80.3(2)
N(7)-Cu(3)	2.017(5)	N(8)-Cu(3)-O(10)	90.5(2)
N(8)-Cu(3)	2.046(5)	N(9)-Cu(3)-O(12)	75.0(2)
N(9)-Cu(3)	2.015(5)	N(8)-Cu(3)-O(12)	90.1(2)
O(15)-Cu(4)	2.375(4)	O(10)-Cu(3)-O(12)	151.23(2)
O(16)-Cu(4)	2.272(5)	O(18)-Cu(4)-N(12)	91.4(2)
O(18)-Cu(4)	1.995(5)	N(11)-Cu(4)-N(12)	175.3(2)
N(10)-Cu(4)	2.026(5)	O(18)-Cu(4)-N(10)	173.7(2)
N(11)-Cu(4)	1.996(5)	O(16)-Cu(4)-O(15)	151.00(2)
N(12)-Cu(4)	2.014(5)	N(11)-Cu(4)-N(10)	81.6(2)
<b>2</b>			
N(1)-Cu(1)	2.007(10)	O(3)-Cu(1)-N(1)	90.0(5)
N(2)-Cu(1)	2.010(12)	O(1)-Cu(1)-N(1)	173.7(5)
O(1)-Cu(1)	1.978(10)	O(1)-Cu(1)-O(3)	95.2(5)
O(2)-Cu(1)	2.313(9)	O(1)-Cu(1)-N(2)	93.9(5)
O(3)-Cu(1)	1.990(10)	O(3)-Cu(1)-N(2)	176.2(5)
O(4)-Cu(1)	2.317(10)	N(1)-Cu(1)-N(2)	80.9(5)
Cu(1)-O(2)	2.313(9)	O(1)-Cu(1)-O(2)	76.9(4)
Cu(1)-O(4)	2.317(10)	O(3)-Cu(1)-O(2)	85.2(4)
		N(1)-Cu(1)-O(2)	99.9(4)
		N(2)-Cu(1)-O(2)	95.3(4)
		O(1)-Cu(1)-O(4)	90.3(4)
		O(3)-Cu(1)-O(4)	78.3(4)
		N(1)-Cu(1)-O(4)	94.2(4)
		N(2)-Cu(1)-O(4)	101.9(4)
		O(2)-Cu(1)-O(4)	159.2(3)

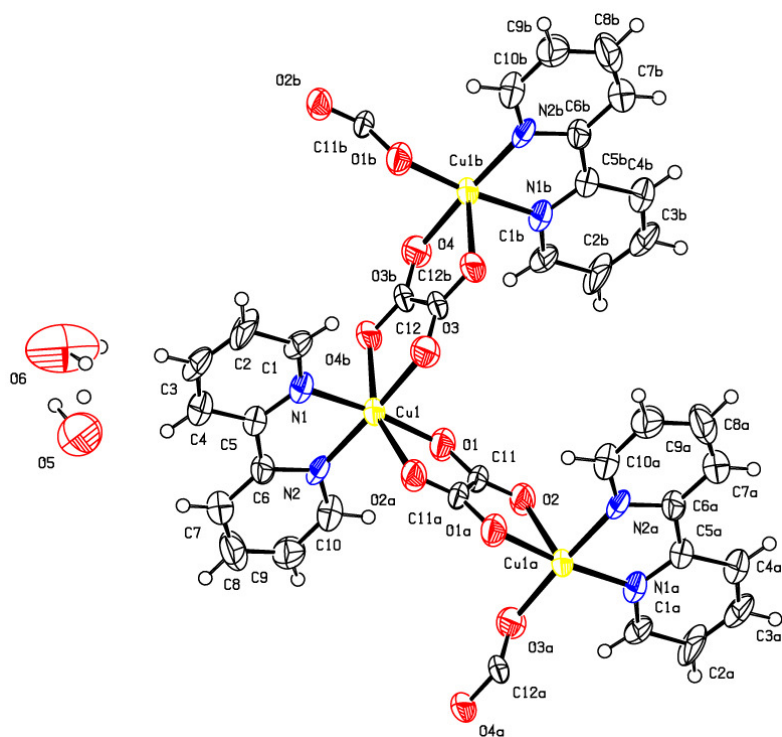


Figure 3. ORTEP diagram of **2** (thermal ellipsoids of 50% probability level).

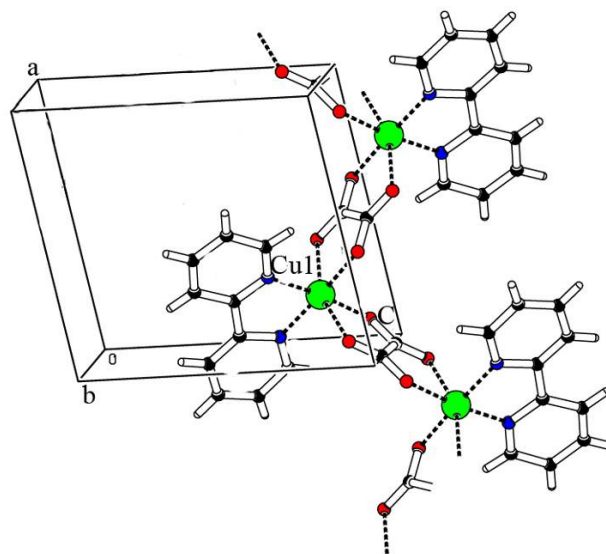


Figure 4. Fragment of infinite chain (along *a*-crystal axis) which formed by coordination interaction.

In the crystal structure of complex **2** there are water molecules of crystallization. Hydrogen bonding interactions between uncoordinated water molecules lead to the formation of infinite chain and therefore the combination of coordinative, hydrogen bonding and  $\pi$ - $\pi$  stacking interactions (Figure 5) with distances of 3.5313(11)Å for  $Cg6 \cdots Cg6$  [ $Cg6$ : N1/C2-C5] and 3.711(11) Å for  $Cg6 \cdots Cg7$  ( $Cg7$ : N2/C6-C10) cause to stabilize of crystal structure.

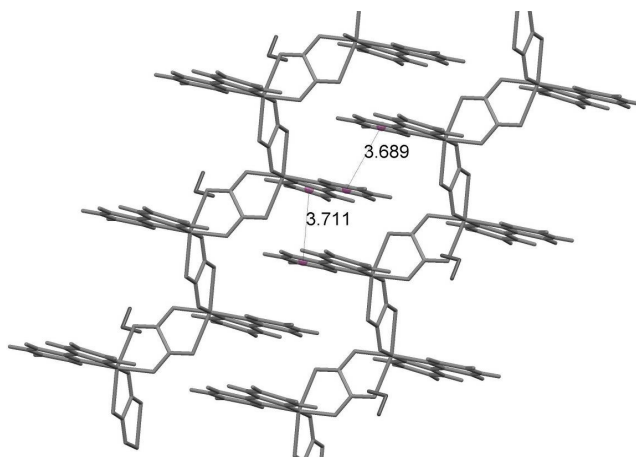


Figure 5. A view of the  $\pi$ - $\pi$  stacking interactions, between the aromatic rings of 2,2'-bipyridine observed in **2**.

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