

NOVEL IRON(II) AND COPPER(II) POLYMERIC COORDINATION COMPOUNDS WITH *N,N'*-BIPYRIDINE-TYPE LIGANDS: SYNTHESIS AND CHARACTERIZATION

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Abstract. Two new coordination compounds $\{(\text{bpyH}_2) \cdot [\text{Fe}(\text{bpy})_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2(\text{H}_2\text{O})\}_n$ (**1**) and $\{[\text{Cu}(\text{bpp})_2(\text{H}_2\text{O})] \cdot (\text{BF}_4)_2 \cdot \text{dmf} \cdot 0.75(\text{H}_2\text{O})\}_n$ (**2**), (where, bpy= 4,4'-bipyridine and bpp= 1,3-bis(4-pyridyl)propane, dmf= *N,N*-dimethylformamide) have been synthesized by slow evaporation method based on rigid and flexible bis(pyridine) ligands. The obtained compounds were characterized by thermal analysis, FT-IR spectroscopy and single crystal X-ray diffraction analysis. The structure of **1** is a channel-containing open framework constructed through the hydrogen-bonding supported by the criss-cross arrangement of the 1D Fe-bpy anionic chains, in which the surrounding of the metal atom is completed by oxygen atoms belonging to water molecules and SO_4^{2-} anions. The structure of **2** is formed by a one-dimensional polymeric cationic chain, in which the four bpp ligands connect with Cu(II) by four nitrogen atoms and one oxygen atom that belongs to a molecule of water that completes the surrounding of each metal atom. The complexes crystallize in the monoclinic space groups *C2/c* and *P2₁* respectively, where Fe(II) and Cu(II) ions present a N_2O_4 octahedral and N_4O square pyramidal environment. The hydrophilic regions absorb bpyH_2^{2+} and water molecules in **1** and BF_4^- anions, water and dmf molecules in **2**, which are held in the crystal lattices *via* hydrogen bonds.

Keywords: crystalline coordination polymer, bridging ligand, supramolecular system, π - π stacking interaction.

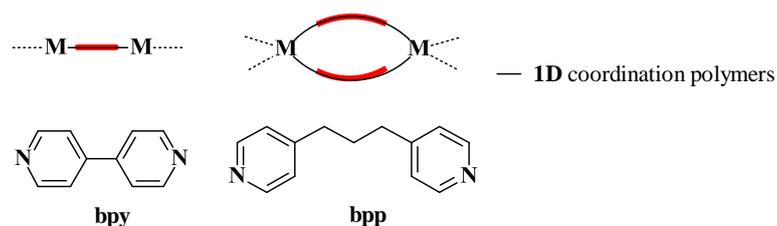
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Introduction

The synthesis and characterization of crystalline coordination polymers has attracted substantial interest due to their potential broad range of applications, catalysis, gas sorption and biological properties [1]. Coordination compounds have advantages over organic compounds, because metals have a variety of coordination geometries and a wide range of physical properties. The organic bridging ligands, such as 4,4'-bipyridine (bpy) and some other bis(pyridyl) derivatives, have recently been used to generate multidimensional hybrid materials, in which the inorganic M(II) (M= Fe, Cu) chains or layers are interlinked by organic bridging ligand [2-4]. These multidimensional hybrid materials can be made porous with large surface areas and tunable pore sizes and topologies, which leads to versatile architectures.

Although up to date an overwhelming number of coordination polymers have been synthesized through various routes using organic bridging ligands, there is still a challenge in predicting the exact conformation of ligands

in the coordination polymers. The use of divergent nitrogen ligands as building blocks in supramolecular chemistry is well known mainly due to their ability to generate multi-dimensional structures. For example, 1,3-bis(4-pyridyl)propane (bpp) ligand through flexible trimethylene group can adopt different structural conformations (*TT*, *TG*, *GG*, and *GG'*, where *T*= trans and *G*= gauche) displaying quite different N...N distances and bend angles [5]. Due to its flexibility and its ability to act in bridging coordination mode, this ligand can provide one-, two-, and three-dimensional coordination polymers with a variety of topologies depending not only on the metal salts employed but also on the synthetic conditions such as solvents, temperature, and pH. In addition, it is well known that the flexible nitrogen ligand bpp is used in the construction of coordination polymers that can show a wide range of interesting topologies as chains (Scheme 1), ladders, grids and adamantoid networks [6].



Scheme 1. Schematic representation of the typical coordination polymers from prototypical neutral nitrogen-heterocycle bridging ligands.

These networks can be formed due to the hydrogen-bonding between suitable organic molecules and cations or anions. Cations and anions are necessary for the charge balance to the metal cations, which typically function as nodes in the scaffolds. In the case of neutral bridging ligands, charge balance is achieved by anions from the original metal salt, for example, SO_4^{2-} and BF_4^- [7].

In this article, the synthesis, crystal structure determination and thermogravimetric analysis of two new one-dimensional coordination compound of *N,N'*-bipyridine-type ligands $\{(\text{bpyH}_2) \cdot [\text{Fe}(\text{bpy})_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2(\text{H}_2\text{O})\}_n$ (**1**) and $\{[\text{Cu}(\text{bpp})_2(\text{H}_2\text{O})] \cdot (\text{BF}_4)_2 \cdot \text{dmf} \cdot 0.75(\text{H}_2\text{O})\}_n$ (**2**), $\text{dmf} = N,N$ -dimethylformamide, are reported.

Experimental

All reagents and solvents were obtained from commercial sources and were used without further purification.

Synthesis of $\{(\text{bpyH}_2) \cdot [\text{Fe}(\text{bpy})_2(\text{H}_2\text{O})_2(\text{SO}_4)_2] \cdot 2(\text{H}_2\text{O})\}_n$ (**1**)

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (278 mg, 0.1 mmol) and 4,4'-bipyridine (19 mg, 0.1 mmol) were dissolved in 6 mL of methanol. Then 10 drops of dmf were added. The reaction mixture was stirred for about 5 min, filtered off and then slowly cooled to room temperature giving brown crystals. Yield: ~33%. Anal. calc. for $\text{C}_{40}\text{H}_{52}\text{Fe}_2\text{N}_8\text{O}_{24}\text{S}_4$ (%): C 42.11; H 4.59; N 9.82. Found: C 41.49; H 4.2; N 9.48. IR (cm^{-1}): 3302 (w), 3202 (w), 1657 (m), 1595 (w), 1530 (m), 1492 (s), 1410 (w), 1324 (s), 1222 (s), 1073 (w), 1044 (m), 993 (m), 809 (m), 737 (m), 675 (m), 460 (w), 410 (w).

Synthesis of $\{[\text{Cu}(\text{bpp})_2(\text{H}_2\text{O})] \cdot (\text{BF}_4)_2 \cdot \text{dmf} \cdot 0.75(\text{H}_2\text{O})\}_n$ (**2**)

$\text{Cu}(\text{BF}_4) \cdot n\text{H}_2\text{O}$ (237 mg, 0.1 mmol) and 1,3-bis(4-pyridyl)propane (15 mg, 0.1 mmol) were dissolved in 10 mL of methanol. Then 8 drops of dmf were added. The reaction mixture was stirred for about 5 min, filtered off and then slowly cooled to room temperature giving blue-violet crystals. Yield: ~75%. Anal. calc. for

$\text{C}_{29}\text{H}_{38.50}\text{B}_2\text{CuF}_8\text{N}_5\text{O}_{2.75}$ (%): C 50.19; H 5.52; N 10.09. Found: C 49.78; H 5.05; N 9.86. IR (cm^{-1}): 3579 (w), 32246 (w), 1655 (m), 1620 (s), 1509 (s), 1433 (m), 1386 (w), 1343 (s), 1231 (m), 1216 (m), 1069 (m), 1027 (m), 992 (m), 822 (m), 806 (m), 758 (m), 665 (w), 569 (m), 441 (m).

Physical measurements

Elemental analysis was performed on an elemental analyser (Vario El III, Elementar Analysensysteme GmbH).

The *IR spectra* were obtained in Nujol on a FT-IR Spectrum-100 Perkin Elmer spectrometer in the range of 400-4000 cm^{-1} .

The *thermogravimetric analysis* (TGA) was carried out with a Derivatograph Q-1500 thermal analyzer in an air flow at a heating rate of 10°C/min in the temperature range of 25-1000°C.

X-ray structure determination. X-Ray diffraction measurements for **1** and **2** were carried out at room temperature on an Xcalibur E diffractometer equipped with CCD area detector and a graphite monochromator utilizing MoK_α radiation. Final unit cell dimensions were obtained and refined on an entire data set. All calculations to solve the structures and to refine the proposed models were carried out with the SHELXS97 program package [8]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms refined isotropically and attached to carbon and oxygen atoms were positioned geometrically using a riding-atom model of SHELXL default parameters with $\text{Uiso}(\text{H}) = 1.2\text{Ueq}(\text{C})$, $\text{Uiso}(\text{H}) = 1.5\text{Ueq}(\text{C})$, $\text{Uiso}(\text{H}) = 1.5\text{Ueq}(\text{N})$ and $\text{Uiso}(\text{H}) = 1.5\text{Ueq}(\text{O})$, respectively. The crystallization water molecules in **2** are localized in two positions with a coefficient of occupancy 0.5 and 0.25. The solvent accessible voids (SAVs) were calculated using PLATON [9].

Crystallographic data for new structures reported herein were deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 1892725 and 1892726. These data can be obtained free of

charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

Both coordination compounds were obtained in the identical synthetic conditions by mixing the warm solutions with *N,N'*-chelating ligands and dmf in methanol. The X-ray data and the details of the refinement for compounds **1** and **2** are summarized in Table 1, selected geometric parameters are given in Tables 2 and 3.

Compound **1** crystallizes in the monoclinic *C2/c* space group (Table 1). This compound consists of a 1D anionic chain of $[\text{Fe}(\text{bpy})_2(\text{H}_2\text{O})_2(\text{SO}_4)_2]^{2n-}$, protonated bpy as organic cations $(\text{bpyH}_2)^{2+}$, and water solvate molecules (Figure 1). In the unit cell there are two crystallographic independent atoms of metal, the Fe(1) atom is located in the centre of symmetry, and Fe(2) on axis *c*, which condition the chains symmetry. The Fe(II) coordination core corresponds to the distorted N_2O_4 octahedral coordination environment. Each Fe atom is coordinated by two pyridine nitrogen donors, Fe–N distances are in the range of 2.222(3)–2.194(5) Å, two sulphate oxygen donors, Fe–O distances are 2.103(3)–2.112(3) Å, and two water molecules, Fe–O 2.158(3)–2.152(3) Å (Table 2). The pair of donor atoms occupy *trans*

position to each other, and the N–Fe–N and O–Fe–O bond angles values are close to 180° (Table 2). The *cis* N–Fe–O and O–Fe–O bond angles are slightly deviated from 90°. The two pyridine rings of each bpy coordinated ligand are co-planar, and in $(\text{bpyH}_2)^{2+}$ the angle between cycles is equal to 5°.

Since a coordinated sulphate anion has a tetrahedral geometry with four oxygen atoms, providing multi-linking sites, this anion can give rise to a well-associated network with metal-bpy modules [10,11]. A relevant synthetic strategy for the channel structure is to use a rod-like bridging ligand 4,4'-bipyridine [12]. The structural characterization of sulphate-bridged coordination polymer, $[\text{Fe}_3(\text{bpy})_3(\text{H}_2\text{O})_6(\text{SO}_4)_4]_n^{2-}$, shows that sulphate anion acts as an effective connector between the Fe centers, the crystal structure affording a 3D porous framework. In **1** we have divided 1D chains formed by alternating Fe (1) and Fe (2) atoms (Figure 2(a)). The network is formed *via* hydrogen bonds between sulphate anions and the coordinated and solvation water molecules $\text{O}(\text{H}_2\text{O})\cdots\text{O}(\text{SO}_4)$ and also by $(\text{bpyH}_2)^{2+}$ cations through the $\text{N}(\text{H}(\text{bpyH}_2))\cdots\text{O}(\text{SO}_4)$ hydrogen bridges and by $\pi\cdots\pi$ interactions as well (Figure 2(b),(c),(d), Table 3).

Table 1

Crystallographic data and structure refinement details for compounds **1** and **2**.

Parameters	Value	
	1	2
Compound	1	2
Empirical formula	$\text{C}_{40}\text{H}_{52}\text{Fe}_2\text{N}_8\text{O}_{24}\text{S}_4$	$\text{C}_{29}\text{H}_{38.50}\text{B}_2\text{CuF}_8\text{N}_5\text{O}_{2.75}$
Formula weight	1268.84	738.31
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2</i> ₁
Z	4	2
<i>a</i> (Å)	22.4227(13)	10.4031(5)
<i>b</i> (Å)	11.5446(6)	16.1225(8)
<i>c</i> (Å)	18.9051(12)	11.4748(5)
β (deg)	98.165(6)	109.513(5)
<i>V</i> (Å ³)	4844.2(5)	1814.1(2)
<i>D</i> _c (g/cm ⁻³)	1.740	1.352
μ (mm ⁻¹)	0.870	0.678
<i>F</i> (000)	2624	761
Crystal size (mm ³)	0.22 x 0.18 x 0.02	0.4 x 0.22 x 0.05
Reflections collected/unique	7853/4281 [<i>R</i> _{int} = 0.0463]	6617/4373 [<i>R</i> _{int} = 0.0296]
Reflections with [<i>I</i> > 2σ(<i>I</i>)]	2774	3364
Parameters	356	444
GOF on <i>F</i> ²	1.005	1.003
Absolute structure parameter	-	-0.01(2)
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0537; 0.1048	0.0626; 0.1595
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0913; 0.1212	0.0846; 0.1752

Table 2

Bond distances (Å) and angles (°) between the crystallographic independent atoms in the 1 and 2 coordination cores.			
1			
Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Fe(1)–O(1)	2.103(3)	Fe(2)–O(5)	2.112(3)
Fe(1)–O(1w)	2.158(3)	Fe(2)–O(2w)	2.152(3)
Fe(1)–N(1A)	2.222(3)	Fe(2)–N(1B)	2.194(5)
		Fe(2)–N(2B) ⁱⁱⁱ	2.232(4)
Angle	ω , deg	Angle	ω , deg
O(1)–Fe(1)–N(1A)	89.06(11)	O(5)–Fe(2)–O(5) ⁱⁱ	172.6(2)
O(1)–Fe(1)–N(1A) ⁱ	90.94(11)	O(5)–Fe(2)–N(1B)	86.27(7)
O(1)–Fe(1)–O(1w)	91.86(11)	O(5)–Fe(2)–N(2B) ⁱⁱⁱ	93.73(7)
O(1)–Fe(1)–O(1w) ⁱ	88.14(11)	O(5)–Fe(2)–O(2w)	91.56(10)
O(1w)–Fe(1)–N(1A)	91.65(11)	O(5)–Fe(2)–O(2w) ⁱⁱ	88.72(10)
O(1w)–Fe(1)–N(1A) ⁱ	88.35(11)	O(2w)–Fe(2)–N(1B)	92.12(7)
		O(2w)–Fe(2)–N(2B) ⁱⁱⁱ	87.88(7)
		O(2w)–Fe(2)–O(2w) ⁱⁱ	175.8(1)
2			
Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Cu(1)–N(1A)	2.024(5)	Cu(1)–N(2B) ⁱ	2.039(6)
Cu(1)–N(2A) ⁱ	2.020(5)	Cu(1)–O(1w)	2.292(6)
Cu(1)–N(1B)	2.023(5)		
Angle	ω , deg	Angle	ω , deg
N(1A)–Cu(1)–N(1B)	88.3(2)	N(1B)–Cu(1)–N(2A) ⁱ	170.0(4)
N(1A)–Cu(1)–N(2B) ⁱ	169.5(4)	N(1B)–Cu(1)–N(2B) ⁱ	92.0(2)
N(1A)–Cu(1)–N(2A) ⁱ	91.17(18)	O(1w)–Cu(1)–N(2A) ⁱ	98.6(3)
N(1A)–Cu(1)–O(1w)	94.4(3)	O(1w)–Cu(1)–N(2B) ⁱ	96.1(3)
N(1B)–Cu(1)–O(1w)	91.4(2)	N(2A) ⁱ –Cu(1)–N(2B) ⁱ	86.7(2)

1: $i -x+1/2, -y+3/2, -z$; $ii -x, y, -z+1/2$; $iii x, y-1, z$.

2: $i x, y, z-1$.

Table 3

Hydrogen bond geometry (Å).				
<i>D</i> – <i>H</i> ··· <i>A</i>	<i>d</i> (<i>H</i> ··· <i>A</i>)	<i>d</i> (<i>D</i> ··· <i>A</i>)	\angle (<i>DHA</i>)	Symmetry transformations for acceptor <i>A</i>
1				
O(1w)–H(1)···O(3w)	1.97	2.758(4)	173	x, y, z
O(1w)–H(2)···O(7)	2.27	3.031(5)	156	$-x+1/2, y+1/2, -z+1/2$
O(2w)–H(1)···O(8)	2.05	2.754(4)	157	$-x, y, -z+1/2$
O(2w)–H(2)···O(3)	1.83	2.695(4)	169	$x, -y+1, z+1/2$
O(3w)–H(1)···O(7)	2.25	3.091(5)	166	$x, y+1, z$
O(3w)–H(1)···O(8)	2.54	3.191(5)	133	$x, y+1, z$
O(3w)–H(2)···O(4)	2.36	3.100(5)	146	x, y, z
O(4w)–H(1)···O(4)	2.11	2.985(5)	166	x, y, z
O(4w)–H(2)···O(3)	2.04	2.910(4)	165	$-x, -y+1, -z$
N(1C)–H(1)···O(6)	1.69	2.628(5)	164	x, y, z
N(2C)–H(2)···O(2)	1.80	2.618(4)	173	$x, -y+2, z+1/2$
2				
O(1w)–H(1)···O(1D)	1.92	2.72(1)	172	x, y, z
O(1w)–H(2)···O(2w)	1.90	2.73(2)	173	$x-1, y, z-1$
O(2w)–H(1)···F(4)	1.77	2.53(3)	172	x, y, z
O(2w)–H(2)···O(3w)	2.13	3.02(4)	179	$x+1, y, z$
O(3w)–H(1)···O(2w)	2.32	3.02(4)	143	$x-1, y, z$
O(3w)–H(2)···F(6)	2.46	3.03(4)	125	x, y, z
O(3w)–H(2)···F(8)	2.12	2.97(4)	179	x, y, z

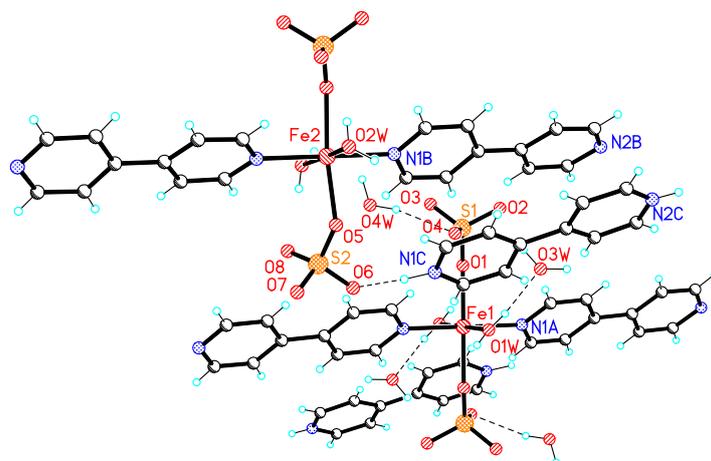


Figure 1. View of the fragment of Fe(II) compound 1 with the numbering scheme of crystallographic independent atoms.

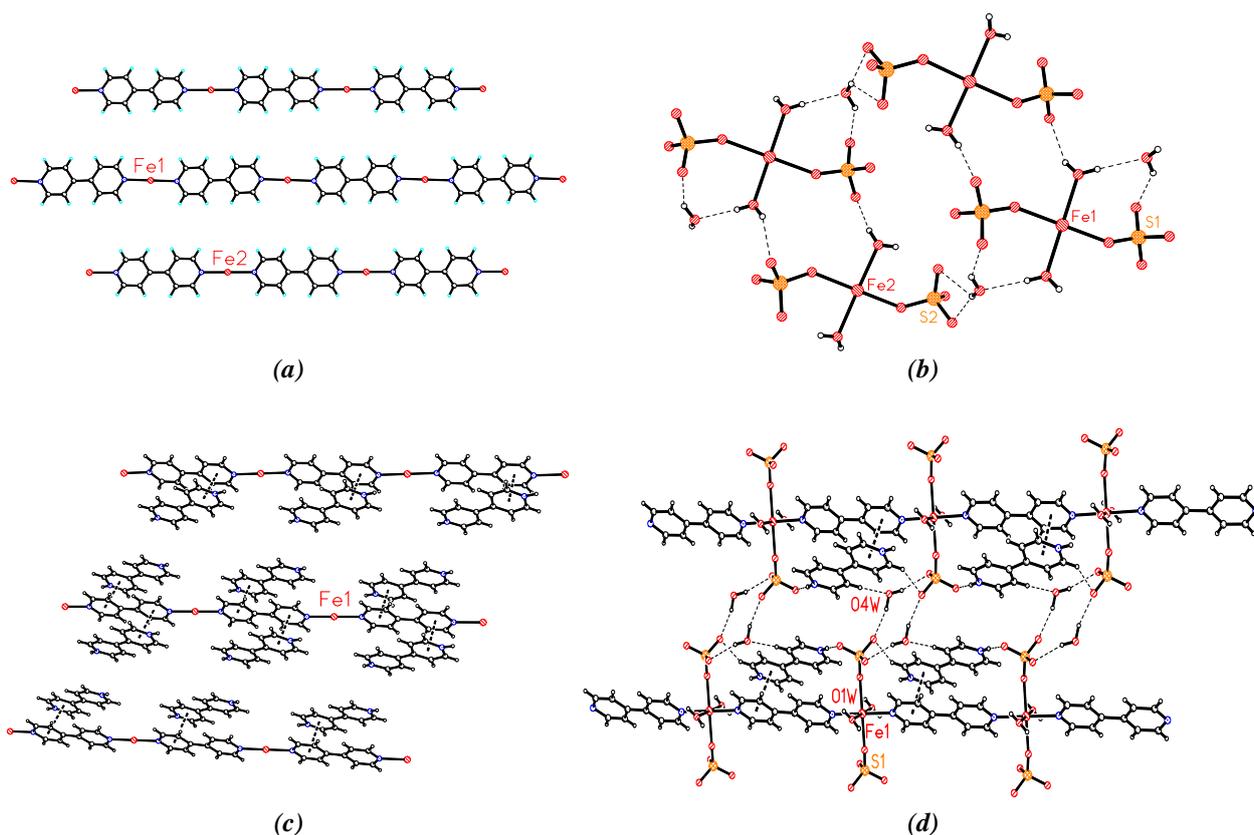


Figure 2. The fragment of 1D chains of polymeric compound 1, the coordinated sulphate anions and H₂O are omitted for clarity (a). The assembly mode of the polymeric chains formed by Fe1 and Fe2 (b). Cation interactions of (bpyH₂)²⁺ with polymer chains (c). The assembly mode of the polymeric chains formed by Fe1 (d).

Intermolecular $\text{O}(\text{H}_2\text{O})\text{--H}\cdots\text{O}(\text{SO}_4^{2-})$ hydrogen bonds involving the coordinating water molecules as donors and the sulphate O atoms as acceptors form zigzag-like hydrogen-bonding chains, which are further assembled *via* hydrogen bonds involving the solvated water molecules and $(\text{bpyH}_2)^{2+}$, thus forming a supramolecular network structure. In the crystal structure it is highlighted that the layer is composed of linear anionic chains formed by Fe(1) lines parallel along the *c*-axis, which are connected by $\pi\cdots\pi$ interactions (3.653 Å) with protonated $(\text{bpyH}_2)^{2+}$ ligands. The molecules $(\text{bpyH}_2)^{2+}$ connected these layers with the chains formed by Fe(2) through hydrogen links (Table 3). The Fe(1) \cdots Fe(1) distance in the same chain is equal to 11.545 Å, Fe(1) \cdots Fe(1) in neighbouring chains is 11.545 Å, Fe(2) \cdots Fe(2) in the same chain 11.545 Å, Fe(1) \cdots Fe(2) into neighbouring chains are 10.186 Å and 9.304 Å.

The interaction in the system $\text{Cu}(\text{BF}_4)_2 - 1,3\text{-bis}(4\text{-pyridyl})\text{propane}$ (bpp) resulted in a new 1D coordination polymer with the composition $\{[\text{Cu}(\text{bpp})_2(\text{H}_2\text{O})]\cdot(\text{BF}_4)_2\cdot\text{dmf}\cdot 0.75(\text{H}_2\text{O})\}_n$ (2),

and this compound was studied by FT-IR spectroscopy, TG analysis and the single crystal X-ray diffraction method. Compound 2 crystallizes in non-centrosymmetric monoclinic $P2_1$ space group (Table 1) and the asymmetric unit comprises one Cu(II) cation, two coordinated bpp ligands, two BF_4^- anions, one molecule of dmf and water molecules of crystallization, occupying two independent crystallographic positions with coefficient 0.5 and 0.25 (Figure 3(a)). The copper atom of the polymer cation is in the square-pyramidal coordination (4N+O). The Cu–N_{bpp} distances are in the range 2.020(5)–2.039(6) Å, the Cu–O_w distance is 2.292(6) Å. The O–Cu–N angles are in the range of 91.4(2)–98.6(3)° (Table 2). Each bpp ligand is linked to two Cu(II) ions in a double-stranded bridge fashion, thus extending the structure to 1D double tape composed of the 24-membered metallic ring with Cu \cdots Cu separation of 11.475 Å across the cavity which are aligned along the *c*-axis (Figure 3(b)).

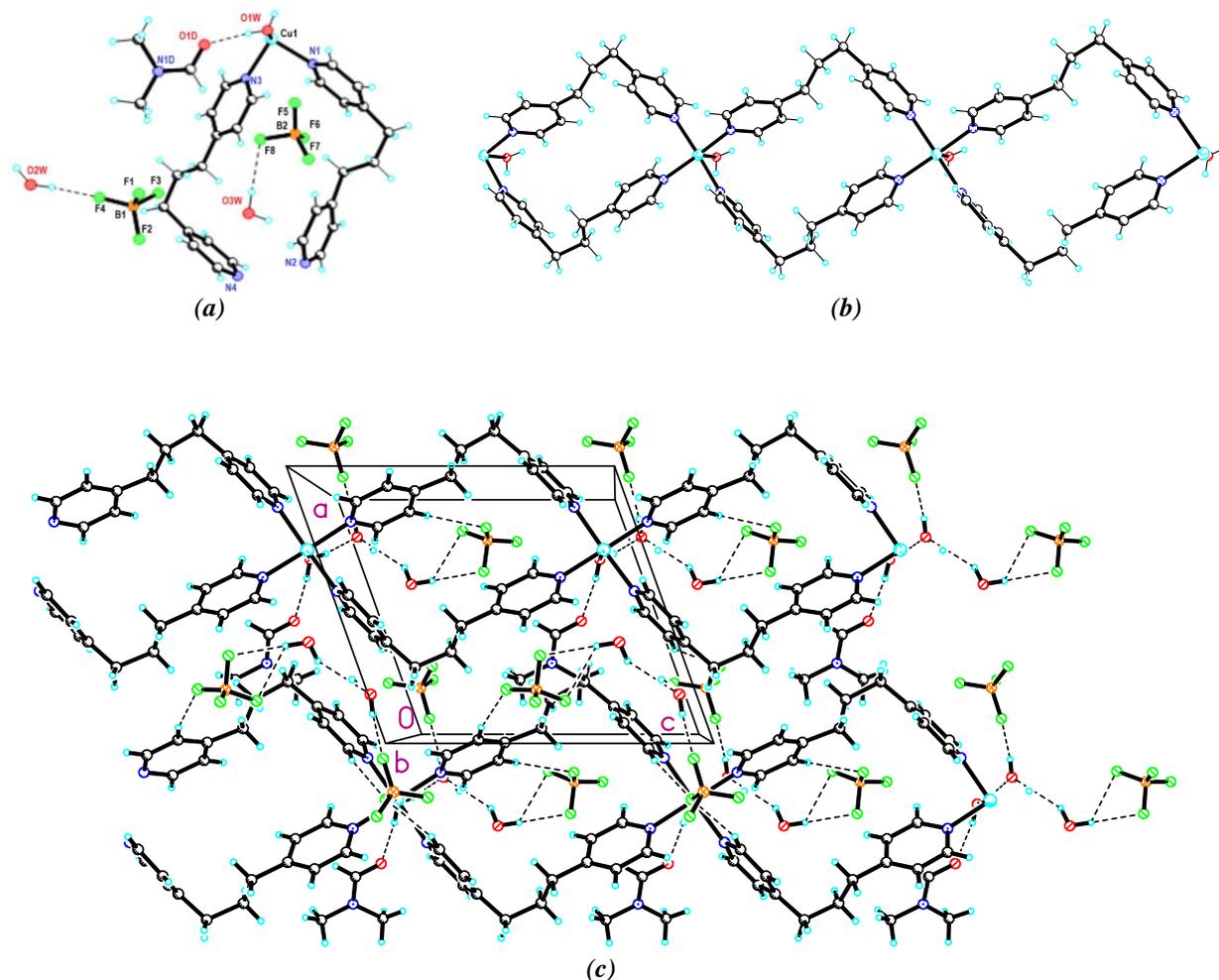


Figure 3. Coordination environment of the Cu(II) ion with the atom labelling (a). Fragment of the double-stranded bridge coordination chain (b). Crystal packing of 2 (c).

The crystallization water and dmf molecules are involved through hydrogen bonds: coordinated water molecule as donor binds with O atom of dmf and one crystallization water molecule. The BF_4^- anions are held in the crystal lattice *via* $\text{OH}\cdots\text{F}$ hydrogen bonds with polymer cation through crystallization water molecules (Table 3, Figure 3(c)). The volume, occupied by solvent molecules as calculated by PLATON comprises 447.9 \AA^3 or (24.7%) of the total unit cell volume, thus indicating a high solvent uptake.

Analysis of the Cambridge Structural Database [13] reveals three Cu(II) coordination 1D polymers built with Cu(II) atoms in the N_4O_2 distorted octahedral [14] and N_4O square-pyramidal coordination environments (Table 4) [15]. Use of the longer bridging bpp ligand causes voids in the crystal lattice and facilitates calculation of solvent accessible voids (SAVs) in these structures with the removed water molecule yields from the total unit cell volume. Among the compounds summarized in Table 4, compound **2** is the best packed and demonstrates the most promising adsorptive properties even after the removal of solvent molecules.

Infrared spectroscopy study

The FT-IR spectra of the both compounds reveal similarities with slight displacement of vibration signals, and are different through

vibrational bands of inorganic anions. FT-IR spectra interpretation was done according to literature data [16]. Both compounds show a broad band in the $3300\text{--}3500 \text{ cm}^{-1}$ region that may be assigned to the (OH) stretching vibration, indicating the presence of water molecules in the structure in accordance with the thermal analysis results. The bands from the range $1657\text{--}1595 \text{ cm}^{-1}$ may be attributed to the pyridyl stretching mode $\nu(\text{C-C})$ and $\nu(\text{C-N})$ of a bpy and bpp ligands. The SO_4^{2-} anion band of compound **1** is observed at 1073 cm^{-1} and the two BF_4^- anion bands are observed in the region $1067\text{--}1027 \text{ cm}^{-1}$. The strong band in the range from 410 to 460 cm^{-1} corresponds to Fe–O vibrations. For the Cu(II) compound, the bands at 440 cm^{-1} and 569 cm^{-1} correspond to elongated vibrations of Cu–O, and Cu–N bonds, respectively.

Thermogravimetric analysis

The decomposition of **2** was investigated by combined TG-DTA (Figure 4). The first weight loss step is observed in the range of $47\text{--}89^\circ\text{C}$, corresponding to the removal of three molecules of water and accompanied by a weak endothermic effect with a 7.26% (7.08% calc.) mass loss. Subsequent heating leads to the loss of a dmf molecule from the outer sphere, with mass loss accounting for 8.37% (9.59% calc.).

Table 4

Selected geometrical and crystal packing parameters in **2** and relative compounds.

Compound	SG	Topology	SAVs, \AA^3 (%)	Refcode CSD, Ref.
$\{[\text{Cu}(\text{bpp})_2(\text{H}_2\text{O})] \cdot (\text{BF}_4)_2 \cdot \text{dmf} \cdot 0.75(\text{H}_2\text{O})\}_n$ (2)	$P2_1$	1D	447.9 (24.7) ^a	Present work
$\{[\text{Cu}(\text{bpp})_2(\text{H}_2\text{O})_2] \cdot \text{tdc} \cdot 5.5\text{H}_2\text{O}\}_n$	$P-1$	1D	380.6 (20.4) ^a	QUJHUZ, [14]
$\{[\text{Cu}(\text{bpp})_2(\text{H}_2\text{O})] \cdot \text{ip} \cdot 7\text{H}_2\text{O}\}_n$	$P2_1$	1D	353.1 (18.6) ^a	OTASOS, [15]
$\{[\text{Cu}(\text{bpp})_2(\text{H}_2\text{O})_2] \cdot \text{tp} \cdot 7\text{H}_2\text{O}\}_n$	$P2_1/n$	1D	857.2 (22.5) ^a	OTASIM, [15]

^aSAVs calculated with the removal of guest molecules (H_2O and dmf).

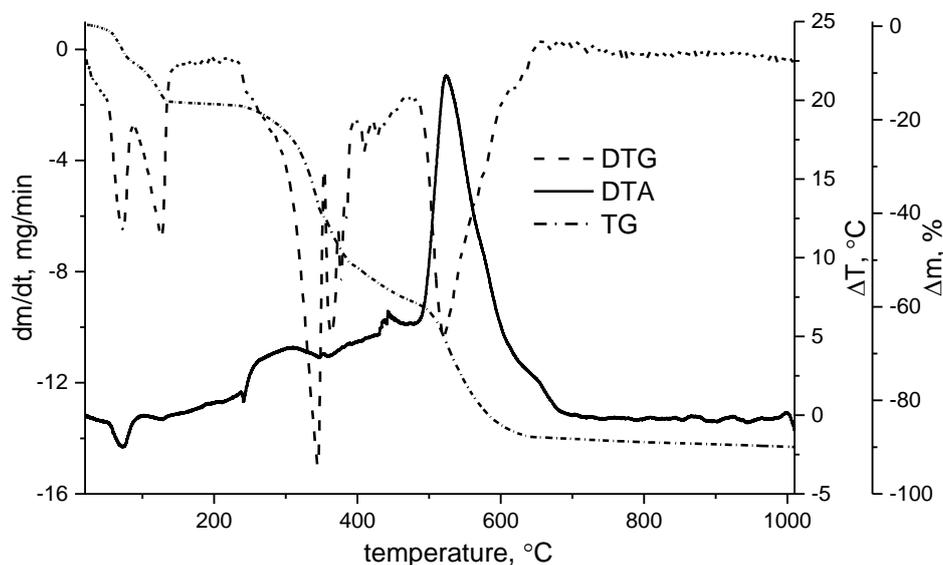


Figure 4. TG-DTA pattern of compound **2**.

At 150°C, a new mass loss is observed, which corresponds to the removal of two BF_4^- anions with a 22.86% loss of mass (22.86% calc.). In the range of 347-680°C degradation of the bpp ligand takes place, this process being strongly exothermic with a maximum at 522°C. The mass fraction of the obtained residue corresponds to CuO , representing 10.91% (10.51% calc.).

Conclusions

In summary, the two new 1D coordination polymers based on octahedral Fe(II) and square-pyramidal Cu(II) complexes and *N,N'*-bipyridine-type ligands were synthesized and characterized. Using the X-ray diffraction it was demonstrated that compound **1** is formed by the polymeric separate $[\text{Fe}_2(\text{bpy})_2]_n^{2-}$ anionic chains with the participation of Fe(1) and Fe(2) atoms. Additionally, it was shown that the $[\text{bpyH}_2]^{2+}$ organic cations and water molecules of crystallization are located between chains. In compound **2** the $[\text{Cu}(\text{bpp})_2(\text{H}_2\text{O})]_n^{2+}$ cations form polymeric double chains, which are linked to BF_4^- anions and crystallization water molecules *via* hydrogen bonds thus determining the polymer packing.

References

- Cussen, E.J.; Claridge, J.B.; Rosseinsky, M.J.; Kepert, C.J. Flexible sorption and transformation behavior in a microporous metal-organic framework. *Journal of the American Chemical Society*, 2002, 124(32), pp. 9574-9581. DOI: [10.1021/ja0262737](https://doi.org/10.1021/ja0262737)
- Jin, H.; Qi, Y.; Wang, E.; Li, Y.; Wang, X.; Qin, C.; Chang, S. Molecular and multidimensional organic-inorganic hybrids based on polyoxometalates and copper coordination polymer with mixed 4,4'-bipyridine and 2,2'-bipyridine ligands. *Crystal Growth & Design*, 2006, 6(12), pp. 2693-2698. DOI: [10.1021/cg060303q](https://doi.org/10.1021/cg060303q)
- Ene, C.D.; Maxim, C.; Rouzieres, M.; Cl  rac, R.; Avarvari, N.; Andruh, M. Enantiopure versus Racemic Mixture in Reversible, Two-Step, Single-Crystal-to-Single-Crystal Transformations of Copper(II) Complexes. *Chemistry a European Journal*, 2018, 24(34), pp. 8569-8576. DOI: <https://doi.org/10.1002/chem.201800404>
- Maxim, C.; Ferlay, S.; Tokoro, H.; Ohkoshi, S.-I.; Train, C. Atypical stoichiometry for a 3D bimetallic oxalate-based long-range ordered magnet exhibiting high proton conductivity. *Chemical Communications*, 2014, 50(42), pp. 5629-5632. DOI: [10.1039/c4cc00607k](https://doi.org/10.1039/c4cc00607k)
- Carlucci, L.; Ciani, G.; Proserpio, D.M.; Rizzato, S. New polymeric networks from the self-assembly of silver(I) salts and the flexible ligand 1,3-bis(4-pyridyl)propane (bpp). A systematic investigation of the effects of the counterions and a survey of the coordination polymers based on bpp. *CrystEngComm*, 2002, 4(22), pp. 121-129. DOI: [10.1039/b201288j](https://doi.org/10.1039/b201288j)
- Biradha, K.; Sarkar, M.; Rajput, L. Crystal engineering of coordination polymers using 4,4'-bipyridine as a bond between transition metal atoms. *Chemical Communications*, 2006, 0(40), pp. 4169-4179. DOI: [10.1039/b606184b](https://doi.org/10.1039/b606184b)
- Janiak, C.; Vieth, J.K. MOFs, MILs and more: concepts, properties and applications for porous coordination networks (PCNs). *New Journal of Chemistry*, 2010, 34(11), pp. 2366-2388. DOI: [10.1039/c0nj00275e](https://doi.org/10.1039/c0nj00275e)
- Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallographica Section C*, 2015, C71, pp. 3-8. DOI: <https://doi.org/10.1107/S2053229614024218>
- Spek, A.L. Structure validation in chemical crystallography. *Acta Crystallographica Section D*, 2009, D65, pp. 148-155. DOI: <https://doi.org/10.1107/S090744490804362X>
- Xu, Z.; Fu, Y.; Zhang, Y. Synthesis, structure and characterization of 4,4'-bipyridine directed isolated cluster and 1D chain of iron sulfates. *Journal of Molecular Structure*, 2008, 876(1-3), pp. 70-76. DOI: <https://doi.org/10.1016/j.molstruc.2007.05.039>
- Geo, P.; Amitava, Ch.; Rao, C.N.R. Organically templated linear and layered iron sulfates. *Chemistry of Materials*, 2003, 15(5), pp. 1174-1180. DOI: [10.1021/cm020772p](https://doi.org/10.1021/cm020772p)
- Moliner, N.; Munoz, M.C.; Real, J.A. Two-dimensional assembling of 4,4'-bipyridine and 4,4'-azopyridine bridged iron(II) linear coordination polymers via hydrogen bond. *Inorganic Chemistry Communications*, 1999, 2(1), pp. 25-27. DOI: [https://doi.org/10.1016/S1387-7003\(98\)00137-3](https://doi.org/10.1016/S1387-7003(98)00137-3)
- Groom, C.R.; Bruno, I.J.; Lightfoot, M.P.; Ward, S.C. The Cambridge structural database. *Acta Crystallographica Section B*, 2016, B72, pp. 171-179. DOI: <https://doi.org/10.1107/S2052520616003954>
- Yu, J.-H.; Wang, Z.-M.; Luo, X.-Z.; Du, H.-G. Synthesis, crystal structures and thermal stabilities of $[\text{Cu}(\text{bpp})_2(\text{bpdc})(\text{H}_2\text{O})_2]_n \cdot 2n\text{H}_2\text{O}$ and $[\text{Cu}(\text{bpp})_2]_n \cdot n(\text{tdc}) \cdot 7.5n\text{H}_2\text{O}$. *Chinese Journal of Chemistry*, 2008, 26(10), pp. 1826-1830. DOI: <https://doi.org/10.1002/cjoc.200890329>
- Luo, G.-G.; Xiong, H.-B.; Dai, J.-C. Syntheses, structural characterization, and properties of $\{[\text{Cu}(\text{bpp})_2(\text{H}_2\text{O})_2]_n(\text{tp}) \cdot 7\text{H}_2\text{O}\}$ and $\{[\text{Cu}(\text{bpp})_2(\text{H}_2\text{O})]_n(\text{ip}) \cdot 7\text{H}_2\text{O}\}$ complexes. New examples of the organic anionic template effect on induced assembly of water clusters (bpp= 1,3-bis(4-pyridyl)propane, tp= terephthalate, ip= isophthalate). *Crystal Growth & Design*, 2011, 11(2), pp. 507-515. DOI: [10.1021/cg1013208](https://doi.org/10.1021/cg1013208)
- Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. Jon Wiley & Sons: New York, 1978, 448 p. DOI: [10.1002/9780470405840](https://doi.org/10.1002/9780470405840)