

Crystal structures of $[\text{Cu}_2(2,2'\text{-bipyridine-N,N}')_2(\text{H}_2\text{O})_2(\mu_2\text{-OH})_2](\text{barbiturate})_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(2,2'\text{-bipyridine-N,N}')(\text{H}_2\text{O})(\text{barbiturate-O})\text{Cl}] \cdot 2\text{H}_2\text{O}$

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Abstract

Two mixed-ligand Cu(II) complexes $[\text{Cu}_2(\text{Bipy})_2(\text{H}_2\text{O})_2(\text{OH})_2](\text{Hba})_2 \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Cu}(\text{Bipy})(\text{H}_2\text{O})(\text{Hba})\text{Cl}] \cdot 2\text{H}_2\text{O}$ (**2**) (Bipy = 2,2'-bipyridine and Hba^- = barbiturate anion) were synthesized and structurally characterized by single crystal X-ray diffraction. In **1**, structural data revealed distorted square-pyramidal geometry for each of two crystallographic independent copper(II) atom with the basal plane formed by two nitrogen atoms of the 2,2'-bipyridine ligand and two oxygen atoms of bridging hydroxo groups. The apical positions are filled by the oxygen atoms from a water molecule. In **2**, the Cu atom is also in distorted square pyramidal geometry, where the equatorial sites are occupied by two N atoms of one Bipy ligand, one O atom of the barbiturate ion and one chloride ion and the apical position by one aqua ligand. Numerous intermolecular hydrogen bonds O–H \cdots O, N–H \cdots O, C–H \cdots O in the structures **1-2** and in addition O–H \cdots Cl, C–H \cdots Cl in the structure **2** form the 3D networks. Topological analysis showed that these H-bonded networks are new. An additional factor that plays a role in the crystal packing of the discussed complexes is the π – π stacking interaction between the aromatic rings of Hba^- and Bipy forming infinite chains –Hba–Bipy–Bipy–Hba–. The spectroscopic and thermal properties of compounds were analyzed.

Keywords: copper(II); barbituric acid; 2,2'-bipyridine; X-ray diffraction; thermal stability

Barbituric acid (H_2ba) and their derivatives are important groups of sedative/hypnotic drugs. The non-covalent interactions, such as hydrogen bonding and π - π stacking, are of great importance in the chemistry of barbiturate compounds. Barbiturate ligands have produced a variety of metal-organic frameworks with diverse topologies and interesting properties [1-3]. However, the crystal structure of the barbiturate complexes with metal ions has been the subject of only few reports [4-14]. Another well-known ligand in supramolecular chemistry is 2,2'-bipyridine (Bipy). Bipy used as auxiliary ligand is excellent candidate for the construction of novel mixed-ligand complexes, since it can form strong bonds with metal ions, and act as a hydrogen bond donor and acceptor, and the pyridine rings can interact to each other or other molecules with π - π stacking interactions [15].

Copper is part of redox-active metalloenzymes and is important for various cellular functions of the body [16]. It is expected that Cu(II) ion also will affect the medical activity of barbituric acid and its derivatives [4]. Therefore, data on the structure and properties of barbiturate copper(II) complexes may be useful for a better understanding of the copper effect on the activity of drugs. The principle interest of the present study is to investigate the solid-state structure of mixed-ligand Cu(II) complexes containing barbiturate anion, 2,2'-bipyridine, chloride ion, coordinated and uncoordinated water molecules. We describe here the synthesis and structures of two new mixed-ligand complexes, $[\text{Cu}_2(\text{Bipy})_2(\text{H}_2\text{O})_2(\text{OH})_2](\text{Hba})_2 \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Cu}(\text{Bipy})(\text{H}_2\text{O})(\text{Hba})\text{Cl}] \cdot 2\text{H}_2\text{O}$ (**2**), where, Hba^- = barbiturate anion. If in compound **1** the Hba^- ion is in the outer sphere, then in **2** it is directly connected with the copper(II) ion. Note that the hydroxo-bridged planar $[\text{Cu}_2(\mu_2\text{-OH})_2]$ core is an important structural unit to build numerous tri-, tetra- and hexa-nuclear Cu(II) complexes with interesting structures, magnetic properties [17-19] and biological activity [20].

The compounds **1** and **2** were prepared by reaction of Bipy, H_2ba with CuCO_3 or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ respectively in water (Scheme 1). The resulting solutions (pH 5-6) were allowed to stand open to the air at room temperature for several days. Large blue block-shaped crystals **1** and dark green rectangular crystals **2** were filtered off and dried in air to a constant mass. Thus, at pH 5-6, the coordination of chloride ions to Cu(II) proved to be more preferable than OH^- ions. The complexes were characterized by single-crystal and powder X-ray diffraction analysis, TG-DSC, and FT-IR. Reagents, syntheses, X-ray diffraction analysis, physical measurements are described in detail in the appendix.

The unit cell of **1** corresponds to triclinic symmetry. Space group $P-1$ was determined from the statistical analysis of reflection intensities. The main crystal data are enumerated in Table S1. The asymmetric unit contains two Cu^{2+} ions, two hydroxo bridging groups, two Bipy molecules, two Hba^- ions and three H_2O molecules (Fig. 1a). Each Cu^{2+} ion is coordinated by Bipy

molecule through two N atoms ($d(\text{Cu-N}) = 2.0023(1) - 2.0100(1) \text{ \AA}$), two OH^- ions ($d(\text{Cu-O}_{\text{OH}}) = 1.9272(1) - 1.9441(1) \text{ \AA}$) and one H_2O forming distorted square pyramid. The Cu-O_{Hba} distances ($2.9278(2) - 3.0725(3) \text{ \AA}$) are long and can be considered as short contacts [21]. The equatorial bonds at each Cu(II) centre comprise two bridging hydroxo oxygen atoms and Bipy nitrogen atoms, generating the N_2O_2 basal planes. The pair of the copper centers forms a four cornered planar Cu_2O_2 core where the two Bipy molecules are *trans* oriented with respect to the Cu_2O_2 core forming five-membered chelate rings with Cu(II). The axial position is occupied by the coordinated water molecule. The axial Cu-O_w distances ($2.356(2)$ and $2.4665(2) \text{ \AA}$) are quite longer than equatorial ones ($d(\text{Cu-O}) = 1.9272(1) - 1.9441(1) \text{ \AA}$) indicating stronger Cu-O-Cu interaction. The elongation of the apical bond length in complex **1** is of comparable magnitude to that observed in the previously reported complexes [18, 19]. The $\text{Cu1}\cdots\text{Cu2}$ distance $2.8644(5) \text{ \AA}$, the angles Cu1-O1w-Cu2 ($95.10(9)^\circ$) and Cu1-O2w-Cu2 ($95.99(9)^\circ$) are similar to those in compounds $[\text{Cu}_2(\text{Bipy})_2(\text{OH})_2(\text{HPO}_4)(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$ [18] and $[\text{Cu}_2(\text{Bipy})_2(\text{H}_2\text{O})(\text{OH})_2(\text{SO}_4)]\cdot 4\text{H}_2\text{O}$ [19]. The main bond lengths and valence angles of Hba^- and Bipy (Table S2) practically coincide with those found earlier in other barbiturate [4-14, 22, 23] and 2,2'-bipyridyl [18, 19, 24-27] compounds. The N-C-C-N torsion angles are $2.2(3)^\circ$ and $-0.4(4)^\circ$. The Bipy molecules are planar, the standard deviation of atoms from corresponding planes are 0.036 \AA for both of them. The N-Cu-N angles are $80.86(9)^\circ$ and $80.73(9)^\circ$ for two crystallographically unique Cu(II) centres, and fall within the range found for similarly coordinated bis- μ_2 -hydroxo-Cu(II) dimers containing Bipy [18, 19].

Sixteen intermolecular hydrogen bonds $\text{O-H}\cdots\text{O}$, $\text{N-H}\cdots\text{O}$ and $\text{C-H}\cdots\text{O}$ in the structure (Table S3) form a 3D network with well-developed 2D network depicted in Fig. 2a. There are several supramolecular motifs $\text{R}_2^2(8)$, $\text{R}_3^2(8)$, $\text{R}_4^3(10)$, $\text{R}_3^3(14)$ and $\text{R}_5^4(14)$ with small cycles can be marked in this 2D layer. Each of μ_2 -hydroxo group forms an intermolecular hydrogen bond to the uncoordinated Hba^- ion of C type (Fig. S1) forming the infinite chain along *a*-axis based on the $\text{C}_2^2(10)$ pattern. The Hba^- ions joint together forming chains along *a*-axis, and they are connected with $[\text{Cu}_2(\text{Bipy})_2(\text{H}_2\text{O})_2(\text{OH})_2]^{2+}$ cations through $\text{C-H}\cdots\text{O}$ hydrogen bonds, forming this 2D layer in *ac*-plane. These layers are linked with each other through $\text{O-H}\cdots\text{O}$ bonds along *b*-axis, and the O4w atoms of water molecules are involved in them. As in **1**, in four complexes of general formula $[\text{M}(\text{bpy})(\text{H}_2\text{O})_4](\text{Hba})_2\cdot 6\text{H}_2\text{O}$ (where $\text{M} = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+} , Zn^{2+} , and $\text{bpy} = 4,4'$ -bipyridine) Hba^- ions are in the outer sphere and they are bound by hydrogen bonds to the molecules of water and bpy [23]. Topological analysis of the net by ToposPro program [28], using simplification and excluding all 0-, 1- and 2-coordinated nodes revealed that this is a 6-nodal $(3\text{-c})(3\text{-c})(3\text{-c})(6\text{-c})(6\text{-c})(7\text{-c})$ net with point symbol $(3.4^3.5^5.6^9.7.8^2)(\{^2.4^4.5^4.6^5\}(4.6^2)(4^3.5^5.6^6.8)(5.6^2)_2$ which is new. Further analysis of interactions

in **1**) reveals π - π interactions between Bipy, Hba⁻ rings which form infinite chain ...-Hba-Bipy-Bipy-Hba-... along *b*-axis (Table S4, Fig. S2a).

The asymmetric unit cell of **2** contains one Cu²⁺ ion, one Bipy molecule, one Hba⁻ ion, one Cl⁻ ion and three water molecules (Fig. 1b). Square-pyramidal geometry about each copper atom is provided by two nitrogen donor atoms ($d(\text{Cu-N}) = 2.008(1)$ – $2.027(1)$ Å) from the Bipy ligand, one oxygen atom from Hba⁻ ion ($d(\text{Cu-O}_{\text{Hba}}) = 1.952(1)$ Å) and Cl⁻ ion ($d(\text{Cu-Cl}) = 2.2763(6)$ Å), which form the N₂OCl basal plane, and axially by an oxygen atom from coordinated H₂O molecule ($d(\text{Cu-O}_{1\text{w}}) = 2.222(1)$ Å). As in **1**, the axial Cu–O_{1w} distance is quite longer than equatorial Cu–O_{Hba} distance. The elongation of the apical bond length in complex **2** is of comparable magnitude to that observed in the previously reported complexes Cu(II) [24–27]. Elongation of the Cu–OH₂ bond leads to the formation of a distorted square pyramidal coordination geometry. In a single structurally characterized complex [Cu(H₂O)₃(Hba)₂] [4], containing Cu(II) and coordinated Hba⁻ ligand, the Cu(II) ion is in the distorted square-pyramidal geometry and the bond length Cu–O_{Hba} (1.952(1) Å) has the same value as in **2**. As in **1**, the main bond lengths and valence angles of Hba⁻ and Bipy in **2** practically coincide with those found earlier in other related compounds [15]. All the C–O distances in **1** and **2** (Table S2) are larger than those in free H₂ba [29], indicating the charge delocalization in the Hba⁻ ion, as in the case of other barbiturate complexes [4–14]. The higher $d(\text{O3B-C6B}) = 1.2834(17)$ Å value as compared with the smaller $d(\text{O1B-C2B}) = 1.2393(18)$ Å and $d(\text{O2B-C4B}) = 1.2567(19)$ Å values can be explained by the coordination of the ligand Hba⁻ to copper(II) *via* an O3B atom. The Bipy molecules are planar, the standard deviation of atoms from corresponding planes are 0.030 Å. The N–C–C–N torsion angle in Bipy is 5.7(2)°, and the N–Cu–N angle is 80.67(5)°. Ten intermolecular hydrogen bonds O–H \cdots O, N–H \cdots O, O–H \cdots Cl, C–H \cdots O and C–H \cdots Cl in the structure (Table S3) form a 3D network. One 2D net can be marked in the plane based on *c* and *a*–*b* vectors (Fig. 2b) and the shortest ring motifs in them are R₂²(8), R₃²(8), R₃²(10) and R₂²(12). Topological analysis [31] of **2** showed that this 3D net is a 3-nodal (3-c)(3-c)(11-c) net with the point symbol (3.4²)(3².4)(3⁶.4¹¹.5¹⁸.6¹⁴.7⁵.8), which is new. The π - π interactions between Bipy, Hba⁻ rings are presented in Fig. S2b and Table S4, and form infinite chain ...-Hba-Bipy-Bipy-Hba- along *a*–*b* direction.

The structural parameters defined by a single crystal analysis were used as base in the powder pattern Rietveld refinement. The refinement was produced using the TOPAS 4.2 program [30]. Low *R*-factor and good refinement results (Table S5, Fig. S3) indicate the phase purity of the powder samples **1** and **2**.

The d–d spectra of aqueous solutions exhibit a broad and featureless band centered at *ca.* 620 nm for **1** and 700 nm for **2**, which are consistent with the presence of a Cu(II) chromophore

with distorted square–pyramidal geometry [31]. This band is assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition of Cu(II) (d^9).

The IR spectra of **1** and **2** are significantly different from the spectra of starting materials (Fig. S4) and this indicates the formation of new compounds. The presence of Hba⁻ ion in compounds is confirmed by very strong bands at 1671 and 1685 cm^{-1} in IR spectra of **1** and **2** (Fig. S4, curve 3 and 4) respectively assigned to the stretching mode of CO in Hba⁻ ion [22, 32]. An intense band at 1600 cm^{-1} in IR spectra of **1-2** is attributed to the $\nu(\text{CC})/\nu(\text{CN})$ stretching modes of the pyridil ring [33]. A broad band in IR spectra of **1** centered at 3396 cm^{-1} is assigned to the $\nu(\text{OH})$ vibrations of μ_2 -hydroxo groups and water molecules. A broad band centered at 3431 cm^{-1} for **2** is assigned to the $\nu(\text{OH})$ vibrations of coordinated and uncoordinated water molecules.

Thermal decomposition of compounds **1** and **2** started with the release of water molecules. The water removal was confirmed by the IR spectroscopic analysis of released gases. The DSC and TG curves of **1** show two-step dehydration (Fig. S5) which is accompanied by two endo effects at 111.1 °C and 131.1 °C. An experimental weight loss (Δm) of 9.1% are observed between 65 and 150 °C, which corresponds to the release of the coordinated and uncoordinated water molecules ($-4\text{H}_2\text{O}$, $\Delta m_{\text{theor}} = 9.0\%$). A weak interaction between the Cu(II) and the axial H_2O molecule is supported by the long bond lengths of Cu–O_w (2.356(2) and 2.4665 (2) Å). The weight of sample remains unchanged up to ~175 °C, and there are no peaks in the DSC curve below this temperature. Compound **1** melts with the decomposition at $T > 175$ °C. These processes are accompanied by a weak endo effect at 206.7 °C and a strong exo effect at ~249 °C. Both the DSC and TG curves of **2** show one-step dehydration at 75–150 °C (Fig. 6S) which is accompanied by endo effect at ~130 °C. The dehydration step resulted in a 12.0% weight loss corresponding to the release of three water molecules per formula unit ($-3\text{H}_2\text{O}$, $\Delta m_{\text{theor}} = 11.9\%$). This corresponds to removal of both the coordinated and uncoordinated water molecules, suggesting a weak Cu–OH₂ bond. Breakdown of the organic components was initiated at ~220 °C and occurs in several steps. These processes are accompanied by a weak endo effect at ~260 °C and a strong exo effect at ~335 °C. According to the IR spectroscopic analysis of the gases evolved at $T > 175$ °C for **1** and $T > 220$ °C for **2**, CO₂, H₂O and NO are formed.

This work is part of our continuing efforts to study metal barbiturate chemistry from a synthetic and structural point of view [7, 10, 11]. Two novel mixed-ligand Cu(II) complexes containing the 2,2'-bipyridine and barbiturate ion are synthesized and characterized by single-crystal X-ray diffraction analysis. The dinuclear compound **1** and mononuclear complex **2** crystallize in the space groups $P-1$ and $C2/c$, respectively. Each copper(II) ion is penta-coordinated having distorted square pyramidal geometry. In **1**, the equatorial sites are occupied

by two N atoms of one Bipy ligand and two O atoms of different μ_2 -OH groups and the apical position by one aqua ligand. This forms a cationic dimer where two uncoordinated barbiturate ligands serve to balance the electrical charge. It is the first of structurally characterized compounds containing symmetric $[\text{Cu}_2(\text{Bipy})_2(\text{H}_2\text{O})_2(\mu_2\text{-OH})_2]^{2+}$ cation. An outstanding feature of **1** is the short Cu...Cu distance (2.8644 (5) Å). The equatorial sites in **2** are occupied by two N atoms of Bipy ligand, one O atom of Htba⁻ ion, one Cl⁻ ion and the apical position by one aqua ligand. As usual, the axial Cu–O distances in **1-2** are longer than equatorial ones. The structures of **1-2** are stabilized by the numerous intermolecular hydrogen bonds. Hba⁻ ions form infinite chains by N–H...O intermolecular hydrogen bonds (based on the R₂²(8) pattern) (Fig. 2a,b). In **1**, the μ_2 -hydroxo groups and uncoordinated Hba⁻ ions are bound by O–H...O_{Hba} intermolecular hydrogen bonds (Fig. S1) forming the infinite chain based on the C₂²(10) pattern. Results of topological analysis [28] demonstrate that these structures are new 3D networks. The π – π interactions between Bipy, Hba⁻ rings form infinite chain ...–Hba–Bipy–Bipy–Hba–... (Fig. S2). Thermal decomposition of **1** and **2** include dehydration, which mainly ends at 150 °C, and an organic ligand oxidation above 170 and 220 °C, respectively.

Supplementary data

The crystallographic data (excluding structure factors) for the structural analysis have been deposited with Cambridge Crystallographic Data Centre ((**1**) - CCDC # 1843895; (**2**) - CCDC # 1843896). The information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk).

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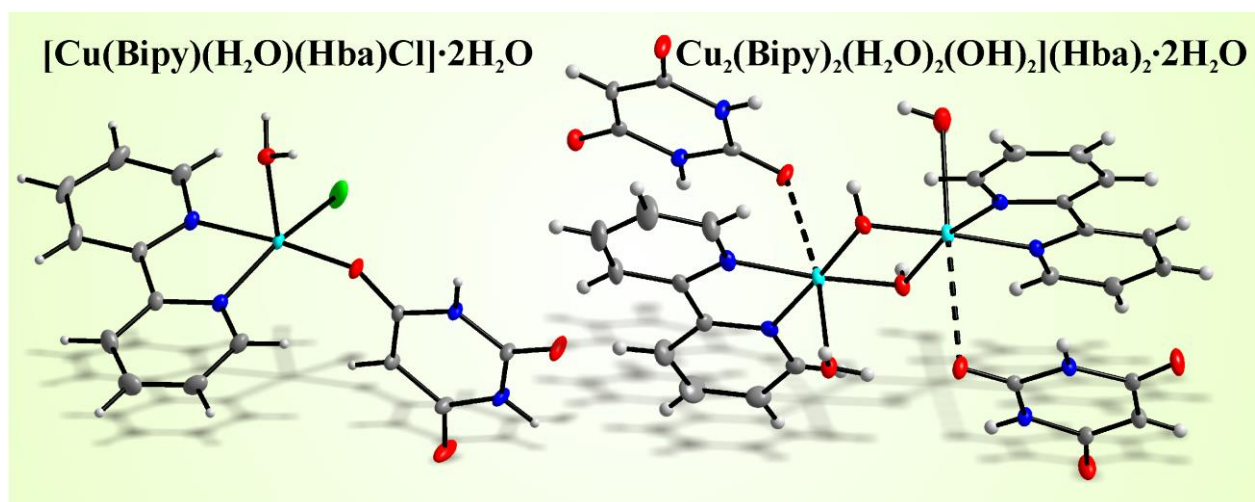
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Graphical Abstract



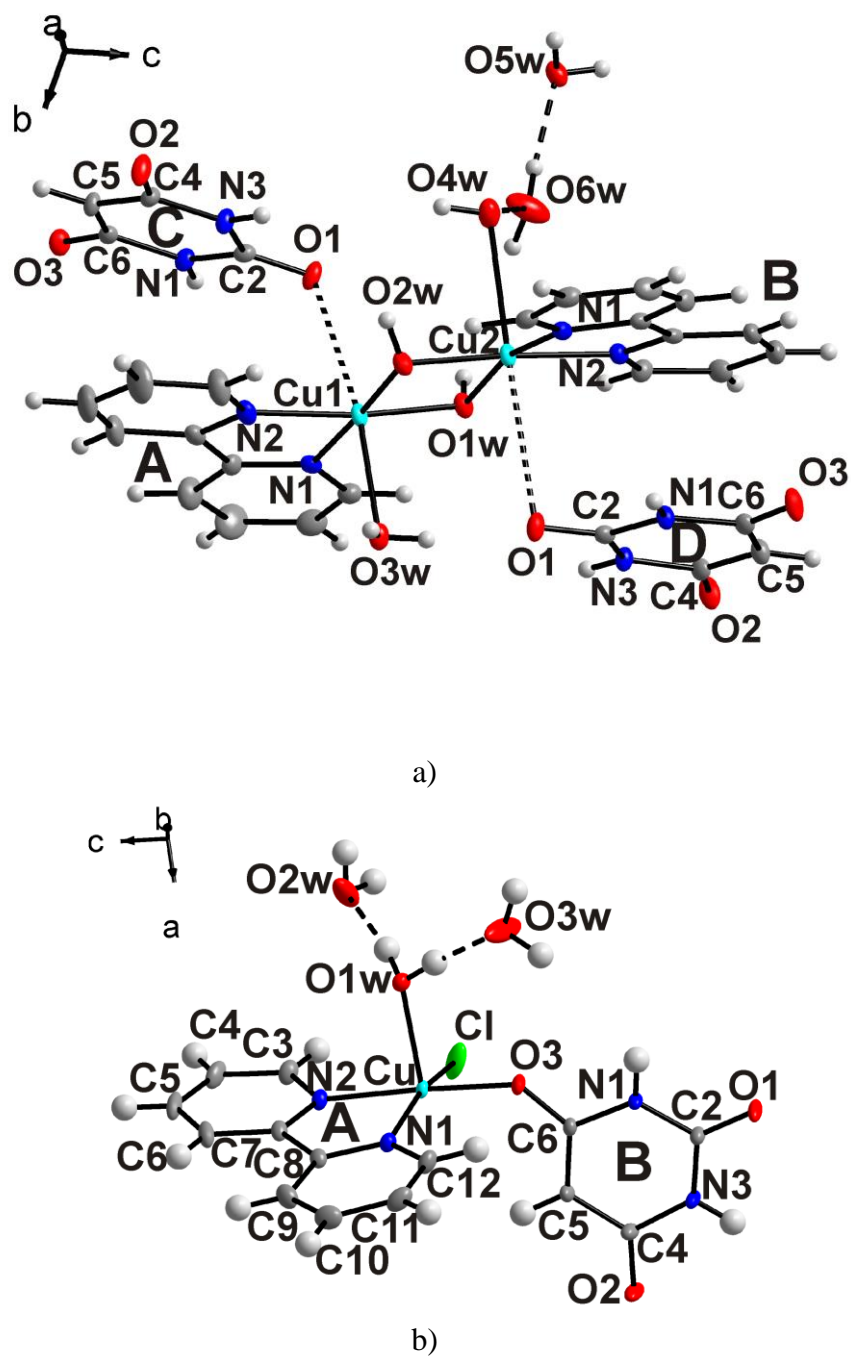
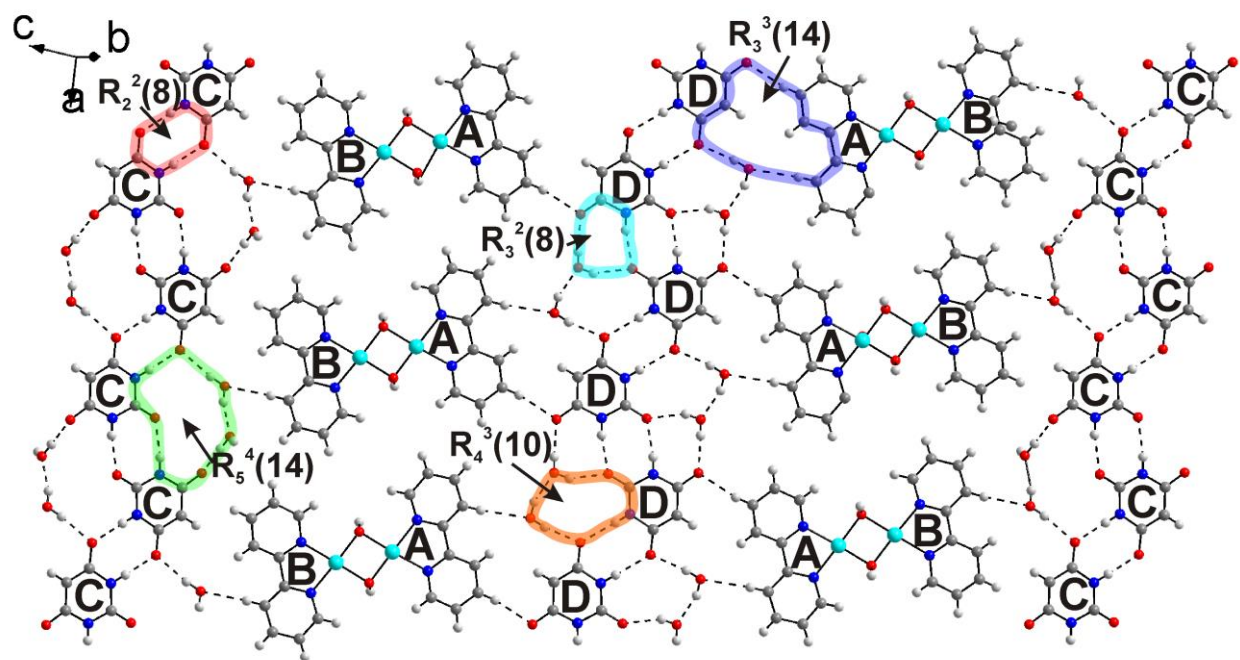
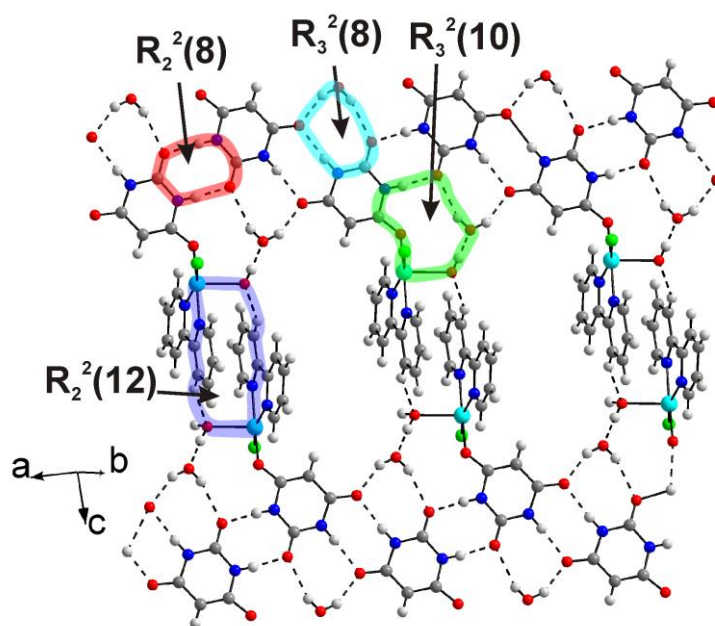


Figure 1. The asymmetric unit of the **1** (a), **2** (b) unit cell. Symmetry independent, different molecules are marked by A, B, C, D labels. Some most important atoms in the asymmetric unit are labeled. The intermolecular hydrogen bonds are represented by dashed lines. The ellipsoids are drawn at the 50% probability level, except for the hydrogen atoms represented by spheres.



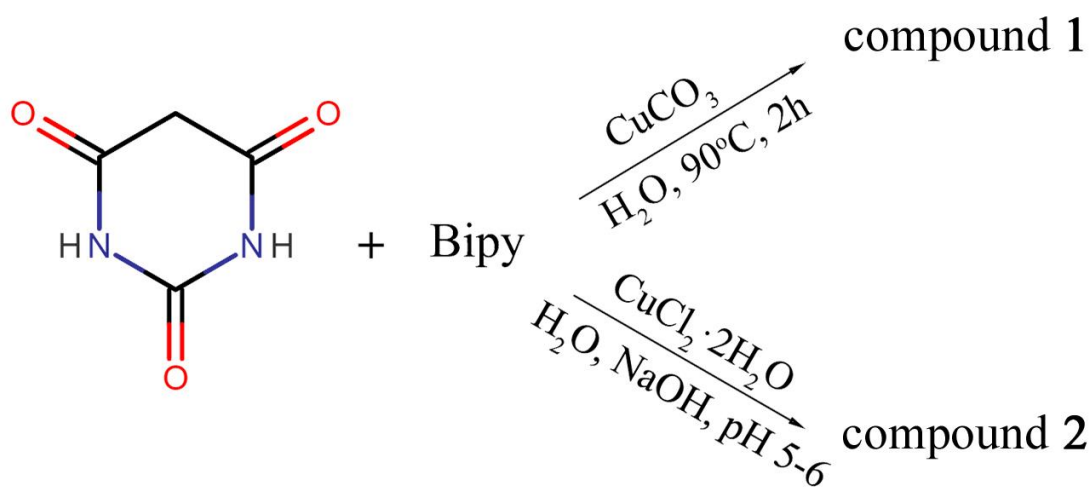
a)



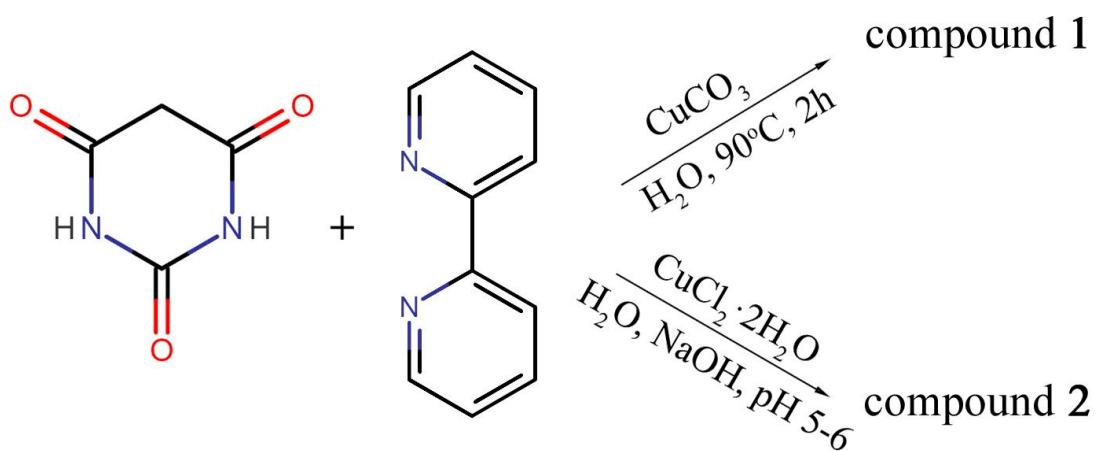
b)

Figure 2. Hydrogen bonding in **1** (a) and **2** (b). The H-bonds are marked by dashed lines, the H-bond motifs are marked by circles. Different ions/molecules are marked by A, B, C, D labels

Scheme 1



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