Crystal structures of $[Cu_2(2,2'\text{-bipyridine}-N,N')_2(H_2O)_2(\mu_2\text{-}OH)_2](\text{barbiturate})_2\cdot 2H_2O$ and $[Cu(2,2'\text{-bipyridine}-N,N')(H_2O)(\text{barbiturate}-O)Cl]\cdot 2H_2O$

Nicolay N. Golovnev[a], Maxim S. Molokeev[b,a,c*], Irina V. Sterkhova[d], Maxim K. Lesnikov[a]
[a] *Siberian Federal University, 79 Svobodny Ave., Krasnoyarsk 660041, Russia*
[b] *Laboratory of Crystal Physics, Kirensky Institute of Physics, Federal Research Center KSC SB RAS, bld. 38 Akademgorodok 50, Krasnoyarsk 660036, Russia*
[c] *Department of Physics, Far Eastern State Transport University, 47 Seryshev Str., Khabarovsk 680021, Russia*
[d] *Favorsky Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, 1 Favorsky, Irkutsk 664033, Russia*

[*] Corresponding author:
Maxim Molokeev
E-mail: msmolokeev@gmail.com
Laboratory of Crystal Physics, Kirensky Institute of Physics, Federal Research Center KSC SB RAS, bld. 38 Akademgorodok 50, Krasnoyarsk 660036, Russia
Tel.: +7-391-249-45-07

---

†Electronic supplementary information (ESI) available. See DOI:xxx

Abstract

Two mixed-ligand Cu(II) complexes $[Cu_2(Bipy)_2(H_2O)_2(OH)_2](Hba)_2\cdot 2H_2O$ (**1**) and $[Cu(Bipy)(H_2O)(Hba)Cl]\cdot 2H_2O$ (**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···O, N–H···O, C–H···O in the structures **1-2** and in addition O–H···Cl, C–H···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 forms 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, $[Cu_2(Bipy)_2(H_2O)_2(OH)_2](Hba)_2{\cdot}2H_2O$ (**1**) and $[Cu(Bipy)(H_2O)(Hba)Cl]{\cdot}2H_2O$ (**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 $[Cu_2(\mu_2\text{-}OH)_2]$ 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 $CuCl_2{\cdot}2H_2O$ 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(Cu–N) = 2.0023(1) – 2.0100 (1) Å), two OH^- ions (d(Cu–O_{OH}) = 1.9272 (1) – 1.9441 (1) Å) and one H_2O forming distorted square pyramid. The Cu–O_{Hba} distances (2.9278(2) – 3.0725 (3) Å) 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–Ow distances (2.356 (2) and 2.4665 (2) Å) are quite longer than equatorial ones ((d(Cu–O) = 1.9272 (1) – 1.9441 (1) Å) 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 Cu1···Cu2 distance 2.8644 (5) Å, the angles Cu1–O1w–Cu2 (95.10 (9)^o) and Cu1–O2w–Cu2 (95.99 (9)^o) are similar to those in compounds $[Cu_2(Bipy)_2(OH)_2(HPO_4)(H_2O)]\cdot 4H_2O$ [18] and $[Cu_2(Bipy)_2(H_2O)(OH)_2(SO_4)]\cdot 4H_2O$ [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)^o and –0.4(4)^o. The Bipy molecules are planar, the standard deviation of atoms from corresponding planes are 0.036 Å for both of them. The N–Cu–N angles are 80.86(9)^o and 80.73(9)^o 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 O–H···O, N–H···O and C–H···O in the structure (Table S3) form a 3D network with well-developed 2D network depicted in Fig. 2a. There are several supramolecular motifs $R_2^2(8)$, $R_3^2(8)$, $R_4^3(10)$, $R_3^3(14)$ and $R_5^4(14)$ 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 $C_2^2(10)$ pattern. The Hba^- ions joint together forming chains along *a*-axis, and they are connected with $[Cu_2(Bipy)_2(H_2O)_2(OH)_2]^{2+}$ cations through C–H···O hydrogen bonds, forming this 2D layer in *ac*-plane. These layers are linked with each other through O–H···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 $[M(bpy)(H_2O)_4](Hba)_2\cdot 6H_2O$ (where M = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and 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-c)(3-c)(3-c)(6-c)(6-c)(7-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 Cu^{2+} 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(Cu–N) = 2.008(1)–2.027(1) Å) from the Bipy ligand, one oxygen atom from Hba^- ion (d(Cu–O_{Hba}) = 1.952(1)Å) and Cl^- ion (d(Cu–Cl) = 2.2763(6) Å), which form the N_2OCl basal plane, and axially by an oxygen atom from coordinated H_2O molecule (d(Cu–O1w) = 2.222(1) Å). As in **1**, the axial Cu–O1w 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–OH_2 bond leads to the formation of a distorted square pyramidal coordination geometry. In a single structurally characterized complex $[Cu(H_2O)_3(Hba)_2]$ [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 H_2ba [29], indicating the charge delocalization in the Hba^- ion, as in the case of other barbiturate complexes [4-14]. The higher d(O3B–C6B) = 1.2834 (17) Å value as compared with the smaller d(O1B–C2B) = 1.2393 (18) Å and d(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···O, N–H···O, O–H···Cl, C–H···O and C–H···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 $R_2^2(8)$, $R_3^2(8)$, $R_3^2(10)$ and $R_2^2(12)$. 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 $(3.4^2)(3^2.4)(3^6.4^{11}.5^{18}.6^{14}.7^5.8)$, 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 ν(CC)/ ν(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 ν(OH) vibrations of μ_2-hydroxo groups and water molecules. A broad band centered at 3431 cm^{-1} for **2** is assigned to the ν(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 ºC and 131.1 ºC. An experimental weight loss (Δm) of 9.1% are observed between 65 and 150 ºC, which corresponds to the release of the coordinated and uncoordinated water molecules ($-4H_2O$, $\Delta m_{theor} = 9.0\%$). A weak interaction between the Cu(II) and the axial H_2O molecule is supported by the long bond lengths of Cu−Ow (2.356(2) and 2.4665 (2) Å). The weight of sample remains unchanged up to ~175 ºC, and there are no peaks in the DSC curve below this temperature. Compound **1** melts with the decomposition at T > 175 ºC. These processes are accompanied by a weak endo effect at 206.7 ºC and a strong exo effect at ~249 ºC. Both the DSC and TG curves of **2** show one-step dehydration at 75−150 ºC (Fig. 6S) which is accompanied by endo effect at ~130 ºC. The dehydration step resulted in a 12.0% weight loss corresponding to the release of three water molecules per formula unit ($-3H_2O$, $\Delta m_{theor} = 11.9\%$). This corresponds to removal of both the coordinated and uncoordinated water molecules, suggesting a weak Cu–OH_2 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 ºC and a strong exo effect at ~335 ºC. According to the IR spectroscopic analysis of the gases evolved at T > 175 ºC for **1** and T > 220 ºC for **2**, CO_2, H_2O 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 *C*2/*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 $[Cu_2(Bipy)_2(H_2O)_2(\mu_2\text{-}OH)_2]^{2+}$ 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 $R_2^2(8)$ 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 $C_2^2(10)$ 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 ºC, 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).

Acknowledgements

The study was carried out within the public task of the Ministry of Education and Science of the Russian Federation to the Siberian Federal University (4.7666.2017/BP) in 2017-2019. X-ray data from single crystals were obtained with use the analytical equipment of Baikal Center of collective use of SB RAS and with use the analytical equipment of Krasnoyarsk Center of collective use of SB RAS.

References

1. K. T. Mahmudov, M. N. Kopylovich, A. M. Maharramov, M. M. Kurbanova, A. V. Gurbanov, A. J. L. Pombeiro, Barbituric acids as a useful tool for the construction of coordination and supramolecular compounds, Coord. Chem. Rev. 265 (2014) 1−37.

2. M. Szostak, B. Sautier, M. Spain, M. Behlendorf, D.J. Procter, Selective reduction of barbituric acids using SmI_2/H_2O: synthesis, reactivity, and structural analysis of tetrahedral adducts, Angew. Chem. Int. Ed. 52 (2013) 12559– 12563.

3. M. Szostak, M. Spain, B. Sautier, J. Procter, Switching between reaction pathways by an alcohol cosolvent effect: SmI_2−ethylene glycol vs SmI_2−H_2O mediated synthesis of uracils, Org. Lett. 16 (2014) 5694–5697.

4. Y. Xiong, C. He, N.-C. An, C.-H. Cha, X.-H. Zhu, An approach to the structure and spectra of copper barbiturate trihydrate, Transition Metal Chem. 28 (2003) 69−73.

5. M. Gryl, Charge density and optical properties of multicomponent crystals containing active pharmaceutical ingredients or their analogues, Acta Crystallogr. B71 (2015) 392-405.

6. J.Chu, Z.Y. Liu, X.J. Zhao, E.C. Yang, The first barbiturate bridged manganese(II) polymer: synthesis, crystal structure, and magnetic properties, Russ. J. Coord. Chem. 36 (2010) 901-905.

7. N.N. Golovnev, L.A. Solovyov, M. K. Lesnikov, S.N. Vereshchagin, V.V. Atuchin, Hydrated and anhydrous cobalt (II) barbiturates: Crystal structures, spectroscopic and thermal properties Inorg. Chim. Acta. 467 (2017) 39-45.

8. D. Braga, F. Grepioni, G.I. Lampronti, L. Maini, A. Turrina, Ionic co-crystals of organic molecules with metal halides: a new prospect in the solid formulation of active pharmaceutical ingredients, Cryst. Growth Des. 11 (2011) 5621-5627.

9. D. Braga, F. Grepioni, L.Maini, G. I. Lampronti, D. Capucci, C. Cuocci, Structure determination of novel ionic co-crystals from powder data: the use of rigid fragments in simulated annealing algorithms, CrystEngComm. 14 (2012) 3521-3527.

10. L. A. Solovyov, N. N. Golovnev, M. S. Molokeev, M. K. Lesnikov, Bis(μ_3-barbiturato−O,O,O′)-(μ_2-aqua)-aqua-barium(II): crystal structure, spectroscopic and thermal properties, J. Coord. Chem. 70 (2017) 1884-1893.

11. N. N. Golovnev, M. S Molokeev, M. K. Lesnikov, S.N.Vereshchagin, Polymeric lithium(I) diaquabarbiturate: Crystal Structure, Russ. J. Inorg. Chem. 62 (2017) 746-750.

12. M. R. Chierotti, K. Gaglioti, R. Gobetto, D. Braga, F. Grepioni, L. Maini, From molecular crystals to salt co-crystals of barbituric acid via the carbonate ion and an improvement of the solid state properties, CrystEngComm. 15 (2013) 7598-7605.

13. M.Gryl, K.Stadnicka, Rubidium 2,4,6-trioxo-1,3-diazinan-5-ide–1,3-diazinane-2,4,6-trione–water (1/1/1), Acta Crystallogr. E67 (2011) m571-m572.

14. D. Braga, F. Grepioni, L. Maini, S. Prosperi, R. Gobetto, M. R.Chierotti, From unexpected reactions to a new family of ionic co-crystals: the case of barbituric acid with alkali bromides and cesium iodide, Chem. Commun. 46 (2010) 7715-7717.

15. Cambridge Structural Database, Univ. of Cambridge, Cambridge, UK, 2017.

16. H. B. Gray, J. S. Valentine, E. I. Stiefel, Biological inorganic chemistry: structure and reactivity, University Science Books, Sausalito, 2007. (не уверен на 100%)

17. V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, W.E. Hatfield, Relation between the singlet-triplet splitting and the copper-oxygen-copper bridge angle in hydroxo-bridged copper dimers, Inorg. Chem. 15 (1976) 2107-2110.

18. R. P. Doyle, M. Julve, F. Lloret, M. Nieuwenhuyzen, P. E. Kruger, Hydrogen-bond tuning of ferromagnetic interactions: synthesis, structure and magnetic properties of polynuclear copper(II) complexes incorporating p-block oxo-anions, Dalton Trans. 17 (2006) 2081-2088.

19. Y.-Q. Zheng, J.-L. Lin, Crystal Structures of $[Cu_2(bpy)_2(H_2O)(OH)_2(SO_4)] \cdot 4H_2O$ and $[Cu(bpy)(H_2O)_2]SO_4$ with bpy = 2,2-Bipyridine, Z. Anorg. Allg. Chem. 629 (2003) 1622-1626.

20. M. Iqbal, S. Ali, M. N. Tahir, N.A. Shah, Dihydroxo-bridged dimeric Cu(II) system containing sandwiched non-coordinating phenylacetate anion: crystal structure, spectroscopic, anti-bacterial, anti-fungal and DNA-binding studies of $[(phen)(H_2O)Cu(OH)_2Cu(H_2O)(phen)]2L.6H_2O$:(HL= phenylacetic acid; phen= 1, 10-phenanthroline), J. Mol. Struct. 1143 (2017) 23-30.

21. M. A. Halcrow, Jahn–Teller distortions in transition metal compounds, and their importance in functional molecular and inorganic materials, Chem. Soc. Rev. 42 (2013) 1784-1795.

22. H. C. Garcia, F. B. de Almeida , R. Diniz, M. I. Yoshida, L. F. C. de Oliveira, Supramolecular structures of metal complexes containing barbiturate and 1, 2-bis (4-pyridyl)-ethane, J. Coord. Chem. 64 (2011) 1125-1138.

23. H. C. Garcia, R. Diniz, M. I. Yoshida, L. F. C. de Oliveira, An intriguing hydrogen bond arrangement of polymeric 1D chains of 4,4′-bipyridine coordinated to Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions having barbiturate as counterions in a 3D network, CrystEngComm. 11 (2009) 881-888.

24. J.-H Zhao, Y.-X. Lin, W. Wu, Z. Zhang, [μ-2, 2′-(1, 4-Phenylene) diacetato-κ2O1: O4] bis [aqua (2, 2′-bipyridine-κ2N, N′) chloridocopper (II)] dihydrate, Acta Crystallogr. E68 (2012) m1114- m1114.

25. Y. Liu, Y.-L. Feng, D.-Z. Kuang, Triaqua-1κO, 2κ2O-bis (2, 2′-bipyridine)-1κ2N, N′; 2κ2N, N′-chlorido-1κCl-μ-terephthalato-1: 2κ2O1: O4-dicopper (II) nitrate monohydrate, Acta Crystallogr. E68 (2012) m746- m747.

26. V. Shivaiah, M. Nagaraju, S.K. Das, Formation of a spiral-shaped inorganic−organic hybrid chain, $[Cu^{II}(2,2'\text{-bipy})(H_2O)_2Al(OH)_6Mo_6O_{18}]_n^{n-}$: influence of intra- and interchain supramolecular interactions, Inorg. Chem. 42 (2003) 6604-6606.

27. K. D. Demadis, A. Panera, Z. Anagnostou, D. Varouhas, A. Kirillov, I. Cisarova, Disruption of “coordination polymer” diarchitecture in Cu^{2+} bis-phosphonates and carboxyphosphonates by use of 2,2′-bipyridine as auxiliary ligand: structural variability and topological analysis, Cryst. Growth Des. 13 (2013) 4480-4489.

28. V. A. Blatov, A. P. Shevchenko, D. M. Proserpio, Applied topological analysis of crystal structures with the program package ToposPro, Cryst. Growth Des. 14 (2014) 3576-3586.

29. T. C. Lewis, D. A. Tocher, S. L. Price, An experimental and theoretical search for polymorphs of barbituric acid: The challenges of even limited conformational flexibility, Cryst. Growth Des. 4 (2004) 979-987.

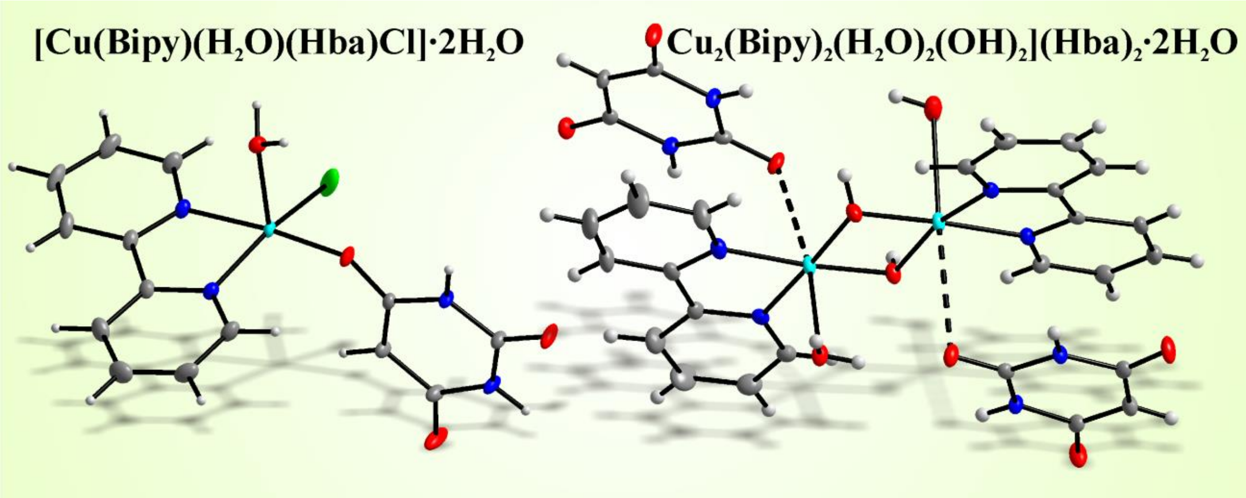
30. Bruker AXS TOPAS V4: General profile and structure analysis software for powder diffraction data. – User’s Manual, Bruker AXS, Karlsruhe, Germany, 2008.

31. A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1968.

32. N. N. Golovnev, M. S. Molokeev, M. K. Lesnikov, I. V. Sterkhova, V. V. Atuchin, Thiobarbiturate and barbiturate salts of pefloxacin drug: growth, structure, thermal stability and IR-spectra, J. Mol. Struct. 1149 (2017) 367-372.

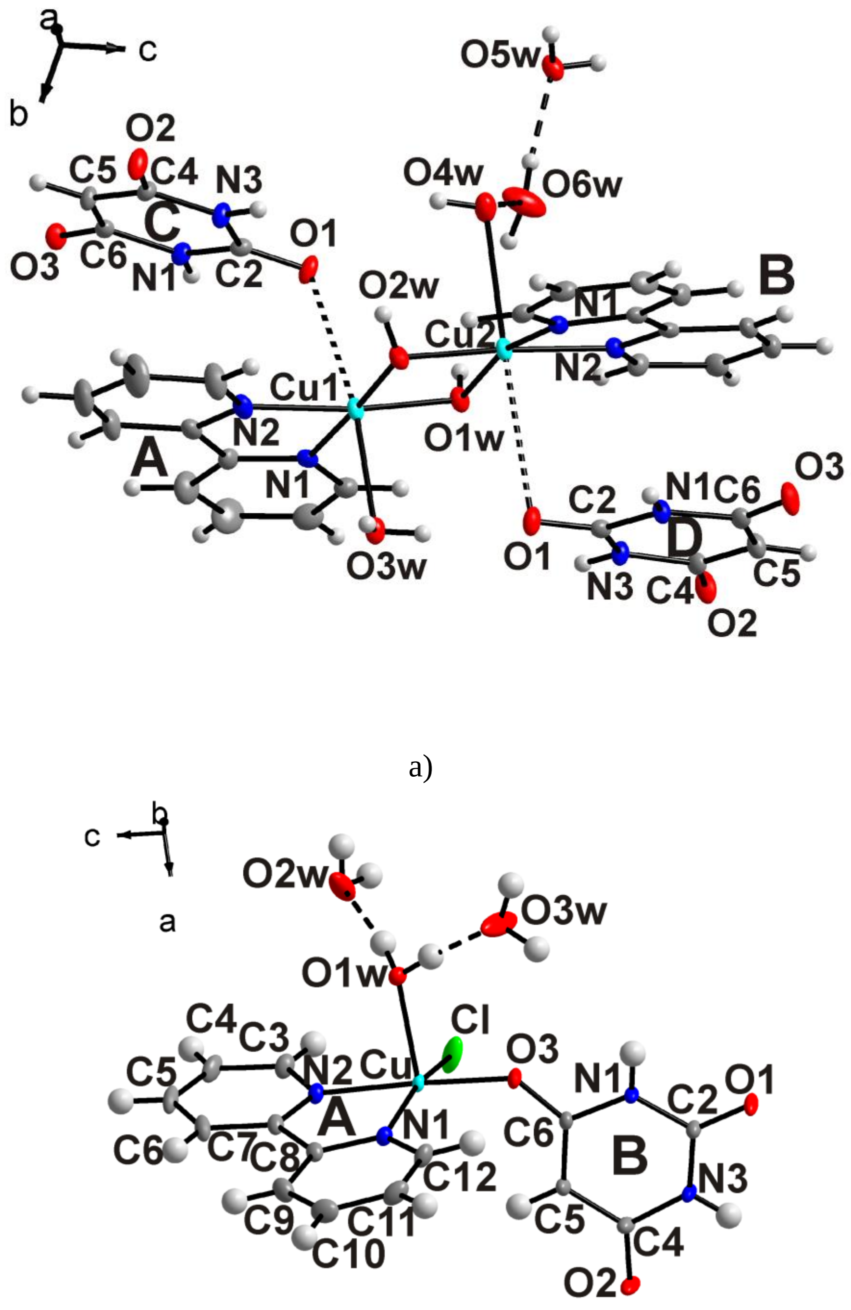
33. T. P. Gerasimova, S. A. Katsyuba, Bipyridine and phenanthroline IR-spectral bands as indicators of metal spin state in hexacoordinated complexes of Fe(II), Ni(II) and Co(II), Dalton Trans. 42 (2013) 1787-1797.

Graphical Abstract



$[Cu(Bipy)(H_2O)(Hba)Cl]\cdot 2H_2O$

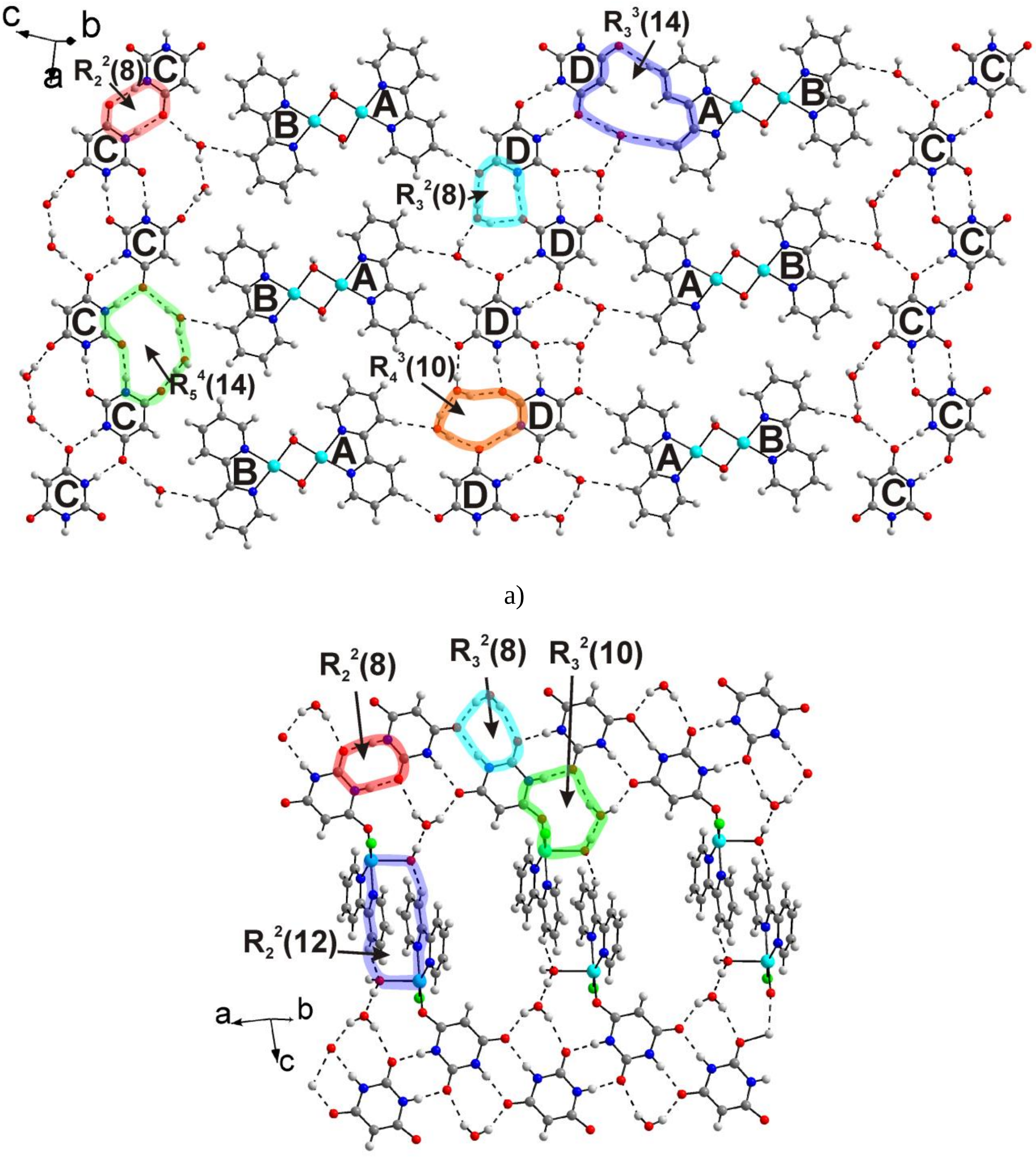
$Cu_2(Bipy)_2(H_2O)_2(OH)_2](Hba)_2\cdot 2H_2O$



a)

b)

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.

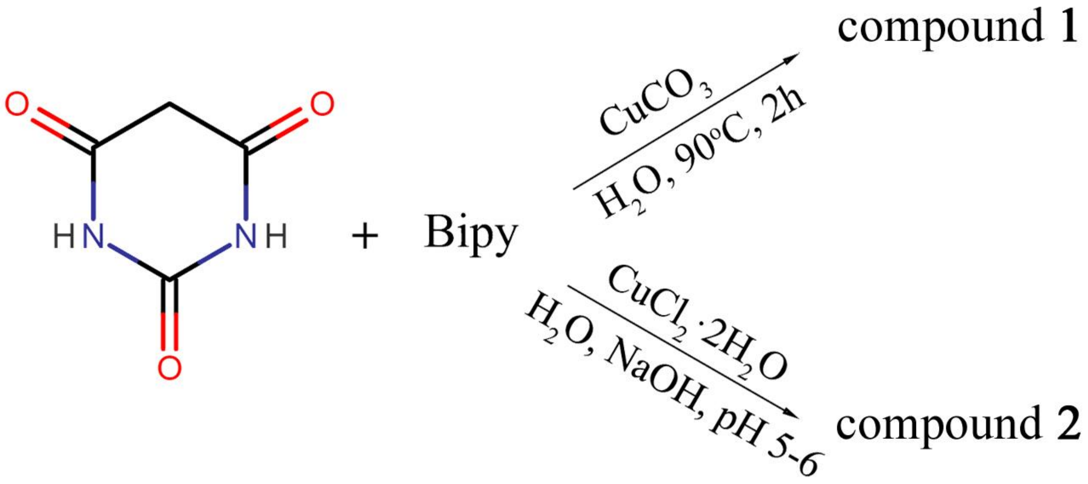


a)

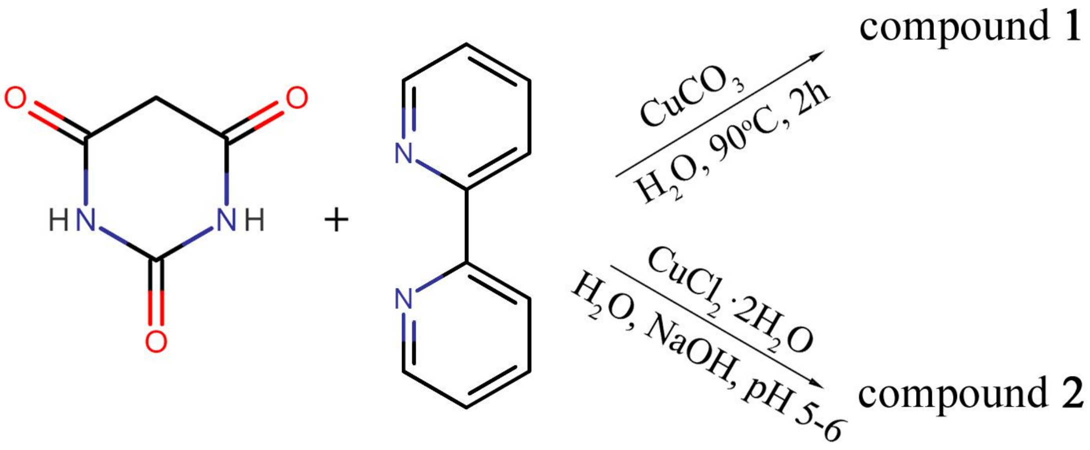
b)

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

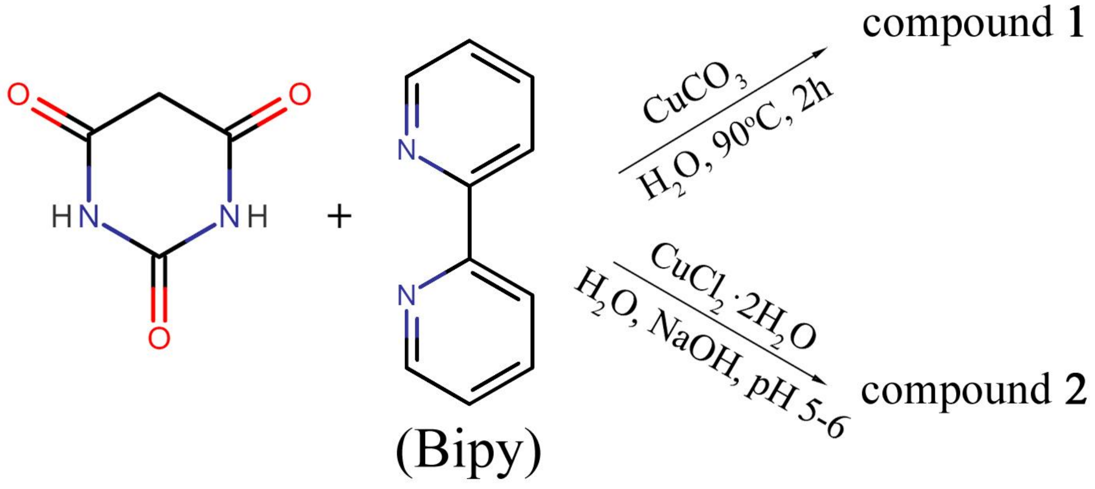
Scheme 1



Или



Или


HN
NH
(Bipy)
CuCO3
H2O, 90ºC, 2h
compound **1**
CuCl2·2H2O
H2O, NaOH, pH 5-6
compound **2**