КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURES OF TWO NEW Cu(II) COMPLEXES

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Two new copper (II) complexes $[Cu(2\text{-}Pic)_2(4\text{-}NPA)_2]$ (**1**) and $[Cu(2\text{-}Pic)_2] \cdot 2H_2O$ (**2**), where 2-Pic is 2-picolinic acid and 4-NPA is 4-nitrophenylamine, are synthesized hydrothermally and their crystal structures are determined and analyzed. Complex **1** is crystallized in the monoclinic system space group $P2_1/c$ and complex **2** is in the triclinic system space group P-1. Single crystal X-ray analysis reveals that the coordination environments around the Cu atoms of two complexes are four-coordinated and six-coordinated respectively. Complex **1** forms a 2D layer of a supermolecular structure through hydrogen bonds, and complex **2** is a 1D stair-stepping polymer chain and two water molecules linked by a hydrogen bond intersperse among the chains.

K e y w o r d s: copper complex, crystal structure, 2-picolinic acid, 4-nitrophenylamine, synthesis.

Currently, much interests have been paid to the constructions of inserting metal ions into organic ligands and to the designing of coordination complexes with specific geometric configurations [1—3]. Copper is an essential element for life; it exists in some native enzymes and is required by all organisms. Due to the important biological relevance of copper complexes, they have been reported more and more in recent years [4—6]. Copper(II) complexes are also of interest due to their capabilities in catalysis, selective separation processes, light-to-energy conversion, electrochemical properties, biological activities, and magnetism, etc. [7—9]. Self-assembly of building components is an effective approach to construct metal-organic frameworks. Generally speaking, strong metal-ligand coordination bonds, metal-metal bonds, weak hydrogen bonds, and π—π stacking interactions have been a protocol to afford multidimensional metal-organic supramolecular entities [10]. We are interested in these approaches for constructing functional polymers through the variabilities of ligand backbones and metal ion coordination environments [11].

In this paper, we reported the syntheses and crystal structures of two new copper(II) complexes with 2-Pic and 4-NPC as ligands. In complex **1**, the Cu(II) ion coordinates to two O and two N atoms from two 2-Pic, while in complex **2**, the Cu(II) ion coordinates to four O and two N atoms from 2-Pic ligands.

EXPERIMENTAL

Materials and physical measurements. All analytical reagents were purchased from commercial sources and used without further purification. Elemental analysis of C, H, and N were performed on a Vario EL III elemental analyzer.

Synthesis of [Cu(2-Pic)₂(4-NPC)₂] (1). CuI (0.0198 g, 0.1 mmol) was added to the MeCN (4 ml) solution containing 2-pyridinecarboxaldehyde (0.1 mmol) and 4-NPC (0.0138 g, 0.1 mmol). While stirring, 4 ml of water were added. The mixture was stirred for 30 min before it was transferred to a 25 ml Teflon-lined stainless steel autoclave and heated to 120 °C for 72 hours. Then it was cooled to room temperature at a rate of 5 °C·h⁻¹. Green columnar crystals of complex **1** were obtained and collected, washed with distilled water and then dried in air. Yield: 45 %. Elemental analyses: chemical formula [$C_{24}H_{20}CuN_6O_8$]; calculated, %: C 49.36, H 3.45, N 14.39; found, %: C 49.33, H 3.47, N 14.4. In addition, a small amount of blue tabular crystals of complex **2** were also obtained in a 10 % yield.

Synthesis of [Cu(2-Pic)₂]·2H₂O (2). A mixture of CuI (0.0384 g, 0.2 mmol), 2-pyridinecarboxal-dehyde (0.2 mmol), acetonitrile (4 ml), and distilled water (4 ml) was sealed in a 25 ml Teflon-lined stainless steel container under autogenous pressure and heated at 120 °C for 72 hours and then cooled to room temperature at a rate of 5 °C·h⁻¹. Blue tabular crystals were collected, washed with distilled water, and then dried in air. Yield: 35 %. Elemental analyses: chemical formula [$C_{12}H_{12}CuN_2O_6$]; cal-culated, %: C 41.92, H 3.52, N 8.12; found, %: C 41.94, H 3.51, N 8.08.

The CuI and 2-pyridinecarboxaldehyde were used in the synthesis of complexes **1** and **2**, but Cu(II) and 2-Pic were found in the two complexes from the crystal structural analysis. This may be due to that CuI and 2-pyridinecarboxaldehyde were oxidized by air before they were transferred to the Teflon-lined stainless steel autoclave [12, 13].

Single crystal X-ray diffraction analysis. Suitable single crystals with the dimensions of 0.30×0.27×0.22 mm and 0.18×0.10×0.08 mm of two complexes were selected for the single crystal X-ray diffraction analysis. The crystallographic data sets were collected on a Bruker SMART CCD diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). Absorption corrections were performed by using the SADABS program [14]. The structures were solved by a direct method

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*Crystallographic data for complexes **1** and **2***

Formula	$C_{24}H_{20}CuN_6O_8$	$C_{12}H_{12}CuN_2O_6$
Molar weight, g/mol	584.0	343.78
Crystal system	Monoclinic	Triclinic
Space group; Z	$P2_1/c$; 2	P-1; 1
Wavelength, Å	0.71073	0.71073
Temperature, K	293(2)	296(2)
a, b, c, Å	13.8985(19), 12.2176(17), 7.1753(10)	5.134(3), 7.646(4), 9.247(5)
α, β, γ, deg.	90.000(0), 99.134(2), 90.000(0)	74.928(7), 84.392(7), 71.464(8)
V, Å³	1203.0(3)	332.3(3)
Range of h, k, l	–17/17, –15/11, –9/8	–6/5, –7/9, –10/10
2θ range, deg.	1.48—26.86	2.28—24.99
d_{calc}, g/cm³	1.612	1.698
$F(000)$	598	171
Reflections collected / unique	6591 / 2531 (R(int) = 0.0251)	1662 / 1155 (R(int) = 0.0119)
Max. and min. transmission	0.8146 and 0.7592	0.8778 and 0.7528
Data / restraints / parameters	2531 / 0 / 178	1155 / 0 / 97
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final R indices $I > 2\sigma(I)$	$R_1 = 0.0382$, $wR_2 = 0.1139$	$R_1 = 0.0363$, $wR_2 = 0.1097$
R indices (all data)	$R_1 = 0.0505$, $wR_2 = 0.1314$	$R_1 = 0.0425$, $wR_2 = 0.1266$
Goodness-of-fit on F^2	1.104	1.199
Absorption coefficient, mm⁻¹	0.972	1.672
Largest diff. peak and hole, e/Å	0.334 and –0.479	0.738 and –0.649

T a b l e   2

Selected bond lengths (Å) *and bond angles* (deg.) *of complexes* **1** *and* **2**

Parametr	Complex **1**		Complex **2**	
Bond lengths	Cu(1)—O(3)	1.9471(17)	Cu(1)—O(1)	1.946(3)
	Cu(1)—N(3)	1.966(2)	Cu(1)—N(1)	1.964(3)
	Cu(1)—N(1)	2.8063(27)	Cu(1)—O(2)#1	2.764(4)
Bond angle	O(3)#1—Cu(1)—N(3)	96.65(8)	O(1)—Cu(1)—N(1)	83.79(12)
	O(3)—Cu(1)—N(3)	83.35(8)	O(1)—Cu(1)—N(1)#1	96.21(12)
	N(1)—Cu(1)—N(3)	95.73(82)	O(1)—Cu(1)—O(2)#1	85.12(10)
	N(1)—Cu(1)—O(3)#1	89.66(79)	N(1)—Cu(1)—O(2)#1	90.60(10)
	N(1)—Cu(1)—O(3)	90.34(79)	N(1)#1—Cu(1)—O(2)#1	90.60(11)
	N(1)—Cu(1)—N(3)#1	84.28(82)	O(1)#1—Cu(1)—O(2)#1	94.88(10)

Symmetry transformations used to generate equivalent atoms: For **1**: #1 $-x+1, -y, -z+1$; For **2**: #1 $-x+1, -y+1, -z$.

and refined by the full-matrix least-squares techniques using the SHELXL-97 program [15]. The crystallographic data and experimental details for structural analysis of the two complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2. The hydrogen bond distances and bond angles are given in Table 3. The CIF files containing complete information on the studied structure were deposited with CCDC, deposition number are 931051 and 931052 for complex **1** and **2** respectively.

RESULTS AND DISCUSSION

Description of the crystal structure of complex 1. Single crystal X-ray analysis reveals that complex **1** is in the monoclinic system space group $P2_1/c$. From the coordination environment of the Cu(II) ion, we can see that the Cu(II) ion lies in the center of symmetry and adopts a *trans* square-planar configuration in the equatorial plane, coordinated by two O and two N atoms from 2-Pic ligands, with the bond lengths of Cu1—O3, Cu1—N3 being 1.9471(17) Å and 1.966(2) Å and bond angles of O3—Cu1—N3 and O3A—Cu1—N3 being 83.35(8)° and 96.65(8)° respectively. Additionally, there exist weak interactions between the Cu(II) ion and two amino nitrogen atoms of 4-NPC (N1—Cu1 = 2.8063(27) Å) from the axial position due to π—π stacking (3.6765(4)) between the neighboring 4-NPC and 2-Pic ligands. The most remarkable structural feature of **1** is the hydrogen bond (N1—H···O4) involving the amino group of the 4-NPC molecule and 2-Pic molecule (Fig. 1, *b* and Table 3), which leads to a 2D network structure.

Description of the crystal structure of complex 2. X-ray crystallography analysis shows that complex **2** is in the triclinic system space group *P*-1, and reveals the presence of a stair-stepping chain

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Hydrogen bonds in complex **1** (Å *and* deg.)

D—H···A	d(D—H)	d(H···A)	d(D···A)	$\angle$(DHA)
N(1)—H(1B)···O(4)#2	0.86	2.38	3.233(3)	171.8
N(1)—H(1A)···O(4)#3	0.86	2.18	2.933(3)	146.7

Symmetry transformations used to generate equivalent atoms: #2 $-x+1$, $y-1/2, -z+1/2$; #3 $x, -y+1/2, z-1/2$.
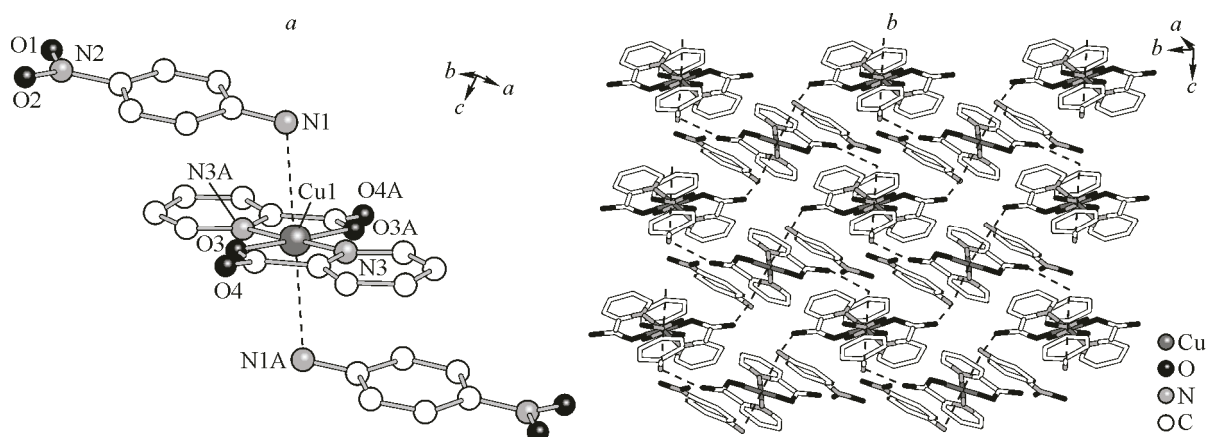
Fig. 1. View of the coordination environment of the Cu(II) ion in complex **1** (*a*); view of the 2D supramolecular network formed by hydrogen bonds N1—H⋯O4 (weak interaction and hydrogen bonds are shown in orange dashes and green dashes, respectively; hydrogen atoms are omitted for clarity) (*b*).
Symmetry code: A = –*x*+1, –*y*, –*z*+1

containing the copper(II) ion in an elongated octahedral geometry. The Cu(II) is coordinated octahedrally by two nitrogen and two oxygen atoms from two 2-Pic ligands in the equatorial plane, and the other two oxygen atoms from two 2-Pic ligands occupy the axial positions (Fig. 2, *a*). The Cu1—O2A bond length (2.7636(36) Å) is significantly longer than Cu1—O1 (1.947(3) Å) and Cu1—N1
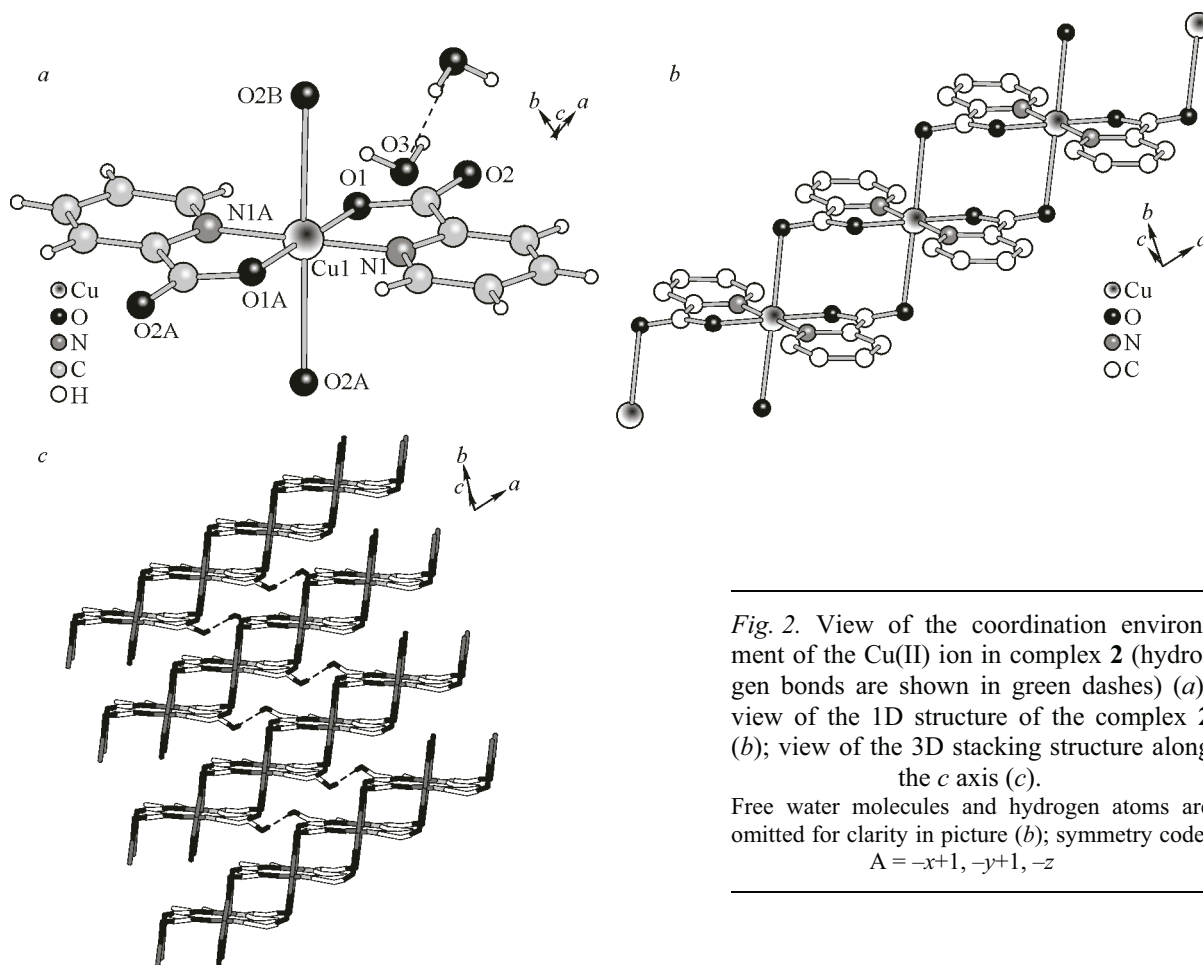

Fig. 2. View of the coordination environment of the Cu(II) ion in complex **2** (hydrogen bonds are shown in green dashes) (*a*); view of the 1D structure of the complex **2** (*b*); view of the 3D stacking structure along the *c* axis (*c*).
Free water molecules and hydrogen atoms are omitted for clarity in picture (*b*); symmetry code: A = –*x*+1, –*y*+1, –*z*

(1.965(3) Å), suggesting that Cu1—O1 is a weak coordination interaction [16] in the axial position and the Cu(II) ion adopts an elongated octahedral coordination environment. There also exist the C—H⋯π stacking (3.4169(14) Å) interactions between the neighboring ligands. In addition, there are two free water molecules in the crystal lattice, and weak hydrogen bond interactions exist between the two water molecules. The carboxyl O atoms of the axial positions bridge the complex to a 1D stair-stepping coordination polymer (Fig. 2, *b*). A quadrilateral porous of 2.7636×3.9358 Å^2 are formed along the 1D chain. The 3D stacking of the 1D chains along the *ab* plane show that these chains are arranged in parallel, and water molecules exist among them (Fig. 2, *c*).

Compared with complex **1**, where the Cu(II) ion is coordinated by two O and two N atoms from 2-Pic and there are weak interactions between the Cu(II) ion and two amino nitrogen atoms of 4-NPA, the Cu(II) ion in complex **2** is coordinated by four O atoms and two N atoms from only 2-Pic ligands. The bond lengths of the axial position in complex **1** are slightly longer than those in complex **2**, due to the different atoms coordinated to Cu(II) and the different π—π stacking interaction.

In conclusion, two new Cu(II) complexes have been prepared and characterized structurally. Complex **1** forms a 2D supermolecular structure through hydrogen bonds among quadrilateral Cu(II) complex molecules coordinated by 2-Pic ligands. In complex **2**, Cu(II) ion is six-coordinated by 2-Pic ligands and the O atoms from carboxyl groups of 2-Pic bridge the complex molecules into a 1D coordination polymer.

REFERENCES

 1. *Desiraju G.R.* // Angew. Chem. Int. Ed. Engl. – 1995. – **34**. – P. 2311 – 2327.
 2. *Yaghi O.M., Li G.* // Angew. Chem. Int. Ed. Engl. – 1995. – **34**. – P. 207 – 209.
 3. *Yaghi O.M., Li H.* // J. Amer. Chem. Soc. – 1995. – **117**. – P. 10401 – 10402.
 4. *Wu Z., Lu Z., Yen Z.* // Trans. Met. Chem. – 1993. – **18**. – P. 291 – 296.
 5. *Basak S., Sen S., Mitra S. et al.* // Struct. Chem. – 2008. – **19**. – P. 115 – 121.
 6. *Li Z.X., Zhang X.L.* // Acta Crystalllogr. – 2008. – **E64**. – P. m216.
 7. a) *Scarpellini M., Neves A., Castellano E.E.* // Polyhedron. – 2004. – **23**. – P. 511 – 518; b) *Lah N., Clérac R.* // Polyhedron. – 2009. – **28**. – P. 2466 – 2472; c) *Naskar J.P., Biswas C., Guhathakurta B.* // Polyhedron. – 2011. – **30**. – P. 2310 – 2319.
 8. *Fujita M., Kwon Y.J., Washizu S.* // J. Amer. Chem. Soc. – 1994. – **116**. – P. 1151 – 1152.
 9. *Çolak A.T., Çolak F., Akduman D.* // Solid State Sci. – 2009. – **11**. – P. 1908 – 1918.
10. a) *MacDonald J.C., Dorrestein P.C., Pilley M.M. et al.* // J. Amer. Chem. Soc. – 2000. – **122**. – P. 11692 – 11702; b) *Noveron J.C., Lak M.S., Del Sesto R.E.* // J. Amer. Chem. Soc. – 2002. – **124**. – P. 6613 – 6625.
11. *Bose D., Mostafa G., Fun H.-K., Ghosh B.K.* // Polyhedron. – 2005. – **24**. – P. 747 – 758.
12. *Jørgensen B., Christiansen S.E., Thomsen M.L.D., Christensen C.H.* // J. Catal. – 2007. – **251**. – P. 332 – 337.
13. *Mannam S., Sekar G.* // Tetrahedron Lett. – 2008. – **49**. – P. 1083 – 1086.
14. *Sheldrick G.M.* SHELXL-97, Program for Crystal Structure Solution, Refinement, version 5.1, University of Göttingen, Germany, 1997.
15. *Sheldrick G.M.* SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1996.
16. *Miroslav B., Marián V. et al.* // Inorg. Chim. Acta. – 2003. – **349**. – P. 111 – 122.