Copper(II) Complexes with 3- and 6-hydroxypicolinic Acid. Preparation, Structural, Spectroscopic and Thermal Study

Boris-Marko Kukovec,[a] Zora Popović[a],* and Gordana Pavlović[b]

[a]*Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia*

[b]*Laboratory of General Chemistry, Department of Applied Chemistry, Faculty of Textile Technology, University of Zagreb, Prilaz baruna Filipovića 28a, HR-10000 Zagreb, Croatia*

* *Corresponding author: E-mail: zpopovic @chem.pmf.hr*
Fax: +385-1-4606341,   Tel. +385-1-4606354

Dedicated to the memory of Professor Ljubo Golič

Abstract

Copper(II) complexes of 3-hydroxypicolinic acid (3-OHpicH), namely [Cu(3-OHpic)$_2$] (**1**), [Cu(3-OHpic)$_2$(4-pic)] (**2**) and of 6-hydroxypicolinic acid (6-OHpicH), namely [Cu(6-OHpic)$_2$(H$_2$O)$_2$] (**3**) and [Cu(6-OHpic)$_2$(4-pic)$_2$] (**4**) were prepared and characterized by IR spectroscopy and thermal analysis (TGA/DTA). Molecular and crystal structures of **2** and **4** were determined by X-ray crystal structure analysis. Complexes **1** and **3** were prepared by reaction of copper(II) sulfate pentahydrate with 3-hydroxypicolinic and 6-hydroxypicolinic acid, respectively, in aqueous solution, while **2** and **4** were prepared by recrystallization of **1** and **3** from 4-picoline solution. Structure analysis revealed square-pyramidal copper(II) coordination in **2**. Copper(II) ion is coordinated by two 3-OHpic ligands in the basal plane of square pyramid and by 4-picoline molecule in the axial position in the structure of **2**. In the structure of **4**, copper(II) is coordinated by two 6-OHpic ligands in the equatorial plane and by two 4-picoline molecules in the axial positions, leading to a distorted 4 + 2 octahedral coordination. The crystal packings of both **2** and **4** are dominated by intermolecular C–H⋯O hydrogen contacts and π⋯π stacking interactions which form a complex three-dimensional supramolecular architectures.

Keywords: Copper(II) complexes; 3- and 6-hydroxypicolinic acids; IR spectroscopy; Thermal analysis (TGA/DTA); Crystal structure; π⋯π stacking interactions

1. Introduction

Supramolecular assembly and crystal engineering of coordination compounds are the central theme in designing of new solid-state structures due to their potential applications as functional materials.[1–4]

In particular, pyridinecarboxylate ligands have been employed to link metals due to their ability to engage in diverse bonding modes allowing wide structural diversity. Hydroxy derivatives of picolinic acid, such as 3-hydroxy (3-OHpicH) and 6-hydroxypicolinic acid (6–OHpicH), have been widely used in the synthesis of complexes containing the first-row transition metal centres.[5–15] By contrast, for the complexes of the second- and the third-row transition metal ions[16–18] as well as with lanthanoids[19, 20] there are a few reports in the literature.

As a part of our continuing interest in copper(II) complexes with molecules of biological importance, we have synthesized and characterized [Cu(3-OHpic)$_2$] (**1**), [Cu(3-OHpic)$_2$(4-pic)] (**2**), [Cu(6-OHpic)$_2$(H$_2$O)$_2$] (**3**) and [Cu(6-OHpic)$_2$(4-pic)$_2$] (**4**) (4-pic = 4-methylpyridine) in order to get some more information on the primary coordination sphere arround Cu^{2+} ion regarding different sterical/electronic demands of the ligands being used. All complexes were identified by elemental analysis and characterized by IR-spectroscopy and thermal mehods (TGA/DTA), while the crystal structures of **2** and **4** were revealed by X-ray crystal structure analysis and discussed

with the data reported earlier for the parent complexes **1** and **3**, respectively, which we have synthesized with practically equal yields, but in a more simpler way than reported in the literature.[6, 9, 12]

2. Experimental

2. 1. Materials and Physical Measurements

All chemicals were used as received without further purification. Copper(II) sulfate pentahydrate was purchased from Merck, 3-hydroxypicolinic acid from Fluka, while 6-hydroxypicolinic acid was purchased from Aldrich.

CHN analyses were performed on Perkin Elmer 2400 Series II CHNS analyser in the Analytical Services Laboratories of the Ruđer Bošković Institute.

The IR spectra were obtained from KBr pellets in the range 4000–450 cm^{-1} with a Perkin-Elmer Spectrum RXI FT-spectrometer.

TGA/DTA measurements were performed at a heating rate of 10 °C/min in temperature range of 25–600 °C, under nitrogen flow of 10 mL/min on instrument Mettler-Toledo TGA/SDTA 851^e. Approximately 10 mg of sample was placed in standard aluminium crucible (40 μL).

2. 2. Bis(3-hydroxypyridine-2-carboxylato-*N,O*)copper(II), [Cu(3-OHpic)$_2$] (1)

Synthesis of **1** was described earlier[6,7] and here we report slightly modified procedure. A solution of 3-hydroxypicolinic acid (0.20 g, 1.44 mmol) in 15 mL of water was added to a solution of copper(II) sulfate pentahydrate (0.18 g, 0.72 mmol) in 5 mL of water. The pH value of the resulting blue solution was 1. The violet-blue product was formed immediately and it was left to stand at room temperature until the next day to complete precipitation. The product was then filtered off, washed with water and dried in a desiccator over CaCl$_2$. Yield: 0.21 g (87.5%). Anal. Calcd for C$_{12}$H$_8$CuN$_2$O$_6$(%): C 42.42, H 2.38, N 8.25. Found: C 42.38, H 2.51, N 7.93. IR (KBr) v 1646(s), 1608(m), 1469(s), 1453(s), 1402(m), 1385(m), 1328(s), 1308(s), 1274(m), 1245(s), 1220(m), 1153(m), 1125(m), 898(m), 825(s), 813(m), 695(s), 587(m) cm^{-1}.

2. 3. Bis(3-hydroxypyridine-2-carboxylato-*N,O*)(4-methylpyridine) copper(II), [Cu(3-OHpic)$_2$(4-pic)] (2)

A solution of **1** (0.09 g, 0.26 mmol) in 5 mL of 4-picoline was left to stand at room temperature for two weeks to give a blue product which was filtered off and dried *in vacuo*. Yield: 0.06 g (54.5%). Anal. Calcd. for C$_{18}$H$_{15}$Cu-N$_3$O$_6$(%):C 49.94, H 3.50, N 9.71. Found: C 49.59,

H 3.75, N 9.43. IR (KBr) v 1646(s), 1613(s), 1470(s), 1402(m), 1333(s), 1310(m), 1254(s), 1225(m), 898(m), 824(m), 695(m) cm^{-1}.

The crystals suitable for X-ray crystal structure analysis were obtained by recrystallization from 4-picoline.

2. 4. *Trans*-diaquabis(6-hydroxypyridine-2-carboxylato-*N,O*)copper(II), [Cu(6-OHpic)$_2$(H$_2$O)$_2$] (3)

Synthesis of **3** was described earlier[12] and here we report a modified procedure. A solution of 6-hydroxypicolinic acid (0.20 g, 1.44 mmol) in 15 mL of water was added to a solution of copper(II) sulfate pentahydrate (0.18 g, 0.72 mmol) in 5 mL of water. The pH value of the resulting blue solution was 1. The blue product was formed immediately and it was left to stand at room temperature until the next day to complete precipitation. The product was then filtered off, washed with water and dried in a desiccator over CaCl$_2$. Yield: 0.24 g (88.9%). Anal. Calcd for C$_{12}$H$_{12}$CuN$_2$O$_8$(%): C 38.35, H 3.23, N 7.46. Found: C 38.71, H 3.56, N 7.08. IR (KBr) v 3487(m), 3096(m), 1665(s), 1617(s), 1576(s), 1456(m), 1394(s), 1320(s), 1255(m), 827(m), 745(m) cm^{-1}.

2. 5. *Trans*-bis(6-hydroxypyridine-2-carboxylato-*N,O*)bis(4-methylpyridine) copper(II), [Cu(6-OHpic)$_2$(4-pic)$_2$] (4)

A solution of **3** (0.10 g, 0.27 mmol) in 5 mL of 4-picoline was left to stand at room temperature for two weeks to give blue crystals which were filtered off and dried *in vacuo*. Yield: 0.05 g (35.7%). Anal. Calcd. for C$_{24}$H$_{22}$Cu-N$_4$O$_6$(%):C 54.80, H 4.22, N 10.65. Found: C 54.67, H 4.51, N 10.27. IR (KBr) v 1685(s), 1620(s), 1577(s), 1485(m), 1454(s), 1367(m), 1321(m), 1281(s), 1254(s), 1170(m), 1147(m), 1072(m), 810(m), 768(s), 552(m), 489(m) cm^{-1}. The obtained crystals were suitable for X-ray crystal structure analysis.

2. 6. X-Ray Single-Crystal Structure Determination

Suitable single crystals of **2** and **4** were selected and mounted in air onto thin glass fibres. The data collection was carried out on Oxford Diffraction Xcalibur four-circle kappa geometry single-crystal diffractometer with Xcalibur Sapphire 3 CCD detector by applying the CrysAlis Software system, Version 171.32.4 at room temperature.[21] Data reduction has been applied by the same programme.[21] Eight runs containing 1234 data collection frames for **2** and **4** were collected at the crystal-detector distance of 60 mm with the exposure time of 10 and 5 s for **2** and **4**, respectively, and with combination of ω and φ scan type for both structures.

The X-ray diffraction data have been corrected for Lorentz-polarization factor and scaled for absorption effects by multi-scan. The structures were solved by direct methods. Refinement procedure by full-matrix least squares methods based on F^2 values against all reflections has been performed including anisotropic displacement parameters for all non-H atoms.

The positions of hydrogen atoms belonging to the carbon atoms Csp^2 and methyl Csp^3 atoms were geometrically optimized applying the riding model [Csp^2-H, Csp^3(methyl)-H, 0.93 Å and 0.96 Å, respectively; U_{iso}(H) = $1.2U_{eq}$(C) for Csp^2 and $1.5U_{eq}$(C) for Csp^3(methyl)]. The position of hydrogen atoms belonging to the hydroxyl O atoms were geometrically optimized applying the riding model [O–H, 0.82 Å; U_{iso}(H) = $1.2U_{eq}$(O)].

Calculations were performed with SHELXS-97,[22] SHELXL-97[22] and PLATON.[23] The molecular graphics were done with ORTEP-3[24] and MERCURY (Version 1.4.2).[25]

CCDC 677241 and 677242 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk]. Structure factors table is available from the authors.

3. Results and discussion

3. 1. Preparation of Complexes

Complex **1** and **3** were prepared by reaction of copper(II) sulfate pentahydrate and 3-hydroxypicolinic acid or 6-hydroxypicolinic acid, respectively, in aqueous solution, while complexes **2** and **4** were obtained by recrystallization of **1** and **3**, respectively, from 4-picoline solution. The complex **1** and **3** were formed even in highly acidic

Table 1. Crystal data and details of the structure determination for [Cu(3-OHpic)$_2$(4-pic)] (**2**) and [Cu(6-OHpic)$_2$(4-pic)$_2$] (**4**)

Compound	2	4
Formula	$C_{18}H_{15}CuN_3O_6$	$C_{24}H_{22}CuN_4O_6$
M_r	432.87	526.00
Colour and habit	blue, plate	blue, block
Crystal system, space group	triclinic, $P\bar{1}$	monoclinic, $C2/c$
Crystal dimensions (mm^3)	$0.43 \times 0.42 \times 0.09$	$0.73 \times 0.50 \times 0.43$
Temperature (K)	296	
Unit cell parameters:		
a (Å)	8.0621(2)	13.7617(4)
b (Å)	10.7717(5)	12.3917(3)
c (Å)	11.4062(5)	14.1337(5)
α (°)	72.343(4)	90
β (°)	77.978(3)	106.649(3)
γ (°)	74.515(3)	90
V (Å^3)	900.83(7)	2309.19(12)
Radiation, MoKα (Å)	0.71073	
Z	2	4
D_{calc}(g cm^{-3})	1.596	1.513
μ (mm^{-1})	1.254	0.995
θ range for data collection (°)	3.97–27.00	4.10–30.00
h,k,l range	–10:10; –13:13, –14:14	–19:19; –17:17, –19:19
Diffractometer	Xcalibur κ geometry with Sapphire 3 CCD detector	
Scan type	ω, φ	
No. measured reflections	14788	21696
No. independent reflections (R_{int})	3909 (0.0286)	3335 (0.0146)
No. observed reflections, $I \geq 2\sigma(I)$	3049	2293
No. refined parameters	256	162
R^a, wR^b [$I \geq 2\sigma(I)$]	0.0495, 0.1373	0.0479, 0.1454
R, wR [all data]	0.0681, 0.1434	0.0672, 0.1641
g_1, g_2 in w^c	0.0381, 1.8052	0.1030, 0.0240
Goodness of fit on F^2, S^d	1.196	1.142
Max., min. electron density (e Å^{-3})	0.614, –0.408	0.981, –0.331
Maximum Δ	<0.001	<0.001
Absorption correction type	multi-scan	multi-scan
Range of transmission factors min., max.	0.590, 0.890	0.560, 0.650

^{a} $R = \Sigma ||F_o| – |F_c||/\Sigma|F_o|$

^{b} w$R = [\Sigma(F_o^2 – F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

^{c} w $=1/[\sigma^2(F_o^2) + (g_1P)^2 + g_2P]$ where $P = (F_o^2 + 2F_c^2)/3$

^{d} $S = \Sigma[w(F_o^2 – F_c^2)^2/(N_{obs} – N_{param})]^{1/2}$

aqueous solution (pH = 1) due to their apparently large complex formation constants (low concentration of anionic ligands is needed). High insolubility of the complexes **1** and **3** in water enables the equilibrium to be shifted towards the formation of **1** and **3**. The same thing was observed in the synthesis of [Cu(3-Mepic)$_2$(4-pic)].[26]

All isolated compounds are air-stable, blue and soluble in solvents with pronounced donor properties (such as *N,N*-dimethylformamide, dimethylsulfoxide, pyridine and 4-picoline).

3. 2. Vibrational Spectroscopy

Infrared spectroscopy data confirm the coordination of 3-OHpic ligand to copper(II) ion *via* the carboxylate group in both **1** and **2**. The spectrum of **1** is in accordance with the data from the literature.[9] In the spectrum of **2** the band associated to the asymmetric stretching vibrational mode, v_{asym}(–COO$^-$) appears at 1646 cm^{-1} (1700 cm^{-1} in the free ligand),[9] while the v_{sym}(–COO$^-$) band at 1333 cm^{-1} (1322 cm^{-1} in the free ligand).[9] The measured values of $\Delta(v_{asym}$(–COO$^-$) – v_{sym}(–COO$^-$)) amounts 313 cm^{-1} indicating the presence of carboxylate groups coordinated to copper(II) ion in unidentate mode[27] which is in agreement with the crystal structure of **2**. The typical stretching v(C–N) vibrational mode of substituted pyridines appears for the uncoordinated 3-OHpic ligand at 1609 cm^{-1} and shows small shifts (4 cm^{-1}) for **2**. This is in a good agreement with *N,O*-chelation, involving the endocyclic nitrogen atom of 3-OHpic ligand.

6-OHpic ligand is also coordinated to copper(II) ion *via* the carboxylate group in **3** and **4** according to infrared spectroscopy data. In the spectra of **3** and **4** the band associated to the asymmetric stretching vibrational mode, v_{asym}(–COO$^-$) appears at 1665 cm^{-1} (**3**) and 1685 cm^{-1} (**4**) (1700 cm^{-1} in the free ligand), while the v_{sym}(–COO$^-$) band at 1320 cm^{-1} (**3**) and 1321 cm^{-1} (**4**) (1295 cm^{-1} in the free ligand). The measured values of $\Delta(v_{asym}$(–COO$^-$) – v_{sym}(–COO$^-$)) amounts 345 cm^{-1} and 364 cm^{-1} for **3** and **4**, respectively, indicating the presence of carboxylate groups coordinated to copper(II) ion in unidentate mode[27] which is in agreement with the crystal structure of both compounds. The typical stretching v(C–N) vibrational mode of substituted pyridines appears for the uncoordinated 6-OHpic ligand at 1606 cm^{-1} and shows relatively small shifts (11 cm^{-1} for **3** and 14 cm^{-1} for **4**), in the agreement with *N,O*-chelation that involves the endocyclic nitrogen atom of 6-OHpic ligand.

3. 3. Structural Description of 2

Crystal data and details of the structure determination for **2** are given in Table 1. ORTEP-3 view of the molecular structure of **2** is depicted in Fig. 1(a) and its crystal structure in Fig. 1(b) and Fig. 1(c). The selected molecular geometry parameters are listed in Table 2, hydrogen bond
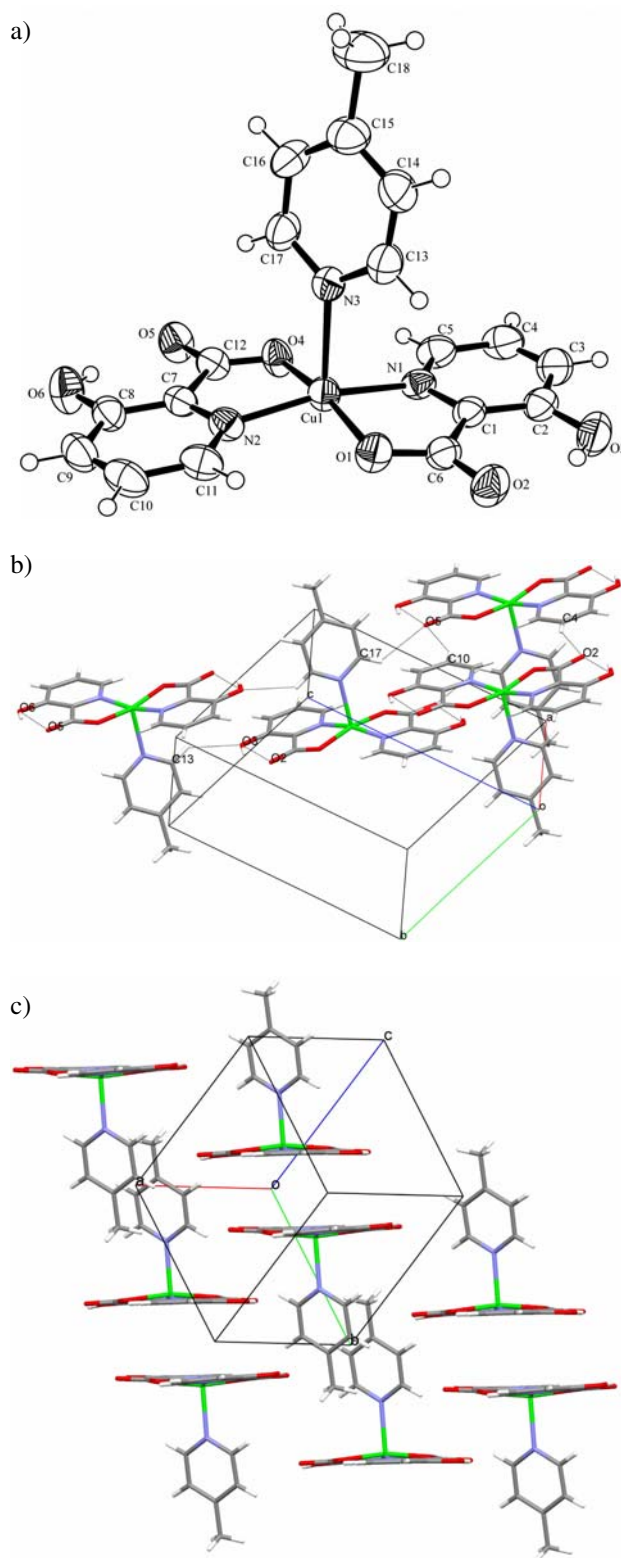
Fig. 1: (a) ORTEP-3 drawing of [Cu(3-OHpic)$_2$(4-pic)] (**2**) with the atomic numbering scheme of the asymmetric unit. The thermal ellipsoids are drawn at the 50% probability level at 296 K.
(b) A view of the packing in the crystal structure of [Cu(3–OH–pic)$_2$(4-pic)] (**2**) (hydrogen bonds are represented by thin lines and selected donor and acceptor atoms are labelled).
(c) π···π stacking interactions in three-dimensional supramolecular architecture of [Cu(3–OHpic)$_2$(4-pic)] (**2**)

Table 2. Selected bond distances (Å) and angles (°) for [Cu(3-OHpic)₂(4-pic)] (**2**) and [Cu(6-OHpic)₂(4-pic)₂] (**4**)

	2		**4**
		Bond distances	
Cu1–O1	1.969(3)	Cu1–O1	1.952(2)
Cu1–O4	1.970(3)	Cu1–N1	1.998(2)
Cu1–N1	1.977(4)	Cu1–N2	2.505(2)
Cu1–N2	1.975(4)	O1–C6	1.314(3)
Cu1–N3	2.273(4)	O2–C6	1.179(3)
O1–C6	1.277(5)		
O2–C6	1.235(5)		
O4–C12	1.270(5)		
O5–C12	1.235(5)		
		Bond angles	
O1–Cu1–O4	168.0(1)	O1–Cu1–N1	83.1(1)
N2–Cu1–N1	167.3(1)	O1–Cu1–N1ⁱ	96.9(1)
O1–Cu1–N2	94.6(1)	O1–Cu1–N2	92.1(1)
O4–Cu1–N2	83.6(1)	O1–Cu1–N2ⁱ	87.9(1)
O1–Cu1–N1	83.8(1)	N1–Cu1–N2	90.3(1)
O4–Cu1–N1	95.5(1)	N1–Cu1–N2ⁱ	89.7(1)
O1–Cu1–N3	98.1(1)		
O4–Cu1–N3	93.9(1)		
N2–Cu1–N3	99.5(1)		
N1–Cu1–N3	93.2(1)		

Symmetry code: (i) –x + ½, –y + 3/2, –z

and contact geometry in Table 3 and geometry of π···π interactions in Table 4.

The coordination environment of the copper(II) ion in **2** can be described as a square pyramid (Fig. 1(a)). The basal plane of the pyramid is defined by two carboxylic O atoms [Cu1-O1 1.969(3) Å, Cu1-O4 1.970(3) Å] in *trans* position and two pyridine N atoms [Cu1-N1 1.977(4) Å, Cu1-N2 1.975(4) Å] (Table 2) from two 3-hydroxypicolinate ligands which are both bound to the copper(II) ion in a bidentate *N,O*-chelated mode forming a five-membered chelate ring. The axial position is occupied by one 4-picoline molecule [Cu1-N3 2.273(4) Å].

The copper(II) ion is nearly situated at the centre of the basal plane with a maximum out-of-plane deviation of 0.212(2) Å in the direction of Cu1-N3 bond. The bond distances Cu1-N1 and Cu1-N2 are in a good agreement within 3σ crystallographic criterion, but the bond distance Cu1-N3 is significantly longer due to the Jahn-Teller effect, typical for d^9 electron configuration. The same distortion of square-pyramidal geometry was reported in the literature for the copper(II) complexes containing picolinic acid and 3-methylpicolinic acid *e.g.* chloro(methylpicolinato-*N,O*)(picolinato-*N,O*)copper(II)[28] and bis(3-

Table 3. Hydrogen bond and contact geometry (Å, °) for [Cu(3-OHpic)₂(4-pic)] (**2**) and [Cu(6-OHpic)₂ (4-pic)₂] (**4**)

D–H···A	D–H	H···A	D···A	∠ DHA	Symmetry code
		[Cu(3-OHpic)₂(4-pic)] (**2**)			
O3–H3···O2	0.82	1.87	2.600(5)	147	–
O6–H6···O5	0.82	1.89	2.607(5)	145	–
C4–H4···O2	0.93	2.51	3.359(7)	152	–1+x, y, z
C10–H10···O5	0.93	2.58	3.409(7)	149	1+x, y, z
C13–H13···O3	0.93	2.49	3.227(7)	136	1–x, 1–y, –z
C17–H17···O5	0.93	2.59	3.258(6)	129	–x, 2–y, 1–z
		[Cu(6-OHpic)₂(4-pic)₂] (**4**)			
O3–H3···O1	0.82	1.81	2.615(3)	166	1/2–x, 1/2–y, 1–z
C10–H10···O3	0.93	2.57	3.474(3)	166	1/2–x, –1/2+y, 1/2–z

Table 4. Geometry of π···π stacking interactions (Å, °) in the crystal structure of [Cu(3-OHpic)₂(4-pic)] (**2**) and [Cu(6-OHpic)₂(4-pic)₂] (**4**)

π···π interaction Cg(I)–Cg(J)ᵃ	Centroid-centroid distance	Cg(I)···P(J)ᵇ	Cg(J)···P(I)ᶜ	Dihedral angle between P(I) and P(J)	Angle defined by Cg(I)→Cg(J) vector and normal to P(I) plane	Angle defined by Cg(I)→Cg(J) vector and normal to P(J) plane
			[Cu(3-OHpic)₂(4-pic)] (**2**)			
Cg(1)–Cg(2)ⁱ	3.859(2)	3.559(2)	3.519(2)	11.5(2)	24.3	22.8
Cg(3)–Cg(4)ⁱ	3.719(3)	3.392(2)	3.382(2)	4.4(2)	24.6	24.2
Cg(1)–Cg(4)ⁱ	3.698(3)	3.537(2)	3.311(2)	10.1(2)	26.5	17.0
			[Cu(6-OHpic)₂(4-pic)₂] (**4**)			
Cg(1)–Cg(1)ⁱⁱ	3.881(1)	3.522(1)	3.522(1)	4.2(1)	24.9	24.9

Symmetry codes: (i) 1–x, 1–y, 1–z; (ii) –x, y, 1/2–z
ᵃRings Cg(1), Cg(2), Cg(3) and Cg(4) are defined as follows:
   Cg(1) five-membered chelate ring 1 defined by atoms Cu1/N1/C1/C6/O1 in **2**
   Cg(2) five-membered chelate ring 2 defined by atoms Cu1/N2/C7/C12/O4 in **2**

Cg(3) pyridine ring 1 defined by atoms N1/C1/C2/C3/C4/C5 in **2**
Cg(4) pyridine ring 2 defined by atoms N2/C7/C8/C9/C10/C11 in **2**
Cg(1) pyridine ring 3 defined by atoms N1/C1/C2/C3/C4/C5 in **4**
ᵇ,ᶜ Cg(I)···P(J) or Cg(J)···P(I) is the perpendicular distance of corresponding centroid on a plane. Planes P(I) or P(J) are defined by the atoms which define the corresponding centroids

methylpicolinato-*N,O*)(4-picoline)copper(II),[26] respectively, and for cyanuric acid adduct with aquabis(picolinato-*N,O*)copper(II).[29] The Cu–N and Cu–O bond distances in **2** are in accordance with the ones found in the literature for square-planar bis(3-hydroxypicolinato-*N,O*)copper(II),[6,9] but longer than the analogous ones in square-pyramidal bis(3-methylpicolinato-*N,O*)(4-picoline)copper(II)[26] which is isostructural with **2**.

The distortion of square pyramid is indicated by the angles from 83.6(1)° to 99.5(1)° for *cis* pairs of the ligating atoms and from 167.3(1)° to 168.0(1)° for *trans* pairs of the ligating atoms. The angles indicating the large distortion from the ideal square-pyramidal geometry are the bite angles O1-Cu1-N1 and O4-Cu1-N2 with values of 83.8(1)° and 83.6(1)°, respectively. For five coordinated structures, the parameter τ [$\tau = (\alpha - \beta) / 60°$, α and β are the largest angles] was introduced.[30] Value τ is 0 for perfectly square-pyramidal geometry and 1 for perfectly trigonal-bipyramidal geometry. In the case of **2**, τ is 0.01 indicating square-pyramidal geometry.

The dihedral angle between the least squares calculated planes through the atoms of pyridine ring (N1/C1-C5) and the corresponding five-membered chelate ring (Cu1/N1/C1/C6/O1) is 5.8(2)°, while the analogous angle (between planes defined by atoms N2/C7-C11 and Cu1/N2/C7/C12/O4) is 1.7(2)°. The dihedral angle between the planes defined by the atoms of pyridine ring (N3/C13-C17) and five-membered chelate ring (Cu1/N1/C1/C6/O1) is 79.0(2)°, while the analogous angle (between planes defined by atoms N3/C13-C17 and Cu1/N2/C7/C12/O4) is 75.8(2)°. The spatial orientation of 4-picoline molecule in relation to equatorial plane of square pyramid is described by twisting around Cu1-N3 bond *i.e.* the torsion angles N2/Cu1/N3/C13 and N1/Cu1/N3/C17 amount 128.0(4)° and 117.8(4)°, respectively.

The bond distances O1-C6 [1.277(5) Å] and O4-C12 (1.270(5) Å] of the carboxylate group are longer than O2-C6 [1.235(5) Å] and O5-C12 (1.235(5) Å] due to the coordination of O1 and O4 atoms to copper(II) ion.

There are two intramolecular hydrogen bonds of the O–H···O type [2.600(5) Å and 2.607(5) Å] in the crystal structure of **2** (Table 3 and Fig. 1(b)). The first one is formed by hydroxyl O3 atom and uncoordinated carboxylate O2 atom, while the second one is formed by hydroxyl O6 atom and uncoordinated carboxylate O5 atom (Table 3). There are also four intermolecular hydrogen contacts of the C–H···O type,[31, 32] formed by pyridine C atoms (C4, C10, C13, C17) as donors and uncoordinated carboxylate O2, O5 atoms and hydroxyl O3 atom as acceptors. Thus, O3 atom acts as a proton donor and acceptor, while O2 atom acts as a double and O5 as a triple proton acceptor (Table 3).

There are also various π···π stacking interactions[33, 34] in the crystal structure of **2**. These interactions are between five-membered chelate rings 1 and 2 [3.859(2) Å], between five-membered chelate ring 1 and pyridine ring 2 [3.698(3) Å] and between pyridine rings 1 and 2 [3.719(3)

Å] (Table 4). These π···π stacking interactions, along with the intermolecular hydrogen contacts of the type C–H···O, link molecules of **2** into a complex three-dimensional supramolecular architecture (Fig. 1(c)).

3. 4. Structural Description of 4

Crystal data and details of the structure determination for **4** are given in Table 1. ORTEP-3 view of the molecular structure of **4** is depicted in Fig. 2(a) and its crystal structure in Fig. 2(b) and Fig. 2(c). The selected molecular geometry parameters are listed in Table 2, hydrogen bond and contact geometry in Table 3 and geometry of π···π interactions in Table 4.

The coordination environment of the copper(II) ion in **4** can be described as a distorted 4 + 2 octahedron, revealing tetragonal elongation due to the Jahn-Teller effect (Fig. 2(a)). Copper(II) ion is situated on a crystallographic inversion centre and coordinated by two 6-hydroxypyridine-2-carboxylate ligands in the equatorial plane (Cu1-N1 1.998(2) Å, Cu1-O1 1.952(2) Å) and by two 4-picoline molecules in axial position (Cu1-N2 2.505(2) Å) (Table 2). 6-OHpic ligands are bound to copper(II) ion in a bidentate *N,O*-chelated mode forming a five-membered chelate ring.

The Cu1-N1 and Cu1-O1 bond distances correspond to the analogous ones in *trans*-diaquabis(6-hydroxypicolinato-*N,O*)copper(II).[12] However, the Cu1-N2 bond distance is longer than Cu1-N1 bond distance due to the Jahn-Teller effect typical for d^9 electron configuration.

The distortion of the octahedron is indicated by the angles from 83.1(1)° to 96.9(1)° for *cis* pairs of the ligating atoms. The angle indicating the large distortion from the ideal octahedral geometry is the bite angle O1-Cu1-N1 with the value of 83.1(1)°.

The dihedral angle between the least squares calculated planes through the atoms of pyridine ring (N1/C1-C5) and the corresponding five-membered chelate ring (Cu1/N1/C1/C6/O1) is 3.2(1)°. The dihedral angle between the planes defined by the atoms of pyridine ring (N2/C7-C11) and five-membered chelate ring (Cu1/N1/C1/C6/O1) is 88.1(1), while the angle between plane formed due to the intramolecular hydrogen bond (Cu1/N1[i]/C5[i]/O3[i]/O1, symmetry code (i) -x + ½, -y + 3/2, -z) and five-membered chelate ring (Cu1/N1/C1/C6/O1) is 3.8(1)°. The hydrogen atom belonging to O3[i] atom is 0.07(4) Å out of plane defined by atoms Cu1/N1[i]/C5[i]/O3[i]/O1. The spatial orientation of 4-picoline molecule in relation to equatorial plane is described by twisting around Cu1-N2 bond (torsion angle N1/Cu1/N2/C7 amounts 75.2(2)°). That reveals different spatial orientation of 4-picoline molecule in **2** in relation to its position in **4**.

The bond distance O1-C6 [1.314(3) Å)] of the carboxylate group is longer than O2-C6 [1.179(3) Å] due to the coordination of O1 atom to copper(II) ion.

There is one intramolecular hydrogen bond (2.615(3) Å) of the type O–HO in the crystal structure of

---

a)

b)

c)
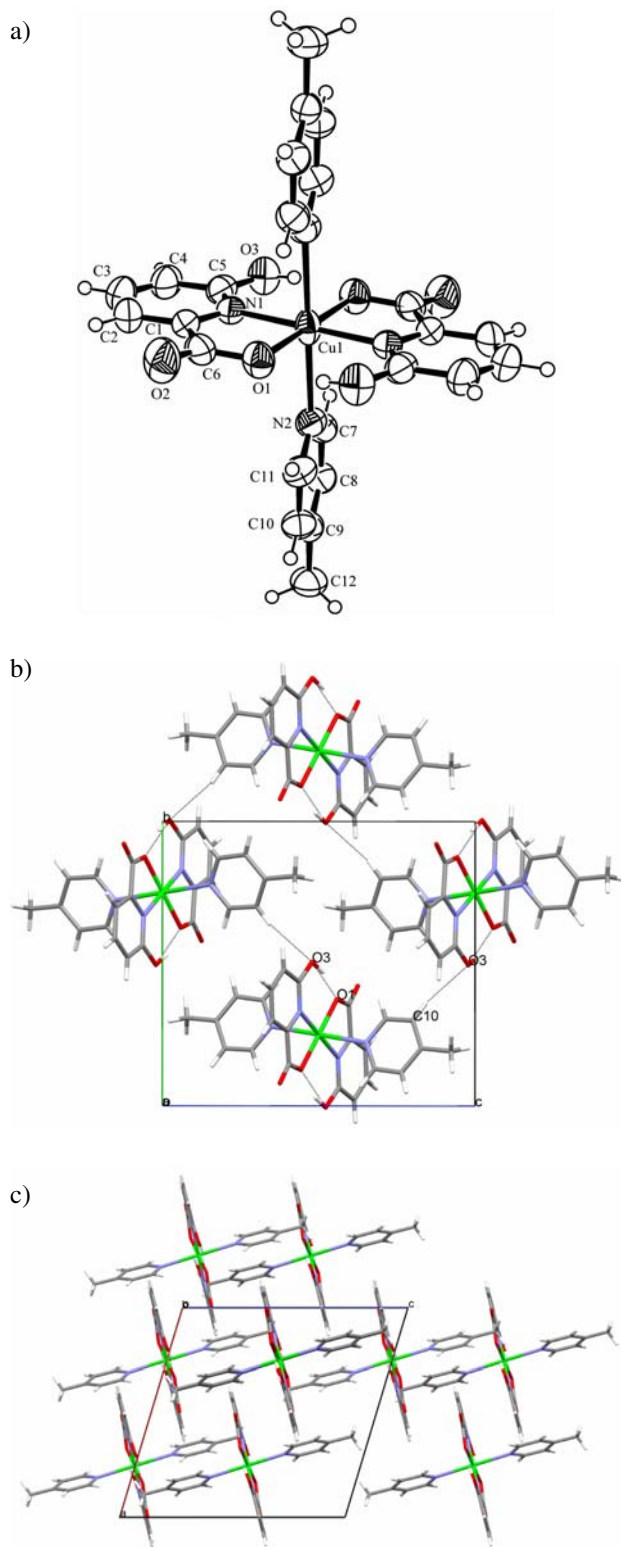
Fig. 2: (a) ORTEP-3 drawing of [Cu(6–OHpic)$_2$(4-pic)$_2$] (**4**) with the atomic numbering scheme of the asymmetric unit. The thermal ellipsoids are drawn at the 50% probability level at 296 K.
(b) A view of the crystal packing of [Cu(6–OHpic)$_2$(4-pic)$_2$] (**4**) in *bc* plane. Hydrogen bonds are represented by thin lines with donor and acceptor atoms labelled.
(c) π···π stacking interactions in three-dimensional supramolecular architecture of [Cu(6–OHpic)$_2$(4-pic)$_2$] (**4**) (view in *ac* plane)

4, formed by hydroxyl O3 atom and coordinated carboxylate O1 atom. There is also one intermolecular hydrogen contact (3.474(3) Å) of the C–H···O type[31, 32] between pyridine C10 atom and hydroxyl O3 atom (Fig. 2(b) and Table 3) and one π···π stacking interaction[33, 34] between pyridine rings 3 [3.881(1) Å] (Table 4), which link molecules of **4** in a complex three-dimensional supramolecular architecture (Fig. 2(c)).

3. 5. Thermal Analysis (TGA/DTA)

The thermal stability of **1**, as determined from TGA and DTA curves, is up to 230 °C. The thermal decomposition of **1** results in a release of one 3-OHpic ligand (observed weight loss 39.6%, calculated 40.6%) during the step with endothermic peak at 306.5 °C. The further decomposition of **1** continues through one step (29.5%) in the temperature range of 360–470 °C (small endothermic peak at 370.8 °C), which corresponds to the decomposition of the second 3-OHpic ligand. The observed residue (30.9%) at 600 °C, remained after total pyrolysis of **1,** is CuO. The results of thermal analysis for **1** reported here are not in accordance with the scarce data from the literature.[9]

Compound **2** is thermally stable up to 75 °C. One 4-picoline molecule was released in a step with endothermic peak at 146.5 °C (observed weight loss 21.0%, calculated 21.6%). The thermal decomposition of **2** continues through step with endothermic peak at 291.5 °C, corresponding to the release of one 3-OHpic ligand (observed weight loss 32.4%, calculated 31.8%). The further step of decomposition (23.1%) occurs in the wide temperature range of 310–475 °C and results with the complete decomposition of **2**. The observed residue (23.5%) at 600 °C is CuO.

Compound **3** is thermally stable up to 75 °C. Two water molecules were evolved in a step with endothermic peak at 134.2 °C (observed weight loss 9.7%, calculated 9.6%), as it was expected for coordinated water molecules and in the accordance with the crystal structure of **3**.[12] The thermal decomposition of **3** finishes with a step with endothermic peak at 369.8 °C, corresponding to the release of both 6-OHpic ligands (62.1%). The observed residue (28.2%) at 600 °C is CuO.

Compound **4** is thermally stable up to 50 °C. Two 4-picoline molecules were evolved in a step with endothermic peak at 130.7 °C (observed weight loss 35.1%, calculated 35.5%). Compound **4** further decomposes with a decomposesin a step with endothermic peak at 369.0 °C, corresponding to the release of both 6-OHpic ligands (45.6%), similar as observed for **3**. The remained residue (19.3%) at 600 °C is CuO.

4. Conclusions

By using 3-hydroxypicolinic and 6-hydroxypicolinic acid as pyridinecarboxylate ligands, we have synthesi-

zed four copper(II) complexes: bis(3-hydroxypyridine-2-carboxylato-*N,O*)copper(II), (**1**), bis(3-hydroxypyridine-2-carboxylato-*N,O*)(4-picoline)copper(II), (**2**), diaquabis(6-hydroxypyridine-2-carboxylato-*N,O*)copper(II), (**3**) and bis(6-hydroxypyridine-2-carboxylato-*N,O*)bis(4-picoline)copper(II), (**4**). Synthesis of **1** and **3** were done in aqueous solution by reaction of copper(II) sulfate pentahydrate and 3-hydroxypicolinic or 6-hydroxypicolinic acid, respectively, while **2** and **4** were obtained by recrystallization of **1** or **3** from 4-picoline solution. All compounds were characterized by elemental analysis, IR spectroscopy and TGA/DTA measurements, while the crystal structures of **2** and **4** were determined by X-ray single-crystal diffractometry method.

X-Ray structure analysis revealed bidentate *N,O*-chelated coordination mode of 3-hydroxypicolinic acid in the structure of **2** and the same one for the 6-hydroxypicolinic acid in the structure of **4**. The IR data are in accordance with the structures of both **2** and **4**. Copper(II) ion has a slightly distorted square-pyramidal coordination in **2** and octahedral coordination in **4**. The difference in the coordination polyhedra around copper(II) in these complexes can be only explained as a consequence of different position of hydroxyl group in ligand pyridine ring (position 3 or 6), leading to a different electron arrangement in the aromatic ring of the ligands.

5. Acknowledgement

6. References

1. J. H. Lehn, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304–1319.
2. O. M. Yaghi, H. L. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474–484.
3. B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658.
4. B. J. Hollyday, C. A. Mirkin, *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 2022–2043.
5. E. Kiss, A. Beneyi, T. Kiss, *Polyhedron* **2003**, *22*, 27–33.
6. C. Sun, X. Zheng, L. Jin, *J. Mol. Struct.* **2003**, *646*, 201–210.
7. M. Nakai, F. Sekiguchi, M. Obata, C. Ohtsuki, Y. Adachi, H. Sakurai, C. Orvig, D. Rehder, S. Yano, *J. Inorg. Biochem.* **2005**, *99*, 1275–1282.
8. A. Shaver, J. B. Ng, D. A. Hall, B. S. Lum, B. I. Posner, *Inorg. Chem.* **1993**, *32*, 3109–3113.
9. P. I. Girginova, F. A. Almeida Paz, H. I. S. Nogueira, N. J. O. Silva, V. S. Amaral, J. Klinowski, T. Trindade, *J. Mol. Struct.* **2005**, *737*, 221–229.
10. B. M. Kukovec, Z. Popović, G. Pavlović, M. Rajić Linarić, *J. Mol. Struct.* **2008**, *882*, 47–55.
11. P. I. Girginova, F. A. Almeida Paz, H. I. S. Nogueira, N. J. O. Silva, V. S. Amaral, J. Klinowski, T. Trindade, *Polyhedron* **2005**, *24*, 563–569.
12. A. Şengül, O. Büyükgüngör, *Acta Cryst.* **2005**, C*61*, m119–m121.
13. B. M. Kukovec, Z. Popović, G. Pavlović, Fifteenth Slovenian-Croatian Crystallographic Meeting, Jezersko, Slovenia, **2006**, Book of Abstracts, 57.
14. Z. Popović, B. M. Kukovec, K. Molčanov, G. Pavlović, M. Rajić Linarić, 1st European Chemistry Congress, Budapest, Hungary, **2006**, Abstract Book, 368.
15. B. M. Kukovec, Z. Popović, G. Pavlović, M. J. Calhorda, P. D. Vaz, International School of Crystallography, 39th Course, Engineering of Crystalline Materials Properties: State-of-the-Art in Modelling, Design, Applications, Erice, Italy, **2007**, Lecture Notes and Poster Abstracts, Part Two, 626.
16. S. M. O. Quintal, H. I. S. Nogueira, V. Felix, M. G. B. Drew, *New J. Chem.* **2000**, *24*, 511–517.
17. S. M. O. Quintal, H. I. S. Nogueira, H. M. Carapuca, V. Felix, M. G. B. Drew, *J. Chem. Soc., Dalton Trans.* **2001**, 3196–3201.
18. S. Gatto, T. I. A. Gerber, G. Bandoli, J. Perils, J. G. H. Du Preez, *Inorg. Chim. Acta* **1998**, *269*, 235–240.
19. P. C. R. Soares-Santos, F. A. Almeida Paz, R. A. Sá Ferreira, J. Klinowski, L. D. Carlos, T. Trindade, H. I. S. Nogueira, *Polyhedron* **2006**, *25*, 2471–2482.
20. C. Y. Sun, L. P. Jin, *J. Mol. Struct.* **2005**, *741*, 241–247.
21. Oxford Diffraction, Oxford Diffraction Ltd., Xcalibur CCD system, CrysAlis Software system, Version 171.32.4, **2007**
22. G. M. Sheldrick, *Acta Cryst.* **2008**, A*64*, 112–122.
23. A. L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7–13.
24. L. J. Farrugić, *J. Appl. Cryst.* **1997**, *30*, 565–565.
25. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Cryst.* **2006**, *39*, 453–457.
26. B.-M. Kukovec, Z. Popović, G. Pavlović, *J. Coord. Chem.* **2008**, *61*, 3092–3101.
27. G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **1980**, *33*, 227–250.
28. M. Bhar, M. Chaudhury, E. R. T. Tiekink, *Acta Cryst.* **2001**, E*57*, m305–m307.
29. A-Q. Wu, G. H. Guo, F. K. Zheng, X. Liu, G. C. Guo, J. S. Huang, *Inorg. Chem. Commun.* **2005**, *8*, 182–185.
30. A. W. Addison, T. Nageswara Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.
31. G. R. Desiraju, T. Steiner: The Weak Hydrogen Bond in Structural Chemistry and Biology, IUCr Monographs on Crystallography, Oxford University Press, Oxford, **2001**

32. G. A. Jeffrey: An Introduction to Hydrogen Bonding, Topics in Physical Chemistry, Oxford University Press, Oxford, **1997**

33. C. A. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.

34. C. Janiak, *J. Chem. Soc., Dalton Trans.* **2000**, 3885–3896.

Povzetek

Pripravljene so bile bakrove(II) kompleksne spojine s 3-hidroksipikolinsko kislino 3-OHpicH)–[Cu(3-OHpic)$_2$] (1), [Cu(3-OHpic)$_2$(4-pic)] (2) in s 6-hidroksipikolinsko kislino (6-OHpicH)–[Cu(6-OHpic)$_2$(H$_2$O)$_2$] (3) in [Cu (6-OHpic)$_2$(4-pic)$_2$] (4) in karakterizirane z IR spektroskopijo in termično analizo (TGA/DTA). Molekularna in kristal-na struktura je bila določena za spojini 2 in 4 z metodo rentgenske strukturne analize. Kristalni gradniki v 2 in 4 so med seboj povezani z intermolekularnimi C–H…O kontakti in π…π interakcijami kar tvori komplicirano tridimenzionalno supramolekularno arhitekturo.