

Synthesis and Characterization of a Copper(II) Complex with 6-Hydroxypicolinic Acid and 3-Picoline[†]

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Abstract. A copper(II) complex with 6-hydroxypicolinic acid (6-OHpicH) and 3-picoline (3-pic), $[\text{Cu}(6\text{-OHpic})_2(3\text{-pic})_2]$ (**1**), was prepared by recrystallization of $[\text{Cu}(6\text{-OHpic})_2(\text{H}_2\text{O})_2]$ from 3-picoline and characterized by IR spectroscopy and thermal methods (TGA/DTA and DSC). The molecular and crystal structure of **1** was determined by single-crystal X-ray structural analysis. The copper(II) ion in **1** has a tetragonally compressed octahedral coordination environment, achieved by two *N,O*-bidentate 6-hydroxypicolinate ligands and by two 3-picoline molecules in *trans* positions. The crystal structure of **1** exhibits one strong intermolecular O–H…O hydrogen bond, one weak intermolecular C–H…O hydrogen bond and one C–H…π interaction. Molecules of **1** are assembled into a 2D network in the (1 0 –1) plane, giving rise to $\text{C}^1_{11}(8)$ graph-set motif. These 2D networks are further assembled into 3D architecture only by weak Van der Waals interactions. A thermogravimetric study showed the initial loss of two coordinated 3-picoline molecules in **1**, followed by a complete decomposition of the compound. (doi: [10.5562/cca2119](http://dx.doi.org/10.5562/cca2119))

Keywords: copper(II), 6-hydroxypicolinic acid, 3-picoline, crystal structure, thermal analysis (TGA/DTA, DSC), tetragonal compression

INTRODUCTION

Metal complexes of pyridine-2-carboxylic acid (picolinic acid, picH) have been widely studied as well as those of its derivatives with electron-withdrawing substituents, such as hydroxyl groups or halogen atoms, due to their great coordination flexibility and wide variety of physiological properties, especially insulinomimetic activity.^{1–7} Until now, there are only few reports regarding insulinomimetic properties of picolinate complexes bearing electron-donating groups such as a methyl group.^{3,8}

Picolinate ligands favor the formation of mononuclear or polynuclear complexes due to their inherent tendency to form a chelate ring. They can also act as bridging ligands (up to four metal ions),⁹ thus offering a possibility of using them as building blocks to assemble multi-dimensional frameworks. Recently, we have explored the coordination modes of hydroxyl derivatives of picolinic acid towards the late 3d-block transition metals, namely cobalt(II), nickel(II) and copper(II).^{10–14}

A lot of copper(II) complexes with picolinic acid derivatives and *N*-donor ligands (pyridine, 4-picoline, 3-picoline) are known from the literature. The pentacoordinated complexes $[\text{Cu}(3\text{-Mepic})_2(4\text{-pic})]$,¹⁵ $[\text{Cu}(3\text{-Mepic})_2(3\text{-pic})]$,¹⁶ $[\text{Cu}(6\text{-Mepic})_2(\text{py})]$,¹⁷ and $[\text{Cu}(3\text{-OHpic})_2(4\text{-pic})]$,¹¹ and octahedral complexes $[\text{Cu}(3\text{-OHpic})_2(3\text{-pic})_2]$,¹⁴ and $[\text{Cu}(6\text{-OHpic})_2(4\text{-pic})_2]$,¹¹ were prepared by recrystallization of the initial complexes $[\text{Cu}(3\text{-Mepic})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$,^{15,16} $[\text{Cu}(6\text{-Mepic})_2(\text{H}_2\text{O})]$,¹⁷ $[\text{Cu}(3\text{-OHpic})_2]$,¹¹ and $[\text{Cu}(6\text{-OHpic})_2(\text{H}_2\text{O})_2]$,^{11,18} from the corresponding solvents (pyridine, 4-picoline, 3-picoline).

As a part of our continuing interest in copper(II) complexes with molecules of biological importance, we have prepared a copper(II) complex with 6-hydroxypicolinic acid (6-OHpicH) and 3-picoline (3-pic), $[\text{Cu}(6\text{-OHpic})_2(3\text{-pic})_2]$ (**1**). The complex was characterized by IR spectroscopy and thermal methods (TGA/DTA, DSC) and its molecular and crystal structure was determined by single-crystal X-ray structural analysis.

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EXPERIMENTAL

Materials and Physical Measurements

All chemicals were of reagent grade, purchased from commercial sources and used as received, without further purification.

CHN analyses were performed by a Perkin-Elmer 2400 Series II CHNS analyzer in the Analytical Services Laboratories of the Ruder Bošković Institute, Zagreb, Croatia.

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 heating rate of 5 °C min⁻¹ in the temperature range of 25–500 °C, under nitrogen flow of 100 mL min⁻¹ by a simultaneous TGA/DTA analyzer TA Instruments, Model SDT 2960. Approximately 10 mg of sample were placed in an open aluminum crucible.

DSC measurements were performed at heating rate of 10 °C min⁻¹ in the temperature range of 25–500 °C, under nitrogen flow of 200 mL min⁻¹ by a Mettler-Toledo DSC 823^e instrument. Approximately 5 mg of sample were placed in closed aluminum crucible (40 µL).

Synthesis of [Cu(6-OHpic)₂(3-pic)₂] (**1**)

A 3-picoline solution (5 mL) of [Cu(6-OHpic)₂(H₂O)₂]¹¹ (0.19 g, 0.51 mmol) was left to stand at room temperature to slowly evaporate. The blue crystals, suitable for X-ray crystal structure analysis, were formed in ten days. The crystals were filtered off, washed with the mother liquor and dried *in vacuo*. Yield: 0.13 g (48%). *Anal. Calcd.* mass fractions of elements, *w* / %, for C₂₄H₂₂CuN₄O₆ (*M_r* = 526.01): C, 54.80; H, 4.22; N, 10.65. *Found:* C, 54.67; H, 4.51; N, 10.27. IR (KBr pellets) *v* / cm⁻¹: 1668 s, 1617 s, 1576 s, 1483 m, 1453 s, 1394 s, 1351 m, 1320 s, 1255s, 1200 w, 1151 m, 1115 w, 1073 m, 1020 m, 1001 w, 969 w, 827 m, 801 m, 779 m, 748 m, 707 m, 659 m, 554 m, 479 m.

Single Crystal X-ray Diffraction Analysis and Structure Determination

A suitable single crystal of **1** was selected and mounted in air onto a thin glass fiber. The data collection for **1** was carried out by an Oxford Diffraction Xcalibur four-circle kappa geometry diffractometer with Xcalibur Sapphire 3 CCD detector, using a graphite monochromated MoK_α ($\lambda = 0.71073 \text{ \AA}$) radiation, and by applying the *CrysAlis* Software system, Version 171.32.29 at room temperature (296(2) K). Data reduction was done by the same program.¹⁹

The X-ray diffraction data were corrected for Lorentz-polarization factor and scaled for absorption

effects by evaluation of multi-scans. The structure was solved by direct methods implemented in SHELXS-97.²⁰ A refinement procedure by full-matrix least-squares methods, based on *F*² values against all reflections, was performed by SHELXL-97,²⁰ including anisotropic displacement parameters for all non-H atoms.

The position of hydrogen atoms belonging to the carbon atoms Csp² and Csp³ and to the hydroxyl O atom were geometrically optimized applying the riding model (Csp²-H, 0.93 Å, *U*_{iso}(H) = 1.2 *U*_{eq}(C); Csp³(methyl)-H, 0.96 Å, *U*_{iso}(H) = 1.5 *U*_{eq}(C); O-H, 0.82 Å, *U*_{iso}(H) = 1.5 *U*_{eq}(O)).

The calculations concerning the molecular geometry, the choice and verification of the space group, the analysis of hydrogen bonds and C–H···π interactions

Table 1. The crystal data and details of the structure refinement for **1**

Formula	C ₂₄ H ₂₂ CuN ₄ O ₆
<i>M_r</i>	526.01
Color and habit	green, prism
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Crystal dimensions / mm ³	0.76 × 0.53 × 0.36
<i>a</i> / Å	9.5380(2)
<i>b</i> / Å	8.49410(10)
<i>c</i> / Å	14.8021(3)
β / °	105.0677(19)
<i>V</i> / Å ³	1157.99(4)
<i>Z</i>	2
<i>D</i> _{calc} / g cm ⁻³	1.509
μ / mm ⁻¹	0.992
<i>F</i> (000)	542
θ range for data collection / °	3.94 – 30.00
<i>h,k,l</i> range	-13:13, -11:11, -20:20
Scan type	ω , φ
Number of measured reflections	21752
Number of independent reflections (<i>R</i> _{int})	3345 (0.0211)
Number of observed reflections, <i>I</i> ≥ 2σ(<i>I</i>)	2505
Number of refined parameters	162
<i>R</i> ^(a) , <i>wR</i> ^(b) [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0298, 0.0823
<i>R</i> , <i>wR</i> [all data]	0.0432, 0.0855
Goodness of fit on <i>F</i> ² , <i>S</i> ^(c)	0.996
Max. and min. electron density / e Å ⁻³	0.47, -0.20

^(a) $R = \sum |F_o| - |F_c| / \sum |F_o|$

^(b) $wR = [\sum (F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$

^(c) $S = [\sum w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$

were performed by PLATON.²¹ The molecular graphics were done with ORTEP-3²² and MERCURY (Version 3.0).²³

The crystal parameters, data collection and refinement results for **1** are summarized in Table 1.

RESULTS AND DISCUSSION

Chemical Studies

Complex $[\text{Cu}(6\text{-OHpic})_2(3\text{-pic})_2]$ (**1**) was prepared by recrystallization of $[\text{Cu}(6\text{-OHpic})_2(\text{H}_2\text{O})_2]$ from 3-picoline. The initial complex $[\text{Cu}(6\text{-OHpic})_2(\text{H}_2\text{O})_2]$ was prepared by the reaction of copper(II) sulfate pentahydrate and 6-hydroxypicolinic acid in the acidic aqueous solution (pH 1).¹¹ The coordinated H_2O molecules in $[\text{Cu}(6\text{-OHpic})_2(\text{H}_2\text{O})_2]$ could be substituted by the 3-picoline molecules during its dissolution in 3-picoline, leading to the formation of **1**. Complex **1** decomposes by prolonged standing in air due to release of coordinated 3-picoline molecules. It is soluble in solvents with pronounced donor properties, such as *N,N*-dimethyl-formamide, dimethylsulfoxide, pyridine and 3-picoline.

Crystal Structure

An ORTEP-3 view of the molecular structure of **1** is depicted in Figure 1 and its crystal structure in Figure 2. The selected molecular geometry parameters are listed in Table 2 and the hydrogen bond geometry in Table 3.

The coordination environment of the copper(II) ion in **1** can be described as a distorted octahedron, revealing tetragonal compression due to the Jahn-Teller effect. The copper(II) ion in **1** is situated on a crystallo-

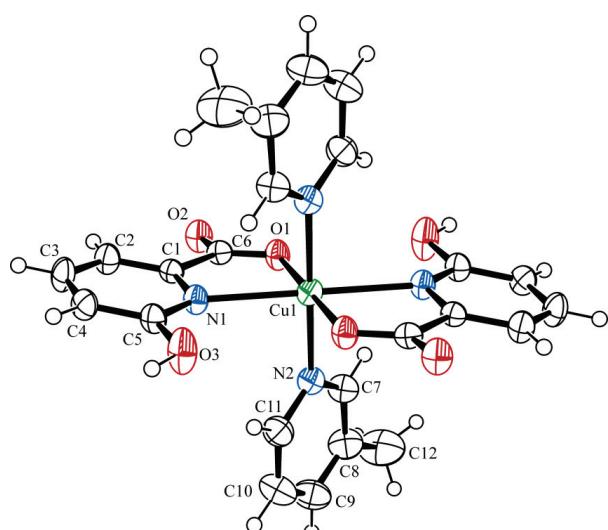


Figure 1. An ORTEP-3 drawing of **1** with the atomic numbering scheme of the asymmetric unit. The thermal ellipsoids are drawn at the 50 % probability level at 296(2) K.

graphic inversion center and it is coordinated by two 6-hydroxypicolinate ligands in the equatorial plane and by two 3-picoline molecules in the axial positions. The 6-hydroxypicolinate ligands are bound to a copper(II) ion in a bidentate *N,O*-chelated mode, forming five-membered rings (Figure 1). The Cu1–N2 bond distance of 2.031(1) Å is significantly shorter than the Cu1–N1 bond distance of 2.328(1) Å, in accordance with the Jahn-Teller effect typical for d^9 electron configuration. The Cu–N and Cu–O bond distances (N and O atoms from 6-hydroxypicolinate) in **1** (Table 2) are longer than the corresponding ones reported in the literature for copper(II) complexes with picolinic,^{24–26} 3-hydroxypicolinic,^{11,14,27,28} 6-hydroxypicolinic,^{11,18,29} 3-methylpicolinic,^{15,16} 6-methylpicolinic¹⁷ and 6-bromopicolinic acid.¹⁷

The bond angles around the copper(II) ion, involving *trans* pairs of donor atoms, are exactly 180° due to the symmetry. The distortion of the octahedron is indicated by the angles with values from 76.37(4)° to 103.63(4)° for *cis* pairs of ligating atoms. One of the angles indicating the largest distortion from the ideal octahedral geometry is the bite angle O1–Cu1–N1 with the value of 76.37(4)° (Table 2).

The pyridine ring (defined by N1/C1/C2/C3/C4/C5 atoms) is not perfectly coplanar with the chelated ring (defined by N1/C1/C6/O1/Cu1 atoms), as it is evident from the value of the dihedral angle between the mentioned rings (9.19(6)°).

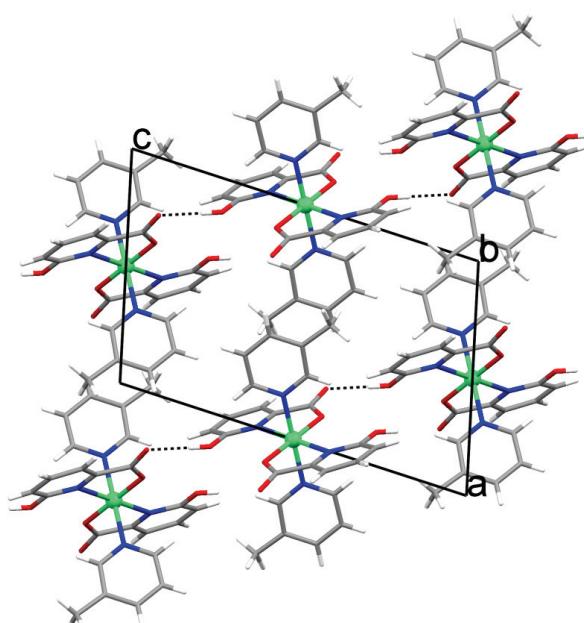


Figure 2. A view of the crystal structure of **1** in the *ac* plane. Molecules are linked by intermolecular hydrogen bonds of the O–H...O type (shown by the dotted lines) into a 2D network, which is represented as a linear chain in this projection. These linear chains extend along the [101] direction and are assembled together only by weak Van der Waals interactions.

Table 2. The selected bond distances (Å) and angles (°) for **1**

Bond distances	
Cu1–O1	2.015(1)
Cu1–N1	2.328(1)
Cu1–N2	2.031(1)
Bond angles	
O1 ⁱ –Cu1–O1	180
O1–Cu1–N2	89.38(4)
O1–Cu1–N2 ⁱ	90.62(4)
N2 ⁱ –Cu1–N2	180
O1 ⁱ –Cu1–N1	103.63(4)
O1–Cu1–N1	76.37(4)
N2 ⁱ –Cu1–N1	90.40(4)
N2–Cu1–N1	89.60(4)
N1–Cu1–N1 ⁱ	180

Symmetry code (*i*): 1-*x*, 1-*y*, -*z*

There are one intermolecular O–H…O and two weak intermolecular C–H…O hydrogen bonds in the crystal packing of **1**. Hydroxyl O3 and pyridine C4 and C9 atoms act as proton donors, while both coordinated (O1 atom) and uncoordinated (O2 atom) carboxylate oxygen atoms act as proton acceptors in hydrogen bonding (Table 3). Molecules of **1** are assembled into a 2D network in the (1 0 -1) plane by intermolecular O–H…O hydrogen bonds, giving rise to C¹(8) graph-set motif.³⁰ If it is viewed in the *ac* plane, this network can be represented as a linear chain, extending along the [101] direction (Figure 2). These 2D networks are further assembled into 3D architecture only by weak Van der Waals interactions. There is also one C–H…π interaction³¹ between the C2 atom and the pyridine ring defined by atoms N2ⁱ/C7ⁱ/C8ⁱ/C9ⁱ/C10ⁱ/C11ⁱ (symmetry operator (*i*): *x*, 1+*y*, *z*; C2…cg distance 3.592(2) Å; C2–H2…cg angle 149°; cg = centroid of the ring) in the crystal structure of **1**.

IR Spectroscopy

Infrared spectroscopy data confirm the coordination of the 6-hydroxypicolinate ligand to the copper(II) ion via carboxylate group in **1**. In the spectrum of **1**, the band associated to the antisymmetric stretching vibrational

mode, $\nu_{\text{asym}}(\text{COO}^-)$, appears at 1668 cm⁻¹ (1700 cm⁻¹ in the uncoordinated ligand). The band associated to the symmetric stretching vibrational mode, $\nu_{\text{sym}}(\text{COO}^-)$, appears at 1320 cm⁻¹ (1295 cm⁻¹ in the uncoordinated ligand). The value of $\Delta(\nu_{\text{asym}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-))$ amounts 348 cm⁻¹, indicating the presence of carboxylate group coordinated to copper(II) ion in monodentate mode^{32,33} which is in agreement with the crystal structure of **1**. The typical stretching vibrational mode of substituted pyridines, $\nu(\text{CN})$, appears for the uncoordinated 6-hydroxypicolinic acid at 1606 cm⁻¹ and it is shifted for 11 cm⁻¹ to higher wavenumbers in **1**. This shift is in agreement with the *N,O*-chelation, involving the pyridine N atom of 6-hydroxypicolinate ligand.

Thermal Analysis (TGA/DTA, DSC)

Complex **1** is thermally stable up to approximately 60 °C and decomposes in two endothermic steps. Two 3-picoline molecules are evolved in the first step (observed weight loss 31.0 %, calculated 35.4 %), with two endothermic peaks in the DTA curve (80.7 °C and 97.4 °C). The complex further decomposes in the second step, revealing the release of both 6-hydroxypicolinate ligands (observed weight loss 51.6 %, calculated 52.5 %), with two endothermic peaks (352.1 °C and 363.5 °C). The remained residue of 17.4 % (calculated 15.1 %) at 500°C is most probably CuO.

The DSC curve of **1** also shows two endothermic peaks for each of the two decomposition steps, similar as the DTA curve. Two peaks at 104.8 °C and 116.9 °C (80.7 °C and 97.4 °C in the DTA curve) in the first step indicate the release of two 3-picoline ligands, while the two peaks at 367.1 °C and 375.1 °C (352.1 °C and 363.5 °C in the DTA curve) in the second step correspond to the decomposition of both 6-hydroxypicolinate ligands. The peaks in the DSC curve are shifted by 10–25 °C to higher temperatures if compared to the peaks in the DTA curve.

The existence of two peaks in DTA and DSC curves for each step suggests that both the release of 3-picoline molecules and the decomposition of 6-hydroxypicolinate ligands may be composed of two different processes. However, this was not confirmed by TGA analysis.

Table 3. The hydrogen bond geometry for **1**

D–H…A	d(D–H) / Å	d(H…A) / Å	d(D…A) / Å	∠(D–H…A) / °	Symmetry code on A
O3–H13O…O2	0.82	1.78	2.584(1)	167	1/2+x, 3/2-y, 1/2+z
C4–H4…O1	0.93	2.54	3.376(2)	149	1/2+x, 3/2-y, 1/2+z
C9–H9…O2	0.93	2.58	3.476(2)	161	-x, 1-y, -z

CONCLUSION

The copper(II) ion in **1** is octahedrally coordinated by two *N,O*-bidentate 6-hydroxypicolinate ligands and two 3-picoline molecules in *trans* position, revealing a tetragonal compression of the octahedron due to the Jahn-Teller effect. This is the first example of tetragonal compression found in octahedral copper(II) complexes with picolinic acid derivatives. Other related octahedral copper(II) complexes with 3-hydroxypicolinic and 6-hydroxypicolinic acid (*e.g.* $[\text{Cu}(6\text{-OHpic})_2(\text{H}_2\text{O})_2]$, $[\text{Cu}(6\text{-OHpic})_2(4\text{-pic})_2]$ ¹¹ and $[\text{Cu}(3\text{-OHpic})_2(3\text{-pic})_2]$ ¹⁴) exhibit a tetragonally elongated copper(II) octahedron.

Supplementary Materials. – CCDC 885975 contains the supplementary crystallographic data for this paper and can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif [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]. The structure factor table is available from the authors.

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