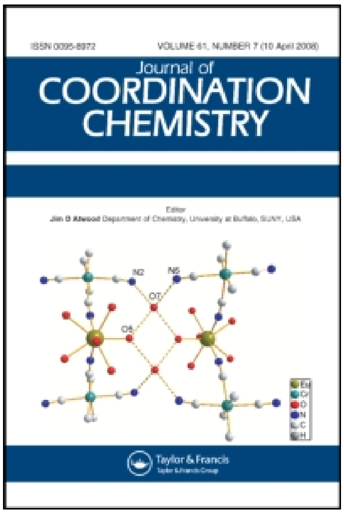

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and characterization of copper(II) complexes with 3-methylpicolinic acid. Crystal and molecular structure of <i>bis</i>(3-methylpicolinato-<i>N</i>,<i>O</i>)(4-picoline)copper(II)

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To cite this Article Kukovec, Boris-Marko , Popović, Zora and Pavlović, Gordana(2008) 'Synthesis and characterization of copper(II) complexes with 3-methylpicolinic acid. Crystal and molecular structure of **<i>bis</i>**(3-methylpicolinato-**<i>N</i>**,**<i>O</i>**)(4-picoline)copper(II)', Journal of Coordination Chemistry, 61: 19, 3092 — 3101

To link to this Article: DOI: 10.1080/00958970802005153

URL: http://dx.doi.org/10.1080/00958970802005153

Journal of Coordination Chemistry
Vol. 61, No. 19, 10 October 2008, 3092–3101

Synthesis and characterization of copper(II) complexes with 3-methylpicolinic acid. Crystal and molecular structure of *bis*(3-methylpicolinato-*N*,*O*)(4-picoline)copper(II)

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(*Received 3 December 2007; in final form 8 January 2008*)

Copper(II) complexes of 3-methylpicolinic acid (3-MepicH), namely $[Cu(3\text{-}Mepic)_2]\cdot 2H_2O$ (**1**) and $[Cu(3\text{-}Mepic)_2(4\text{-}pic)]$ (**2**) were prepared and characterized by IR spectroscopy and thermal analysis (TGA/DTA). Crystal structure for **2** was determined by X-ray crystal structure analysis. **1** was prepared by reaction of copper(II) sulfate pentahydrate and 3-methylpicolinic acid in aqueous solution, while **2** was prepared by recrystallization of **1** from 4-picoline solution. Structure analysis revealed square-pyramidal copper(II) coordination and *N*,*O*-chelating mode of 3-methylpicolinic acid in **2**. Copper(II) is coordinated by two 3-Mepic ligands in the basal plane of a square pyramid and by 4-picoline in the apical position. Crystal packing of **2** is dominated by weak intermolecular C–H $\cdots$ O hydrogen bonds and $\pi\cdots\pi$ stacking interactions forming a complex three-dimensional supramolecular architecture.

Keywords: Copper(II) complexes; 3-Methylpicolinic acid; IR spectroscopy; Thermal analysis (TGA/DTA); Crystal structure

1. Introduction

There has been considerable interest in design and synthesis of complexes with carboxylate ligands due to various coordination modes with metals and increasing recognition of metals' role in biological systems. Many transition metal complexes with picolinic acid have been investigated as well as complexes of its derivatives, mostly 3-hydroxypicolinic acid (3-OHpicH).

Less attention has been given to the complexes of derivatives of picolinic acid, such as 3-methyl or 6-methylpicolinic acid (6-MepicH). Zinc complexes of 6-MepicH and 3-MepicH were reported, $[Zn(6\text{-}Mepic)_2]$, $[Zn(3\text{-}Mepic)_2]$ [1] and $[Zn(6\text{-}Mepic)_2(H_2O)]\cdot H_2O$ [2]. Interestingly, $[Zn(6\text{-}Mepic)_2(H_2O)]\cdot H_2O$ shows *in vitro* insulin

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802005153

mimetic activity. Cadmium with 6-MepicH forms a one-dimensional coordination polymer $[Cd(6\text{-}Mepic)_2]_n$ [3]. Several complexes of 3d metals were structurally characterized, mononuclear Co^{II}, *cis*-$[Co(6\text{-}Mepic)_2(H_2O)_2]$ [4], heterobinuclear complex containing Cr^{III} and Sn^{IV}, $[(C_6H_5)_3SnClCr(6\text{-}Mepic)_3][(C_6H_5)_3SnCl(MeOH)]$ [5], $[Ni(6\text{-}Mepic)_2(H_2O)_2]\cdot 2H_2O$ and its anhydrous form [6]. Silver salts react with 6-MepicH and give different complexes, but only [Ag(6-Mepic)(6-MepicH)] was structurally determined [7]. In platinum group metals two complexes were reported, *cis*- and *trans*-$[Ru(tpy)(6\text{-}Mepic)(DMSO)](OSO_2CF_3)$ (tpy = 2,2′ : 6′,2″-terpyridine; DMSO = dimethylsulfoxide) [8] and [PdR(6-Mepic)L] ($R{=}CH_3$; $L{=}P(C_6H_5)_3$) [9].

There is a lack of data concerning metal complexes with 3-MepicH and here we report the synthesis of two copper(II) complexes with 3-MepicH, $[Cu(3\text{-}Mepic)_2]\cdot 2H_2O$ (**1**) and $[Cu(3\text{-}Mepic)_2(4\text{-}pic)]$ (**2**), their characterizations by IR spectroscopy and thermal methods and crystal and molecular structure of **2**.

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, while 3-methylpicolinic acid was purchased from Aldrich.

CHN analyses were performed in the Analytical Services Laboratories of the Ruđer Bošković Institute.

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

Data collection for **2** was carried out on an 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 ambient temperature [10]. Data reduction was done by the same program [10]. Thirteen runs containing 1591 data collection frames were collected at the crystal-detector distance of 60 mm with exposure time of 7 s and with ω scan type.

TGA/DTA measurements were performed at heating rate of $10^{\circ}C\,min^{-1}$ from 25–600°C under nitrogen flow of $10\,mL\,min^{-1}$ on a Mettler-Toledo TGA/SDTA 851^e. Approximately 10 mg of the sample was placed in standard aluminium crucible (40 μL).

2.2. *$[Cu(3\text{-}Mepic)_2]\cdot 2H_2O$ (1)*

A solution of 3-methylpicolinic acid (0.10 g, 0.73 mmol) in 15 mL of water was added to a solution of copper(II) sulfate pentahydrate (0.09 g, 0.36 mmol) in 5 mL of water. The pH of the resulting blue solution was 1. The violet-blue product formed after a couple of minutes and 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: 0.12 g (92.3%). Anal. Calcd for $C_{14}H_{16}CuN_2O_6$ (%): C, 45.2; H, 4.4; N, 7.5. Found: C, 45.3; H, 4.5; N, 8.0. IR data (KBr pellet, cm^{-1}): 3451(m), 1637(s), 1588(m), 1425(m), 1365(m), 1349(s), 1280(m), 1247(m), 1203(m), 1136(m), 871(m), 697(m).

2.3. *[Cu(3-Mepic)$_2$(4-pic)] (2)*

A solution of **1** (0.06 g, 0.16 mmol) in 5 mL of 4-picoline was left to stand at room temperature for one week to give a violet-blue product which was filtered off and dried in air. Yield: 0.06 g (85.7%). Anal. Calcd for $C_{20}H_{19}CuN_3O_4$ (%): C, 56.0; H, 4.5; N, 9.8. Found: C, 55.8; H, 4.7; N, 10.1. IR data (KBr pellet, cm^{-1}): 1666(s), 1655(s), 1611(m), 1588(m), 1327(s), 1268(m), 1242(m), 1132(m), 869(m), 804(m), 695(m).

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

2.4. *X-ray crystal structure analysis*

X-ray diffraction data for **2** were corrected for Lorentz-polarization factor and scaled for absorption effects by multi-scan. The structure was solved by the Patterson method. 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 carbon atoms Csp^2 and methyl Csp^3 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 distance between C1 and C6 and between C8 and C13 was restrained to the average value of 1.34(1) Å using SHELXL-97 DFIX instruction.

Calculations were performed with SHELXS-97 [11] and SHELXL-97 [12]. The molecular graphics were done with ORTEP-3 [13] and MERCURY (Version 1.4.2) [14].

3. Results and discussion

3.1. *Preparation of complexes*

Complex **1** was prepared by reaction of copper(II) sulfate pentahydrate and 3-methylpicolinic acid in aqueous solution, while **2** was obtained by recrystallization of **2** from 4-picoline solution. Complex **1** formed even in highly acidic aqueous solution (pH = 1) due to its large formation constant (low concentration of anionic ligand is needed). High insolubility of **1** in water enables the equilibrium to be shifted towards formation of **1** as observed in the synthesis of [Ni(6-OHpic)$_2$(H$_2$O)$_2$] [15], [Ni(3-OHpic)$_2$(H$_2$O)$_2$] [16] and copper(II) complexes with 6-methylpicolinic and 6-bromopicolinic acid (not published yet).

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

3.2. *Vibrational spectroscopy*

Infrared data indicate coordination of 3-Mepic ligand to copper(II) ion *via* carboxylate in both compounds. In the spectra of **1** and **2** the asymmetric stretching $\nu_{asym}(-COO^-)$

is shifted 28 cm^{-1} (**1**) and 10 cm^{-1} (**2**) to lower wavenumbers, while the symmetric stretching ν_{sym}(–COO$^-$) is shifted 53 cm^{-1} (**1**) and 31 cm^{-1} (**2**) to higher wavenumbers compared to free ligand. The measured values of $\Delta(\nu_{\mathrm{asym}}(\text{–COO}^-) - \nu_{\mathrm{sym}}(\text{–COO}^-))$ of 288 cm^{-1} and 328 cm^{-1} for **1** and **2**, respectively, indicate carboxylate coordinated unidentate to copper(II) [17], in agreement with the crystal structure of **2**. The typical ν(C–N) of substituted pyridines appears for the uncoordinated ligand at 1601 cm^{-1} and shifts (13 cm^{-1}) to lower wavenumber for **1** and **2**. This indicates *N*,*O*-chelation, involving the endocyclic nitrogen of 3-Mepic, confirmed by X-ray crystal structure analysis of **2**.

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 figure 1 and its crystal structure in figure 2(a) and figure 2(b). Selected molecular parameters are listed in table 2, hydrogen bond geometry in table 3 and geometry of $\pi \cdots \pi$ interactions in table 4.

The coordination environment of copper(II) in **2** can be described as a square pyramid (figure 1). The basal plane of the pyramid is defined by two carboxylic O atoms [Cu1–O1 1.936(1) Å, Cu1–O3 1.929(1) Å] in *trans* position and two pyridine N atoms [Cu1–N1 1.967(2) Å, Cu1–N2 1.970(2) Å] (table 2) from two 3-methylpicolinic ligands, which are both bound to the copper(II) ion in a bidentate *N*,*O*-chelated mode forming a five-membered chelate ring. The apical position is occupied by one 4-picoline molecule [Cu1–N3 2.352(2) Å].

The copper(II) is situated nearly at the center of the basal plane with a maximum out-of-plane deviation of 0.171(1) Å in the direction of Cu1–N3. The bond distances Cu1–N1 and Cu1–N2 are the same within 3σ crystallographic criterion, but the Cu1–N3 bond distance is significantly longer due to the Jahn-Teller effect, typical for d^9 configuration. The same distortion of square-pyramidal geometry was reported in the literature for copper(II) complexes containing picolinic acid e.g. chloro(methylpicolinato-*N*,*O*)(picolinato-*N*,*O*)copper(II) [18] and cyanuric acid adduct with aquabis(picolinato-*N*,*O*)copper(II) [19]. There are several copper(II) complexes with picolinic acid and its hydroxyl derivatives comprising other coordination geometries, square-planar {$\mathrm{Cu(pic)_2}$ [20], $\mathrm{Cu(pic)_2 \cdot 2H_2O}$ [21, 22]} and octahedral {$\mathrm{Cu(pic)_2(H_2O)_2}$ [23], $\mathrm{Cu(3\text{-}OHpic)_2}$ [24, 25], $\mathrm{Cu(6\text{-}OHpic)_2(H_2O)_2}$ [26]}.

Distortion of the square pyramid is indicated by angles from 82.3(1)° to 101.3(1)° for *cis* pairs of ligating atoms and from 168.9(1)° to 170.9(1)° for *trans* pairs of the ligating atoms. Angles with the largest distortion from the ideal square-pyramidal geometry are the bite angles O1–Cu1–N1 and O3–Cu1–N2 at 82.3(1)°. For five-coordinated structures, the parameter τ [$\tau = (\alpha - \beta)/60$, α and β are the largest angles] was introduced [27]; τ is 0 for perfectly square-pyramidal geometry and 1 for perfectly trigonal-bipyramidal geometry. In the case of **2**, τ is 0.033 indicating square-pyramidal geometry.

The dihedral angle between the least squares calculated planes through the atoms of pyridine ring (N1/C1/C2/C3/C4/C5) and the corresponding five-membered chelate ring (Cu1/N1/C1/C6/O1) is 3.2(1)° while the analogous angle (between planes defined by N2/C8/C9/C10/C11/C12 and Cu1/N2/C8/C13/O3) is 9.0(1)°.

Table 1. Crystal data and details of the structure determination for $[Cu(3\text{-Mepic})_2(4\text{-pic})]$ (**2**).

Compound	**2**
Formula	$C_{20}H_{19}CuN_3O_4$
M_r	428.92
Color and habit	Blue, plate
Crystal system, space group	Triclinic, $P\bar{1}$
Crystal dimensions (mm^3)	$0.30 \times 0.26 \times 0.09$
Temperature (K)	296
Unit cell parameters (Å, °)	
a	8.0776(2)
b	10.3696(5)
c	11.8857(5)
α	75.244(4)
β	76.947(3)
γ	86.444(3)
V (Å^3)	937.84(7)
Radiation, Mo-Kα (Å)	0.71073
Z	2
D_{Calcd} ($g\,cm^{-3}$)	1.519
μ (mm^{-1})	1.197
θ range for data collection (°)	4–30
Index ranges	$-11 \le h \le 11$ $-14 \le k \le 14$ $-16 \le l \le 16$
Diffractometer	Xcalibur κ geometry with Sapphire 3 CCD detector
Scan type	ω
No. measured reflections	26959
No. independent reflections (R_{int})	5450 (0.0318)
No. observed reflections, $I \ge 2\sigma(I)$	3238
No. refined parameters	256
R^a, wR^b [$I \ge 2\sigma(I)$]	0.0333, 0.0805
R, wR [all data]	0.0597, 0.0870
g_1, g_2 in w^c	0.05, 0
Goodness of fit on F^2, S^d	0.961
Max., min. electron density (e Å^{-3})	0.361, −0.398
Maximum Δ/σ	0.001
Absorption correction type	Multi-scan
Range of transmission factors min., max.	0.71, 0.90

[a] $R = \Sigma||F_o| - |F_c|/\Sigma|\ F_o||$.
[b] $wR = [\Sigma(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.
[c] $w = 1/[\sigma^2(F_o^2) + (g_1 P)^2 + g_2 P]$ where $P = (F_o^2 + 2F_c^2)/3$.
[d] $S = \Sigma[w(F_o^2 - F_c^2)^2/(N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

The bond distances O1–C6 [1.287(2) Å) and O3–C13 (1.286(2) Å] of the carboxylate group are longer than O2–C6 [1.212(2) Å) and O4–C13 (1.210(2) Å] due to the coordination of O1 and O3 to copper(II).

There are two weak intermolecular hydrogen bonds [3.421(2) Å and 3.205(3) Å] of the type C–H $\cdots$ O [28, 29] in the crystal structure of **2** (table 3 and figure 2(a)). The first is formed by pyridine C4 atom and coordinated carboxylate O1 atom, while the second is formed by pyridine C19 atom and uncoordinated carboxylate O4 atom (table 3). There are also various $\pi \cdots \pi$ stacking interactions [30, 31] in the crystal structure of **2** (figure 2(b)). These interactions are between five-membered chelate rings defined by Cu1/N1/C1/C6/O1 and Cu1/N2/C8/C13/O3 [3.794(1) Å], between

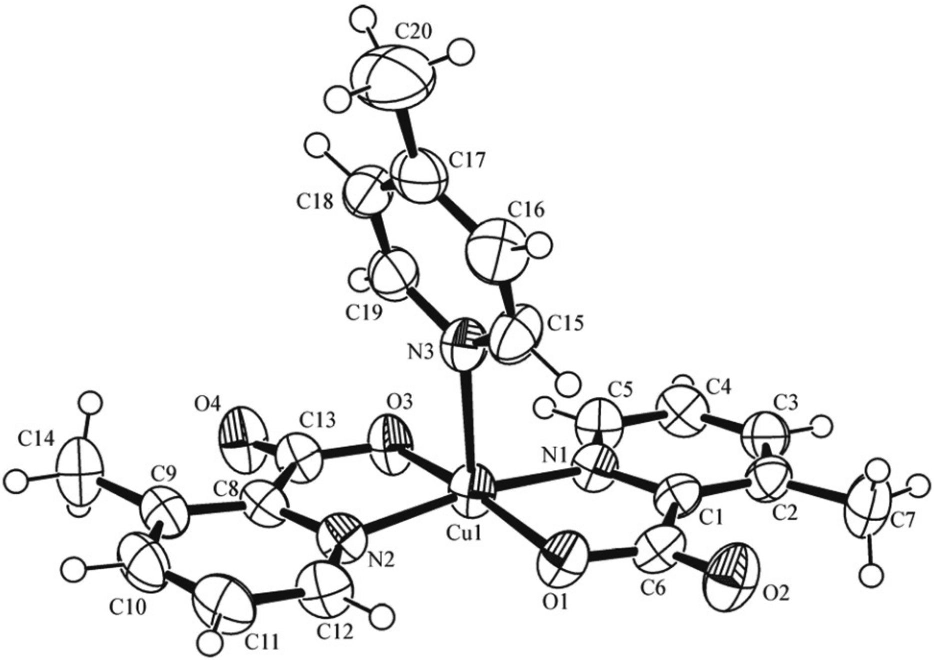

Figure 1. ORTEP-3 drawing of [Cu(3-Mepic)$_2$(4-pic)] (**2**) with the atomic numbering scheme of the asymmetric unit. Thermal ellipsoids are drawn at the 50% probability level at 296 K.

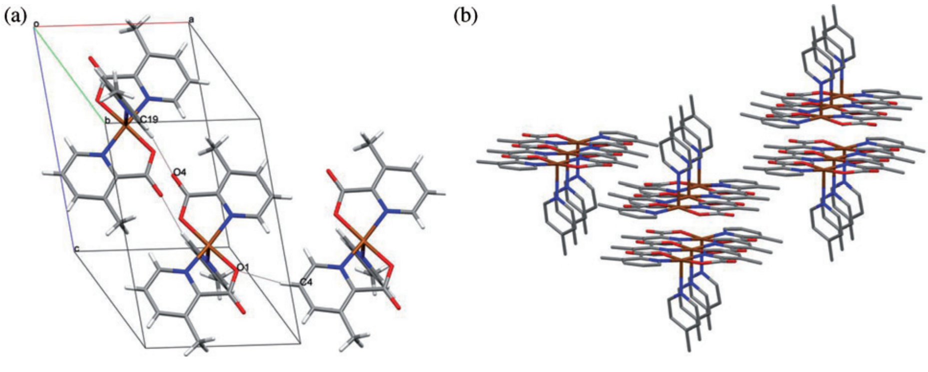

Figure 2. MERCURY view of the packing in the crystal structure of **2** (weak hydrogen bonds are represented by thin lines) (a), $\pi \cdots \pi$ stacking interactions in three-dimensional supramolecular architecture of [Cu(3-Mepic)$_2$(4-pic)] (**2**) (b).

five-membered chelate ring defined by Cu1/N2/C8/C13/O3 and pyridine ring (N1/C1/C2/C3/C4/C5) [3.675(1) Å], between pyridine rings defined by N1/C1/C2/C3/C4/C5 and N2/C8/C9/C10/C11/C12 [3.746(1) Å] and between pyridine rings defined by N3/C15/C16/C17/C18/C19 [3.915(1) Å] (table 4). These $\pi \cdots \pi$ stacking interactions, along with the weak intermolecular hydrogen bonds C–H $\cdots$ O, link molecules of **2** into a complex three-dimensional supramolecular architecture (figure 2(b)).

Table 2. Selected bond distances (Å) and angles (°) for $[Cu(3\text{-}Mepic)_2(4\text{-}pic)]$ (**2**).

Cu1–O3	1.929(1)
Cu1–O1	1.936(1)
Cu1–N1	1.967(2)
Cu1–N2	1.970(2)
Cu1–N3	2.352(2)
O1–C6	1.287(2)
O2–C6	1.212(2)
O3–C13	1.286(2)
O4–C13	1.210(2)
O3–Cu1–O1	170.9(1)
N1–Cu1–N2	168.9(1)
O3–Cu1–N1	95.4(1)
O1–Cu1–N1	82.3(1)
O3–Cu1–N2	82.3(1)
O1–Cu1–N2	98.3(1)
O3–Cu1–N3	98.1(1)
O1–Cu1–N3	91.0(1)
N1–Cu1–N3	101.3(1)
N2–Cu1–N3	89.8(1)

Table 3. Hydrogen bond geometry (Å, °) for $[Cu(3\text{-}Mepic)_2(4\text{-}pic)]$ (**2**).

D–H···A	D–H	H···A	D···A	∠DHA	Symmetry code
C4–H4···O1	0.93	2.51	3.421(2)	165	$1+x, y, z$
C19–H19···O4	0.93	2.47	3.205(3)	136	$1-x, 1-y, 1-z$

3.4. *Thermal analysis (TGA/DTA)*

The thermal stability of **1**, as determined from TGA and DTA curves, is to 90°C. Two molecules of crystal water are evolved at 90°C (observed weight loss 9.1%, Calcd 9.7%). Thermal decomposition of **1** continues through one step (62.3%) in the temperature range 280–310°C, corresponding to total decomposition of 3-Mepic. The observed residue (28.6%) at 600°C, after total decomposition of **1**, is CuO.

Compound **2** is thermally stable to 115°C as determined from TGA and DTA curves. One molecule of 4-picoline is released at 115°C (observed weight loss 20.6%, Calcd 21.7%). The thermal decomposition of **2** continues through one step (55.2%) in the temperature range 270–300°C, corresponding to decomposition of 3-Mepic ligands. The observed residue (24.2%) at 600°C is CuO, as well.

4. Conclusion

By using 3-methylpicolinic acid as ligand, we have synthesized two copper(II) complexes, *bis*(3-methylpicolinato)copper(II) dihydrate (**1**) and *bis*(3-methylpicolinato-*N*,*O*)(4-picoline)copper(II) (**2**). Synthesis of **1** was done in aqueous solution, while **2** was obtained by recrystallization of **1** from 4-picoline. All compounds were

Table 4. Geometry of $\pi \cdots \pi$ stacking interactions (Å, °) in the crystal structure of [Cu(3-Mepic)$_2$(4-pic)] (**2**).

$\pi \cdots \pi$ interaction $Cg(I)$–$Cg(J)$[a]	Centroid–centroid distance	$Cg(I) \cdots P(J)$[b]	$Cg(J) \cdots P(I)$[c]	Dihedral angle between $P(I)$ and $P(J)$	Angle defined by $Cg(I) \rightarrow Cg(J)$ vector and normal to $P(I)$ plane	Angle defined by $Cg(I) \rightarrow Cg(J)$ vector and normal to $P(J)$ plane
Cg(1)–Cg(2)^{i}	3.794(1)	3.608	3.566	6.90	19.98	18.02
Cg(2)–Cg(3)^{i}	3.675(1)	3.548	3.450	5.33	20.15	15.10
Cg(3)–Cg(4)^{i}	3.746(1)	3.468	3.489	4.25	21.35	22.20
Cg(5)–Cg(5)^{ii}	3.915(1)	3.634	3.634	0.02	21.83	21.83

Symmetry codes: (i) = $1-x, -y, 1-z$; (ii) = $1-x, 1-y, -z$.

[a] Rings Cg(1), Cg(2), Cg(3), Cg(4) and Cg(5) are defined as follows: Cg(1) five-membered chelate ring defined by atoms Cu1/N1/C1/C6/O1; Cg(2) five-membered chelate ring defined by atoms Cu1/N2/C8/C13/O3; Cg(3) pyridine ring defined by atoms N1/C1/C2/C3/C4/C5; Cg(4) pyridine ring defined by atoms N2/C8/C9/C10/C11/C12; Cg(5) pyridine ring defined by atoms N3/C15/C16/C17/C18/C19.

[b,c] $Cg(I) \cdots P(J)$ or $Cg(J) \cdots P(I)$ 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.

characterized by elemental analysis, IR spectroscopy and TGA/DTA measurements and the crystal structure of **2** was determined by X-ray single-crystal diffractometry.

X-ray structure analysis revealed bidentate *N*,*O*-chelated coordination of 3-methylpicolinic acid in **2**, confirmed by IR data for both **1** and **2**. Copper(II) ion has a slightly distorted square-pyramidal coordination in **2**. The crystal packing of **2** is dominated by weak interactions such as C–H $\cdots$ O hydrogen bonds and $\pi \cdots \pi$ stacking interactions.

TGA/DTA measurements showed weight loss corresponding to two crystal water molecules for **1** and to one 4-picoline for **2**. Both **1** and **2** decomposed in one step afterwards. The observed residue after total decomposition of **1** and **2** was CuO.

Supplementary data

CCDC 668274 contains 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.

Acknowledgements

This work was supported by the Ministry of Science, Education and Sports of the Republic of Croatia within the scientific project under the title ‘‘Chemistry of metal complexes in reactions of biological importance and new materials’’ (No. 119-1193079-1332) and in the framework of the scientific programme ‘‘Ligands, complexes, proteins – synthesis and structure – properties relationship’’.

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