

# Synthesis, Characterization, Crystal Structures and Fungicidal Activity of Some Copper(II) Carboxylates with 3-Hydroxypyridine<sup>†</sup>

Amalija Golobič<sup>a</sup>, Ljerka Ožbolt<sup>a</sup>, Franc Pohleven<sup>b</sup>, Ivan Leban<sup>a</sup> and Primož Šegedin<sup>a</sup>

<sup>a</sup>Faculty of Chemistry, University of Ljubljana, Aškerčeva 5, P.O.Box 537, 1001 Ljubljana, Slovenia, e-mail:primoz.segedin@fkkt.uni-lj.si

<sup>b</sup>Biotechnical Faculty, University of Ljubljana, Rožna dolina, C. VIII/34, 1000 Ljubljana, Slovenia

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<sup>†</sup> Dedicated to the memory of Prof. Dr. Davorin Dolar

## Abstract

Different synthetic routes were applied for preparation of some copper(II) carboxylates with 3-hydroxypyridine (3-pyOH). Monomeric and dimeric complex of copper(II) acetate were isolated,  $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(3\text{-pyOH})_2]$ , **1**, and  $[\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(3\text{-pyOH})_2]$ , **2**, respectively. A covalently linked 2D  $\text{Cu}^{\text{II}}$  compounds of general formula  $[\text{Cu}(\text{O}_2\text{CR})_2(3\text{-pyOH})_2]_n$  were prepared with benzoate ( $\text{R}=\text{C}_6\text{H}_5$ , **3**), hexanoate ( $\text{R}=\text{CH}_2(\text{CH}_2)_4$ , **4**), and heptanoate ( $\text{R}=\text{CH}_2(\text{CH}_2)_5$ , **5**) ligands. The crystal structures of all five compounds were determined by X-ray structure analysis. The compounds were tested for fungicidal activity against two fungal species *Trametes versicolor* and *Antrodia vaillantii*. Complete growth retardation for *Antrodia vaillantii* was noticed for compounds **3**, **4**, and **5** at concentrations of  $5 \cdot 10^{-3} \text{ mol L}^{-1}$ ,  $1 \cdot 10^{-3} \text{ mol L}^{-1}$ , and  $5 \cdot 10^{-4} \text{ mol L}^{-1}$ , while in the case of *Trametes versicolor* complete growth retardation was observed for the same three compounds only at the highest tested concentration.

**Key words:** copper(II) carboxylates, 3-hydroxypyridine, fungicidal activity, X-ray structure analysis

## 1. Introduction

Small low-molecular-weight Cu(II) coordination compounds with *N*-donor ligands have frequently been used to model the active site in copper proteins with the aim to obtain insight into the correlation between structure and the spectroscopic and magnetic behaviour.<sup>1</sup> Our recent investigations include efforts to find new synthetic methods for preparation of copper carboxylates with additional *N*-donor ligands. Choice of ligands with hydrogen-bonding functionality could lead to the formation of useful inorganic materials with desired physical properties. In this sense complexes of hydroxypyridine are of considerable interest.<sup>2</sup> Despite such interest only few coordination compounds of copper(II) carboxylates with 3-hydroxypyridine (3-pyOH) have been structurally characterised so far. Two-dimensional network linked by hydrogen bonds between the trifluoroacetate ligand and the 3-pyOH ligand is present in compound  $[\text{Cu}(\text{O}_2\text{CCF}_3)_2(3\text{-pyOH})_2](\text{THF})_2$ .<sup>3</sup> Presence of bifunctional 3-pyOH ligand (ligand that is capable of forming both metal-ligand bonds and hydrogen bonds) results in extended two-dimensional sheet structure also in  $[\text{Cu}(\text{O}_2\text{CCF}_3)_2(3\text{-pyOH})_2]_n$ .<sup>4</sup> A one dimensional

extended complex was found in bis-didentate oxalato-bridged compound  $[\text{Cu}(\text{ox})(3\text{-pyOH})_2]_n$ .<sup>5</sup> In this work we present synthesis, characterization and crystal structures of five 3-pyOH derivatives of copper(II) carboxylates together with the results of screening tests on their fungicidal activity. Structures of **3**, **4** and **5** are new, while room temperature structures of **1** and **2** were published recently.<sup>6,7</sup> Since the present structure determination was done at 150 K structural data of **1** and **2** still represent a new information.

## 2. Experimental

### 2.1. Synthesis and Characterization

$[\text{Cu}_2(\text{O}_2\text{CC}_6\text{H}_5)_4(\text{C}_6\text{H}_5\text{COOH})_2]$  was prepared from hot aqueous solution of copper(II) sulphate, benzoic acid and sodium benzoate by precipitation method.  $[\text{Cu}_2(\text{O}_2\text{CC}_n\text{H}_{2n+1})_4]$  ( $n = 5, 6$ ) were synthesized according to precipitation method described in the literature.<sup>8</sup> Sodium carboxylates were prepared by evaporating equimolar aqueous solution of appropriate carboxylic acid and sodium hydroxide to dryness. All other chemicals were of reagent grade and were used without further purification. The procedures for obtaining IR, UV-Vis, powder X-ray diffraction patterns,

effective magnetic moment and elemental analysis results were as previously described.<sup>9</sup> Compounds were tested for fungicidal activity for wood decay fungi *Trametes versicolor* (L. ex Fr.) Pilat and *Antrodia vaillantii* (DC. ex Fr.) Ryv. by standard procedure.<sup>10</sup>

**[Cu(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(3-pyOH)<sub>2</sub>], 1**

Solution prepared by stirring 0.40 g (1 mmol) of [Cu<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] in 13 mL of absolute ethanol was filtered onto solution of 1.14 g (12 mmol) of 3-hydroxypyridine (3-pyOH) in 7.6 mL of absolute ethanol. Violet crystals of compound **1** precipitated from the solution which has been kept at ~0 °C over night. They were filtered off and dried in desiccator over KOH for 12 h. Average yield of synthesis was 77%. Anal. Calcd. for [Cu(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(3-pyOH)<sub>2</sub>]: C, 45.22%; H, 4.34%; N 7.53%; Cu, 17.09%. Found C, 45.3%; H, 4.26%; N 7.51%; Cu, 17.1%. IR (KBr, cm<sup>-1</sup>): 1544vs (ν<sub>as</sub>(CO<sub>2</sub>)); 1467vs (ν<sub>s</sub>(CO<sub>2</sub>)). UV/Vis (Nujol, λ<sub>max</sub>/nm): 316, 558, 629sh. μ<sub>eff</sub>(RT): 1.93 BM. Single crystals of compound **1** were obtained by similar procedure from more diluted solutions.

**[Cu<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>(3-pyOH)<sub>2</sub>], 2**

Solution prepared by stirring 0.80 g (2 mmol) of [Cu<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] in 26 mL of absolute ethanol was filtered onto solution of 0.38 g (4 mmol) of 3-pyOH in 4 mL of absolute ethanol. Green crystals of compound **2** precipitated from the solution almost immediately together with grass-green amorphous substance which almost or totally disappeared if the solution was left in refrigerator over night. The remaining crystals were filtered off next day and dried in desiccator over KOH for 12 h. Average yield of synthesis was 93%. Individual crystals of compound **1** were sometimes present and were removed manually. Anal. Calcd. for [Cu<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>(3-pyOH)<sub>2</sub>]: C, 39.06%; H, 4.01%; N 5.06%; Cu, 22.96%. Found C, 37.9%; H, 3.96%; N 4.62%; Cu, 22.7%. IR (KBr, cm<sup>-1</sup>): 1625vs (ν<sub>as</sub>(CO<sub>2</sub>)); 1445vs (ν<sub>s</sub>(CO<sub>2</sub>)). UV/Vis (Nujol, λ<sub>max</sub>/nm): 298, 379sh, 732 μ<sub>eff</sub>(RT): 1.51 BM/Cu atom. Single crystals of compound **2** were obtained by similar procedure from more diluted solutions.

**[Cu(O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(3-pyOH)<sub>2</sub>]<sub>n</sub>, 3**

Solution prepared by dissolving 0.43 g (0.5 mmol) of [Cu<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>COOH)<sub>2</sub>] in 30 mL of hot CH<sub>3</sub>CN was filtered onto solution of 0.76 g (8 mmol) of 3-pyOH in 35 mL of CH<sub>3</sub>CN. Violet plate-like crystals precipitated from solution almost immediately. The solution was left at room temperature over night, the obtained product was filtered off and dried in air and in desiccator over KOH. Average yield was 89%. Anal. Calcd. for [Cu(O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(3-pyOH)<sub>2</sub>]: C, 58.12%; H, 4.06%; N 5.65%; Cu, 12.81%. Found C, 57.7%; H,

4.12%; N 6.47%; Cu, 12.8%. IR (KBr, cm<sup>-1</sup>): 1538s (ν<sub>as</sub>(CO<sub>2</sub>)); 1385vs (ν<sub>s</sub>(CO<sub>2</sub>)). UV/Vis (Nujol, λ<sub>max</sub>/nm): 298, 553, 690sh. μ<sub>eff</sub>(RT): 1.94 BM/Cu atom. Single crystals of compound **3** were formed from the solution obtained by mixing 30 mL of saturated solution of [Cu<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>COOH)<sub>2</sub>] in methanol, prepared at room temperature with solution of 0.05 g (0.5 mmol) of 3-pyOH in 1.2 mL of methanol.

**[Cu(O<sub>2</sub>C(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>(3-pyOH)<sub>2</sub>]<sub>n</sub>, 4**

0.29 g (0.5 mmol) of copper(II) hexanoate [Cu(O<sub>2</sub>C(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>] were dissolved in 12 mL of hot CH<sub>3</sub>OH and CH<sub>3</sub>CN mixture (1 : 1, v/v) and the hot solution filtered onto solution of 0.10 g (1 mmol) of 3-pyOH in 2 mL of the same mixture of solvents. The obtained solution was cooled to room temperature and left at -20 °C for 5 days. Blue-violet crystals of **4** were filtered off and dried in desiccator over KOH for 24 h. Average yield was 40%. The same compound was obtained by mixing water solution of copper sulphate pentahydrate with water solution of sodium hexanoate and 3-pyOH with higher yields (60%), but small amounts of unknown impurities were often present. Anal. Calcd. for [Cu(O<sub>2</sub>C(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>(3-pyOH)<sub>2</sub>]: C, 54.59%; H, 6.66%; N 5.79%; Cu, 13.13%. Found C, 53.8%; H, 6.95%; N 5.90%; Cu, 13.0%. IR (KBr, cm<sup>-1</sup>): 1604s, 1544m (ν<sub>as</sub>(CO<sub>2</sub>)); 1439s (ν<sub>s</sub>(CO<sub>2</sub>)). UV/Vis (Nujol, λ<sub>max</sub>/nm): 303, 574, 710sh. μ<sub>eff</sub>(RT): 1.98 BM/Cu atom. Single crystals of compound **4** were obtained from the solution prepared by mixing hot solution of 0.29 g (0.5 mmol) of copper(II) hexanoate in 15 mL of methanol and solution of 0.10 g (1 mmol) of 3-pyOH in 1 mL of methanol. Solution was left to concentrate slowly at room temperature and after 14 days blue-violet plate-like crystals were obtained.

**[Cu(O<sub>2</sub>C(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>)<sub>2</sub>(3-pyOH)<sub>2</sub>]<sub>n</sub>, 5**

Similar procedures with slightly different concentrations of solutions as for compound **4** were used for the preparation of analogous heptanoato coordination compound. Average yields were 44% (70%). Anal. Calcd. for [Cu(O<sub>2</sub>C(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>)<sub>2</sub>(3-pyOH)<sub>2</sub>]: C, 56.29%; H, 7.09%; N 5.47%; Cu, 12.41%. Found C, 55.6%; H, 7.33%; N 5.25%; Cu, 12.3%. IR (KBr, cm<sup>-1</sup>): 1605s, 1540m (ν<sub>as</sub>(CO<sub>2</sub>)); 1427s, 1407s (ν<sub>s</sub>(CO<sub>2</sub>)). UV/Vis (Nujol, λ<sub>max</sub>/nm): 288, 573, 715sh. μ<sub>eff</sub>(RT): 1.94 BM/Cu atom. Single crystals of compound **5** crystallized from the solution obtained by mixing 35 mL of saturated solution of copper heptanoate in ethyl acetate and solution of 0.10 g (1 mmol) of 3-pyOH in 10 mL ethyl acetate. A grass-green substance (not identified) precipitated from solution almost immediately and blue-violet crystals of **5** appeared after approximately 30 minutes and were left in solution to grow for 24 h.

## 2.2. X-ray Structure Analysis

Diffraction data for all five compounds were collected on a Nonius Kappa CCD diffractometer at 150(2) K using graphite monochromated MoK $\alpha$  radiation. The data were processed using DENZO<sup>11</sup> program. Structures were solved by direct methods: **1** to **4** using SHELXS-97<sup>12</sup> and **5** SIR97<sup>13</sup> program, respectively. Structures of **1** to **4** were refined by full matrix least squares on F<sup>2</sup> using SHELXL-97.<sup>14</sup> Non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed at ideal positions with the displacement parameters taken as 1.2 times (aromatic) and 1.5 times (methyl) of their parent atoms. For structure **5** a full-matrix least-squares refinement on F magnitudes with anisotropic displacement factors for all non-hydrogen atoms using Xtal3.6<sup>15</sup> was employed. The positions of hydrogen atoms were obtained from the difference Fourier map. The parameters of hydrogen atoms were refined isotropically. The resulting crystal data and details concerning data collection and refinement for all five compounds are quoted in Table 1. The crystallographic data for compounds **1** to **5** have also been deposited with the Cambridge Crystallographic Data Center as supplementary material with the deposition numbers: CCDC 612814 - 612818, respectively. Copies of the data can be obtained, free of charge via <http://www.ccdc.cam.ac.uk/const/retrieving.html>.

## 3. Results and Discussion

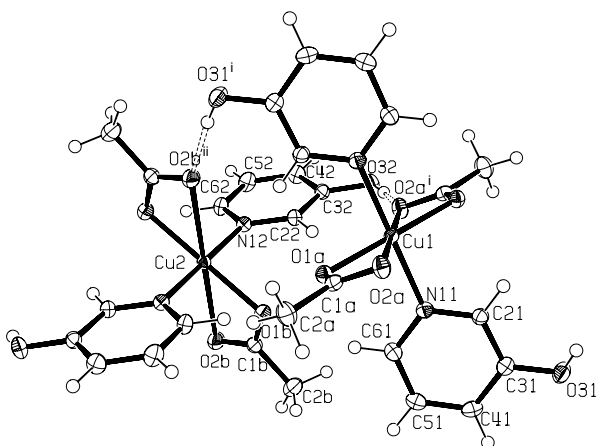
Different synthetic routes were applied and optimized procedures for preparation of five new copper(II) carboxylates with 3-hydroxypyridine (3-pyOH) are presented in experimental section. Monomeric and dimeric complex of copper(II) acetate were isolated, [Cu(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(3-pyOH)<sub>2</sub>], **1**, and [Cu<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>(3-pyOH)<sub>2</sub>], **2**, respectively. A covalently linked 2D Cu<sup>II</sup> compounds of general formula [Cu(O<sub>2</sub>CR)<sub>2</sub>(3-pyOH)<sub>2</sub>]<sub>n</sub> were prepared with benzoate (R=C<sub>6</sub>H<sub>5</sub>, **3**), hexanoate (R=CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>, **4**), and heptanoate (R=CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>, **5**) ligands. The measured XRD powder patterns of all prepared compounds are in good agreement with those calculated from single crystal data, thus confirming together with their IR spectra that all products were obtained as pure single phases. The obtained UV-Vis spectra and room temperature magnetic moments of all five compounds are in agreement with their crystal structures.

### 3.1. Description of the Crystal Structures

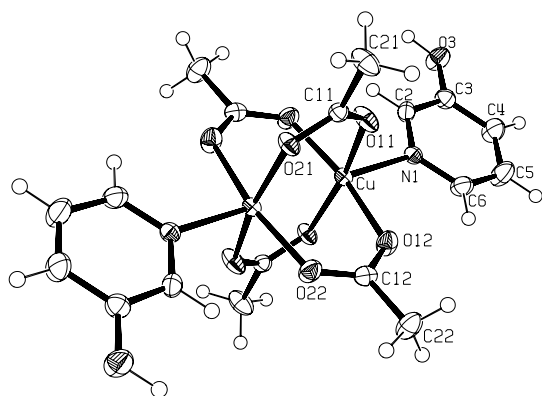
Figures 1-5 present ORTEP-III<sup>16</sup> drawings of complex molecules of compounds **1** to **5**, respectively. Table 2 contains coordination bond lengths and angles of all five compounds.

**Table 1.** Crystal data, data collection and structure refinement for compounds **1** to **5**.

	Compound <b>1</b>	Compound <b>2</b>	Compound <b>3</b>	Compound <b>4</b>	Compound <b>5</b>
Formula	C <sub>14</sub> H <sub>16</sub> CuN <sub>2</sub> O <sub>6</sub>	C <sub>9</sub> H <sub>11</sub> CuNO <sub>5</sub>	C <sub>24</sub> H <sub>20</sub> CuN <sub>2</sub> O <sub>6</sub>	C <sub>22</sub> H <sub>32</sub> CuN <sub>2</sub> O <sub>6</sub>	C <sub>24</sub> H <sub>36</sub> CuN <sub>2</sub> O <sub>6</sub>
<i>M<sub>r</sub></i>	371.83	276.73	495.96	484.04	512.10
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> -1, No. 2	<i>Pcab</i> , No. 61	<i>P</i> 2 <sub>1</sub> , No. 4	<i>P</i> 2 <sub>1</sub> / <i>a</i> , No. 14	<i>P</i> 2 <sub>1</sub> / <i>c</i> , No. 14
<i>a</i> (Å)	8.8859(2)	8.4619(1)	10.9221(2)	10.7241(5)	12.8516(3)
<i>b</i> (Å)	10.1093(2)	13.1660(2)	9.5674(2)	9.6013(5)	9.6675(2)
<i>c</i> (Å)	10.0985(3)	19.8127(4)	11.1563(2)	12.2743(5)	10.4773(3)
$\alpha$ (°)	114.962(2)	90	90	90	90
$\beta$ (°)	100.011(1)	90	111.7069(9)	113.219(2)	100.929(1)
$\gamma$ (°)	100.251(1)	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	777.14(3)	2207.32(6)	1083.12(4)	1161.5(1)	1278.12(5)
<i>Z</i>	2	8	2	2	2
Color, shape	blue, prism	green, prism	blue, prism	blue, plate	blue, plate
$\rho$ (Mg m <sup>-3</sup> )	1.589	1.665	1.521	1.384	1.330
<i>T</i> (K)	150(2)	150(2)	150(2)	150(2)	150(2)
Total reflect.	9905	19467	10980	9950	15546
<i>R<sub>int</sub></i>	0.024	0.047	0.026	0.052	0.054
Independ. refl.	3575	2509	4596	2641	2930
Observed refl.	3207	2038	4349	2112	2368
Refinement on	F <sup>2</sup>	F <sup>2</sup>	F <sup>2</sup>	F <sup>2</sup>	F
Final <i>R</i> and <i>R<sub>w</sub></i>	0.026, 0.070	0.032, 0.070	0.028, 0.063	0.056, 0.151	0.041, 0.039
Contribut. refl.	3575	2509	4596	2641	2720
Parameters	220	150	308	147	223
$\Delta\rho_{\max,\min}$ (e Å <sup>-3</sup> )	0.380, -0.389	0.386, -0.382	0.249, -0.374	1.063, -0.608	0.690 -1.140



**Figure 1.** A view of monomeric complex molecules  $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(3\text{-pyOH})]_1$ , **1**, with labelling of nonhydrogen atoms of asymmetric unit. Additionally are labeled symmetry related O atoms that form intermolecular hydrogen bonds, i:  $-x, -y+1, -z+1$ ; ii:  $-x, -y, -z$ . (Ellipsoids are at 50% probability level.)



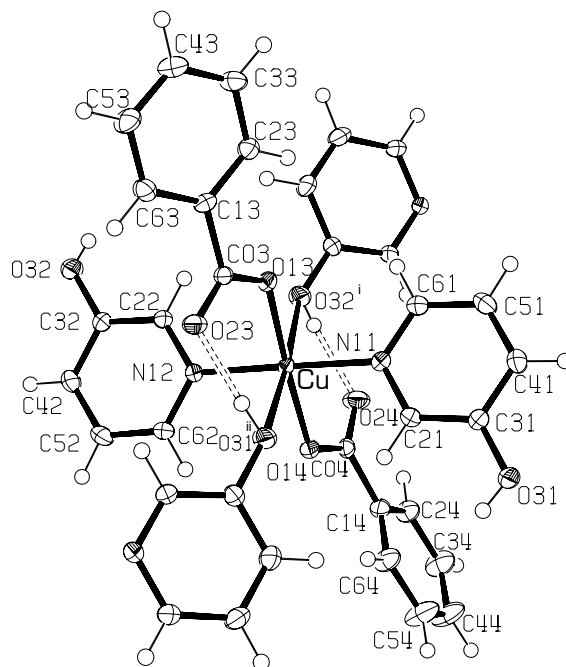
**Figure 2.** A view of the dimeric complex molecule  $[\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(3\text{-pyOH})_2]_2$ , **2**, with labelling of nonhydrogen atoms of asymmetric unit. (Ellipsoids are at 50% probability level.)

The structures of compounds **1** and **2** at 150 K are very similar to those at room temperature.<sup>6,7</sup> As it is expected at low temperature the unit cells are smaller than at room temperature. The comparison of bond lengths and contact distances shows that the contraction of structures is mostly due to the contraction of contact distances and less affected by changes of the geometrical parameters of the complex molecules.

The asymmetric unit of **1** consists of two half-units of  $[\text{Cu}(\text{ac})_2(3\text{-pyOH})_2]$ .  $\text{Cu}^{2+}$  ion lies on inversion centre and is surrounded by two (nearly coplanar) 3-pyOH ligands, *trans* coordinated through N atom and two acetato ligands coordinated in *trans* asymmetric chelate mode. Bond lengths and angles (Table 2) show

distorted octahedral (4+2) coordination. Hydroxy O atoms are not involved in coordination bonds. They form intermolecular hydrogen bonds with O2a and O2b atoms of acetato ligands linking the complex molecules in a chain running along [011] direction. The  $\text{O31}^i \dots \text{O2b}^{ii}$  and  $\text{O32} \dots \text{O2a}^i$  distances are 2.607(2) and 2.620(2) Å, and  $\text{O31}^i\text{-H}^i \dots \text{O2b}^{ii}$  and  $\text{O32-H} \dots \text{O2a}^i$  angles 175(2) and 171(3)°, respectively, i:  $-x, -y+1, -z+1$ ; ii:  $-x, -y, -z$ . The Cu...Cu contact distance within the chain is 5.4316(1) Å. The crystal packing is additionally stabilized by  $\pi \dots \pi$  and  $\pi \dots \sigma$  interactions among stacked heteroaromatic rings. Distance among ring centroids is 3.7055(11) Å. Dihedral angle between planes of these rings is 0° and the angle between centroid vector and normal to ring plane is 24.6°.

The conformation of complex molecules of **2** is of a *paddle-wheel* type. The molecules are centrosymmetric dimers with four *syn-syn* bridging acetato ligands and two apical 3-pyOH ligands coordinated through N atoms. The coordination polyhedron of Cu is slightly distorted square pyramid,  $\tau$  is 0.004.<sup>17</sup> The apical Cu-N distance 2.162(2) Å is significantly longer than Cu-O distances (average 1.976(11) Å). The Cu...Cu separation within a dimer is 2.6543(5) Å. Hydroxy group is uncoordinated. It forms intermolecular hydrogen bond with O21 atom of symmetry related acetato ligand linking the dimeric complex molecules in a two dimensional layer structure perpendicular to *c* edge. The  $\text{O3} \dots \text{O21}^i$  distance is 2.720(3) Å and  $\text{O3-H} \dots \text{O21}^i$  angle is 165(4)°, i:  $-x+3/2, y-1/2, -z+1$ .



**Figure 3.** A view of the complex molecule  $[\text{Cu}(\text{O}_2\text{CC}_6\text{H}_5)_2(3\text{-pyOH})_2]_n$ , **3**, (Ellipsoids are at 50% probability level.) The dashed lines indicate intramolecular hydrogen bond (i:  $-x+2, y-1/2, -z$ ; ii:  $-x+2, y+1/2, -z+1$ ).

**Table 2.** Selected bond distances (Å) and angles (°) for compounds **1** to **5**.

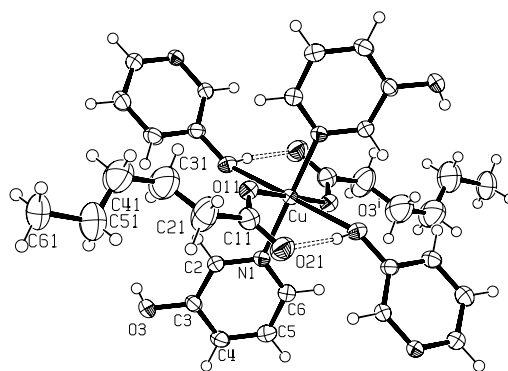
Compound 1			
Cu1-O1a	1.980(1)	O1a-Cu1-N11	90.07(6)
Cu2-O1b	1.986(1)	O1a-Cu1-O2a	55.49(5)
Cu1-N11	2.005(1)	O1b-Cu2-N12	90.18(6)
Cu2-N12	1.995(2)	O1b-Cu2-O2b	56.26(4)
Cu1-O2a	2.608(2)	O2a-Cu1-N11	90.11(6)
Cu2-O2b	2.566(1)	O2b-Cu2-N12	86.10(5)
Compound 2			
Cu-O11	1.971(2)	O11-Cu-O21 <sup>i</sup>	167.49(7)
Cu-O21 <sup>i</sup>	1.993(2)	O11-Cu-O12	89.57(8)
Cu-O12	1.972(2)	O11-Cu-O22 <sup>i</sup>	89.60(7)
Cu-O22 <sup>i</sup>	1.969(2)	O11-Cu-N1	97.57(7)
Cu-N1	2.161(2)	O21 <sup>i</sup> -Cu-O12	90.39(7)
O12-Cu-O22 <sup>i</sup>	167.72(7)	O21 <sup>i</sup> -Cu-O22 <sup>i</sup>	87.79(7)
O12-Cu-N1	96.47(7)	O21 <sup>i</sup> -Cu-N1	94.87(7)
O22 <sup>i</sup> -Cu-N1	95.79(7)		
Compound 3			
Cu-N11	2.001(2)	N11-Cu-O31 <sup>ii</sup>	84.41(7)
Cu-N12	2.003(2)	N11-Cu-N12	178.8(1)
Cu-O13	1.950(2)	N11-Cu-O32 <sup>iii</sup>	97.72(8)
Cu-O14	1.970(2)	N11-Cu-O13	89.33(8)
Cu-O31 <sup>ii</sup>	2.691(2)	N11-Cu-O14	87.45(8)
Cu-O32 <sup>iii</sup>	2.629(2)	N12-Cu-O32 <sup>iii</sup>	82.33(7)
O31 <sup>ii</sup> -Cu-O14	87.89(7)	N12-Cu-O13	91.86(8)
O32 <sup>iii</sup> -Cu-O13	85.31(7)	N12-Cu-O14	91.36(8)
O32 <sup>iii</sup> -Cu-O14	95.33(7)	O31 <sup>ii</sup> -Cu-N12	95.61(7)
O13-Cu-O14	176.77(8)	O31 <sup>ii</sup> -Cu-O32 <sup>iii</sup>	176.20(7)
O31 <sup>ii</sup> -Cu-O13	91.59(7)		
Compound 4			
Cu-N1	2.013(3)	N1-Cu-O11	89.3(1)
Cu-O3 <sup>iv</sup>	2.524(4)	N1-Cu-O3 <sup>iv</sup>	95.0(1)
Cu-O11	1.949(2)	O3 <sup>iv</sup> -Cu-O11	88.9(1)
Compound 5			
Cu-N1	2.012(2)	N1-Cu-O1 <sup>v</sup>	83.97(7)
Cu-O1 <sup>v</sup>	2.497(2)	N1-Cu-O11	89.59(9)
Cu-O11	1.961(2)	O1 <sup>v</sup> -Cu-O11	91.89(8)

i: 1-x, 1-y, 1-z; ii: 2-x, 1/2+y, 1-z; iii: 2-x, -1/2+y, -z;

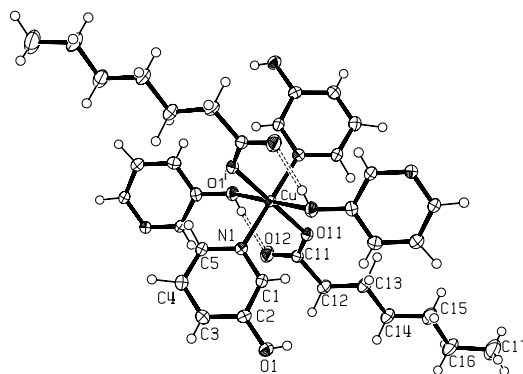
iv: -3/2+x, -1/2-y, z; v: -x, -1/2+y, 3/2-z

Compounds **3**, **4** and **5** contain 3-pyOH ligand and besides also benzoato, hexanoato or heptanoato ligand which is larger in comparison with the acetato ligand in **1** and **2**. This is probably the reason that they have very similar structure which differs completely from that of **1** or **2**. In all three structures both, N and hydroxy O atom form coordination bond, resulting in a two-dimensional covalently bonded extended structure analogous to the trifluoroacetato coordination compound<sup>4</sup>, with the same linkage pattern. Hydroxy O atom in all three compounds forms additionally an intramolecular hydrogen bond with the non-coordinated O atom of carboxylato ligand which has the consequence that also the coordination sphere is very similar. Carboxylate is in all three cases bonded as *trans* monodentate ligand with Cu-O distance 1.950(2), 1.970(2), 1.949(3) and 1.901(2) Å in **3**, **3**, **4**, and **5**, respectively. Cu-N distances are 2.003(2), 2.001(2), 2.013(3) and 2.012(2) Å, respectively. The distances between Cu and hydroxy O atoms from another pair of

(symmetry related) *trans* coordinated 3-pyOH ligands are significantly longer: 2.691(2), 2.629(2), 2.524(4), 2.497(2) Å in **3**, **3**, **4**, and **5**, respectively. In all three cases there is a distorted (4+2) octahedral arrangement of bonded ligands. Similar bond lengths and angles are also observed in [Cu(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(3-pyOH)<sub>2</sub>]<sub>n</sub>.<sup>4</sup> Cu atom in **4** and **5** lies at inversion centre, while the complex molecule of **3** does not possess the centre of inversion. Not only the conformations of all three complexes are very similar, also the packing motif is nearly the same, which can be seen from Figure 6 and also from the similarity of unit cell parameters and space groups. Space group of **4** and **5** is the same, *P*2<sub>1</sub>/*c* (if we exchange *a* and *c* axes of unit cell of **4**, *P*2<sub>1</sub>/*a* is transformed to the conventional *P*2<sub>1</sub>/*c*). Adding a centre of inversion to *P*2<sub>1</sub>, space group of **3**, would also result to its super-group *P*2<sub>1</sub>/*c*. The common feature of packing of complex molecules in all three structures are π...π and π...σ stacking interactions among 3-pyOH rings. The heteroaromatic rings are stacked in all three cases in the same way, with distance among ring centroids



**Figure 4.** A view of the complex molecule [Cu(O<sub>2</sub>CCH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>)<sub>2</sub>(3-py(OH)<sub>2</sub>)<sub>n</sub>, **4**. The dashed lines indicate intramolecular hydrogen bond, i: -x+1/2, y-1/2, -z. (Ellipsoids are at 50% probability level.)



**Figure 5.** A view of the complex molecule [Cu(O<sub>2</sub>CCH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>)<sub>2</sub>(3-py(OH)<sub>2</sub>)<sub>n</sub>, **5**, with labelling of nonhydrogen atoms of asymmetric unit. The dashed lines indicate intramolecular hydrogen bond, i: -x, y-1/2, -z+3/2. (Ellipsoids are at 50% probability level.)

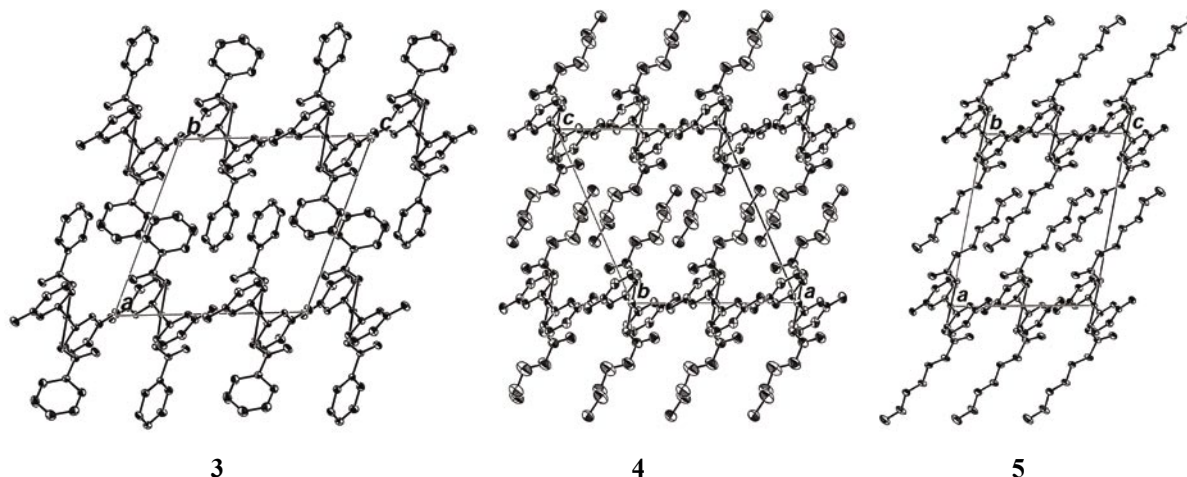


Figure 6. The packing of complex molecules of compound 3, 4, and 5, viewed along the *b* axis.

4.193(2), 4.193(2), 4.010(2) and 4.116(2) Å, dihedral angles between planes of these rings 9.89, 9.89, 0.04 and 0.00° and the angle between centroid vector and normal to ring plane 33.24, 28.05, 32.23 and 32.65° in 3, 3, 4, and 5, respectively.

### 3.2. Fungicidal activity

Results of screening for fungicidal activity against two fungal species *Trametes versicolor* and *Antrodia vaillantii* are presented in Table 3. Complete growth retardation for *Antrodia vaillantii* was noticed for compounds 3, 4, and 5 at concentrations  $5 \cdot 10^{-3}$  mol L<sup>-1</sup>,  $1 \cdot 10^{-3}$  mol L<sup>-1</sup>, and  $5 \cdot 10^{-4}$  mol L<sup>-1</sup>, while in the case of *Trametes versicolor* complete growth retardation was observed for the same three compounds only at the highest tested concentration. Compounds described in this paper show significantly lower fungicidal activity as compared with some other copper carboxylate complexes with different *N*-donor ligands.<sup>18</sup> In some cases the dissolved compound at lower concentration even enhance the fungal growth in comparison with pure solvent.

Table 3. Fungicidal activity for species *Trametes versicolor* (*T.v.*) and *Antrodia (Poria) vaillantii* (*A.v.*) at different concentrations, seven days after inoculation<sup>a</sup>

c/mol L <sup>-1</sup> Compound	5.0×10 <sup>-3</sup>		1.0×10 <sup>-3</sup>		5.0×10 <sup>-4</sup>	
	<i>T.v.</i>	<i>A.v.</i>	<i>T.v.</i>	<i>A.v.</i>	<i>T.v.</i>	<i>A.v.</i>
3-pyOH	2	2-3	1	2-3	1	2-3
1	1	3	1	3	1	3
2	3	5	1	3	1	2-3
3	5	5	3	5	1	5
4	5	5	3	5	1	5
5	5	5	3-4	5	1-2	5

<sup>a</sup> - The numbers in the table have the following meaning: 1, normal growth, no retardation; 2, slightly visible signs of retardation; 3, significant retardation; 4, retardation is very strong; 5, no fungal growth.

The value for the control without dissolved compounds: water 1, DMSO 2-3.

## 4. Acknowledgement

The diffraction data for all five compounds were collected on the Kappa CCD Nonius diffractometer in the Laboratory of Inorganic Chemistry, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia. We acknowledge with thanks the financial contribution of the Ministry of Higher Education, Science and Technology of the Republic of Slovenia through grants X-2000 and PS-511-103, which thus made the purchase of the apparatus possible.

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## Povzetek

Uporabljene so bile različne sintezne poti za pripravo petih bakrovih(II) karboksilatov z 3-hidroksipiridinom. Sintetizirana sta bila monomerni in dimerni kompleks bakrovega(II) acetata,  $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(3\text{-pyOH})_2]$ , **1**, in  $[\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(3\text{-pyOH})_2]$ , **2**. Pripravljene so bile tudi spojine  $\text{Cu}^{\text{II}}$  z dvodimenzionalnimi kovalentnimi povezavami s splošno formulo  $[\text{Cu}(\text{O}_2\text{CR})_2(3\text{-pyOH})_2]_n$ , in naslednjimi karboksilati: benzoatom ( $\text{R}=\text{C}_6\text{H}_5$ ), **3**, heksanoatom ( $\text{R}=\text{CH}_3(\text{CH}_2)_4$ ), **4** in heptanoatom ( $\text{R}=\text{CH}_3(\text{CH}_2)_5$ ), **5**. Kristalne strukture vseh petih spojin so bile določene z rentgensko strukturno analizo. Spojine so bile testirane za fungicidno aktivnost dveh vrst gliv: *Trametes versicolor* in *Antrodia vaillantii*. Spojine **3**, **4** in **5** s koncentracijo  $5 \cdot 10^{-3} \text{ mol L}^{-1}$ ,  $1 \cdot 10^{-3} \text{ mol L}^{-1}$  in  $5 \cdot 10^{-4} \text{ mol L}^{-1}$  so povzročile popoln zastoj rasti glive *Antrodia vaillantii*. V primeru glive *Trametes versicolor* pa je bil opažen za iste tri spojine popoln zastoj rasti samo pri najvišji testirani koncentraciji.