

## Fatty Acid Copper(II) Carboxylates with Nicotinamide – Characterization and Fungicidal Activity. Crystal Structures of Two Heptanoate Forms and Nonanoate\*

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Several new compounds of the composition  $[\text{Cu}_2(\text{OOCCH}_n\text{H}_{2n+1})_4(\text{nia})_2]$  (nia = nicotinamide;  $n = 6$  to 11) were synthesized, characterized and tested for fungicidal activity. Crystal structure determinations revealed dinuclear structures of the copper(II) acetate hydrate type for compounds  $[\text{Cu}_2(\text{OOCCH}_6\text{H}_{13})_4(\text{nia})_2]$ -A (**1A**),  $[\text{Cu}_2(\text{OOCCH}_6\text{H}_{13})_4(\text{nia})_2]$ -B (**1B**) and  $[\text{Cu}_2(\text{OOCCH}_8\text{H}_{17})_4(\text{nia})_2]$  (**3**). Other applied characterization methods indicate dimeric structures for all synthesized compounds [ $\mu_{\text{eff}}$  (298 K) = 1.43–1.50 BM; characteristic band in UV-Vis spectra in the region  $\lambda = 350$ –400 nm]. The same conclusion may also be deduced from the IR ( $\Delta = \nu_{\text{asym}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-) = 183$ –189  $\text{cm}^{-1}$ ) and EPR spectra, though some differences were observed for heptanoate modification **1A**, probably due to a different hydrogen bonding scheme. Screen-

\* Dedicated to Professor Boris Kamenar on the occasion of his 70<sup>th</sup> birthday.

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ing for fungicidal activity against the wood-rotting fungus *Trametes versicolor* (L. ex Fr.) Pilat shows that the compounds dissolved in DMSO completely stop mycelium growth at a concentration of  $1.0 \times 10^{-3}$  mol L<sup>-1</sup>. Some of them ( $n = 8, 9, 10$ ) show strong activity also in more diluted solutions ( $1.0 \times 10^{-4}$  mol L<sup>-1</sup>).

*Key words:* copper(II) carboxylates, fatty acids, nicotinamide, crystal structure, EPR, fungicidal activity.

## INTRODUCTION

The fungicidal activity of copper(II) carboxylates have already been studied.<sup>1-3</sup> It was noticed that not only the nature of the ligands around the metal ion but also their mode of coordination plays an important role in the complex activity. During the investigations, it was found that dimeric complexes involving bridging fatty acids are especially interesting.<sup>4,5</sup> The influence of dimers in biological systems may also vary with the different apically positioned ligand that is already bioactive, *e.g.* nicotinamide in this study. In general, copper(II) carboxylates exhibit the dinuclear paddle-wheel cage type structure. Although more than 250 X-ray crystal structures containing the [Cu<sub>2</sub>(OOCR)<sub>4</sub>] core can be found in the Cambridge Structural Database<sup>6</sup> and over a hundred of the type [Cu<sub>2</sub>(OOCR)<sub>4</sub>L<sub>2</sub>] (L is an apical ligand with an oxygen or a nitrogen donor atom), only a few of the former are with higher carboxylic acids,<sup>7-10</sup> of which only one is of the type [Cu<sub>2</sub>(OOCR)<sub>4</sub>L<sub>2</sub>].<sup>10</sup>

In this paper, the synthesis and characterization of the fatty acid copper(II) carboxylates with nicotinamide [Cu<sub>2</sub>(OOCCH<sub>n</sub>H<sub>2n+1</sub>)<sub>4</sub>(nia)<sub>2</sub>] ( $n = 6$  for **1A**, **1B**; 7 for **2**; 8 for **3**; 9 for **4**; 10 for **5**; 11 for **6**) are presented, and for **1A**, **1B** and **3**, their crystal structures are reported. The results of preliminary studies concerning compounds **2** and **3** have already been reported.<sup>4</sup>

## EXPERIMENTAL

### *Syntheses*

Nicotinamide (nia) and all solvents were purchased from commercial sources and used without further purification. The other starting substances [Cu<sub>2</sub>(OOCCH<sub>n</sub>H<sub>2n+1</sub>)<sub>4</sub>] ( $n = 6$  to 11) were synthesized according to the precipitation method described in the literature.<sup>11</sup>

Copper carboxylate was added to acetonitrile acidified by the appropriate carboxylic acid, under stirring. After the addition, the temperature was raised to boiling point and the solution was kept at that temperature for 15 minutes while stirring was continued. Obtained transparent solution was added to the solution of

nicotinamide (2 mol *per* 1 mol of copper carboxylate) dissolved in a minimal volume of acetonitrile. After cooling to room temperature, the green tabular or needle-like crystals precipitated. They were filtered off in a few days and dried in a desiccator over KOH for several hours. Average yield is over 80% for all compounds except for **1B** (45%). Because of lower solubility of starting copper carboxylates for **4**, **5** and **6**, the absolute ethanol was mixed with acetonitrile at the beginning of the synthesis. In order to prevent precipitation of turquoise coloured starting carboxylates, instead of the desired green compounds with nicotinamide, a higher amount of nicotinamide was used. An excess of nicotinamide was used also for **1A** to avoid appearance of the **1B** modification. Single crystals of X-ray quality for **1A** and **1B** were obtained by the above methods. For **3**, the crystals were grown on copper metal sheets in the acetonitrile solution of sodium nonanoate and nicotinamide after ten months.

Metal analyses were carried out electrogravimetrically with Pt electrodes.

C, H, N analyses were performed at the Department of Organic Chemistry, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia.

The results of elemental analyses are available from the authors upon request.

### Physical Measurements

Interplanar spacings ( $d$ -values) were obtained using a Guinier-de-Wolf camera (Enraf Nonius) and Cu-K $\alpha$  radiation. Infrared spectra were measured on mineral oil mulls between CsI plates using a Perkin-Elmer FT-IR 1720X spectrometer in the range 4000–400 cm<sup>-1</sup>. Electronic spectra were recorded as Nujol mulls (200–860 nm) with a Perkin-Elmer UV/VIS/NIR Spectrometer Lambda 19. Magnetic susceptibility of the substances was determined at room temperature by the Evans method using powdered samples and a Sherwood Scientific MSB-1 balance with Hg[Co(NCS)<sub>4</sub>] as a calibrant. Diamagnetic corrections were estimated from Pascal's constants and the effective magnetic moments were calculated using the equation:  $\mu_{\text{eff}} = 2.828(\chi_{\text{M}}T)^{1/2}$ . EPR spectra of the powdered samples were recorded at 150 K and at room temperature on a Bruker ESP-300 X band spectrometer at the Department of Solid State Physics-EPR Center, "Jožef Stefan" Institute, Ljubljana, Slovenia. Parameters  $g_{\perp}$ ,  $g_{\parallel}$ ,  $D$  and  $J$  were calculated directly with the field positions  $H_{\perp}$ ,  $H_{z1}$  and  $H_{z2}$  from the spectra, as described in the literature.<sup>12,13</sup> Compounds were tested for fungicidal activity as described earlier.<sup>14</sup>

### *X-ray Crystallography of Tetrakis( $\mu$ -heptanoato-O,O')-bis(nicotinamide) dicopper(II)-A (1A), Tetrakis( $\mu$ -heptanoato-O,O')-bis(nicotinamide)dicopper(II)-B (1B) and Tetrakis( $\mu$ -nonanoato-O,O')-bis(nicotinamide)dicopper(II) (3)*

Room temperature data for **1A** were collected on a Siemens P4/PC diffractometer with Cu-K $\alpha$  radiation and for **1B** and **3** on a Nonius KappaCCD CAD-4 diffractometer with Mo-K $\alpha$  radiation, using graphite monochromator in both cases. Common data corrections for variations in reference reflections and Lorentz-polarization effects were applied. An empirical absorption correction for **1A** was performed,<sup>15</sup> but absorption for **1B** and **3** was done by scaling (the internal consistency factors were low). The crystallographic data are summarized in Table I. All three structures were solved by direct methods using SHELXS86<sup>16</sup> and all non-hydrogen atoms were re-

TABLE I  
Crystal data, data collection and structure refinement parameters for **1A**, **1B** and **3**

	Compound <b>1A</b>	Compound <b>1B</b>	Compound <b>3</b>
Molecular formula	Cu <sub>2</sub> (OCC <sub>6</sub> H <sub>13</sub> ) <sub>4</sub> (nia) <sub>2</sub>	Cu <sub>2</sub> (OCC <sub>6</sub> H <sub>13</sub> ) <sub>4</sub> (nia) <sub>2</sub>	Cu <sub>2</sub> (OCC <sub>8</sub> H <sub>17</sub> ) <sub>4</sub> (nia) <sub>2</sub>
Molecular weight	888.0	888.0	1000.3
Crystal color	dark green	dark green	dark green
Crystal system	monoclinic (no. 14)	monoclinic (no. 15)	monoclinic (no. 15)
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	9.358(3)	23.193(5)	50.77(1)
<i>b</i> /Å	18.878(4)	9.886(2)	9.955(2)
<i>c</i> /Å	27.348(7)	20.942(4)	21.894(4)
$\beta$ /°	98.83(3)	99.68(3)	92.84(3)
<i>V</i> /Å <sup>3</sup>	4774(2)	4733.3(2)	11051(4)
Density (calcd.) /g cm <sup>-3</sup>	1.236	1.246	1.202
<i>Z</i>	4	4 <sup>a</sup>	8
$\lambda$ /Å	1.54178	0.71073	0.71073
Scan mode	$\omega$	– CCD detector was used –	–
Max $\theta$ /°	59.97	26.38	26.31
Data measured	7585	9176	20110
Unique data	7090	4769	10520
Observed data $ F_o  > 4\sigma F_o $	2661	3186	4058
Goodness of fit on $F^2$	1.016	0.954	0.848
Final $R_1$ indices $ F_o  > 4\sigma F_o $	0.1191	0.0440	0.0508
$wR_2$ indices $ F_o  > 4\sigma F_o $	0.3276	0.1260	0.1350
$R_1$ indices (all data)	0.2791	0.0687	0.1361
$wR_2$ indices (all data)	0.5452	0.1378	0.1214
Extinction coefficient	0.0005(2)	0.0028(6)	0.0006(1)
Max., min. residue /e Å <sup>-3</sup>	0.54, –0.77	0.40, –0.27	0.27, –0.32
Mean, max. shift / error	0.001, –0.065	0.001, –0.024	0.032, 0.208
Absorption coefficient /cm <sup>-1</sup>	15.3	9.5	8.2

<sup>a</sup> The complex has crystallographic  $C_i$  symmetry.

fined anisotropically. Carbon atoms at the ends of the alkyl chains showed significant thermal motion, resulting in low accuracy in carbon–carbon interatomic distances. There is a considerable disorder in three of the four alkyl chains in the structure of **1A**, leading to rather high final residuals ( $R_1 = 0.119$ ,  $wR_2 = 0.328$  for the observed reflections). Obtained geometrical parameters are not of high quality, but the chemical structure is reliable.

Refinements were performed by full-matrix least squares based on  $F^2$  using SHELX97.<sup>15</sup> In **1B**, the amino hydrogen atoms were located from  $\Delta F$  map and refined isotropically. Positions of the remaining hydrogen atoms were calculated and refined as riding atoms with isotropic displacement parameters taken from those of the attached heavy atoms and multiplied by 1.5 (options AFIX 93, 43, 23 and 33 of SHELX97). All of the N–H distances of amino groups for **1A**, **1B** and **3** have been normalized to 0.90 Å.

## RESULTS AND DISCUSSION

Several new compounds of the composition  $[\text{Cu}_2(\text{OOC}C_n\text{H}_{2n+1})_4(\text{nia})_2]$  (nia = nicotinamide;  $n = 6$  to 11) were synthesized. In the cases of heptanoates – **1A**, **1B** and nonanoate – **3** crystals suitable for X-ray structural analysis were obtained. Structures of the two polymorphic modifications of heptanoates, **1A** and **1B**, and the structure of nonanoate **3** were determined. Crystal structures and the results of other characterization methods of the compounds are compared and discussed. Also, observations concerning their fungicidal activity are reported and described herein.

### *Crystal Structures*

The results of the crystal structure determination show that in three synthesized compounds  $[\text{Cu}_2(\text{OOC}C_n\text{H}_{2n+1})_4(\text{nia})_2]$ , [ $n = 6$  for **1A** (Figure 1), **1B** (Figure 2); 8 for **3** (Figure 3)] copper ions are bridged by four carboxylate groups, forming usual dinuclear complexes of the acetate hydrate type<sup>17</sup> with nicotinamide ligands (nia) instead of water molecules in the axial positions, coordinated through pyridine nitrogen atoms. Despite the number of crystal structures with  $[\text{Cu}_2(\text{OOCR})_4\text{L}_2]$  core, the search through the Cambridge Structural Database<sup>6</sup> revealed only one other example with fatty acid carboxylate.<sup>10</sup>

Small differences in the Cu–Cu separation were observed in the three related structures (see figure captions). The copper atoms are displaced from the basal  $\text{O}_4$  planes by between 0.193(6) to 0.208(6) Å values, considered normal for this type of compound.<sup>18</sup> The amide groups are rotated by *ca.* 23° out of the plane of pyridine rings in heptanoates, while the twist angles between amide groups and their associated pyridine rings in nonanoate are *ca.* 20° and 16°, respectively. Coordination geometries about the copper

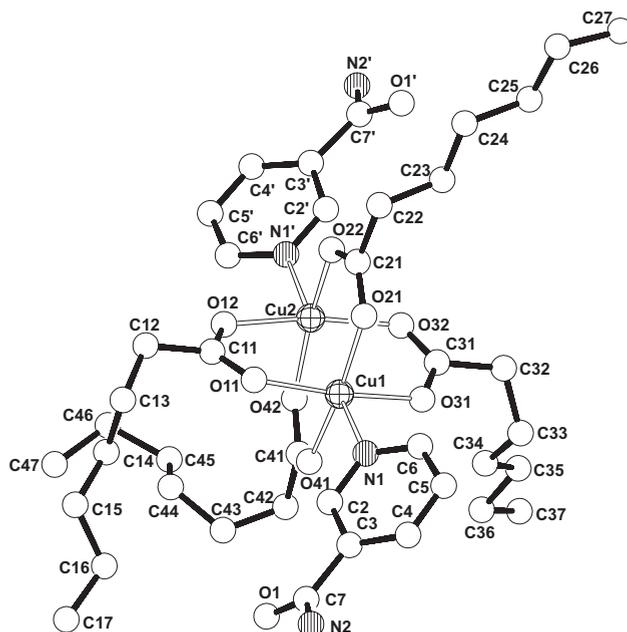


Figure 1. The molecular structure of **1A**. The Cu–Cu separation is 2.604(3) Å. Only one of the alternate orientations of the disordered alkyl chains is illustrated.

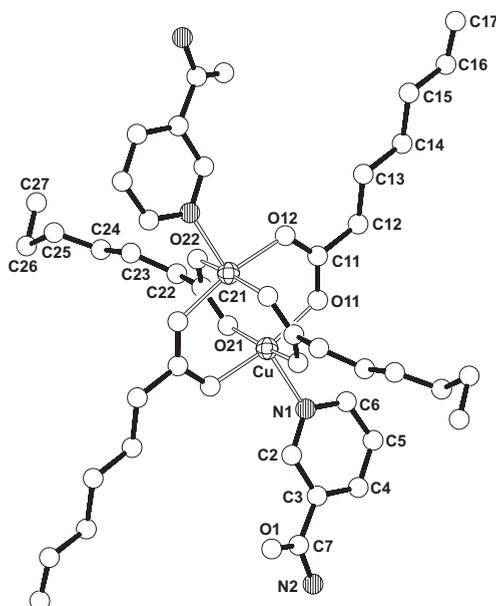


Figure 2. The molecular structure of **1B**. The Cu–Cu separation is 2.612(7) Å.

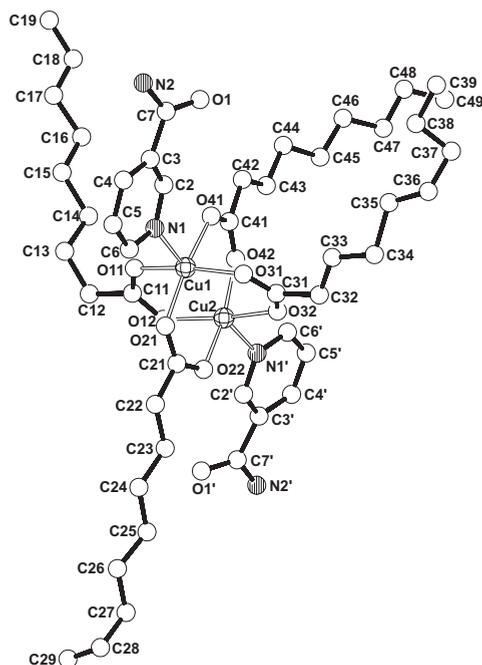


Figure 3. The molecular structure of **3**. The Cu–Cu separation is 2.618(7) Å.

centers are typical for this type of compounds. Selected bond lengths and angles are presented in Table II.

### *Structures of Heptanoates – 1A and 1B*

The main difference between the two polymorphic forms of heptanoates is the existence of  $C_i$  symmetry for **1B** complex in the space group  $C2/c$ , whereas this is not the case of **1A** complex, which crystallizes in the space group  $P2_1/c$ . Furthermore, the existence of the two polymorphic modifications was confirmed by different powder diffraction patterns. The two forms have considerably different hydrogen bonding schemes (Figure 4). In **1A**, only amide-amide hydrogen bonds are observed, being linked head-to-head and tail-to-tail *via* pairs of N–H $\cdots$ O hydrogen bonds. These chains criss-cross to form a honeycomb-like network (Figure 5), the pores being populated by the bulky alkyl chains. Adjacent crossing chains are hydrogen-bonded *via* additional N–H $\cdots$ O hydrogen bonds, utilizing the N–H hydrogen atoms not involved in chain formation. There are also some differences in the orientation of nicotinamide groups with respect to the carboxylic parts. The pyridine rings adopt an almost bisecting geometry between the planes of

TABLE II  
Selected bond lengths /Å and angles /° with estimated standard deviations  
in parentheses

Compound <b>1A</b>					
Cu1–O11	1.91(1)	Cu2–O12		1.97(1)	
Cu1–O21	1.93(1)	Cu2–O22		1.98(1)	
Cu1–O31	1.95(1)	Cu2–O32		1.97(1)	
Cu1–O41	1.97(1)	Cu2–O42		1.98(1)	
Cu1–N1	2.14(1)	Cu2–N1'		2.16(1)	
<i>Structural parameters suggesting hydrogen bonding</i>					
N2...O1 <sup>i</sup>	2.965(12)	H5...O1 <sup>i</sup>	2.11	N2–H5...O1 <sup>i</sup>	175
N2...O1 <sup>ii</sup>	2.796(15)	H6...O1 <sup>iii</sup>	2.06	N2–H6...O1 <sup>iii</sup>	144
N2'...O1 <sup>iii</sup>	2.989(12)	H11...O1 <sup>iii</sup>	2.15	N2'–H11...O1 <sup>iii</sup>	164
N2'...O1 <sup>iv</sup>	2.868(15)	H12...O1 <sup>iv</sup>	2.19	N2'–H12...O1 <sup>iv</sup>	136
Symmetry code: <sup>i</sup> $-x, -y, -z$ ; <sup>ii</sup> $-x, 2+y, 2-z$ ; <sup>iii</sup> $1-x, 1-y, 1-z$ ; <sup>iv</sup> $1-x, 2+y, 2-z$ .					
Compound <b>1B</b>					
Cu–O11	1.957(2)	Cu–O21		1.964(2)	
Cu–O12a	1.961(2)	Cu–O22a		1.983(2)	
Cu–N1	2.172(2)				
<i>Structural parameters suggesting hydrogen bonding</i>					
N2...O1 <sup>i</sup>	3.107(3)	H31...O1 <sup>i</sup>	2.09	N2–H31...O1 <sup>i</sup>	157
N2...O22 <sup>ii</sup>	3.215(4)	H32...O22 <sup>ii</sup>	2.37	N2–H32...O22 <sup>ii</sup>	177
Symmetry code: <sup>i</sup> $2-x, 2+y, \frac{3}{2}-z$ ; <sup>ii</sup> $x, 1-y, -2+z$ ; a $\frac{1}{2}-x, \frac{1}{2}-y, 2-z$ .					
Compound <b>3</b>					
Cu1–O11	1.983(3)	Cu2–O12		1.987(3)	
Cu1–O21	1.956(3)	Cu2–O22		1.959(3)	
Cu1–O31	1.969(3)	Cu2–O32		1.956(3)	
Cu1–O41	1.954(3)	Cu2–O42		1.957(3)	
Cu1–N1	2.188(3)	Cu2–N1'		2.173(3)	
<i>Structural parameters suggesting hydrogen bonding</i>					
N2...O12 <sup>i</sup>	3.161(4)	H5...O12 <sup>i</sup>	2.31	N2–H5...O12 <sup>i</sup>	170
N2...O1 <sup>i</sup>	2.992(4)	H6...O1 <sup>i</sup>	2.15	N2–H6...O1 <sup>i</sup>	168
N2'...O41 <sup>ii</sup>	3.161(4)	H11...O41 <sup>ii</sup>	2.39	N2'–H11...O41 <sup>ii</sup>	149
N2'...O1 <sup>ii</sup>	2.978(4)	H12...O1 <sup>ii</sup>	2.15	N2'–H12...O1 <sup>ii</sup>	162
Symmetry code: <sup>i</sup> $x, 2-y, -2+z$ ; <sup>ii</sup> $x, 2-y, 2+z$ .					

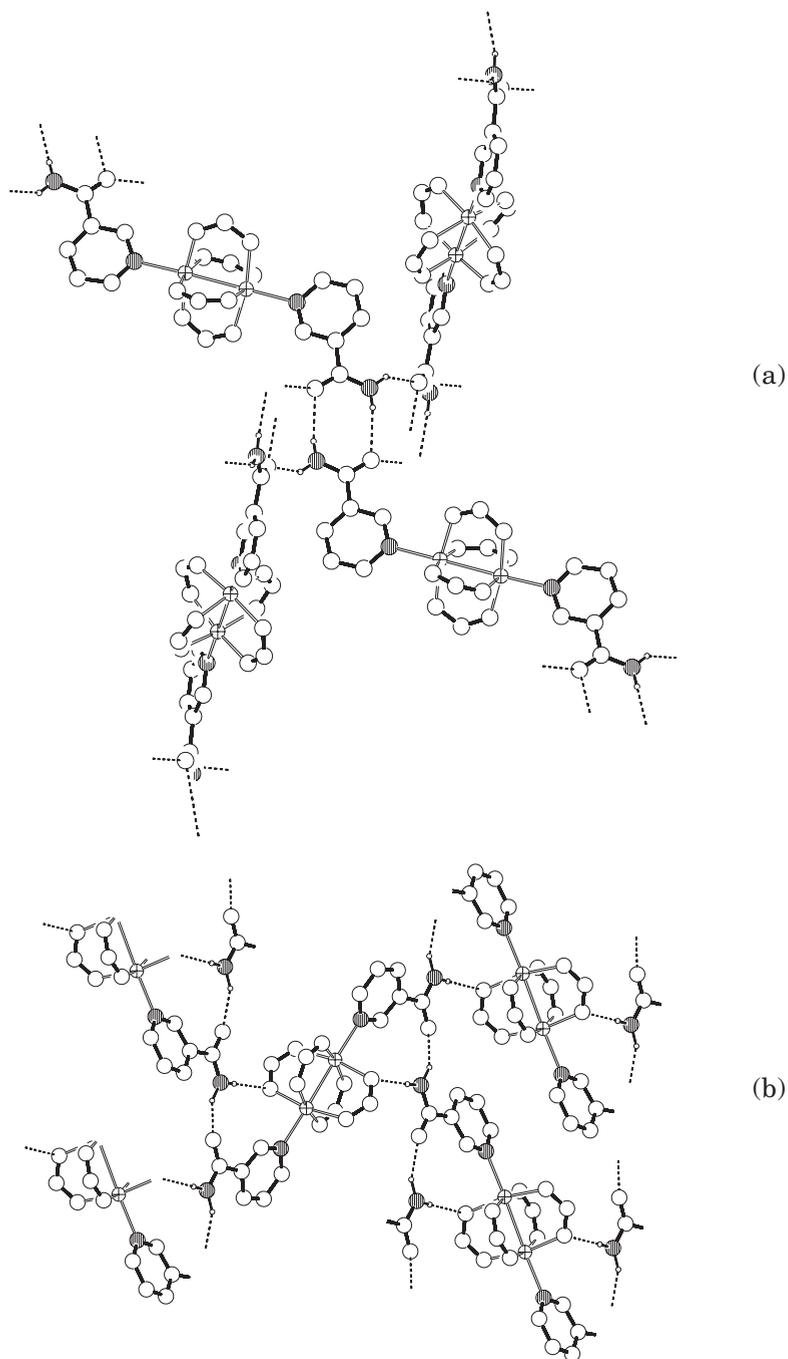


Figure 4. Hydrogen-bonding schemes in the two polymorphic forms of heptanoates: (a) for **1A** and (b) for **1B**. The void-filling alkyl chains have been omitted for clarity.

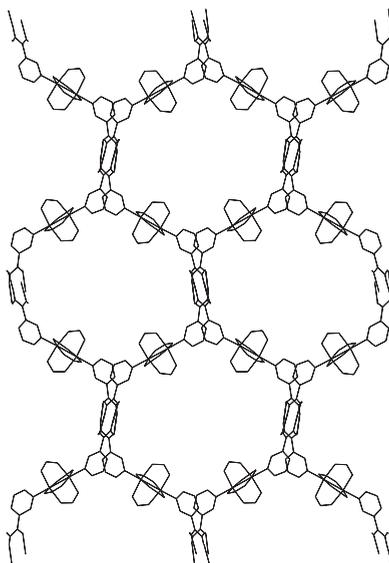


Figure 5. The honeycomb-like pattern of cross-linking chains present in the crystals of **1A**. The void-filling alkyl chains have been omitted for clarity.

two carboxylate groups in **1A**, whereas in **1B** they are almost coincident with the planes ( $13^\circ$ ). A detailed analysis of the pattern of bonding for **1A** is not realistic due to the disorder that is present in three of the four aliphatic chains, which limits the precision of the structure.

In **1B**, the dimers pack *via* pairs of N–H...O hydrogen bonds from the amide nitrogen to the amide and carboxylate oxygen atoms of adjacent dimers to form an extended sheet, as illustrated in Figure 4b.

#### *Structure of Nonanoate – 3*

Structures of compounds **1B** and **3** are more closely related than the two heptanoate forms. Both complexes **1B** and **3** crystallize in the space group *C2/c* with the nearly double unit-cell dimension of 50.77(1) Å in **3**, compared to 23.193(5) Å in **1B** (Table I). The hydrogen-bonding scheme observed for **3** is almost identical to that of **1B**.

#### *Spectroscopic Data*

Ambient EPR spectra of all nicotinamide complexes exhibit broad features characteristic of a triplet state, at  $-2J$  above the singlet level (the figure is available from the authors upon request). A typical binuclear copper

TABLE III

Room temperature EPR parameters for the studied copper(II) carboxylates with nicotinamide

Compound	$g_{\parallel}$ ( $\pm 0.01$ )	$g_{\perp}$ ( $\pm 0.005$ )	$D$ ( $\pm 0.004$ ) /cm <sup>-1</sup>	$ 2J $ ( $\pm 20$ ) /cm <sup>-1</sup>
<b>1A</b>	2.35	2.090	0.347	300
<b>1B</b>	2.35	2.090	0.347	330
<b>2</b>	2.35	2.090	0.347	/
<b>3</b>	2.35	2.090	0.347	300
<b>4</b>	2.35	2.090	0.347	/
<b>5</b>	2.34	2.090	0.345	/
<b>6</b>	2.35	2.080	0.345	/

Where the Cu–Cu distance ( $r$ ) was known, singlet–triplet energy gap was calculated from the following expression:<sup>13</sup>  $D = -J/8 [1/4(g_{\parallel} - 2)^2 - (g_{\perp} - 2)^2] - [g_{\parallel}^2 + 1/2(g_{\perp}^2)] \beta^2/r^3$ .

compound with a triplet state EPR spectrum is copper(II) acetate hydrate.<sup>11,19,20</sup> Besides this classic example, EPR spectroscopic data of numerous binuclear copper complexes can be found in the literature.<sup>11,13,21,22</sup> A comparison of these data with our measurements shows that the values of  $g_{\perp}$ ,  $g_{\parallel}$ , zero-field splitting parameter  $D$  and the singlet–triplet energy gap  $|2J|$ , calculated for the studied carboxylates containing nicotinamide ligand (Table III), lie within the expected range. Besides three triplet state transitions, EPR spectra of the complexes, with the exception of copper(II) octanoate adduct, contain additional resonance lines at 320 mT. These lines arise from the so-called mononuclear impurities, which can be found in similar systems.<sup>12,23</sup> Values of parameter  $g$  for the observed mononuclear impurities, from 2.065 to 2.090, correspond to the perpendicular part of axial Cu(II) EPR spectrum, resulting from a spin doublet state.<sup>24</sup> Mononuclear  $g_{\parallel}$  could not be resolved. In some cases, intensities of mononuclear resonance lines were rather high but recrystallization resulted in their significant decrease (Figure 6). The exception was **1A**: several attempts to lower the content of "mononuclear" impurities by recrystallization and therefore intensity of the corresponding EPR signal were not successful because the compound converts to **1B**. We managed to synthesize compound **1A** repeatedly only by following the already described procedure. We can also see (the figure is available from the authors upon request) that the lineshape of the spectrum is different from the other spectra in the part where "mononuclear" signals are expected. Interestingly, also the hydrogen-bonding scheme for compound **1A** differs significantly from that in **1B** and **3**. Spectrum of **1A** powder was recorded also at 150 K (the figure is available from the authors upon request). The only difference from the ambient temperature spectrum

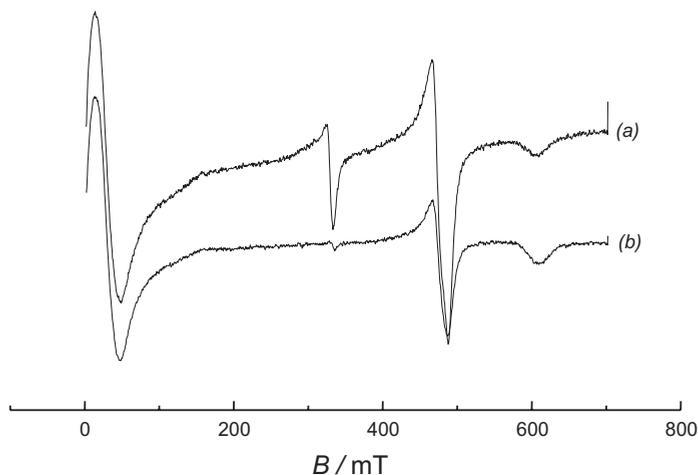


Figure 6. Room temperature EPR spectra of **5** before (a) and after (b) recrystallization.

is in the triplet feature  $B_{z1}$  at about 25 mT. Splitting into a septet, due to interaction of the unpaired electrons with two equivalent copper nuclei within the dimer unit, was observed.

In the IR spectra, several bands in two regions are characteristic of carboxylate stretching vibrations. The difference between the strongest symmetric and asymmetric bands ( $\Delta = \nu_{\text{asym}} - \nu_{\text{nsym}}$ )<sup>25</sup> in these regions is in the range between 183 and 189  $\text{cm}^{-1}$ . Some differences for heptanoate **1A** (198  $\text{cm}^{-1}$ ) were observed. Significant deviations in the region between 3100 and 3400  $\text{cm}^{-1}$ , characteristic of N–H bonds, were noticed. Two bands are present in the spectrum of **1A**, however for the others at least four bands that are relatively weaker compared to those of **1A** appeared. As mentioned above, a significant difference in hydrogen bonding scheme for this compound was observed. Only amide-amide intermolecular hydrogen bonds are present in **1A**, whereas for **1B** and **3** that have almost the same hydrogen-bonding scheme, linkages between amide and carboxylate groups are also present. Different surroundings of the coordinated ligands may therefore lead also to deviations in the EPR spectrum.

In the UV-Vis spectra recorded as Nujol mull, the band between 350 and 400 nm, characteristic of dimeric structure, was observed.<sup>26</sup> The values for room temperature magnetic moments lie in the range between 1.43 and 1.50 BM.

The results of X-ray analyses reveal dinuclear copper(II) acetate hydrate type structures for both heptanoates (**1A** and **1B**) and nonanoate (**3**). From the results of the applied spectroscopic methods and magnetic measure-

ments described above, we suggest a similar nature also for the other investigated compounds of the composition  $[\text{Cu}_2(\text{OOC}_n\text{H}_{2n+1})_4(\text{nia})_2]$  (nia = nicotinamide;  $n = 6$  to 11).<sup>25,26,27</sup> Different IR and EPR spectra of complex **1A**, compared to the spectra of the other compounds, are in the agreement with the results of the X-ray structure analysis.

### *Fungicidal Activity*

Dissolved in DMSO, the synthesized compounds show strong fungicidal activity against the wood-rotting fungus *Trametes versicolor* (L. ex Fr.) Pilat. The mycelium growth is completely stopped at a concentration of  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> for all investigated complexes. Some of them (**4**, **5**, **6**) show strong activity also in more diluted solutions ( $1.0 \times 10^{-4}$  mol L<sup>-1</sup>). The weaker influence noticed for heptanoate complexes in concentrated solution is probably due to the shorter chain of the fatty acid.<sup>4,5,28</sup> The length of the chain influences also the solubility of the substances, as it was observed for undecanoate and especially dodecanoate complex. Partial recrystallization in the cooled culture medium leads to lower concentration and therefore weaker activity of the solution of dodecanoate complex.

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## SAŽETAK

### Mješoviti kompleksi bakra(II) s karboksilnim kiselinama i nikotinamidom – opis svojstava i fungicidna djelotvornost. Kristalne strukture dvaju polimorfa heptanoatnog i jednog nonanoatnog kompleksa

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Opisani su priprava, fizikalna i kemijska svojstva, stereokemija i ispitivanje fungicidne djelotvornosti nekoliko novih kompleksnih spojeva bakra(II) opće formule  $[\text{Cu}_2(\text{OOC}C_n\text{H}_{2n+1})_4(\text{nia})_2]$  (nia = nikotinamid;  $n = 6$  do 11). Određivanjem kristalne strukture ustanovljeno je da spojevi  $[\text{Cu}_2(\text{OOC}C_6\text{H}_{13})_4(\text{nia})_2]$ -A (**1A**),  $[\text{Cu}_2(\text{OOC}C_6\text{H}_{13})_4(\text{nia})_2]$ -B (**1B**) i  $[\text{Cu}_2(\text{OOC}C_8\text{H}_{17})_4(\text{nia})_2]$  (**3**) po građi odgovaraju tipu strukture dinuklearnog akvakompleksa bakrova(II) acetata. Druge primijenjene metode istraživanja fizikalnih i kemijskih značajki ukazuju da svi priređeni spojevi imaju dimernu građu [ $\mu_{\text{eff}}$  (298 K) iznosi 1,43 do 1,50 BM; svojstvena vrpca u UV-Vis spektru nalazi

se u području 350 do 400 nm]. Do istih se zaključaka može doći raščlambom spektara IR ( $\Delta = \nu_{\text{asym}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-) = 183 - 189 \text{ cm}^{-1}$ ) i EPR, premda su opažene neke razlike za modifikaciju heptanoatnog kompleksa **1A** koje su najvjerojatnije prozročene različitom shemom vodikovih veza. Ispitivanjem fungicidne djelotvornosti prema gljivicama truljenja drveta *Trametes versicolor* (L. ex Fr.) Pilat pokazalo je da spojevi otopljeni u DMSO pri koncentraciji  $1,0 \times 10^{-3} \text{ mol L}^{-1}$  u potpunosti zaustavljaju rast micelija. Neki od spojeva ( $n = 8, 9$  i  $10$ ) pokazuju još izrazitiju fungicidnu djelotvornost čak i u razrjeđenijim otopinama ( $1,0 \times 10^{-4} \text{ mol L}^{-1}$ ).