COPPER(II) CARBOXYLATES - SYNTHESIS, STRUCTURE AND BIOLOGICAL ACTIVITY. IV. FATTY ACID COPPER(II) CARBOXYLATES WITH UREA[†]

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Abstract

During the investigations of fatty acid copper(II) carboxylates with biologically important ligands, several compounds of the composition $[Cu_2(O_2CC_nH_{2n+1})_4(urea)]$ (n = 5 to 11) and $[Cu_2(O_2CC_5H_{11})_4(urea)_2]$ were prepared. The molecular structure of the compound $[Cu_2(O_2CC_5H_{11})_4(urea)_2]$ was determined by X-ray diffraction analysis. The compounds were characterized by standard physical and chemical methods and tested for their fungal mycelial growth activity with mycelium of two wood decay fungi *Trametes versicolor* and *Antrodia vaillantii*. The results of the characterization are in agreement with the values typical for dimeric copper(II) carboxylates. In the electronic spectra the difference between both types of hexanoate compounds is observed, however in vibrational spectra also the differences among the compounds where one molecule of urea is bonded on each dimer were noticed. Significantly higher growth inhibition for the whole series for *Antrodia vaillantii* was observed.

Introduction

Synthesis, structure and properties of copper(II) carboxylates with nitrogen donor ligands have been already studied.[1-3] The results of the experiments showed increased activity of metal ions in the compounds with selected biologically active molecules. Many of these complexes are used as pharmaceuticals.[4] Our interest in coordination chemistry of copper(II) carboxylates originates from the fact that this type of compounds may be used for wood protection.[5-7] It was noticed that coordination of the ligands around metal ion in the complex plays an important role in the fungal growth retardation activity. In this group of the compounds, the dimers with fatty acid carboxylates showed the strongest activity.[8] Due to the known influence of urea molecules in biological processes

the coordination compounds with urea are therefore potentially interesting. Synthesis and characterization of the coordination compounds in the family of copper(II) carboxylates with urea and the subsequent testing of their fungicidal activity was the main aim of our investigations.

Experimental

Materials: Commercially available substances as $CuSO_4 \cdot 5H_2O$, fatty acids ($C_nH_{2n+1}COOH$; n = 5 – 11), urea and all solvents were used without further purification. Sodium carboxylates ($C_nH_{2n+1}COONa$; n = 5 – 11) were prepared by the reaction of sodium hydroxide and stoichiometrical amount of appropriate saturated carboxylic (fatty) acid in aqueous solution by evaporation of the solvent. The syntheses of fatty acid copper(II) carboxylates ($[Cu_2(O_2CC_nH_{2n+1})_4]$; n = 5 – 11) were carried out from $CuSO_4 \cdot 5H_2O$ and corresponding sodium carboxylates in aqueous solution by the precipitation method.[1]

Synthesis: The guidance for the synthesis of copper(II) coordination compounds with urea has already been described.[9]

$[Cu_2(O_2CC_nH_{2n+1})_4(OCN_2H_4)]$; n = 5 - **1a**, 6 - **2**, 7 - **3**, 8 - **4**, 9 - **5**, 10 - **6**, 11 - **7**. Copper(II) carboxylate was dissolved in 10 mL of absolute ethanol. Because of better solubility of the complexes with urea with shorter aliphatic chains (lower yield) we subsequently added lower amount of starting copper(II) carboxylate with lenghtening of the chains (from 1.4 mmol of hexanoate to 0.11 mmol of dodecanoate). The starting carboxylates did not dissolve quantitatively at room temperature therefore heating to boiling point of the solution was applied. The prepared hot solution was added to the solid urea (from 3.0 mmol at hexanoate to 0.92 mmol at dodecanoate) which dissolved during stirring. Precipitated turquoisegreen product (the colour is very similar to the colour of starting carboxylates) were filtered off next day and than dried another day in the desiccator over KOH. The average yields of the syntheses were between 50 and 80%.

d-Spacings (Å) (relative intensities are in parentheses - I/I_0): **1a** - 16.6(10), 10.2(1), 8.7(1), 8.2(2), 6.95(1), 5.48(1), 5.08(1), 4.34(1), 4.10(1), 4.04(2); **2** - 18.6(10), 10.1(1),

9.3(2), 8.8(1), 8.4(1), 7.00(1), 6.75(1), 6.65(1), 6.23(1), 5.68(1), 4.05(3); **3** - 20.9(10), 10.4(2), 8,7(1), 8.3(1), 6.90(3), 6.30(1), 5.35(1), 4.75(1), 4.32(1), 4.09(4); **4** - 22.6(10), 11.4(2), 9.6(1), 8.6(1), 8.5(1), 8.05(1), 7.50(3), 6.95(2), 6.80(2), 6.55(1), another intense line at 3.97(6); **5** - 12.5(10), 8.7(1), 8.3(5), 6.90(2), 6.53(1), 6.40(1), 6.30(1), 5.81(1), 5.62(1), 4.65(2), 4.05(7); **6** - 13.6(8), 9.0(9), 8.5(1), 8.2(1), 7.50(1), 6.95(2), 6.55(1), 6.45(1), 5.85(1), 5.33(1), 3.99(10); **7** - 13.4(10), 9.0(9), 8.5(1), 7.45(1), 6.95(1), 6.55(1), 6.45(1), 5.80(1), 4.34(1), 4.23(2), 3.98(6).

Table 1: Selected parameters of the characterization methods. Magnetic measurements μ_{eff} / BM; Vibrational spectra: $\nu_{as}(O_2C)$, $\nu_s(O_2C)$, $\Delta = \nu_{as} - \nu_s$ / cm^{-1}; Electronic spectra: λ / nm.

compound	μ_{eff}	$\nu_{as}(O_2C)$	$\nu_s(O_2C)$	Δ	λ_1	λ_2	λ_3
1a	1.42	1588	1428	160	267	377	691
1b	1.39	1583	1429	154	272	369	740
2	1.43	1587	1423	164	276	378	692
3	1.43	1588	1422	166	271	379	684
4	1.40	1589	1422	167	264	378	675
5	1.40	1588	1422	166	267	382	681
6	1.41	1588	1422	166	277	378	673

[$Cu_2(O_2CC_5H_{11})_4(OCN_2H_4)_2$]; ***1b***. Substance was synthesized by similar procedure as described above. Copper(II) hexanoate (1.24 mmol) was dissolved in 5.0 mL of methanol and the solution was added to the solid urea (9.09 mmol). The solution with dissolved urea was cooled in refrigerator for a day (253 – 258 K) and bright green aggregated crystals were filtered off. The average yield of the syntheses was 50%. The crystals suitable for X-ray structure analysis were obtained by similar procedure, but a lower concentration of the starting compound was used. Attempts for the synthesis of the other

bright green compounds with two molecules of urea per dimeric unit were successful only for heptanoate modification. Due to lower stability, this compound partially converts to turquoise "hemiurea"[9] heptanoate modification and was not obtained in pure state.

Table 2: Measured and calculated values for *d*-spacings (Å) and their relative intensities [a] for hexanoate modification with urea **1b**.

d_m	14.1	7.60		7.00		6.80			5.59	
I/I$_0$	10	1		1		1			3	

d_c	14.0	7.52	7.04	7.02	6.81	6.80	6.28	5.62	5.60	5.52
I/I$_0$	100	6	8	4	2	2	5	3	5	3

[a] The calculated values for the intensities of nine presented *d*-spacings (without 14.0(100) are very weak, therefore different scale as for measured intensities was used. Nevertheless, there is strong agreement between measured and calculated values, where only one line 6.28(5) was not visually observed.

Table 3: Elemental analysis of the complexes with urea (found and calculated (calc.) values).

compound	Cu[%] found	Cu[%] calc.	C[%] found	C[%] calc.	H[%] found	H[%] calc.	N[%] found	N[%] calc.
1a	19.3	19.6	46.1	46.4	7.13	7.47	4.21	4.32
1b	17.7	18.0	43.4	44.1	7.29	7.40	8.35	7.92
2	17.9	18.1	49.0	49.5	7.87	8.02	4.27	3.98
3	16.4	16.7	51.8	52.2	9.01	8.49	3.60	3.69
4	15.4	15.6	54.2	54.5	9.52	8.89	3.50	3.43
5	14.1	14.6	56.4	56.5	9.95	9.25	3.04	3.21
6	13.3	13.7	58.3	58.2	10.3	9.56	2.91	3.02
7	12.4	12.9	59.8	59.7	10.5	9.83	2.79	2.85

Metal analysis was carried out electrogravimetrically with Pt electrodes. *C, H, N* analysis was performed at the Department of Organic Chemistry, Faculty of Chemistry and Chem. Technology, University of Ljubljana, Slovenia with Perkin Elmer, Elemental Analyzer 2400 CHN.

X-ray diffraction work: Single crystal diffraction measurement was carried out on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Unit cell dimensions were obtained from 75 selected reflections in θ range 8.27 -14.68° using PARAM from XRAY76.[10] Common data corrections for variations in reference reflections and Lorentz-polarization effects were applied (DATRD2 in NRCVAX).[11] Absorption correction was performed by Gaussian integration methods (ABSORP in NRCVAX).[11] Structure was solved by SHELXS-86[12] and refined by SHELXL-97.[13] Details of crystal data as well as the data collection and structure refinement summary

Table 4: Crystal and data collection summary for $[Cu_2(O_2CC_5H_{11})_4(OCN_2H_4)_2]$

Asymmetric Unit Formula	$Cu(O_2CC_5H_{11})_2(OCN_2H_4)$
Crystal System	monoclinic
Space Group	$P2_1/c$ No. 14
a (Å)	14.484(3)
b (Å)	9.029(2)
c (Å)	14.024(3)
β (°)	104.26(1)
Volume (Å^3)	1777(1)
Z	4
D_x (Mg/m^3)	1.239
μ (mm^{-1})	1.245
Crystal Colour	green
Crystal Shape	prism
Crystal Size (mm)	0.17 x 0.38 x 0.42
Intensity Decay (%)	1.4
T_{min}/T_{max}	0.816/0.623
Radiation	Mo $K\alpha$, $\lambda = 0.710730$ Å
Diffractometer	Enraf-Nonius CAD-4
Scan Type	$\omega/2\theta$
Measured Reflections	4253
Observed Reflections [I>2(σ)I]	1968
R_1 (all reflections)	0.166
R_1 ([I>2(σ)I])	0.067

are presented in Table 4. Large thermal displacement parameters for the urea moiety as well as for hexanoate chains suggest disorder, which was resolved only in case of urea molecules on apical positions. After isotropic refinement coordinates of urea molecule were split to two positions with occupancy of 47.2 (52.8)%. Rather high value of final R_1 could be ascribed to additional disorder of hexanoate chains, which is typical for similar systems but was not resolved. H atoms were placed at idealized positions with isotropic thermal displacement parameters taken from the parent non-H atoms and multiplied by 1.2 for CH_2 and NH_2 groups and by 1.5 for CH_3 groups. Additional crystallographic data for the structure reported in this paper are available at the Cambridge Crystallographic Data Center and can be obtained on request.[14]

Physical measurements: Interplanar spacings were obtained by the Guinier camera (Enraf Nonius) with Cu $K\alpha$ radiation. The data were recorded at Ceramics Department, "Jožef Stefan" Institute, Ljubljana, Slovenia. Line intensities were estimated visually. The magnetic susceptibility of the substances was determined at room temperature by powdered samples with a Sherwood Scientific MSB-1 balance using $Hg[Co(NCS)_4]$ as a calibrant. Instrument uses Evans method. Diamagnetic corrections were estimated from Pascal's constants[15] and the effective magnetic moments were calculated using the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$. Molar magnetic susceptibility was calculated per one copper atom. Infrared spectra were measured on mineral oil (poly-(chlortrifluorethylene) and Nujol) mulls between CsI plates using Perkin-Elmer FT-IR 1720X spectrometer in the range 4000-400 cm^{-1}. Electronic spectra were recorded as Nujol mulls (200-860 nm) with Perkin-Elmer UV/VIS/NIR spectrometer Lambda 19. Compounds were tested for fungicidal activity for wood decay fungi *Trametes versicolor* (L. ex Fr.) Pilat and *Antrodia vaillantii* (DC. ex Fr.) Ryv.. The procedure was already described.[16]

Results and discussion

Dimeric copper(II) carboxylates with urea ($[Cu_2(O_2CC_nH_{2n+1})_4(OCN_2H_4)]$; n = 5–11 and $[Cu_2(O_2CC_5H_{11})_4(OCN_2H_4)_2]$) were synthesized. The purity of the compounds was checked by powder diffraction technique and vibrational spectroscopy. Calculated *d-*

values were obtained by the program DISPOW of the NRCVAX system.[11] The results of X-ray structural analysis for hexanoate modification with two urea molecules per dimeric unit **1b** reveal dimeric copper(II) cage structural type (Figure 1). Selected interatomic distances are presented in Table 5. Comparison with the other urea complexes with simple carboxylate ligands (formate[17], acetate[18] and benzoate[19]) show similar coordination sphere around copper(II) atoms. The Cu–O (carboxylate) distances for formate, benzoate and hexanoate lie in the range between 1.94 and 1.97 Å, however significantly longer distances for acetate were noticed (2.00 – 2.01 Å). The reason for the lengthening of these coordination bonds is probably due to the presence of water molecule in near coordination sphere of central copper(II) atom (Cu – O (H_2O) 2.20 Å).
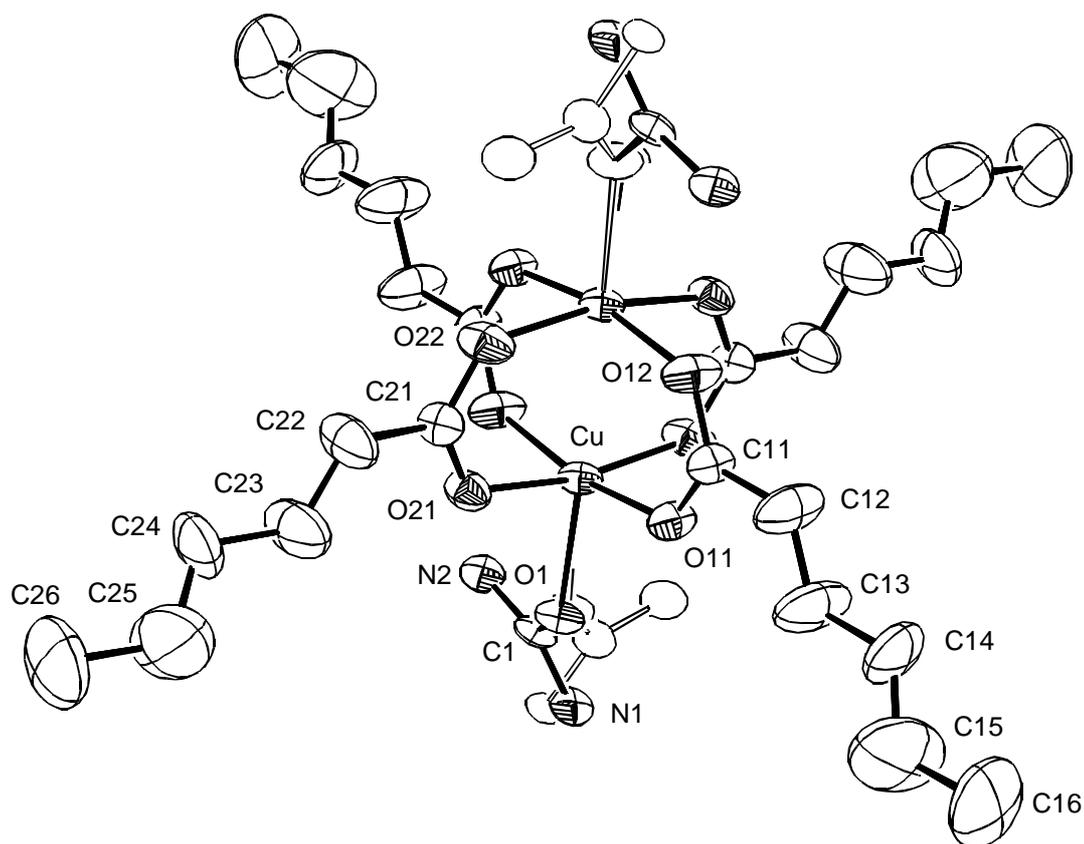

Figure 1: ORTEP-III [20] view of $[Cu_2(O_2CC_5H_{11})_4(OCN_2H_4)_2]$. Thermal displacement ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. The Cu – Cu separation is 2.644(2) Å.

The urea molecules are axially coordinated on tetracarboxylate framework via oxygen atom. Characteristic for these urea complexes is also the presence of several hydrogen bonds that connect the dimers in the network. The strongest hydrogen bond is in all cases intramolecular N–H•••O (carboxylate) bond. Between compared complexes the shortest bond is noticed in hexanoate complex [N2(N2')•••O12^i(O22^i); 2.88 (2.86) Å]. Longer distances were observed in acetate 2.91 Å, formate 2.99 Å and especially in benzoate complex (3.10 and 3.11 Å). Different values are probably due to the steric factors (size and shape of carboxylate tail) which lead also to two bonds observed in benzoate.

Table 5: Interatomic distances (Å) with estimated standard deviations.

Cu-O11	1.961(4)	O11-C11	1.252(7)
Cu-O12^i	1.967(4)	O12-C11	1.240(7)
Cu-O21	1.974(4)	O21-C21	1.253(7)
Cu-O22^i	1.971(4)	O22-C21	1.255(7)
Cu-O1	2.10(4)	Cu-O1'	2.16(3)
O1-C1	1.44(3)	O1'-C1'	1.13(3)
C1-N1	1.29(5)	C1'-N1'	1.42(3)
C1-N2	1.37(2)	C1'-N2'	1.34(2)

Symmetry code: i) −x+1, −y+1, −z

O1', C1', N1' and N2' are the atoms of the disordered urea molecule which is not labeled in Figure 1.

The results of room temperature magnetic measurements for all series lie in the range between 1.39 and 1.43 BM. Antiferromagnetic properties with a singlet ground state are characteristic for copper(II) carboxylates with four bridging carboxylate ligands. Magnetic properties of such complexes result from the coupling of the unpaired electrons in the $d_{x^2-y^2}$ orbitals of Cu^{2+} ions through the bridging ligands (spin superexchange pathway).[21]

Similar conclusions may be found also from the electronic spectra. For all compounds a broad band at 700 nm ($d \rightarrow d$ transition) in the visible part and two bands at higher energies are present (LMCT). The band between 350 and 400 nm has relatively

weak intensity however the third band nearby is much stronger (the origin is partially also in the transitions between orbitals of the ligand ($\pi \rightarrow \pi^*$)[22] (Figure 2). The second band is commonly attributed as characteristic for dimeric compounds.[23] The spectra of the compounds differ only in the visible part. In the series with one urea molecule very broad band with peak between 673 and 691 nm is observed, while the band for **1b** is not so broad and lies at lower energies (740 nm). It is interesting to note that corresponding series of dimeric complexes without urea [$Cu_2(O_2CC_nH_{2n+1})_4$] shows the band at 670 nm. The colour of the compounds from this series is turquoisegreen and is almost identical to the colour of "hemiurea" series but differ significantly from the brightgreen crystals of **1b**.
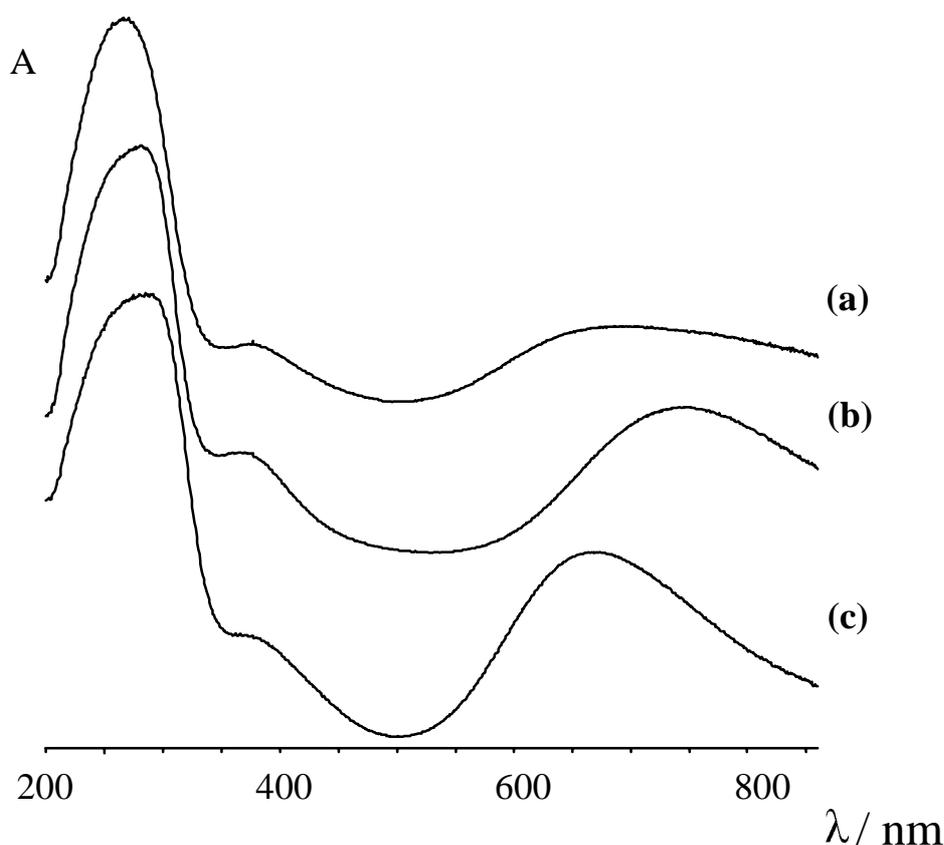

Figure 2: Electronic spectra of dimeric complexes with urea **1a** (a), **1b** (b) and [$Cu_2(O_2CC_5H_{11})_4$] (c) in the region 200 - 860 nm.

The comparison of the vibrational spectra of both hexanoate complexes with urea **1a** and **1b** in the region 1750 – 1300 cm^{-1} shows that the position of the bands is almost identical (Figure 3). The position for asymmetric $\nu_{as}(O_2C)$ and symmetric $\nu_s(O_2C)$

stretching vibration of carboxylate group do not differ significantly though smaller value between them (Δ) for **1b** was noticed (Table 1). According to the position of the carboxylate bands (1600 – 1570, 1430 – 1400 cm^{-1}), methyl and methylene bands (1470 – 1420 cm^{-1}), the spectra in these regions are more similar between "hemiurea" (Table 1) and $[Cu_2(O_2CC_nH_{2n+1})_4]$ series ($\Delta = 162 – 172$ cm^{-1})[24] although partial overlapping of the bands in the region 1430 – 1420 cm^{-1} limits the qualitative analysis. More significant difference is found between 1630 – 1610 cm^{-1} where the bands are assigned to amide NH$_2$ bending vibration.[25] In the spectrum of **1b** (the compound with known

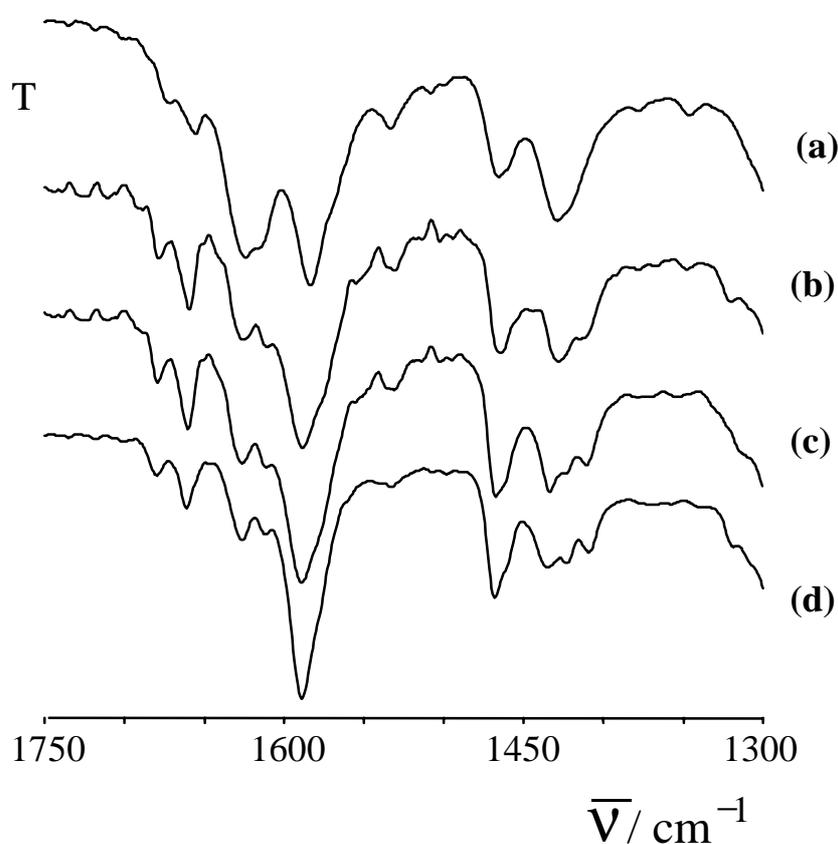Figure 3: Vibrations in the region 1750 − 1300 cm^{-1}. Spectra of the compounds **1b** (a), **1a** (b), **4** (c) and **7** (d) were recorded in poly-(chlortrifluorethylene) oil.

crystal structure where urea coordinates via oxygen atom) the intensity of two bands is significantly stronger than in the spectrum of **1a** (Figure 3). We assume that the bands are stronger in **1b** because both NH$_2$ groups remain uncoordinated (only hydrogen bonds are present). Coordination of NH$_2$ group would lower the intensity of the amide NH$_2$ bending

vibration, so we believe that in **1a** urea bonds via oxygen atom to copper atom of one dimeric unit and via nitrogen atom to copper atom of another dimeric unit. Such type of bonding leads to connection of dimeric tetracarboxylate units by bridging urea molecules in infinite chain. The spectra of the series of other "hemiurea" complexes are almost identical to the spectra of **1a** therefore similar structure is predicted for them. Polynuclear tetracarboxylate structure of $[Cu_2(O_2CC_nH_{2n+1})_4]$ (where the distance of copper atom to the oxygen atom of the neighbouring tetracarboxylate unit in heptanoate structure is 2.22 Å)[26] is therefore also in agreement with the results of spectroscopic characterization for "hemiurea" and $[Cu_2(O_2CC_nH_{2n+1})_4]$ series.

The influence of the compounds on fungal growth: All compounds dissolved in DMSO show very strong mycelium growth inhibition of *Antrodia vaillantii* (Table 6). Mycelium growth was noticed only for both hexanoate modifications at the lowest concentration $(1.0 \times 10^{-4}$ mol/L). Weaker activity was observed for species *Trametes versicolor*, where only octanoate and nonanoate compound show appropriate retardation activity at the highest used concentration 1.0×10^{-3} mol/L. Comparison with the other compounds from investigated series shows weakening of the retardation activity if the aliphatic chains are shorter. Similar effect for the compounds with longer chains is probably due to their lower solubility that lead to lower concentration, as was already noticed for the series with nicotinamide[8] and *N,N*-diethylnicotinamide.[27] The activity of nonbonded urea molecules did not deviate from the effect of the solvent.

Table 6: The results [a] for the testing of fungicidal activity for *Trametes versicolor* (*T.v.*) and *Antrodia vaillantii* (*A.v.*) at diferrent concentrations, seven days after inoculation. Values for the control without dissolved compound 1-2 (*T.v.*) and 3 (*A.v.* – stronger partial influence of the solvent).

c \ mol / L	1.0×10^{-4}		5.0×10^{-4}		1.0×10^{-3}	
compound	*T.v.*	*A.v.*	*T.v.*	*A.v.*	*T.a.*	*A.v.*
1a	1-2	3-4	1-2	<u>5</u>	2-3	5
1b	1-2	3-4	2	<u>5</u>	2-3	5
2	1-2	<u>5</u>	2	5	<u>4</u>	5
3	1-2	<u>5</u>	2	5	<u>5</u>	5
4	1-2	<u>5</u>	2	5	<u>5</u>	5
5	1	<u>5</u>	2-3	5	3	5
6	1-2	<u>5</u>	2-3	5	2-3	5
7	1-2	<u>4-5</u>	2	4-5	2	4-5

[a] - The numbers in the table have the following meaning: 1 - normal growth, no retardation (as control – only water); 2 - slightly visible signs of retardation; 3 - significant retardation; 4 - retardation is very strong; 5 - no fungal growth.

Acknowledgements

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Povzetek

Pri raziskavah bakrovih(II) karboksilatov maščobnih kislin z biološko pomembnimi ligandi smo pripravili spojine s sečnino (ureo): $[Cu_2(O_2CC_nH_{2n+1})_4(urea)]$ (n = 5 - 11) in $[Cu_2(O_2CC_5H_{11})_4(urea)_2]$. Molekulska struktura spojine $[Cu_2(O_2CC_5H_{11})_4(urea)_2]$ je bila določena z rentgensko difrakcijsko metodo. Vse sintetizirane spojine smo karakterizirali s standardnimi fizikalnimi in kemijskimi metodami ter testirali njihovo učinkovitost pri zaviranju rasti micelija gliv pisane ploskocevke *Trametes versicolor* in bele hišne gobe *Antrodia vaillantii*. Rezultati karakterizacije se skladajo z vrednostmi, ki so značilne za dvojedrne bakrove(II) karboksilate. V elektronskih spektrih je opazna razlika med obema tipoma heksanoatnih spojin, v vibracijskih pa tudi razlike med spojinami, ki imajo na en dimer vezano le eno molekulo sečnine. Pri celotni seriji spojin smo opazili izrazito večje zaviranje rasti pri beli hišni gobi.