COPPER(II) BENZOATES AND ACETATES WITH 2-AMINOPYRIDINE[#]

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[#]This paper is dedicated to Professor Dr. D. Dolar on the occasion of his 80th birthday

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Abstract

Two monomeric and two dimeric copper(II) benzoate and acetate coordination compounds with 2-aminopyridine were synthesized. The crystal structures of benzoate compounds were determined by X-ray diffraction analysis. The monomeric benzoate form $[Cu(O_2CC_6H_5)_2(2apy)_2]$ (2apy = 2-aminopyridine) is composed of *trans* oriented ligands around central copper(II) atom, where benzoates act as asymmetrical chelates (Cu – O 1.97 and 2.65 Ĺ). On the other hand, dimeric form $[Cu_2(O_2CC_6H_5)_4(2apy)_2]$ reveals *paddle - wheel* type structure where 2-aminopyridine acts as axial ligand *via* pyridine nitrogen atom. All compounds were characterized by standard physico-chemical methods and tested for their fungal mycelial growth retardation activity for wood decay fungi *Trametes versicolor* and *Antrodia vaillantii.*

Introduction

Copper carboxylates are well known to form a variety of structures even with the ligands of the same homologous series.[1] The main reason for such diversity are ligand basicity, steric factors, hydrogen bonding, concentration of the starting compounds in the solution and their ratio. Several possible modifications also lead to different properties of the compounds even though the constituents are similar or the same. Our investigation is aimed towards finding new synthetic routes for preparation of known copper carboxylates and synthesis of new stoichiometric types of the compounds and their characterization. We try to find such compounds that will have satisfactory fungicidal action together with their physical and chemical properties that further research in the field of their application will be worthwhile. Therefore in this work we report the synthesis, characterization and fungicidal activity of monomeric and dimeric copper(II) benzoates and acetates with 2-aminopyridine.

Experimental

Materials: $[Cu_2(O_2CC_6H_5)_4(C_6H_5COOH)_2]$ was prepared from hot aqueous solution of copper(II) sulphate, benzoic acid and sodium benzoate by precipitation method. The other starting substances and solvents were purchased from commercial sources and used without previous purification.

Synthesis: Monomeric benzoate complex $[Cu(O_2CC_6H_5)_2(2apy)_2]$ **1** (2apy = 2-aminopyridine) was prepared by modified procedure as already described.[2] In 25 mL of acetonitrile 0.50 mmol of $[Cu_2(O_2CC_6H_5)_4(C_6H_5COOH)_2]$ was dissolved due to stirring and heating. This solution was added to 4.0 mmol of 2-aminopyridine in 1.0 mL of acetonitrile. After 24 hours, violet crystalline product was filtered off and than dried in a desiccator over KOH overnight.

For the dimeric benzoate compound $[Cu_2(O_2CC_6H_5)_4(2apy)_2]$ **2** four times lower amount of 2-aminopyridine was used but other applied procedure was the same as for monomeric compound **1**.

Starting copper compound for both acetate complexes was $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ and the procedure was different as described.[3,4] The molar ratio of the starting compounds for acetate complexes ($[Cu_2(O_2CCH_3)_4(H_2O)_2]$ and 2apy) was the same as for benzoates **1** and **2**. Monomeric acetate compound $[Cu(O_2CCH_3)_2(2apy)_2]$ **3** was prepared similarly as monomeric benzoate **1** but higher concentrations of the reactants were used. Compound **3** crystallize from acetonitrile solution (as benzoates) however dimeric compound $[Cu_2(O_2CCH_3)_4(2apy)_2]$ **4** from acetone (2,0 mmol 2-aminopyridine in 20 mL of acetone was added to 1.0 mmol $[Cu_2(O_2CCH_3)_4(H_2O)_2]$). Both synthesized acetate complexes were filtered off after the solution was left in a refrigerator (~ 6 °C) for 24 hours. The average yields for all synthesized compounds were between 85 and 95%.

d-spacings (Å) and their relative intensities, from X-ray powder diffraction data for all compounds described herein, are in agreement with the calculated values [5] from crystal structure analysis.[3,4]

Table 1: Elemental analysis (w / %). Found and calculated (calc.) values.

	Cu		C		H		N	
compound	**found**	**calc.**	**found**	**calc.**	**found**	**calc.**	**found**	**calc.**
1	12.9	12.9	57.6	58.4	3.91	4.49	11.4	11.3
2	15.5	15.9	56.8	57.1	3.92	4.03	7.40	7.01
3	16.8	17.2	45.3	45.5	4.52	4.91	14.9	15.2
4	22.8	23.0	39.2	39.2	4.22	4.39	10.1	10.2

X-ray diffraction work: Single crystal diffraction measurements were carried out on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo *Kα* radiation. Unit cell dimensions were obtained from 25 reflections in the θ range 8-16º. Common data corrections for variations in reference reflections and Lorentz polarization effects were applied.[5] No absorption correction was performed. Structures were solved by direct methods implemented in SHELXS-97[6] and refined by full matrix least squares on F^2 by SHELXL-97.[6] Non-hydrogen atoms were refined anisotropically, hydrogen atoms were generated geometrically, assigned appropriate isotropic thermal displacement parameters and allowed to ride on their parent atoms. Details on crystal data and data collection summary are presented in Table 2. Additional crystallographic data for the structure reported in this paper are available at the Cambridge Crystallographic Data Center and can be obtained on request.[7]

Physical measurements: *Metal analysis* was carried out electrogravimetrically with Pt electrodes. *C, H, N* analysis was performed with Perkin Elmer, Elemental Analyzer 2400 CHN. Interplanar spacings were obtained by the Guinier camera (Enraf Nonius) with Cu *Kα* radiation. 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. Diamagnetic corrections were estimated from Pascal's

constants. Infrared spectra were measured on mineral mulls between CsI plates, using Perkin-Elmer FT-IR 1720X spectrometer. 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. at the Department of Wood Science and Technology, Biotechnical Faculty, University of Ljubljana, as described.[8]

Table 2: Relevant crystal data and data collection summary

Formula	$C_{24}H_{22}CuN_4O_4$ **1**	$C_{38}H_{32}Cu_2N_4O_8$ **2**
Formula weight	494.00	799.76
Crystal system	orthorhombic	triclinic
Space group	Pbca	P8
a (Å)	8.724(8)	10.206(3)
b (Å)	20.288(5)	10.942(4)
c (Å)	12.360(8)	16.166(5)
α (°)	90	79.390(6)
β (°)	90	88.930(6)
γ (°)	90	89.530(3)
V (Å^3)	2252(3)	1774.1(1)
Z	4	2
D_x (g/cm^3)	1.457	1.497
μ (mm^{-1})	1.008	1.258
Crystal colour	violet	green
Crystal shape	prism	prism
Crystal size (mm)	0.20 x 0.25 × 0.30	0.30 x 0.30 x 0.35
Intensity decay (%)	1.5	1.3
Scan type	ω/2θ	ω/2θ
θ range (º)	1.95 - 28.01	1.28 - 18.17
R_{int}	0.0861	0.0562
Total data	20144	17309
Independent data	2717	8656
Observed data [I>2σ(I)]	1547	4939
R_1 (observed)	0.0394	0.0519
wR_2 (observed)	0.0900	0.1275

Results and discussion

Description of the crystal structures: The stereochemistry of the monomeric complex **1** (Figure 1) could be described as pseudo-octahedral with the copper atom on the inversion center. Benzoate and 2-aminopyridine ligands are arranged around the copper atom in a *trans* mode. Equatorial plane is constituted of two pyridine nitrogen atoms from the 2-aminopyridine ligands (Cu-N1 2.014(2) Å) and two benzoate oxygen atoms (O11) on the distance of 1.967(2) Å from the copper ion. The distance of the remaining carboxylate oxygens (Cu-O12 2.646(2) Å) is substantially longer than Cu-O11 distance, but shorter than the sum of the van der Waals radii, which indicates a weak interaction between the two atoms. Therefore, 4+2 coordination was proposed. Although the *cis* arrangement of the ligands around the copper center was observed for monomeric complexes with aliphatic carboxylates and the 2-aminopyridine as N-donor ligand,[3,9] the *trans* arrangement is more commonly observed for similar complexes.[10]

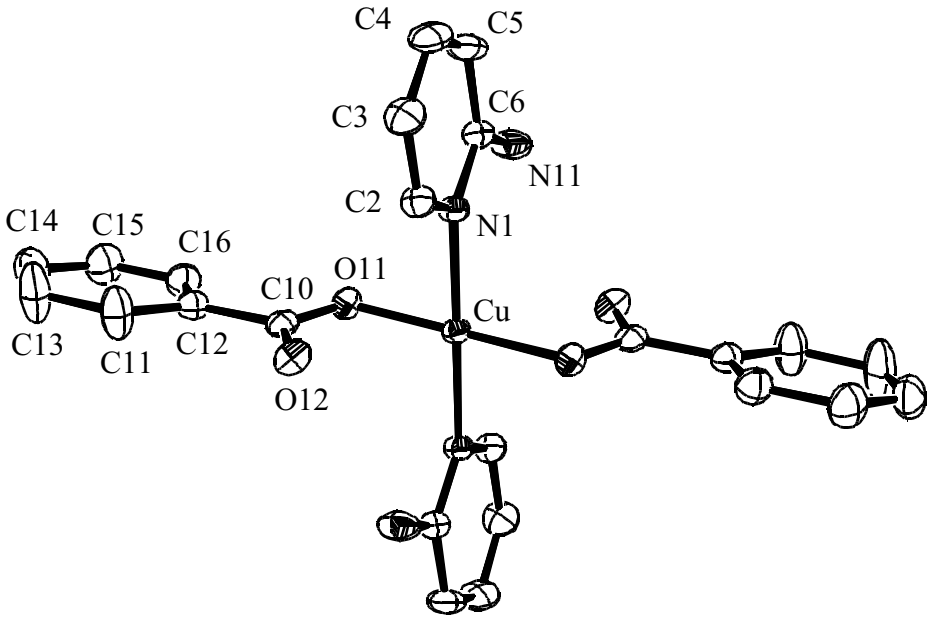

Figure 1: ORTEP view of monomeric copper(II) benzoate complexes with 2-aminopyridine. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 30% probability level.

Table 3: Selected geometrical parameters (Å, º) for monomeric **1** and dimeric **2** Cu(II) benzoates with 2-aminopyridine

1				
Cu-O11	1.9666(12)			
Cu-O12	2.646(2)			
Cu-N1	2.014(2)			
Hydrogen bonds		H···A	D···A	D-H···A
N11···O12		2.29	2.935(4)	131.9
N11···O12 (-x+0.5, -y+1, z-0.5)		2.12	2.953(3)	164.5
2				
Cu1-O11	1.957(2)	Cu2-O31		1.969(3)
Cu1-O12^{i}	1.959(2)	Cu2-O32^{ii}		1.950(3)
Cu1-O21	1.968(2)	Cu2-O41		1.963(3)
Cu1-O22^{i}	1.969(3)	Cu2-O42^{ii}		1.962(3)
Cu1-N1	2.180(3)	Cu2-N2		2.174(3)
Cu1-Cu1^{i}	2.6435(11)	Cu2-Cu2^{ii}		2.6649(9)
Hydrogen bonds		H···A	D···A	D-H···A
N11···O11		2.36	3.060(2)	138.2
N21···O31		2.43	3.192(5)	148.2
N21···O41		2.59	3.113(5)	119.8

i) -x, -y+1, -z+1, ii) -x, -y, -z+2

Within the molecule an intramolecular hydrogen bond through amino group and semi-coordinated carboxylate oxygen is observed. Additional intermolecular hydrogen bond links monomeric units into two-dimensional network nearly parallel to ac plane. Selected geometrical parameters are presented in Table 3.

Dimeric complex has the expected *paddle-wheel* type structure. Two crystallographically independent centrosymmetric dimers are present in the unit cell. Ortep view of one of the dimers is presented in Figure 2. The nearest neighbours of each copper atom are the four oxygen atoms of the bridging benzoate groups in a square planar arrangement. The Cu-O distances span the range from 1.957 to 1.969 Å, which is normal for similar type of compounds.[11] A square-based pyramidal arrangement around the copper atom is completed by the endocyclic nitrogen atom of the 2-aminopyridine ligand. The copper atom is shifted towards the apical position for 0.2164(13) Å in one

and for 0.2254(13) Å in the second dimer. Molecular geometry is similar to those observed for dimeric complexes with aliphatic carboxylate and 2-aminopyridine.[4,9] Recently, the structure of similar complex with solvated tetrahydrofuran molecules was reported.[12] The Cu-Cu distance in the reported structure is 2.641 Å, while in the present structure Cu-Cu distances are 2.6435(11) and 2.6649(9) Å in the two independent dimers. The geometries of pyridine and phenyl rings are normal.

Amino groups of the 2apy ligand are involved in intramolecular hydrogen bonds. Interestingly, each of the two dimers has each own hydrogen bond scheme. Amino N11 atom is involved in formation of H bond to O11 only, while other amino N21 atom is hydrogen bonded to O31 and O41 of the same molecule. For geometrical details see Table 3.

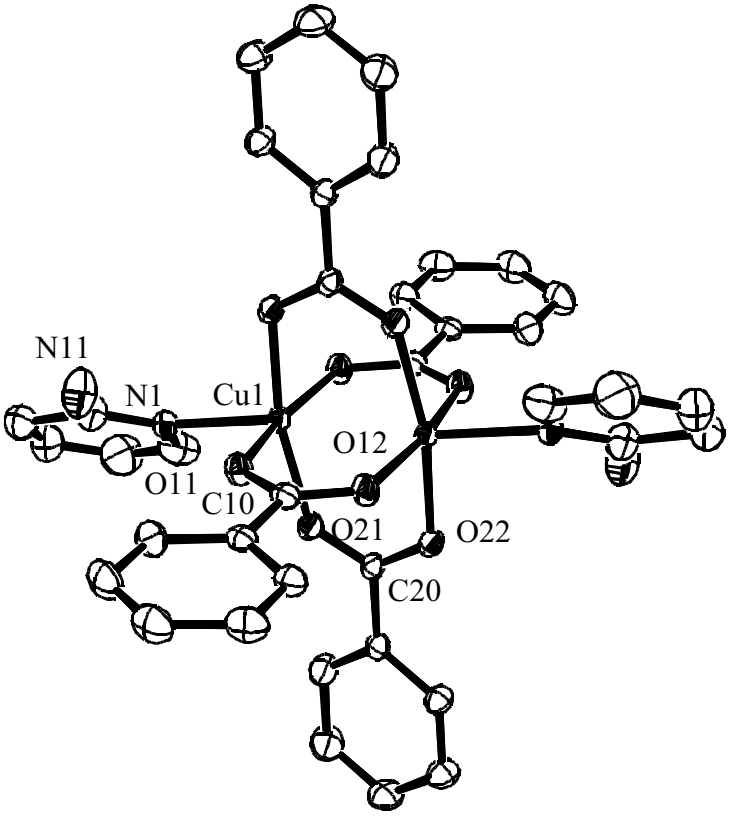

Figure 2: ORTEP view of one of the two crystallographically independent dimeric units of copper(II) benzoate with 2-aminopyridine. Hydrogens are omitted for clarity.

Magnetic measurements and spectroscopy: The results of magnetic measurements are in agreement with monomeric and dimeric nature of the compounds (Table 4). Similar values for **1** (1.99 BM) [2] and $[Cu_2(O_2CC_6H_5)_4(2apy)_2]\cdot(C_4H_8O)_2$ - solvate analogue of **2** (1.45 BM) [12] were reported but different for **3** (1.78 BM).[3]

Table 4: Selected parameters of the characterization methods (sh - shoulder).

compound	μ_{eff} / BM	λ_1 / nm	λ_2 / nm	λ_3 / nm
1	1.97	$265_{(sh)}$, 320	$400_{(sh)}$	545, $700_{(sh)}$
2	1.48	$260_{(sh)}$, 302	$400_{(sh)}$	726
3	1.98	248, 310	$410_{(sh)}$	609
4	1.50	$260_{(sh)}$, 310	$390_{(sh)}$	727

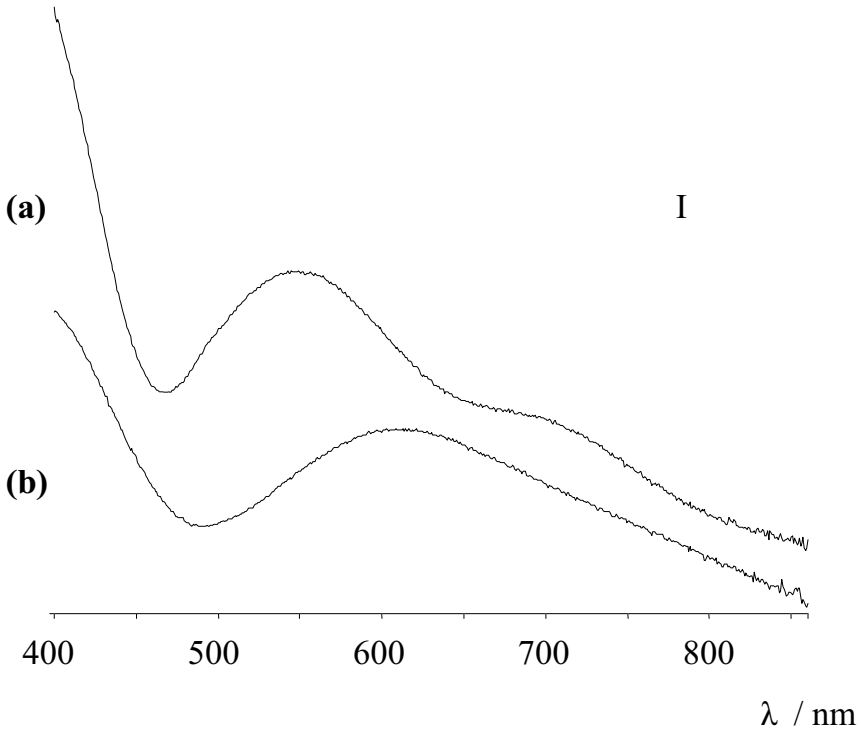

Figure 3: Visible part of electronic spectra for monomeric compounds **1** (a) and **3** (b).

In the visible part of the electronic spectra, the bands for *d-d* transitions are found. For dimeric compounds **2** and **4**, with square pyramidal geometry of the first coordination sphere around copper, one band in the 700 – 750 nm region is observed (Table 4). Meanwhile in the spectra of six coordinated monomeric compounds **1** and **3**, the bands are shifted to higher energies (Figure 3). Similar appearance were noticed also for the other copper(II) carboxylates with different pyridine ligands.[13,14] The positions of the bands in the spectra of monomeric **1** and **3** are in agreement with the reports for electronic reflectance spectra (λ / nm : **1 -** 600, 700; **3 -** 248, 290, 312, 395, 615).[2,3]

All compounds show strong similarity in the vibrational spectra for ring stretching vibrations, but some deviations for the band at 1600 cm^{-1} were observed (Figure 4, Table 5).

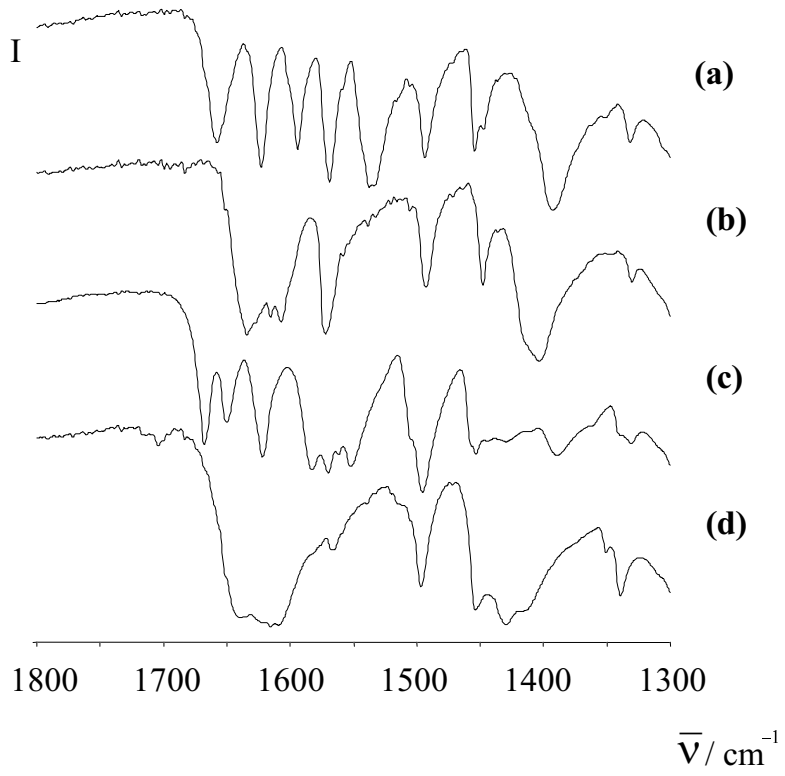

Figure 4: The vibrational spectra of the investigated compounds in the region 1800 – 1300 cm^{-1}: **1** (a), **2** (b), **3** (c), and **4** (d).

On the other hand, the amine bands and Δ (= $\nu_{as} - \nu_s$) of carboxylate asymmetric and symmetric vibrations differ significantly as expected for the compounds with the same carboyxlate ligand. Nevertheless some correlations between both monomeric (**1**, **3**) and dimeric (**2**, **4**) complexes are noticed, where also more similar hydrogen-bonding scheme is expected. The NH_2 stretching vibrations in the range 3500 – 3000 cm^{-1} for both monomeric complexes are in the lower energy region (2 inter and 2 intramolecular hydrogen bonds), than in the spectra of dimeric compounds (only intramolecular hydrogen bonds). (For **1** and **2** see Table 3; **3:** inter: 2,916(5) Å, 2,928(5) Å, intra: 3.027(6) Å, 2,945(6) Å; **4**: intra: 2 × 2,868(6) Å).[3,4] One band for NH_2 bending

Table 5: Assignation of the bands in the vibrational spectra in the range 4000 – 3000 and 1800 – 1300 cm^{-1}. The average values for the positions of carboxylate bands were used for Δ.

1	**2**	**3**	**4**	**2apy** [15]	**assignation**
3356, 3328	3488	3349	3474	3443, 3305	$\nu_{as}(NH_2)$
3209	3386	3195	3320, 3208	3168	$\nu_s(NH_2)$
				3071	ν_s(arCH)
1657	1634	1667, 1649	1639	1628	$\delta(NH_2)$
1622		1621			
1594	1615, 1607	1582	1608	1599	ν(C=Cring)
1568		1569	1566	1560	ν(C=Cring)
1537, 1533	1572	1561, 1552	1615		$\nu_{as}(O_2C)$
1493	1492	1495	1496	1490	ν(C=Cring)
1454, 1447	1447	1457, 1453	1454	1442	ν(C=Cring)
1393	1403	1429, 1389	1431		$\nu_s(O_2C)$
1331	1329	1339, 1330	1339	1340, 1325	ν(C-NH_2)
145	169	147	184		Δ

vibration at 1640 cm^{-1} in the spectra of dimeric complexes is noticed, while two for monomeric benzoate **1** and three for acetate **3**. Four different hydrogen bonds in **3** may also play a key role in splitting of the carboxylate asymmetric and symmetric stretching vibrations (Figure 4). The assignation of the carboxylate bands for **1** ($\bar{\nu}$ / cm^{-1}: ν_{as} 1565, 1535; ν_s 1380) [2] and for solvate analogue of **2** (ν_{as} 1570; ν_s 1402) [12] is close to our values. Because of the similarity to the other investigated compounds, we assigned the 1568 cm^{-1} band in the spectrum of **1** as ν(C=Cring).

The influence of the compounds on fungal growth: The preliminary tests on fungal growth for the species *Trametes versicolor* and *Antrodia vaillantii* did not show any significant retardation activity for the investigated compounds.

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Povzetek

Sintetizirani sta bili dve enojedrni in dve dvojedrni koordinacijski spojini bakrovega benzoata in acetata z 2-aminopiridinom. Z rentgensko difrakcijsko analizo je bila določena kristalna struktura obeh benzoatnih spojin. V enojedrni benzoatni obliki $[Cu(O_2CC_6H_5)_2(2apy)_2]$ (2apy = 2-aminopiridin) so koordinirani ligandi v *trans* položaju okoli osrednjega bakrovega(II) atoma, kjer so benzoati asimetrični kelati (Cu – O 1.97 in 2.65 Ĺ). Po drugi strani dvojedrno obliko $[Cu_2(O_2CC_6H_5)_4(2apy)_2]$ predstavlja strukturni tip 'mlinskega kolesa' z 2-aminopiridinom, ki se veže aksialno preko piridinskega dušikovega atoma. Vse spojine so bile karakterizirane s standardnimi fizikalno-kemijskimi metodami in testirane za njihovo zaviralno aktivnost pri rasti micelija lesnih gliv pisane ploskocevke in bele hišne gobe.