

SYNTHESIS, CRYSTAL STRUCTURE AND SPECTRAL PROPERTIES OF COPPER(II) 2-CHLORONICOTINATO COMPLEXES WITH N-HETEROCYCLIC LIGANDS

JOZEF MIKLOVIČ¹, DUŠAN VALIGURA¹, INGRID SVOBODA²,
JÁN MONCOL³, MILAN MAZÚR⁴

¹ Department of Chemistry, Faculty of Natural Sciences, University of SS. Cyril and Methodius in Trnava, Nám. J. Herdu 2, Trnava, SK-917 01, Slovak Republic
(jozef.miklovic@ucm.sk)

² Material Sciences, Darmstadt University of Technology, Darmstadt, 64287, Germany

³ Institute of Inorganic Technology, FCHPT, Slovak University of Technology, Bratislava, SK-812 37, Slovak Republic

⁴ Institute of Physical Chemistry and Chemical Physic, FCHPT, Slovak University of Technology, Bratislava, SK-812 37, Slovak Republic

Abstract: The synthesis and characterization of nine new copper(II) complexes $[\text{Cu}(\text{2-Clnic})_2\text{L}_2]$ (where 2-Clnic is 2-chloronicotinate anion, L is imidazole – Im, benzimidazole – Bim, furo[3,2-c]pyridine – FP, 2-methylfuro[3,2-c]pyridine – MFP, or [1]benzofuro[3,2-c]pyridine – BFP), $[\text{Cu}(\text{2-Clnic})_2(\text{INA})]$ (where INA is isonicotinamide), $[\text{Cu}(\text{2-Clnic})_2(\text{4-py})]\cdot\text{H}_2\text{O}$ (where 4-py is 4-methylpyridine) and $[\text{Cu}_2(\text{2-Clnic})_4(\text{IQ})_2]$ (where IQ is isoquinoline) are reported. The characterizations were based on elemental analysis, infrared, electronic and EPR spectra. The dimeric character of $[\text{Cu}_2(\text{2-Clnic})_4(\text{IQ})_2]$ is assumed on the EPR spectrum and the other spectral methods. The crystal structure of the $[\text{Cu}(\text{2-Clnic})_2(\text{Bim})_2]$ and $[\text{Cu}(\text{2-Clnic})_2(\text{FP})_2]$ complexes have been determined by X-ray crystal structure analysis. Both complexes exhibit the hexacoordination coordination polyhedra around copper atom that lies in the crystallographic center of symmetry. The distorted tetragonal-bipyramidal (4+2) arrangement is in good agreement with spectral data that have suggested an asymmetric chelate coordination of the carboxylic group.

Key words: complex, copper(II), crystal structure, carboxylate, IR, electronic and EPR spectra

1. Introduction

The metal carboxylates are interesting from a chemical point of view as the carboxylate ion can coordinate to metals in number of ways: as a unidentate ligand, as a chelating ligand, as a bridging ligand, or as a monoatomic bridging ligand. This causes the existence of a rich family of compounds with various structures (DEACON and PHILLIPS 1980, RAO *et al.*, 2004). Moreover pyridinecarboxylates due to presence of pyridine nitrogen atom can act as *N*-donor ligands in addition to their carboxylate *O*-donor ability. Some crystal structures of copper(II) 2-chloronicotinate complexes have been published (JIN *et al.*, 2012; 2014; 2015; MONCOL *et al.*, 2002; 2006; 2007).

In this paper, we described synthesis, spectral properties and crystal structure of 2-chloronicotinate copper(II) complexes with *N*-heterocyclic ligands: $[\text{Cu}(2\text{-Clnic})_2(\text{L})_2]$ ($\text{L} = \text{Im}, \text{Bim}, \text{FP}, \text{MFP}, \text{BFP}$); $[\text{Cu}_2(2\text{-Clnic})_4(\text{IQ})_2]$; $[\text{Cu}(2\text{-Clnic})_2(4\text{-py})_2] \cdot \text{H}_2\text{O}$; $[\text{Cu}(2\text{-Clnic})_2(\text{INA})]$; $[\text{Cu}(2\text{-Clnic})_2(3,5\text{-py})(\text{MeOH})]$. The crystal and molecular structure of the complexes under study $[\text{Cu}(2\text{-Clnic})_2(\text{Bim})_2]$ and $[\text{Cu}(2\text{-Clnic})_2(\text{FP})_2]$ has also been studied by X-ray structure analyses. Sketch and abbreviations of 2-chloronicotinate and heterocyclic ligands used in assembling new Cu(II) complexes are presented in Fig. 1.

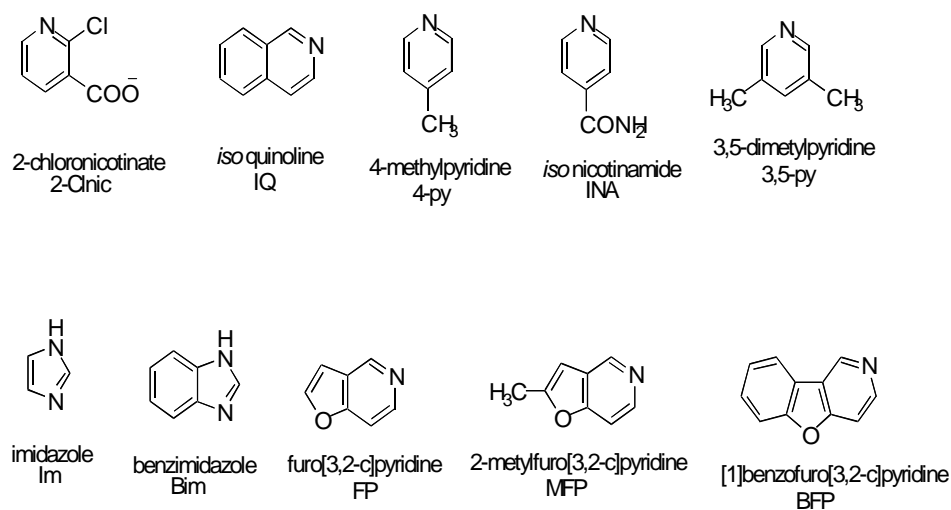


Fig. 1. Sketch and abbreviations of 2-chloronicotinate and *N*-heterocyclic ligands.

2. Material and Methods

2.1. Chemical reagents, analysis and physical measurements

All used chemicals were of reagent grade and used without further purifications. Derivatives of furo[3,2-c]pyridine (FP, MFP and BFP) have been prepared using Eloy-Deryckere procedure (ELOY and DERYCKERE, 1971). The complex $[\text{Cu}_2(2\text{-Clnic})_4(\text{H}_2\text{O})_2]$ was prepared by procedure described in (MONCOL *et al.*, 2006).

Carbon, hydrogen, nitrogen and sulfur were determined by microanalytical methods (Thermo Electron Flash EA 1112). Analytical data for the complexes are given in Table 1. Electronic spectra ($9\,000 - 50\,000\text{ cm}^{-1}$) of the powdered samples were recorded on a Specord 200 (Karl-Zeiss). IR spectra were recorded on FT-IR spectrometer (Nicolet 5700, Thermo Scientific) with a SmartOrbit™ diamond ATR accessory in range of $4\,000 - 400\text{ cm}^{-1}$ at room temperature (r.t.). EPR spectra of powdered samples were measured a Bruker 200D SRC X-band (9.4 GHz) at room

temperature. The simulations of the EPR spectra were performed using the commercially available program SIMFONIA (Bruker).

Table 1. Analytical data for the Cu(II) complexes.

Compound	Empirical formula	Formula weight (g mol ⁻¹)	Calc / Found (%)		
			C	H	N
[Cu ₂ (2-Clnic) ₄ (IQ) ₂] 1	C ₄₂ H ₂₆ Cl ₄ Cu ₂ N ₆ O ₈	1011.60	49.87 50.12	2.59 2.46	8.31 8.30
[Cu(2-Clnic) ₂ (4-py) ₂ ·H ₂ O] 2	C ₂₄ H ₂₂ Cl ₂ CuN ₄ O ₅	580.91	49.62 49.14	3.82 3.51	9.64 9.54
[Cu(2-Clnic) ₂ (INA)] 3	C ₁₈ H ₁₂ Cl ₂ CuN ₄ O ₅	498.77	43.34 43.28	2.42 2.43	11.23 10.91
[Cu(2-Clnic) ₂ (3,5-py)(MeOH)] 4	C ₂₀ H ₁₉ Cl ₂ CuN ₃ O ₅	515.83	46.57 46.91	3.71 3.88	8.15 8.62
[Cu(2-Clnic) ₂ (Im) ₂] 5	C ₁₈ H ₁₄ Cl ₂ CuN ₆ O ₄	512.80	42.16 42.07	2.75 2.64	16.39 16.12
[Cu(2-Clnic) ₂ (Bim) ₂] 6	C ₂₆ H ₁₈ Cl ₂ CuN ₆ O ₄	612.92	50.95 51.30	2.96 2.87	13.71 13.68
[Cu(2-Clnic) ₂ (FP) ₂] 7	C ₂₆ H ₁₆ Cl ₂ CuN ₄ O ₆	614.88	50.79 50.56	2.62 2.52	9.11 9.07
[Cu(2-Clnic) ₂ (MFP) ₂] 8	C ₂₈ H ₂₀ Cl ₂ CuN ₄ O ₆	642.94	52.31 52.40	3.13 3.11	8.71 8.54
[Cu(2-Clnic) ₂ (BFP) ₂] 9	C ₃₄ H ₂₀ Cl ₂ CuN ₄ O ₆	715.00	57.11 57.63	2.82 2.86	7.83 8.00

2.2. Crystallography

Data collection and cell refinement of **1** and **2** were carried out using a κ -axis diffractometer Xcalibur S CCD (Oxford Diffraction) with graphite monochromated MoK α radiation. The diffraction intensities were corrected for Lorentz and polarization factors. The structures were solved using program SHELXT (SHELDRICK, 2015a) or Olex2.solve (BOURHIS *et al.*, 2015) and refined by the full-matrix least-squares procedure with SHELXL (version 2016/4) (SHELDRICK, 2015b). Geometrical analyses were performed with SHELXL. The structures were drawn using the OLEX2 package (DOLOMANOV *et al.*, 2009). Crystal data and conditions of data collection and refinement are reported in Table 2.

2.3. Preparation of the complexes

[Cu₂(2-Clnic)₄(IQ)₂] **1**; [Cu(2-Clnic)₂(4-py)₂·H₂O] **2**; [Cu(2-Clnic)₂(INA)] **3**; [Cu(2-Clnic)₂(3,5-py)(MeOH)] **4**: Complex [Cu₂(2-Clnic)₄(H₂O)₂] (0.5 mmol; 0.395 g) was suspended in methanol (20 cm³) and ligand 2 mmol (IQ = 0.258 g; 4-py = 0.186 g; INA = 0.244 g; 3,5-py = 0.214 g) in methanol (10 cm³) was added. Solution was then heated to reflux for 15 minutes and then filtered off. Mixture then evaporated at r. t. and subsequent crystals were separated, washed with methanol

and dried at r. t.. Yield: complex **1** – 0.3 g (59 %, green); **2** – 0.17 g (29 %, blue); **3** – 0.39 g (78 %, blue green); **4** – 0.32 g (62 %, blue).

Table 2. Crystallographic data for the reported compounds.

Compound	6 [Cu(2-Clnic) ₂ (Bim) ₂]	7 [Cu(2-Clnic) ₂ (FP) ₂]
Empirical formula	C ₂₆ H ₁₈ CuN ₆ O ₄	C ₂₆ H ₁₆ CuN ₄ O ₆
Formula weight	612.90	614.87
Temperature (K)	293(1)	293(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>
a (Å)	7.6684(3)	12.9680(4)
b (Å)	22.9040(10)	13.2636(4)
c (Å)	7.6341(5)	7.3937(2)
α (°)	90	90
β (°)	107.504(6)	99.284(3)
γ (°)	90	90
V (Å ³)	1278.74(12)	1255.08(6)
Z, ρ _{calc} g.cm ⁻³	2, 1.592	2, 1.627
Radiation type	Mo-K _α	Mo-K _α
μ (mm ⁻¹)	1.109	1.134
F (000)	622	622
Crystal size (mm)	0.20x0.36x0.40	0.16x0.50x0.50
2θ Ranges (°)	5.57 to 55.35	8.30 to 52.73
Final R indices [I > 2σ(I)]	R ₁ = 0.0353 wR ₂ = 0.0823	R ₁ = 0.0493 wR ₂ = 0.1203
R indices (all data)	R ₁ = 0.0418 wR ₂ = 0.0865	R ₁ = 0.0616 wR ₂ = 0.1297
S	1.099	1.038
CCDC number	1511127	1511128

[Cu(2-Clnic)₂(Im)₂] **5**; [Cu(2-Clnic)₂(Bim)₂] **6**: Complex [Cu₂(2-Clnic)₄(H₂O)₂] (0.5 mmol; 0.395 g) was suspended in methanol (20 cm³) and ligand **2** mmol (Im = 0.136 g; Bim = 0.236 g) in methanol (10 cm³) was added. Solution was then heated to reflux for 15 minutes and then filtered off. Mixture was then evaporated at r. t.. Solid was recrystallized from ethanol and dried at r. t.. Yield: complex **5** – 0.15 g (29 %, blue); **6** – 0.21 g (34 %, blue).

[Cu(2-Clnic)₂(FP)₂] **7**; [Cu(2-Clnic)₂(MFP)₂] **8**; [Cu(2-Clnic)₂(BFP)₂] **9**: Copper(II) acetate monohydrate (0.5 mmol, 0.1 g) was dissolved in mixture of methanol (10 cm³) and water (1 cm³). To this solution was added ligand (FP = 0.26 g; MFP = 0.29 g; BFP = 0.37 g) in methanol (5 cm³). 2-Chloronicotinic acid (1 mmol, 0.157 g) in methanol (10 cm³) was then added to the solution. Reaction mixture was stirred for 1 hour and filtered off. Mixture was then evaporated at r. t. and crystals were formed and separated. Yield: **7** – 0.2 g (65 %, blue); **8** – 0.15 g (47 %, blue); **9** – 0.3 g (84 %, blue).

3. Results and Discussion

3.1. Description of crystal structure of $[\text{Cu}(2\text{-Clnic})_2(\text{Bim})_2](\mathbf{6})$ and $[\text{Cu}(2\text{-Clnic})_2(\text{FP})_2](\mathbf{7})$

Molecular structure of complexes **6** and **7** are given in Fig. 2. Both cases crystallize in monoclinic system with space group $P2_1/c$. The molecular structures show the both compound have mononuclear units with a *trans* square planar configuration, in which the copper(II) atoms are coordinated by carboxylate oxygen atoms of two 2-chloronicotinate anions and two nitrogen atoms of benzimidazole (**6**) or furo[3,2-*c*]pyridine (**7**) ligands. The distances of Cu–O1 are 1.961(1) and 2.160(3) Å, respectively, and Cu–N1 are 1.920(2) and 1.998(3) Å, respectively. The remaining carboxylate oxygen atoms of both complexes, which are weakly (**6**) or more strongly (**7**) bonded to the copper atom [Cu2–O2 = 2.890(2) Å or 2.281(4) Å, respectively] in the direction of the Cu1–O2 bonds, lie at 50.14(6) and 58.59(11)°, respectively, from the normal to the CuO₂N₂ plane and complete a tetragonal-bipyramidal (4+2) coordination. The complexes **6** and **7** represent two opposite examples of variability of the tetragonal-bipyramidal coordination of copper(II) carboxylate complexes (MONCOL *et al.*, 2004).

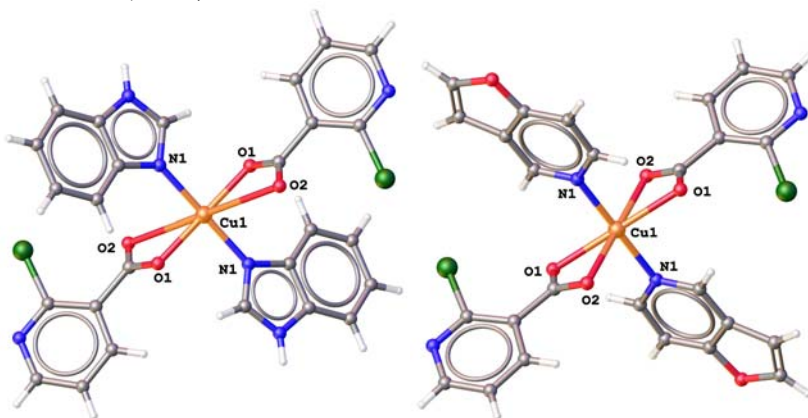


Fig. 2. The molecular structures of $[\text{Cu}(2\text{-Clnic})_2(\text{Bim})_2]$ (left) (**6**) and $[\text{Cu}(2\text{-Clnic})_2(\text{FP})_2]$ (right) (**7**).

The complex molecules of **6** are linked through N–H \cdots O hydrogen bonds between imidazole nitrogen atoms (N2) and carboxylate oxygen atoms (O2) of neighboring complex molecules [N2–H2 \cdots O2 ($-x, 1-y, 2-z$) with N2 \cdots O distance of 2.757(2) Å and N2–H2 \cdots O angle of 160°] into 1D supramolecular chains (Fig. 3). The crystal structure of **6** contains also π – π stacking interactions (JANIÁK, 2000) between imidazole rings of benzimidazole ligands [angle between two planes of π – π stacking interactions of 0.0°, the centroid-centroid distance of 3.88Å with shift distance of 1.66Å], and between pyridine rings of 2-chloronicotinate ligands [angles between two planes of π – π stacking interactions of 5.4°, the centroid-centroid distances of 3.86 and 3.87Å with shift distances of 1.10 and 1.28Å] (Fig. 4). The π – π stacking

interaction (JANIÁK, 2000) have been also observed in crystal structure of **7** between pyridine rings of furo[3,2-*c*]pyridine ligands [angles between two planes of π - π stacking interactions of 12.4° , the centroid-centroid distances of 3.88\AA with shift distances of 1.93 and 1.38\AA] (Fig. 4).

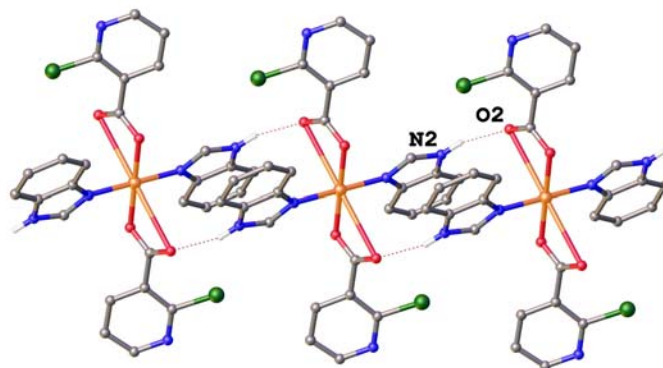


Fig. 3. Supramolecular chain formed from connecting complex molecules of **6** through N-H \cdots O hydrogen bonds. The hydrogen atoms are omitted for clarity.

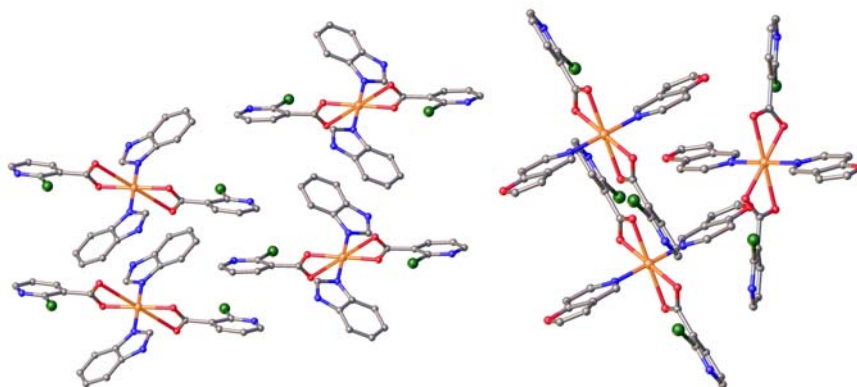


Fig. 4. The π - π stacking interactions in crystal structures of **6** (top) and **7** (bottom). The hydrogen atoms are omitted for clarity.

Table 3. Selected bond lengths and angles of **6** and **7**.

Compound	6	7
	[Cu(2-Clnic) ₂ (Bim) ₂]	[Cu(2-Clnic) ₂ (FP) ₂]
Cu1–O1 [*]	1.961(1)	2.160(3)
Cu1–O2 [*]	2.890(2)	2.281(4)
Cu1–N1 [*]	1.982(2)	1.998(3)
O1–Cu1–O2	50.14(6)	58.59(11)
N1–Cu1–O1	92.28(6)	89.59(10)
N1–Cu1–O2	81.41(6)	89.34(10)

^{*}Also for Cu1–D^{*} symmetry codes: 1-*x*, 1-*y*, 2-*z* (for **6**), 1-*x*, 1-*y*, 1-*z* (for **7**).

3.2. IR, electronic and EPR data

All the typical features of IR spectra are clearly compatible with the structural characteristics of the complexes under study. Some characteristic IR bands of the sodium salt 2-Clnic Na·H₂O as well as of Cu(II) complexes are given in Table 4. The IR spectrum of complex **2** shows absorption bands in the region from 3 200 to 3 500 cm⁻¹. These bands correspond to the antisymmetric and symmetric OH stretch and confirm the presence of water. IR spectrum of the complex **4** has sharp band at 3 492 cm⁻¹. This is stretching vibration of OH and confirms presence of methanol in complex structure that is in good agreement with elemental analyses.

Table 4. Spectroscopic data^a (in cm⁻¹) of Cu(II) complexes.

Compound	Infrared data			Electronic data	
	Carboxyl group			Band I	Band II
$\nu_{as}(\text{COO}^-)$	$\nu_s(\text{COO}^-)$	Δ^b			
2-ClnicNa	1577s	1383vs	194	-	-
[Cu ₂ (2-Clnic) ₄ (IQ) ₂] 1	1574s	1377vs	197	13 200	25 100sh
[Cu(2-Clnic) ₂ (4-py) ₂ ·H ₂ O] 2	1576vs	1389vs	187	16 700	-
[Cu(2-Clnic) ₂ (INA)] 3	1573vs	1376vs	197	14 400	-
[Cu(2-Clnic) ₂ (3,5-py)(MeOH)] 4	1573s	1374vs	199	16 400	-
[Cu(2-Clnic) ₂ (Im) ₂] 5	1572vs	1390vs	182	17 300 14 600sh	-
[Cu(2-Clnic) ₂ (Bim) ₂] 6	1593vs	1365vs	228	18 100 14 400sh	28 600
[Cu(2-Clnic) ₂ (FP) ₂] 7	1575vs	1374vs	201	16 800	-
[Cu(2-Clnic) ₂ (MFP) ₂] 8	1590s	1382vs	208	13 100	-
[Cu(2-Clnic) ₂ (BFP) ₂] 9	1574vs	1382vs	192	16 800	-

^a vs – very strong; s – strong; m – medium; br – broad; sh – shoulder, ^b $\Delta = \nu_{as}(\text{COO}^-) - \nu_s(\text{COO}^-)$.

The difference between the antisymmetric stretch and symmetric stretch (Δ) gives information on carboxylic bonding mode for the complexes after comparison with Δ of compounds with ionic carboxylic groups (NAKAMOTO, 1977). The difference between the antisymmetric stretch and symmetric stretch for 2-Clnic complexes could not be determined accurately due to an overlap of $\nu_{as}(\text{COO}^-)$ with the stretching vibration of C=N of the pyridine ring. For sodium 2-chloronicotinate, the Δ value is 194 cm⁻¹. Similar Δ value for the complex **1** (197 cm⁻¹) and **3** suggest bridging carboxylic group. For complex **1** it is confirm from electronic spectra. The greater Δ value for the complexes **4** (199 cm⁻¹), **6** (228 cm⁻¹), **7** (201 cm⁻¹) and **8** (208 cm⁻¹) suggest, that carboxylic group is probably coordinated in an asymmetric chelating manner. In this case, the Δ values are comparable to those of unidentate complexes (NAKAMOTO, 1977). The lower Δ value for the complexes **2** (187 cm⁻¹) and **5** (182 cm⁻¹) suggest, that carboxylic group is probably coordinated in chelating manner.

The positions of bands which correspond to pyridine ring deformation of neutral ligands are shifted to higher wavenumbers [IQ (601 \rightarrow 641 cm^{-1}), FP (602 \rightarrow 648 cm^{-1}), MFP (601 \rightarrow 648 cm^{-1}) and BFP (596 \rightarrow 648 cm^{-1})] show, that these ligands are coordinated through the nitrogen atom of the pyridine ring (NAKAMOTO, 1977).

The positions of band to the skeletal vibrations for 4-py (802 and 995 cm^{-1}) and 3,5-py (858 and 1064 cm^{-1}) for free ligands are shifted to higher wavenumbers 847, 1033 cm^{-1} ; complex **2**, and 867, 1064 cm^{-1} , complex **4** respectively. This shift suggest coordination these ligand via nitrogen atom of pyridine ring (MILATA *et al.*, 2008).

The band of stretching vibration amide group C=O is at 1 626 cm^{-1} for free ligand, and is shifted to 1 686 cm^{-1} in the complex **3**. This suggests that ligand INA is in the complex **3** as bridging.

Table 5. The EPR data of monomeric Cu(II) complexes.

Compound	EPR data				
	g_{\parallel}	g_i	g_{\perp}	g_{av}^*	G^*
[Cu(2-Clnic) ₂ (4-py) ₂ ·H ₂ O] 2	2.28		2.07	2.14	4
[Cu(2-Clnic) ₂ (INA)] 3		2.16			-
[Cu(2-Clnic) ₂ (3,5-py)(MeOH)] 4	2.37		2.07	2.17	5.3
[Cu(2-Clnic) ₂ (Im) ₂] 5	2.25		2.08	2.14	3
[Cu(2-Clnic) ₂ (Bim) ₂] 6	2.26		2.07	2.13	3.8
[Cu(2-Clnic) ₂ (FP) ₂] 7	2.41		2.09	2.2	4.5
[Cu(2-Clnic) ₂ (MFP) ₂] 8	2.39		2.10	2.2	3.9
[Cu(2-Clnic) ₂ (BFP) ₂] 9	2.39		2.09	2.19	4.3

* $g_{av} = 1/3(2g_{\perp} + g_{\parallel})$; $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$.

The solid state electronic spectra of complex **1** show a broad absorption band (band I) v visible region with maximum at 13 200 cm^{-1} (Table 4), which is assigned to a $d_{xy,yz} \rightarrow d_{x^2-y^2}$ transition (KATO and MUTO, 1988). Moreover, the spectrum of complex **1** displays a shoulder at about 25 100 cm^{-1} (band II). Band II has been assigned to charge transfer absorption and is believed to be indicate of dimeric complex. Finally, complex **1** displays band I and II in the usual range for Cu(II) compounds in square-pyramidal CuO₄N environment. Electronic spectra of all other copper(II) complexes under study exhibit a asymmetrical broad ligand field band with a maximum at from 13 100 cm^{-1} to 18 100 cm^{-1} . This type of d-d spectra for complexes **2** – **9** is typical for tetragonally distorted octahedral copper(II) complexes (LEVER, 1984). In the complexes **5** and **6** it is possible watch little evolve shoulders near 14 600 and 14 400 cm^{-1} by Jahn-Teller effect. In others complexes is splitting d-d transition very little of shining and it is not possible determination of position individual bands.

The solid state EPR spectra of complexes **2**, **4**, **5**, **6**, **7**, **8** and **9** are of monomeric type, exhibiting allowed transitions ($\Delta M_S=1$) characteristic of species with $S=1/2$.

The EPR spectra exhibit axial symmetry pattern giving g -tensor values listed in Table 5. The axial character with $g_{\parallel} > g_{\perp}$. G values close to four are in agreement with the elongated pseudooctahedral geometry having a $d_{x^2-y^2}$ ground state.

Acknowledgements: This work was financially supported by the Grants APVV-14-0073, VEGA 1/0534/16 of the Slovak Grant Agency for Science.

References

- BOURHIS, L.J., DOLOMANOV, O.V., GILDEA, R.J., HOWARD, J.A.K., PUSCHMANN, H.: The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment - *Olex2* dissected. *Acta Crystallogr. Sect. A*, 71, 2015, 59-75.
- DEACON, G.B., PHILLIPS, R.J.: Relationships between the carbon-oxygen stretching frequencies of carboxylate complexes and the type of carboxylate coordination. *Coord. Chem. Rev.*, 33, 1980, 227-250.
- DOLOMANOV, O.V., BOURHIS, L.J., GILDEA, R.J., HOWARD, J.A.K., PUSCHMANN, H.: *OLEX2*: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.*, 42, 2009, 339-341.
- ELOY, F., DERYCKERE, A.: Sur la synthèse des furo[3,2-*c*]pyridines. *J. Heterocycl. Chem.*, 8, 1971, 57-60.
- JANIAK, C.: A critical account on π - π stacking in metal complexes with aromatic nitrogen-containing ligands. *J. Chem. Soc., Dalton Trans.*, 21, 2000, 3885-3896.
- JIN, S.W., WANG, D.Q., XU, Y.C.: Five new metal(II) complexes with 3-D network structures based on carboxylate and bis(imidazole) ligands: syntheses and structures. *J. Coord. Chem.*, 65, 2012, 1953-1969.
- JIN, S.W., YE, X.H., JIN, L., ZHENG, L., LI, J.W., JIN, B.P., WANG, D.Q.: Syntheses and structural characterization of nine coordination compounds assembled from copper acetate, 3,5-dimethylpyrazole and carboxylates. *Polyhedron*, 81, 2014, 382-395.
- JIN, S.W., LIU, H., CHEN, G.Q., AN, Z.Y., LOU, Y.L., HUANG, K., WANG, D.Q.: Syntheses and crystal structures of copper(II), zinc(II) and cadmium(II) complexes containing pyridine, quinoline and 2-methylquinoline. *Polyhedron*, 95, 2015, 91-107.
- KATO, M., MUTO, Y.: Factors affecting the magnetic properties of dimeric copper(II) complexes. *Coord. Chem. Rev.*, 92, 1988, 45-83.
- LEVER, A.B.P.: *Inorganic electronic spectroscopy*, 2nd Ed., Elsevier, Amsterdam, 1984, 480 p.
- MILATA, V., SEGĽA, P., GATIAL, A., KOVÁČIK, V., MIGLIERINI, M., STANKOVSKÝ, Š., ŠÍMA, J.: *Aplikovaná molekulová spektroskopia*, Vydavateľstvo STU, 2008; 600 p.
- MONCOL, J., PALICOVÁ, M., SEGĽA, P., KOMAN, M., MELNÍK, M., VALKO, M., GLOWIAK, T.: Crystal and spectral study of copper(II) pyridinecarboxylates: Crystal and molecular structure of *trans*-diaqua-bis(*N,N*-diethylnicotinamide-*N*)bis(2-chloronicotinate-*O*)copper(II). *Polyhedron*, 21, 2002, 365-370.

- MONCOL, J., MÚDRA, M., , LONNECKE, P., KOMAN, M., MELNÍK, M.: Copper(II) halogenopropionates: Low-temperature crystal and molecular structure of bis(2,2-dichloropropionato)-di(methyl-3-pyridylcarbamate)copper(II) and bis(2-bromopropionato)-di(2-pyridylmethanol)copper(II). *J. Coord. Chem.*, 57, 2004, 1065-1078.
- MONCOL, J., SEGĽA, P., , MIKLOŠ, D., MAZÚR, M., MELNÍK, M., GLOWIAK, T., VALKO, M., KOMAN, M.: Structural diversity of coordination polymers with bridging 3-pyridylmethanol ligand: New type of coordination polymer with different stereochemistry of copper(II) atom. *Polyhedron*, 25, 2006, 1561-1566.
- MONCOL, J., KORABIK, M., SEGĽA, P., KOMAN, M., MIKLOŠ, D., JAŠKOVÁ, J., GLOWIAK, T., MELNÍK, M., MROZINSKI, J., SUNDBERG, M.R.: Preparation, structure, and magnetic properties of copper(II) halogenonicotinate: Crystal and molecular structure of tetrakis(μ -2-chloronicotinato-*O,O'*)-diaquadicopper(II). *Z. Anorg. Allg. Chem.*, 633, 2007, 298-305.
- NAKAMOTO, K.: Infrared and Raman spectra of inorg. and coord. compounds, Part B, 5th Edition, New York, 1997, 384-387.
- RAO, C.N.R., NATARAJAN, R., VAIDHYANATHAN, R.: Metal carboxylates with open architectures. *Angew. Chem., Int. Ed.*, 43, 2004, 1466-1496.
- SHELDRICK, G.M.: *SHELXT* - Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A*, 71, 2015a, 3-8.
- SHELDRICK, G.M.: Crystal structure refinement with *SHELXL*. *Acta Crystallogr. Sect. C*, 71, 2015b, 3-8.

Received 16 November 2016

Accepted 5 December 2016