



J. Serb. Chem. Soc. 75 (2) 229–242 (2010)
JSCS–3955

Synthesis and structural studies of complexes of Cu, Co, Ni and Zn with isonicotinic acid hydrazide and isonicotinic acid (1-naphthylmethylene)hydrazide

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(Received 15 April, revised 11 September 2009)

Abstract: Eight new complexes of Cu(II), Co(II), Ni(II) and Zn(II) with isonicotinic acid hydrazide (isoniazid, (INH)) and isonicotinic acid (1-naphthylmethylene)hydrazide (INNMH), having the formula of the type $[M(INH)(ac)_2]$ or $[M(INNMH)(ac)_2]$ ($M = Co(II), Ni(II)$ and $Zn(II)$) and $[Cu(INH)(ac)_2]_2$, $[Cu(INNMH)(ac)_2]_2$, were synthesized and characterized. All complexes were characterized based on elemental analyses, and IR, UV–VIS–NIR and EPR spectroscopy, as well as by thermal analysis and determination of their molar conductivity and magnetic moments. The structure of INNMH was established by single crystal X-ray analysis. In all complexes, both ligands were coordinated to the metal *via* N and O. The complexes of Cu (II) were dimeric, with four bridges between acetate ions and Cu(II).

Keywords: isoniazid; isonicotinic acid (1-naphthylmethylene)hydrazide; template synthesis; X-ray study; transition metal complexes.

INTRODUCTION

Isonicotinic acid hydrazide (isoniazid, INH) is a known tuberculostatic agent. It forms metal chelates with many bivalent ions. These complexes have been used in the determination of the structure of isoniazid.^{1,2}

Numerous research papers have described the bactericide and fungicide properties of various mixed ligand complexes of metal ions with isoniazid and hydrazone derivatives.^{3,4}

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doi: 10.2298/JSC1002229K

Hydrazones play an important role in inorganic chemistry, as they easily form stable complexes with most transition metal ions. The development of the field of bioinorganic chemistry has increased the interest in hydrazone complexes, since it was recognized that many of these complexes may serve as models for biologically important species.⁵⁻⁹ In context to previous research,^{10,11} a number of complexes of transition metals with isonicotinoylhydrazone ligands were obtained and characterized.

In the present paper, the synthesis and characterization of eight new complexes of Cu(II), Co(II), Ni(II) and Zn(II) acetate with isoniazid (INH) and isonicotinic acid (1-naphthylmethylene)hydrazide (INNMH) are reported. The structural formula of isoniazid is shown in Fig. 1a and a molecular drawing and the atom labeling scheme of isonicotinic acid (1-naphthylmethylene)hydrazide are shown in Fig. 1b.

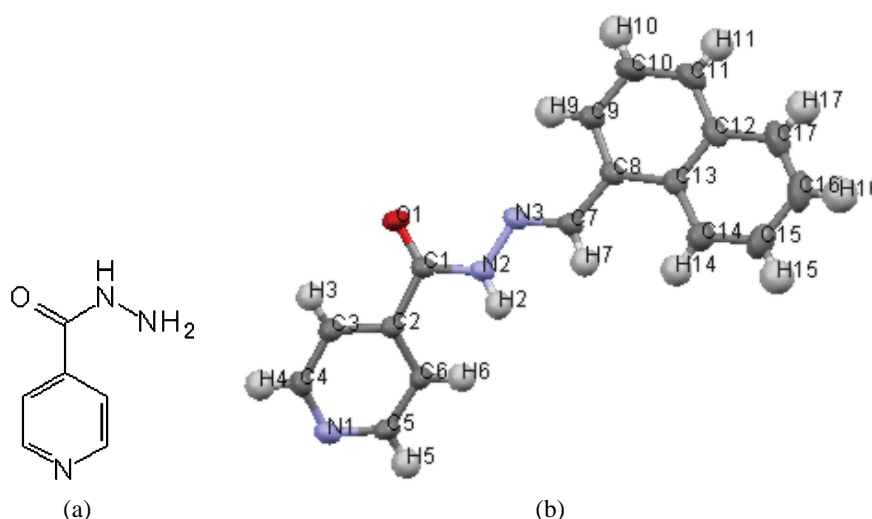


Fig. 1. a) The structural formula for isoniazid, INH, and b) the crystal structure of isonicotinic acid (1-naphthylmethylene)hydrazide, INNMH.

EXPERIMENTAL

Isonicotinic acid (1-naphthylmethylene)hydrazide, INNMH, was obtained by refluxing a mixture of isoniazid and 1-naphthaldehyde (1:1 molar ratio) on a water bath for 5 h. Methanol (30 ml) was used as the solvent. After cooling, a brilliant yellowish white precipitate formed, which was filtered, washed with methanol and dried under vacuum over CaCl₂. Single crystals were separated from the solid and subjected to a single crystal X-ray study whereby their crystal structure was determined.

Synthesis of the complexes

To a methanolic solution (30 ml) of the required metal acetate with crystal water (0.001 mol) was added a methanolic solution of isoniazid (INH) in a 1:1 molar ratio. The resulting precipitates **1–4** were filtered, washed with methanol and dried under vacuum over CaCl_2 .

For the complexes with the hydrazone, isoniazid (0.0020 mol in 30 ml of methanol) was added to a methanolic solution of 1-naphthaldehyde (0.0020 mol in 30 ml methanol). The mixture was stirred at 50 °C for 30 min, cooled to room temperature and to this was added under stirring, a methanolic solution of Cu(II), Co(II), Ni(II) or Zn(II) acetate (0.0010 mol in 15 ml methanol). Immediately, the metallic complexes precipitated. The solid products **5–8** were filtered, washed with methanol and dried under vacuum over anhydrous CaCl_2 .

Instrumentation

The elemental analyses (C, H, N) were realized with an elemental combustion system CHNS-O, using a Costech device, type ECS 4010, and the metal contents were determined by gravimetric methods.¹²

The IR spectra (4000–400 cm^{-1}) were recorded in KBr pellets using a Bio-Rad FTS-135 spectrometer. The UV–VIS–NIR electronic spectra (200–2200 nm) were recorded by diffuse reflection using a Jasco V 670 UV–VIS–NIR spectrophotometer.

The magnetic susceptibility of the complexes was determined at room temperature, using the Faraday method. The electronic paramagnetic resonance (EPR) spectra of the Cu complexes were recorded at room temperature on a Jeol JESS FA 100 spectrometer, with a 100 Hz field modulation.

The thermal analyses were performed with a Perkin Elmer Diamond instrument at a heating of 5 °C/min under a dynamic air atmosphere (150 ml/min). All complexes were investigated in the temperature range 20–800 °C, with the exception of the cobalt complexes, which were investigated up to 960 °C.

Single-crystal X-ray diffraction was used for crystal structure determination of isonicotinic acid (1-naphthylmethylene)hydrazide. The XRD data were collected at room temperature on a Stoe IPDS II diffractometer operating with an Mo $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) X-ray tube with a graphite monochromator. Data collection and cell refinement were realized using Stoe X-AREA.¹³ The structures were solved by direct methods and refined with anisotropic displacement parameters based on F^2 , using SHELXS-97¹⁴ and SHELXL-97¹⁵ crystallographic software packages.

RESULTS AND DISCUSSION

By the reaction of Co(II), Ni(II) and Zn(II) acetate with INH, complexes of the type $[\text{M}(\text{INH})(\text{ac})_2] \cdot x\text{H}_2\text{O}$ ($x = 3$, $\text{M} = \text{Co}$ and $x = 2$, $\text{M} = \text{Ni}$ and Zn ; $\text{INH} =$ isoniazid) were obtained and by the reaction of Cu(II) acetate with INH in 1:1 molar ratio, the dimer $[\text{Cu}(\text{INH})(\text{ac})_2]_2 \cdot 3\text{H}_2\text{O}$ was obtained. The complexes were insoluble or slightly soluble in usual organic solvents (methanol, ethanol, DMF, acetone, diethyl ether and chloroform).

The structure of INNMH (isonicotinic acid (1-naphthylmethylene)hydrazide) was determined in a single crystal X-ray diffraction study. Details of crystal structure determination are summarized in Table I, and the bond lengths and angles in Table II.

The complexes with INNMAH were obtained by template synthesis. The compounds were soluble in DMF and insoluble in other common (methanol, ethanol, acetone, diethyl ether and chloroform.) organic solvents. Molar conductivity measurements in DMF showed that they were non-electrolytes.

TABLE I. Crystallographic data, details of data collection and structure refinement parameters for INNMA

Chemical formula	$C_{17}H_{13}N_3O_1$
$M / g \text{ mol}^{-1}$	275.30
T / K	293(2)
$\lambda / \text{\AA}$	0.71073
Crystal system	Monoclinic
Space group	P21/n
$a / \text{\AA}$	9.1732(9)
$b / \text{\AA}$	11.342(1)
$c / \text{\AA}$	13.161(1)
$\alpha / ^\circ$	90.00
$\beta / ^\circ$	99.400(7)
$\gamma / ^\circ$	90.00
$V / \text{\AA}^3$	1350.9(2)
Z	4
$\rho / g \text{ cm}^{-3}$	1.354
$F(000)$	576
R_{int}	0.0421
Reflections collected	5171
Unique reflections	3440
Goodness-of-fit on F^2	1.073

TABLE II. Bond distances and angles for INNMAH

C1–O1 1.2158(2)	C13–C14 1.418(2)	C13–C8–C7 120.70(1)
C1–N2 1.3567(2)	C14–C15 1.368(3)	C8–C9–C10 121.83(2)
C1–C2 1.5071(2)	C15–C16 1.400(3)	C11–C10–C9 119.95(2)
C2–C6 1.383(2)	C16–C17 1.352(3)	C10–C11–C12 121.04(2)
C2–C3 1.386(2)	N2–N3 1.3781(16)	C11–C12–C17 121.43(2)
C3–C4 1.384(2)	O1–C1–N2 124.00(13)	C11–C12–C13 119.72(2)
C4–N1 1.333(2)	O1–C1–C2 120.83(1)	C17–C12–C13 118.83(2)
C5–N1 1.338(2)	N2–C1–C2 115.16(1)	C14–C13–C12 118.01(1)
C5–C6 1.388(2)	C6–C2–C3 118.18(1)	C14–C13–C8 123.86(1)
C7–N3 1.2680(2)	C6–C2–C1 123.25(1)	C12–C13–C8 118.12(1)
C7–C8 1.4693(2)	C3–C2–C1 118.36(1)	C15–C14–C13 120.81(2)
C8–C9 1.375(2)	C4–C3–C2 118.74(1)	C14–C15–C16 120.97(2)
C8–C13 1.434(2)	N1–C4–C3 123.97(1)	C17–C16–C15 120.03(2)
C9–C10 1.402(2)	N1–C5–C6 123.57(1)	C16–C17–C12 121.28(2)
C10–C11 1.354(3)	C2–C6–C5 118.86(1)	C4–N1–C5 116.69(1)
C11–C12 1.408(3)	N3–C7–C8 121.11(1)	C1–N2–N3 118.50(1)
C12–C17 1.422(2)	C9–C8–C13 119.25(1)	C7–N3–N2 115.72(1)
C12–C13 1.429(2)	C9–C8–C7 119.92(1)	

Results of the elemental analyses of the obtained complexes are listed below (ac = C₂H₃O₂⁻).

[Cu(INH)(ac)₂]₂·3H₂O (**1**). Anal. Calcd. for Cu₂C₂₀H₃₂N₆O₁₃: C, 34.711; H, 4.665; N, 12.157; Cu, 18.382. Found: C, 34.989; H, 4.873; N, 12.449; Cu, 18.618.

[Co(INH)(ac)₂]₂·3H₂O (**2**). Anal. Calcd. for CoC₁₀H₁₉N₃O₈: C, 34.246; H, 4.894; N, 12.005; Co, 16.832. Found: C, 34.011; H, 4.678; N, 12.120; Co, 16.630.

[Ni(INH)(ac)₂]₂·2H₂O (**3**). Anal. Calcd. for NiC₁₀H₁₇N₃O₇: C, 31.427; H, 4.487; N, 10.999; Ni, 15.370. Found: C, 31.771; H, 4.621; N, 11.100; Ni, 15.600.

[Zn(INH)(ac)₂]₂·2H₂O (**4**). Anal. Calcd. for ZnC₁₀H₁₇N₃O₇: C, 30.559; H, 5.390; N, 10.703; Zn, 16.652. Found: C, 30.711; H, 5.604; N, 10.912; Zn, 16.705.

[Cu(INNMH)(ac)₂]₂·4H₂O (**5**). Anal. Calcd. for Cu₂C₄₂H₄₄N₆O₁₆: C, 51.192; H, 4.607; N, 8.538; Cu, 12.909. Found: Cu, C, 51.316; H, 4.982; N, 8.611; 12.800.

[Co(INNMH)(ac)₂]₂·4H₂O (**6**). Anal. Calcd. for CoC₂₁H₂₆N₃O₉: C, 46.650; H, 5.038; N, 7.780; Co, 10.909. Found: C, 46.510; H, 5.103; N, 7.610; Co, 10.872.

[Ni(INNMH)(ac)₂]₂·2H₂O (**7**). Anal. Calcd. for NiC₂₁H₂₂N₃O₇: C, 51.649; H, 4.751; N, 8.614; Ni, 12.029. Found: C, 51.712; H, 4.842; N, 8.702; Ni, 12.200.

[Zn(INNMH)(ac)₂]₂·2H₂O (**8**). Anal. Calcd. for ZnC₂₁H₂₂N₃O₇: C, 50.949; H, 4.687; N, 8.497; Zn, 13.220. Found: C, 50.732; H, 4.502; N, 8.378; Zn, 13.310.

Some physical properties (color, melting point, molar conductivity) of the complexes are given in Table III.

TABLE III. Selected physical and chemical properties of the complexes **1–8** (INH = isoniazid; INNMH = isonicotinic (1-naphthylmethylene)hydrazide; ac = CH₃COO⁻)

Complex	Color	Melting point, °C	$\Lambda_M^a / \text{cm}^2 \text{mol}^{-1}$	μ_{eff} / μ_B
[Cu(INH)(ac) ₂] ₂ ·3H ₂ O (1)	Green	277	–	2.180
[Co(INH)(ac) ₂] ₂ ·3H ₂ O (2)	Brown	280 ^b	–	4.32
[Ni(INH)(ac) ₂] ₂ ·2H ₂ O (3)	Green	299 ^b	–	3.386
[Zn(INH)(ac) ₂] ₂ ·2H ₂ O (4)	Yellowish	263	–	Diamagnetic
[Cu(INNMH)(ac) ₂] ₂ ·4H ₂ O (5)	Green	193	9.04	2.39
[Co(INNMH)(ac) ₂] ₂ ·4H ₂ O (6)	Brown	233	8.88	5.02
[Ni(INNMH)(ac) ₂] ₂ ·2H ₂ O (7)	Grey	317	8.85	2.801
[Zn(INNMH)(ac) ₂] ₂ ·2H ₂ O (8)	Yellowish	206	8.44	Diamagnetic

^a10⁻³ M Solution in DMF; ^bcarbonization

IR spectra

The main bands in the IR spectra of INH and its metal complexes **1–4** are presented in Table IV and the bands in the IR spectra of INHNA and its metal complexes **5–8** are given in Table V.

In the IR spectrum of isoniazid, very intense bands appeared at 3302, 3112, 1667 and 1555 cm^{-1} , which were assigned to the vibration frequencies $\nu(\text{NH}_{\text{as}})$ and $\nu(\text{NH}_{\text{sym}})$ and to amide-I and amide-II-groups. The average intensity band at 887 cm^{-1} was assigned to the N–N vibration frequency.¹⁶

TABLE IV. Selected infrared frequencies (cm^{-1}) of isoniazid (INH) and its complexes **1–4** ($\text{ac} = \text{CH}_3\text{COO}^-$)

Complex	$\nu(\text{OH})$	$\nu(\text{N–H})$	$\nu(\text{C=O})$ Amide I	ν Amide II	$\nu(\text{N–N})$	$\nu(\text{COO})$		
						ν_{as}	ν_{sym}	$\Delta\nu$
INH	–	3302 3112	1667	1555	887	–	–	–
[Cu(INH)(ac) ₂] ₂ ·3H ₂ O (1)	3429	–	1627	1499	837	1561	1418	143
[Co(INH)(ac) ₂] ₂ ·3H ₂ O (2)	3363	3245	1650	1549	832	1596	1416	180
[Ni(INH)(ac) ₂] ₂ ·2H ₂ O (3)	3380	3257	1660	1550	857	1580	1416	164
[Zn(INH)(ac) ₂] ₂ ·2H ₂ O (4)	3421	3211	1634	1547	855	1580	1408	172

TABLE V. Selected infrared frequencies (cm^{-1}) of isonicotinic acid (1-naphthylmethylene)-hydrazide (INNMH) and complexes **5–8** ($\text{ac} = \text{CH}_3\text{COO}^-$)

Complex	$\nu(\text{OH})$	$\nu(\text{N–H})$	$\nu(\text{C=O})$ Amide I	$\nu(\text{C=N})$ Azomethine	$\nu(\text{COO})$		
					ν_{as}	ν_{sym}	$\Delta\nu$
INNMH	–	3175 3011	1675	1552	–	–	–
[Cu(INNMH)(ac) ₂] ₂ ·4H ₂ O (5)	3416	–	1623	1521	1557	1419	138
[Co(INNMH)(ac) ₂] ₂ ·4H ₂ O (6)	3416	3196 3047	1654	1516	1598	1419	179
[Ni(INNMH)(ac) ₂] ₂ ·2H ₂ O (7)	3416	3201 3057	1649	1516	1577	1419	158
[Zn(INNMH)(ac) ₂] ₂ ·2H ₂ O (8)	3416	3180 3052	1654	1506	1593	1398	195

In the complexes **1–4**, the band corresponding to the amide-I group is shifted towards lower values by $\Delta\nu$ between 7 and 40 cm^{-1} , which indicates the involvement of the carbonyl group in the coordination.¹⁷ The $\nu(\text{N–H})$ vibration frequencies are strongly displaced in all complexes. The movement of the band 3302 cm^{-1} to lower wave numbers suggests the involvement of the amino nitrogen in the coordination to the metal ions. This conclusion is supported by the movement of the $\nu(\text{N–N})$ frequency vibration towards lower values in the complexes.

The spectrum of complexes show bands which could be assigned to both bridging and chelating binding coordination mode of the acetate anion.¹⁸ A correlation between the infrared antisymmetric and symmetric absorption frequencies of the carboxylate group and the type of carboxylate group has been developed. The acetate ion in aqueous solution is characterized by bands at 1578 and 1411 cm^{-1} , which are commonly assigned to the antisymmetric (ν_{as}) and the

symmetric (ν_{sym}) stretching vibrations of the carboxylate group. These frequencies and, in particular, their difference, $\Delta\nu = \nu_{\text{as}} - \nu_{\text{sym}}$, have been used as empirical indicators of coordination modes of the acetate group. According to Deacon and Phillips,¹⁸ a difference larger than 200 cm^{-1} indicates a monodentate coordination, whereas a difference smaller than 150 cm^{-1} indicates a bridging coordination mode. Moreover, it is accepted that a values of $\Delta\nu$ smaller than 200 cm^{-1} can indicate a bidentate coordination mode. In complexes **1–4**, the frequencies of the vibration $\nu_{\text{as}}(\text{COO})$ appears in the range $1561\text{--}1596 \text{ cm}^{-1}$, while those characteristic of the $\nu_{\text{sym}}(\text{COO})$, ranged from 1408 to 1418 cm^{-1} . For complex **1**, a value of $\Delta\nu < 150 \text{ cm}^{-1}$, which is indicative of a bridge in the coordination of the acetate group.¹⁸ However, for the complexes **2–4**, $\Delta\nu$ is $>150 \text{ cm}^{-1}$, which leads to the conclusion that the acetate group is a chelating binding ligand in these complexes.

Bands in the region $3363\text{--}3429 \text{ cm}^{-1}$ in the IR spectra of the complexes suggests the presence of crystallization water.¹⁹ In the region $400\text{--}500 \text{ cm}^{-1}$, there are bands that can be attributed to modes of vibration $\nu(\text{M–N})$ and $\nu(\text{M–O})$. All this data supports the idea that in the metal complexes, the isoniazid was coordinated through the amino nitrogen and the carbonyl oxygen.

In the IR spectrum of INNMH, intense bands appear at 1675 and 1552 cm^{-1} , which were assigned to the vibrations $\nu(\text{C=O amide I})$ and $\nu(\text{C=N azomethine})$.

For the complexes **5–8**, the band corresponding to amide I was shifted by $21\text{--}53 \text{ cm}^{-1}$ toward lower frequencies, which indicates the involvement of carbonyl group in coordination.¹⁷ In addition, a shift towards lower values by $31\text{--}46 \text{ cm}^{-1}$ was observed for the bands characteristic of the azomethine group of metal complexes with INHNA. This suggests involvement of the azomethine nitrogen in the coordination with the metal ions.¹⁷ The $\nu_{\text{as}}(\text{COO})$ vibration band appeared in the domain $1557\text{--}1598 \text{ cm}^{-1}$ in the spectra of the complexes **5–8**, while those characteristic of the $\nu_{\text{sym}}(\text{COO})$ appeared in the $1398\text{--}1419 \text{ cm}^{-1}$ range. For complex **5**, $\Delta\nu$ was $<150 \text{ cm}^{-1}$, suggesting that the acetate group is coordinated in a bridge. In complexes **6–8**, $\Delta\nu$ was $>150 \text{ cm}^{-1}$ which leads to the conclusion that the acetate group in these complexes was in a chelating binding mode.¹⁸

The IR spectral data showed that isonicotinic acid (1-naphthylmethylene)-hydrazide was coordinated to the metal ions through the azomethine nitrogen and the carbonyl oxygen.

Magnetic properties

The magnetic moments calculated for complexes **1** and **5** (at room temperature) of 2.18 and $2.39 \mu_{\text{B}}$, respectively, reasonably correspond to octahedral geometry of the Cu(II) complexes.²⁰

For the Co (II) complexes **2** and **6**, the magnetic moments were 4.32 and $5.02 \mu_{\text{B}}$, respectively, indicating a high-spin character, excluding the oxidation to

Co(III). These values are within the range (4.3–5.7 μ_B) corresponding to an octahedral geometry for the Co(II) ion.²⁰

For the Ni(II) complexes **3** and **7**, the values for the magnetic moments were 3.38 and 2.80 μ_B , respectively. These values are within the range (2.8–3.5 μ_B) found for paramagnetic complexes of Ni(II) with octahedral geometry.²⁰

The Zn(II) complexes **4** and **8** were diamagnetic, as expected for complexes of metal ions with a d^{10} configuration.

Electronic spectra

The data of the electronic spectra of the ligands and those of complexes **1–8** are given in Table VI. The spectrum of isoniazid presented two bands in the UV interval at 42372 and 37037 cm^{-1} , assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, and that of INNMH also exhibited two bands at 39682 and 30864 cm^{-1} , assigned to the same transitions, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively.

TABLE VI. Electronic spectral data and geometries for the ligands and their complexes

Complex	ν / cm^{-1}	Assignments	Geometry	$10Dq / \text{cm}^{-1}$	B	β
INH	42372	$\pi \rightarrow \pi^*$	–	–	–	–
	37037	$n \rightarrow \pi^*$				
[Cu(INH)(ac) ₂] ₂ ·3H ₂ O (1)	34482	$\pi \rightarrow \pi^*$	Octahedral	–	–	–
	29411	$n \rightarrow \pi^*$				
	13404	$xy \rightarrow x^2-y^2$				
	11467	$z^2 \rightarrow x^2-y^2$				
[Co(INH)(ac) ₂] ₂ ·3H ₂ O (2)	40983	$\pi \rightarrow \pi^*$	Octahedral	2188	592	0.609
	36764	$n \rightarrow \pi^*$				
	24390	${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$				
	11037	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$				
	8849	${}^4T_{1g} \rightarrow {}^4T_{2g}$				
	40000	$\pi \rightarrow \pi^*$				
[Ni(INH)(ac) ₂] ₂ ·2H ₂ O (3)	33745	$n \rightarrow \pi^*$	Octahedral	9225	893.2	0.867
	25641	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$				
	15432	${}^3A_{2g} \rightarrow {}^3T_{1g}$				
	9225	${}^3A_{2g} \rightarrow {}^3T_{2g}$				
	39062	$\pi \rightarrow \pi^*$				
	34246	$n \rightarrow \pi^*$				
INHNA	39682	$\pi \rightarrow \pi^*$	–	–	–	–
	30864	$n \rightarrow \pi^*$				
[Cu(INNMH)(ac) ₂] ₂ ·4H ₂ O (5)	39062	$\pi \rightarrow \pi^*$	Octahedral	–	–	–
	28409	$n \rightarrow \pi^*$				
	14204	$xy \rightarrow x^2-y^2$				
	7246	$z^2 \rightarrow x^2-y^2$				
[Co(INNMH)(ac) ₂] ₂ ·4H ₂ O (6)	45045	$\pi \rightarrow \pi^*$	Octahedral	–	–	–
	28409	$n \rightarrow \pi^*$				
	17667	${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$				
	10000	${}^4T_{1g} \rightarrow {}^4T_{2g}$				

TABLE VI. Continued

Complex	ν / cm^{-1}	Assignments	Geometry	$10Dq / \text{cm}^{-1}$	B	β
[Ni(INNMH)(ac) ₂].2H ₂ O (7)	37593	$\pi \rightarrow \pi^*$	Octahedral	10309	10140.984	
	28901	${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$				
	17241	${}^3A_{2g} \rightarrow {}^3T_{1g}$				
	10309	${}^3A_{2g} \rightarrow {}^3T_{2g}$				
[Zn(INNMH)(ac) ₂].2H ₂ O (8)	31250	$n \rightarrow \pi^*$	Octahedral	–	–	–

The electronic spectrum of complex **1** had two bands at 13404 and 11467 cm^{-1} , which can be attributed to the transitions $xy \rightarrow x^2-y^2$ and $z^2 \rightarrow x^2-y^2$, characteristic for a Cu(II) ion in an octahedral environment. The electronic spectrum of complex **5** showed a broad band at 14204 cm^{-1} attributed to the transition $xy \rightarrow x^2-y^2$, also corresponding to an octahedral Cu(II) ion.²¹

The electronic spectrum of the complex **2** displayed three bands at 24390, 11037 and 8849 cm^{-1} , attributed to the d–d transitions: ${}^4T_{1g} \rightarrow {}^4T_{1g}(\text{P})$, ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}$, and ${}^4T_{1g} \rightarrow {}^4T_{2g}$, respectively. The electronic spectrum of complex **6** displayed two bands at 17667 cm^{-1} and 10000 cm^{-1} . These transitions are consistent with the characteristic octahedral geometry.²¹

Both electronic spectra of the Ni(II) complexes, **3** and **7**, exhibited three bands at: 25641, 15432 and 9225 cm^{-1} , and 28901, 17241 and 10309 cm^{-1} , respectively, attributed to the transitions ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$, ${}^3A_{2g} \rightarrow {}^3T_{1g}$ and ${}^3A_{2g} \rightarrow {}^3T_{2g}$, respectively, which are characteristic of an octahedral geometry.²¹

The values for the parameters $10Dq$, B and β for the Co and Ni complexes were calculated using formulas of König²² and they are presented in Table VI.

In the spectra of the Zn(II) complexes **4** and **8**, as expected, there were only the bands characterizing the ligand, but displaced to lower values compared with the corresponding bands in the spectrum of the free ligand, which proves the coordination of the ligands to the metal ion.

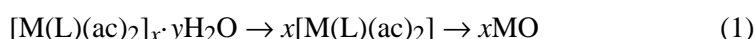
EPR spectra

The EPR spectra of the Cu(II) complexes **1** and **5** (Figs. 2a and 2b, respectively), measured at room temperature using polycrystalline powders, were analyzed. Complex **1** exhibited no signal, while for complex **5**, the “g” parameter had only one value ($g_{\text{isotropic}} = 2.1$). These values and the spectral rate indicate that both Cu(II) complexes could be dimeric.

Thermogravimetric analysis

The results of the thermal analysis of complexes **1–8** are given in Table VII.

The TG curves of these complexes indicated the presence of water molecules outside the coordination and the final products were the corresponding metal oxides. The decomposition occurred in three stages, represented generally as follows:



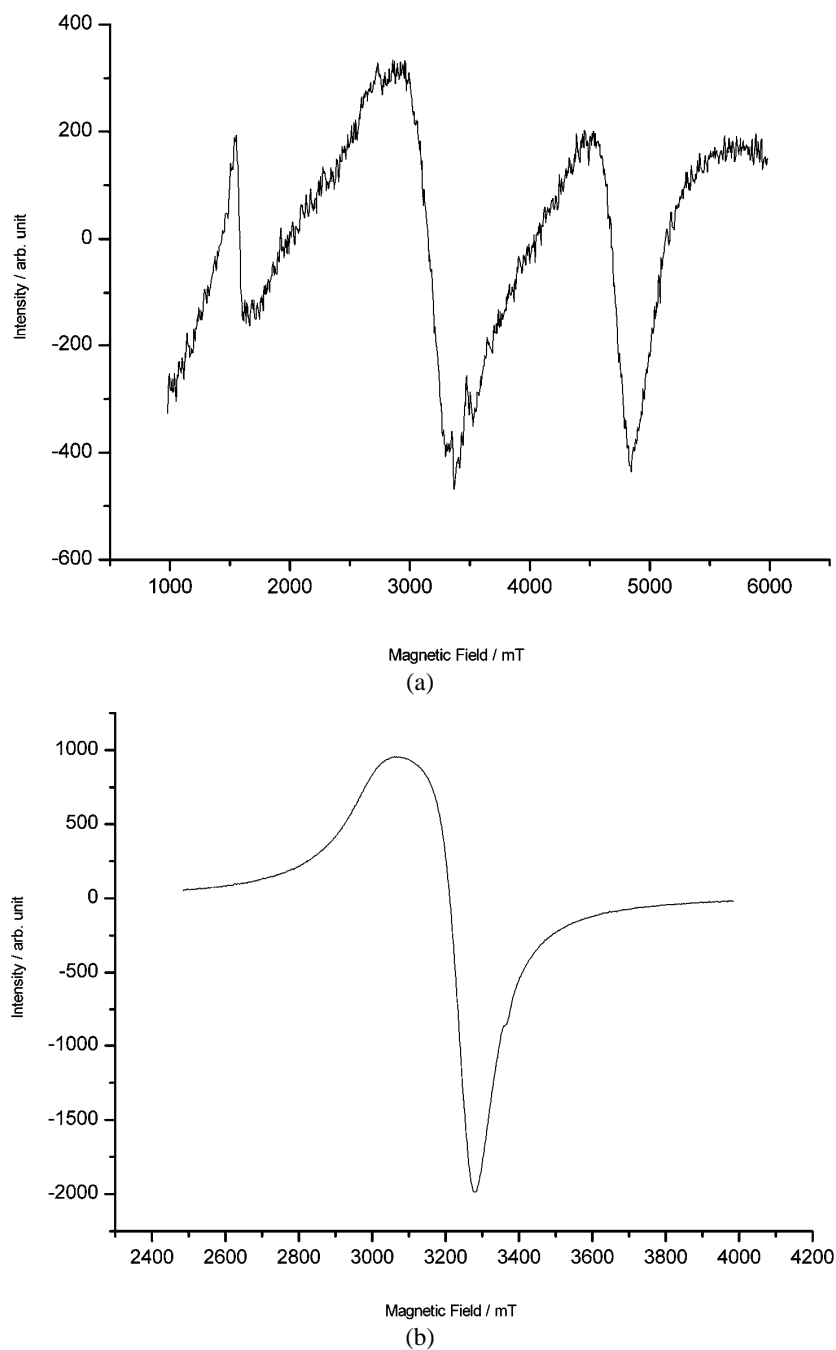


Fig. 2. The room temperature EPR spectra for complex **1** (a) and **5** (b).

where L = INH or INNMH; M = Co, $x = 1$, $y = 3$ for INH and $y = 4$ for INNMA; M = Ni or Zn, $x = 1$, $y = 2$ in for both ligands; M = Cu, $x = 2$, $y = 3$ for INH and $y = 4$ for INNMA.

The mass losses were accompanied by exothermic effects.

TABLE VII. Thermal data for the complexes 1–8

Complex	Decomp. temp. °C	Lost fragment	Weight loss, %	
			Experimental	Theoretical
[Cu(INH)(ac) ₂] ₂ ·3H ₂ O (1)	19–119	3H ₂ O	8.619	8.019
	119–800	2INH, 2CO ₂	52.389	53.78
	>800	residue 2CuO	32.054	31.406
[Co(INH)(ac) ₂] ₂ ·3H ₂ O (2)	25–113	3H ₂ O	15.767	14.67
	113–928	INH, 2CO ₂	60.384	61.125
	>928	residue CoO	23.849	20.350
[Ni(INH)(ac) ₂] ₂ ·2H ₂ O (3)	20–103	2H ₂ O	10.238	10.685
	103–400	INH, 2CO ₂	63.968	63.942
	400–800	residue NiO	21.223	24.009
[Zn(INH)(ac) ₂] ₂ ·2H ₂ O (4)	18–227	2H ₂ O	11.605	10.10
	227–360	2CO ₂	31.039	30.83
	360–472	INH	38.864	38.45
	472–800	residue ZnO	23.74	22.82
[Cu(INNMH)(ac) ₂] ₂ ·4H ₂ O (5)	20–201	4H ₂ O	8.52	7.267
	201–280	INNMH	29.519	28.046
	280–807	INNMH	27.982	28.046
	>807	residue 2CuO	32.106	33.764
[Co(INNMH)(ac) ₂] ₂ ·4H ₂ O (6)	51–202	4H ₂ O	10.38	11.155
	202–407	INNMH, 2CO ₂	75.705	74.97
	407–943	residue CoO	13.91	15.34
[Ni(INNMH)(ac) ₂] ₂ ·2H ₂ O (7)	20–110	2H ₂ O	9.323	7.378
	110–800	INNMH, 2CO ₂	74.224	75.0014
	>800	residue NiO	15.978	15.711
[Zn(INNMH)(ac) ₂] ₂ ·2H ₂ O (8)	18–272	2H ₂ O	6.595	7.281
	272–513	INHNA, 3CO ₂	80.659	82.875
	513–800	Residue ZnO	12.746	13.44

CONCLUSIONS

Eight new complexes of Cu(II), Co(II), Ni(II) and Zn(II) with isoniazid (INH) and isonicotinic acid (1-naphthylmethylene)hydrazide (INNMA) ligands were synthesized and characterized. Based on all results obtained by elemental analysis, IR, electronic and EPR spectroscopy, magnetic measurements and thermogravimetric analysis, the structural formulae presented in Figs. 3a–d are proposed for complexes 1–8.

The structure of the INNMH was established in a single crystal X-ray study. Both ligands act as a bidentate through the oxygen and nitrogen in the Co(II), Ni(II) and Zn(II) complexes. The Cu(II) complexes are dimeric, with four brid-

ges between the acetate ions and Cu(II). The number of water molecules of crystallization was determined by differential thermal analysis.

Supplementary material. Crystallographic data for the structure in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC number: CCDC 727344. This data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/deposit> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Tel: (44) 1223 762910; Fax: (44) 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

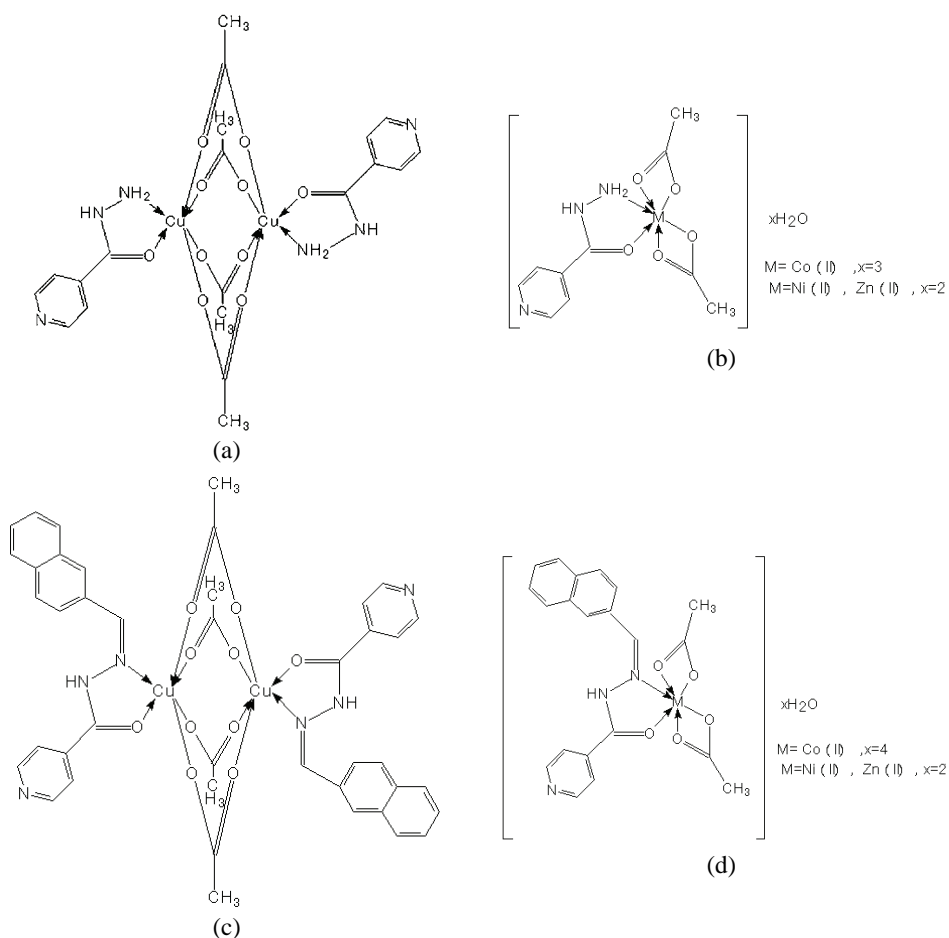


Fig. 3. The structural formula proposed for the a) $[\text{Cu}(\text{INH})(\text{ac})_2]_2$ complex, b) $[\text{M}(\text{INH})(\text{ac})_2]$ type of complexes, $\text{M} = \text{Co}(\text{II}), \text{Ni}(\text{II})$ or $\text{Zn}(\text{II})$, c) $[\text{Cu}(\text{INNMH})(\text{ac})_2]_2$ complex and d) $\text{M}(\text{INNMH})(\text{ac})_2]$ type of complexes, $\text{M} = \text{Co}(\text{II}), \text{Ni}(\text{II})$ or $\text{Zn}(\text{II})$.

ИЗВОД

СИНТЕЗА И СТРУКТУРНО ПРОУЧАВАЊЕ КОМПЛЕКСА Cu, Co, Ni И Zn СА ХИДРАЗИДОМ
ИЗОНИКОТИНСКЕ КИСЕЛИНЕ И (1-НАФТИЛМЕТИЛЕН)ХИДРОЗИДОМ
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Добијено је и окарактерисано осам нових комплекса Cu(II), Co(II), Ni(II) и Zn(II) са изонијазидом (INH) и (1-нафтилметилен)хидразидом изоникотинске киселине (INNMH) опште формуле $[M(INH)(ac)_2]$, $[M(INNMH)(ac)_2]$ (M = Co(II), Ni(II) и Zn(II)), односно $[Cu(INH)(ac)_2]_2$, $[Cu(INNMH)(ac)_2]_2$. Сви комплекси су окарактерисани елементалном анализом, IR, UV-VIS-NIR и EPR спектроскопијом, као и термичком анализом, одређивањем моларне проводљивости и магнетних момената. Структура INNMH хидразона је утврђена рендгенском структурном анализом на моно-кристалу. Оба лиганда се координују за метал преко N, O у свим комплексима. Комплекси Cu(II) су димерни, са четири ацетато јона који премошћују Cu(II).

(Примљено 15. априла, ревидирано 11. септембра 2009)

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