Spectral and Thermal Studies about the Complexes of Some Divalent Transitional Metals with Isonicotinic Acid Hydrazide

ANGELA KRIZA[1], LUCICA VIORICA ABABEI[2]*, NICOLAE STĂNICĂ[3], ILEANA RAU[4], ELENA ADINA ROGOZEA[3]

[1]University of Bucharest, Chemistry Faculty, 23 Dumbrava Rosie Str., Bucharest, Romania
[2]The House of Teaching Staff Giurgiu, 8 Nicholae Droc Barcian Str., Giurgiu, Romania
[3]Romanian Academy, Chemistry-Physics Institute, 202 Independence Avenue, 77208 Bucharest, Romania
[4]Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Science, 1 Polizu Str., 011061, Bucharest, Romania

We synthesized and characterized five new complexes of some transitional metals sulphates with isonicotinic acid hydrazide (isoniazid - INH), having formula of type $[M(INH)(SO_4)(H_2O)_2] \cdot xH_2O$ (x =1, M = Cu(II), and x=0, M = Zn(II)), and $[M(INH)(SO_4)(H_2O)_2]_2$, M = Co(II), Ni(II) and Mn(II). All complexes were characterized on the basis of elemental analyses, IR spectroscopy, UV-Vis-NIR, EPR, as well as thermal analysis and determination of magnetic moments. The thermal behaviour of complexes was studied using thermogravimetry (TG) and differential thermal analysis (DTA). The ligand works as bidentate NO, being coordinated through the imine nitrogen and carbonylic oxygen. Complexes of Cu (II) and Zn(II) are monomeric and complexes of Co(II), Ni(II) and Mn(II) are dimeric.

Keywords: isoniazid, dimeric complexes, thermal analysis

Isoniazid (INH) is one of the most common and efficient drugs used in treatment of tuberculosis [1], because it has a very high *in vivo* inhibitory activity towards *Mycobacterium tuberculosis* H37Rv [2]. Its activity is enhanced by chelation with metals. The structure, stability and consecutive formation constants of metal chelates of isoniazid with different metal ions, have been studied [3-6]. According to previous investigations [7] first we had as a task the synthesis of new complexes combination with izoniazid and derivate hydrazones [8,9].

In the present paper, we report synthesis and characterization of five combinations of Cu (II), Co (II), Ni (II), Mn (II) and Zn(II) sulphate with isoniazid (INH). The structural ligand formula is shown in figure1.
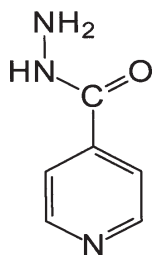

Fig. 1. Ligand formula

Experimental part
Synthesis of the complexes
To methanolic solution of Cu (II), Co (II), Ni (II) and Mn (II) sulphate (0.001 moles in 15 mL methanol), a methanol solution of izoniazid (INH) is added, in a molar ratio 1:1, under continuous stirring. Immediately, the metallic complexes are precipitates. The solid products are filtered, washed with methanol and dried in vacuum over anhydrous $CaCl_2$.

Materials and methods
The elemental analyses (C, H, N) were made with an Elemental Combustion System CHNS-O, using a Costech device, type ECS 4010, and the metal content was determined by gravimetric methods: Cu with salicylaldoxime, Ni with dimethilglioxime, and Co, Mn and Zn as pyrophosphates.

The melting temperatures of complexes were directly measured with SMPI Melting Point Apparatus (Stuart Scientific).

The IR spectra (4000 - 400 cm^{-1}) were recorded in KBr tablet, using a BIO-RAD FTS-135 spectrometer, and the UV-Vis-NIR electronic spectra (200 - 2200 nm) were recorded with a UV-Vis-NIR spectrophotometer in diffuse reflectance, JASCO V 670.

The measurements of magnetic susceptibility were determined at room temperature, using the Faraday method, and electronic paramagnetic resonance (EPR) spectra of Cu(II) complex 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 with a heating of 5^0C/min in synthetic air atmosphere (150 mL / min). All complexes have been investigated in the range 20-800^{0}C.

Results and discussions
By reaction of sulphate of some transitional metals with INH, in 1:1 molar ratio, were obtained the monomeric complexes, type $[M(INH)(SO_4)(H_2O)_2].xH_2O$ (x = 1, M = Cu (II) and x = 0, M = Zn (II)) and dimeric complexes, type $[M(INH)(SO_4)(H_2O)_2]_2$ (M = Co(II), Ni(II) and Mn(II)).

The compounds are thermally stable and they are insoluble in common organic solvents (methanol, ethanol, acetone, diethyl ether, chloroform, DMF).

Elemental analysis and some physical properties (colours, melting point) of the complexes are given in table1.

IR Spectra
The main bands from IR spectra for the ligand and its metal complexes are presented in table 2.

In the izoniazid IR spectrum very intense bands appear at 3302 cm^{-1}, 3112 cm^{-1}, 1667 cm^{-1} and 1555 cm^{-1}, that are

* email: lucica_32@yahoo.com; Tel 0723637890

Table1

ELEMENTAL ANALYSIS DATA, COLOURS AND MELTING POINTS OF COMPLEXES

	Complex	colour	melting point, (^{0}C)	Elemental analysis Found (calcd)			
				M%	C%	H%	N%
1.	$[Cu(INH)(SO_4)(H_2O)_2].H_2O$	Bleu	250[*]	17.321 (!7.818)	19.998 (20.187)	3.402 (3.674)	13.218 (13.458)
2.	$[Co(INH)(SO_4)(H_2O)_2]_2$	Pink	>325	17.046 (17.186)	22.002 (22.158)	3.128 (3.412)	12.746 (12.925)
3.	$[Ni(INH)(SO_4)(H_2O)_2]_2$	Blue cristals	314[*]	17.580 (17.906)	21.786 (21.965)	3.106 (3.382)	12.916 (12.813)
4.	$[Mn(INH)(SO_4)(H_2O)_2]_2$	yellow	>325	16.804 (16.954)	22.305 (22.220)	3.126 (3.421)	12.794 (12.961)
5.	$[Zn(INH)(SO_4)(H_2O)_2]$	yellow	>325	19.003 (19.205)	21.025 (21.146)	3.075 (3.256)	13.995 (14.097)

* carbonisation

Table 2

INFRARED FREQUENCIES (cm^{-1}) OF INH AND COMPLEXES

	Complex	v(OH)	vN-H	vC=O amideI	vPy ring	v amide II	vSO$_4^{2-}$ dicoord	δH$_2$O coord	vN-N
	INH	-	3302 3112	1667	1602	1555	-	-	887
1.	$[Cu(INH)(SO_4)(H_2O)_2].H_2O$	3413	3248 3119	1654	1603	1540	1215 1042 969	911	864
2.	$[Co(INH)(SO_4)(H_2O)_2]_2$	3444	3272 3168	1657	1603	1547	1211 1060 984	894	855
3.	$[Ni(INH)(SO_4)(H_2O)_2]_2$	3381	3211	1658	1604	1552	1224 1060 977	905	852
4.	$[Mn(INH)(SO_4)(H_2O)_2]_2$	3446	3283 3180	1659	1603	1541	1203 1070 978	891	860
5.	$[Zn(INH)(SO_4)(H_2O)_2]$	3462	3257 3103	1664	1603	1547	1209 1065 983	896	855

assigned to the vibration frequency $v(NH_{as})$, $v(NH_{sim})$ and are due to amide-I groups and amide-II. The band of medium intensity from 887 cm^{-1} is due to the vibration frequency vN-N [10].

In the complexes, the corresponding band of amide-I group appears displaced towards lower values, which indicates the involvement of carbonyl group in coordination [11].

The vibration frequencies vN-H is strongly displaced in all complexes. The displacement towards lower values by comparison with the ligand spectra, suggests the involvement of the imino nitrogen in coordination with metallic ions. In accordance with this is the fact that the vibration frequency vN-N is displaced towards lower values in complexes [10].

The bands attributed to pyridine vibration mode remain almost unchanged in the spectra of the complexes,

suggesting that the pyridine nitrogen is not involved in the coordination of the metal ions.

All data support the idea that in the metallic complexes, the ligand works as bidentate NO, being coordinated through the imine nitrogen and carbonylic oxygen.

The bands in the domain 3462-3381 cm^{-1} and 911 - 894 cm^{-1}, from IR spectra of the complexes, suggest the existence of coordination water [12].

The presence of SO_4^{2-} anionic in the coordination sphere of the complexes is supported by the emergence of three bands in the domain 969 - 984 cm^{-1}, 1042 - 1070 cm^{-1} and 1203 - 1224 cm^{-1} [12].

In all the complexes, in the range 400 – 500 cm^{-1}, new lower intensity bands appear, that show the presence of some M-O and M-N bonds.

Electronic spectra

The isoniazid presents in UV two bands, at 45454 cm^{-1} and 38461 cm^{-1}, assigned to transitions $\pi \rightarrow \pi^*$ respectively $n \rightarrow \pi^*$.

The electronic spectrum of the Cu(II) complex, presents a large band at 13123 cm^{-1}, which can be attributed to the transition $^2E_g \rightarrow ^2T_{2g}$, proper for an octahedral geometry [13].

The Co(II) complex presents three bands in the electronic spectrum, at 8333 cm^{-1}, 16025, 19157 cm^{-1}, attributed to the transitions d-d, $^4T_{1g} \rightarrow ^4T_{2g}$, $^4T_{1g}(F) \rightarrow ^4A_{2g}$, and $^4T_{1g} \rightarrow ^4T_{1g}(P)$. These transitions and the values of the field parameters correspond to those characteristic for an octahedral geometry [13].

The electronic spectrum of Ni(II) complex (fig. 2), presents three bands at 10080 cm^{-1}, 16286 cm^{-1}, 26737 cm^{-1}, attributed to the transitions $^3A_{2g} \rightarrow ^3T_{2g}$, $^3A_{2g} \rightarrow ^3T_{1g}$ and respectively $^3A_{2g} \rightarrow ^3T_{1g}$ (P), proper to an octahedral geometry for the Ni(II) ion [13].

The ligand field splitting energy (10Δq), interelectronic repulsion parameter (B) and nephelauxetic ratio (β) for the Co(II) and Ni(II) complexes were calculated using the secular equations given by König [14] and the values are presented in table 3.
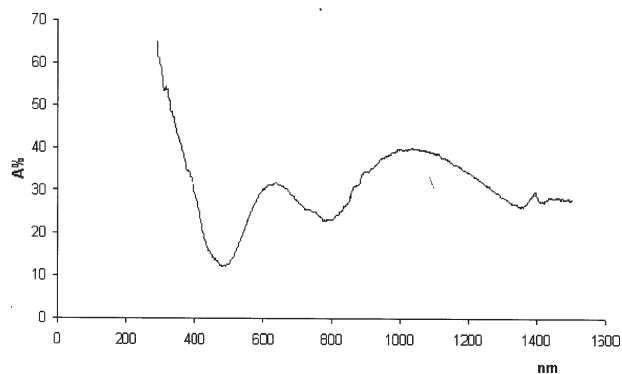

Fig 2 . UV-Vis-NIR spectra for complex 3

The Mn(II) complex presents a signal in UV domain at 31250 cm^{-1} assigned to a change transfer of electric load, how the theory foresees for a d^5 ion [15].

In the spectrum of Zn(II) complex, as expected, it can be noticed only the ligand bands, displaced to lower values.

Magnetic moments

The magnetic moment determined for the complex of Cu (II) is 1.889 MB and reasonably corresponds in the range (1.8 – 2.2 BM) specific to complexes of Cu (II) with octahedral geometry [16].

The complex of Zn (II) is diamagnetic, as expected for the configuration of d^{10} [17].

It is known that in the approximation "spin only" can be calculated magnetic moment of a compound based on the hypothesis non-matched number of electrons, so the value of the spin associated of the paramagnetic ions components: validity of the hypothesis results from comparing the magnetic moment calculated with that determined from measurements. In so far as the compounds whose magnetic moment is determined, containing several paramagnetic ions, when produced experimentally at room temperature, the measured susceptibility can be typically played by the relationship "spin only":

Table 3

ELECTRONIC SPECTRA (cm^{-1}), MAGNETIC MOMENTS AND GEOMETRIES FOR LIGAND AND COMPLEXES

	Complex	Freqencies, cm^{-1}	Assignments	10Δq	B	β	μ_{eff} B.M.	Environment
	INH	45454 38461	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-	-	-	-
1	$[Cu(INH)(SO_4)(H_2O)_2].H_2O$	13123	$^2E_g \rightarrow ^2T_{2g}$	-	-	-	1,89	Octahedral
2	$[Co(INH)(SO_4)(H_2O)_2]_2$	19157 16025 8333	$^4T_{1g} \rightarrow ^4T_{1g}(P)$ $^4T_{1g}(F) \rightarrow ^4A_{2g}$ $^4T_{1g} \rightarrow ^4T_{2g}$	7692	678,866	0,699	5,70	Octahedral
3	$[Ni(INH)(SO_4)(H_2O)_2]_2$	26737 16286 10080	$^3A_{2g} \rightarrow ^3T_{1g}$ (P) $^3A_{2g} \rightarrow ^3T_{1g}$ $^3A_{2g} \rightarrow ^3T_{2g}$	10080	852,2	0,827	3,21	Octahedral
4	$[Mn(INH)(SO_4)(H_2O)_2]_2$	31250	TS				5,65	Octahedral
5	$[Zn(INH)(SO_4)(H_2O)_2]$	30120	$n \rightarrow \pi^*$	-	-	-	Dia	Octahedral

$$M = \frac{N\mu_B^2}{3k} \sum_{i=1}^{n} g_i S_i (S_i + 1) \qquad (1)$$

(expression of the calculated magnetic moment in Bohr magnetons, assuming no magnetic exchange interaction of intra and inter molecular and assuming the neglect of orbital magnetic moment contribution),
where:

- n is the number of paramagnetic ions in the compound
- g_i, S_i are the giromagnetic factors, respectively the timing of the spin relative to the indices paramagnetic ion indicated with "i" in the composition of the molecule
- N, μ_B, k is Avogadro's number, the magneton Bohr and his constant Boltzmann.

The relationship (1) is based essentially on the assumption of no interaction among the paramagnetic centers inside a molecule and leads to the formula

$$\chi_{molar} T = \frac{N\mu_B^2}{3k} \sum_{i=1}^{n} g_i S_i (S_i + 1) \qquad (1')$$

so

$$\frac{3k}{N\mu_B^2} \chi_{molar} T = \sum_{i=1}^{n} g_i S_i (S_i + 1) \qquad (1'')$$

where further

$$\sqrt{\frac{3k}{N\mu_B^2} \chi_{molar} T} = \sqrt{\sum_{i=1}^{n} g_i S_i (S_i + 1)} \qquad (1''')$$

By the expression 1''' on the left is evaluated "the experimental magnetic moment" and the term 1''' on the right is evaluated "the magnetic theoretical moment", based on approximation" spin only ".

The difference between the two values can be interpreted as being due to interaction between paramagnetic centers (interactive ferro or antiferro-magnetic) and / or orbital magnetic moment contribution. In the latter option, you turned to theoretical models more developed, given that "spin only" approximation from before expressions neglects both contributions.

Nothing is changed if considered only one molecule or more, as long as we use the assumption of no interaction among the paramagnetic centers within a molecule, intermolecular dipolar interaction or orbital contributions.

Based on this hypothesis and determined the susceptibility values at room temperature were calculated magnetic moments for complexes of Co (II), Ni (II) and Mn (II). Thus:

- for the complex Co (II), the experimentally determined magnetic moment is 5.7 MB, indicating a high spin and excluding the oxidation to Co(III). The value determined is perfectly in the 4.3 - 5.7 MB, which corresponds to an octahedral geometry for the ion Co(II) [16].

- for the complex of Ni (II) the amount determined for the magnetic moment is 3.21 MB. This value is in the range (2.8 - 3.5) for complexes of Ni (II) with octahedral geometry [16].
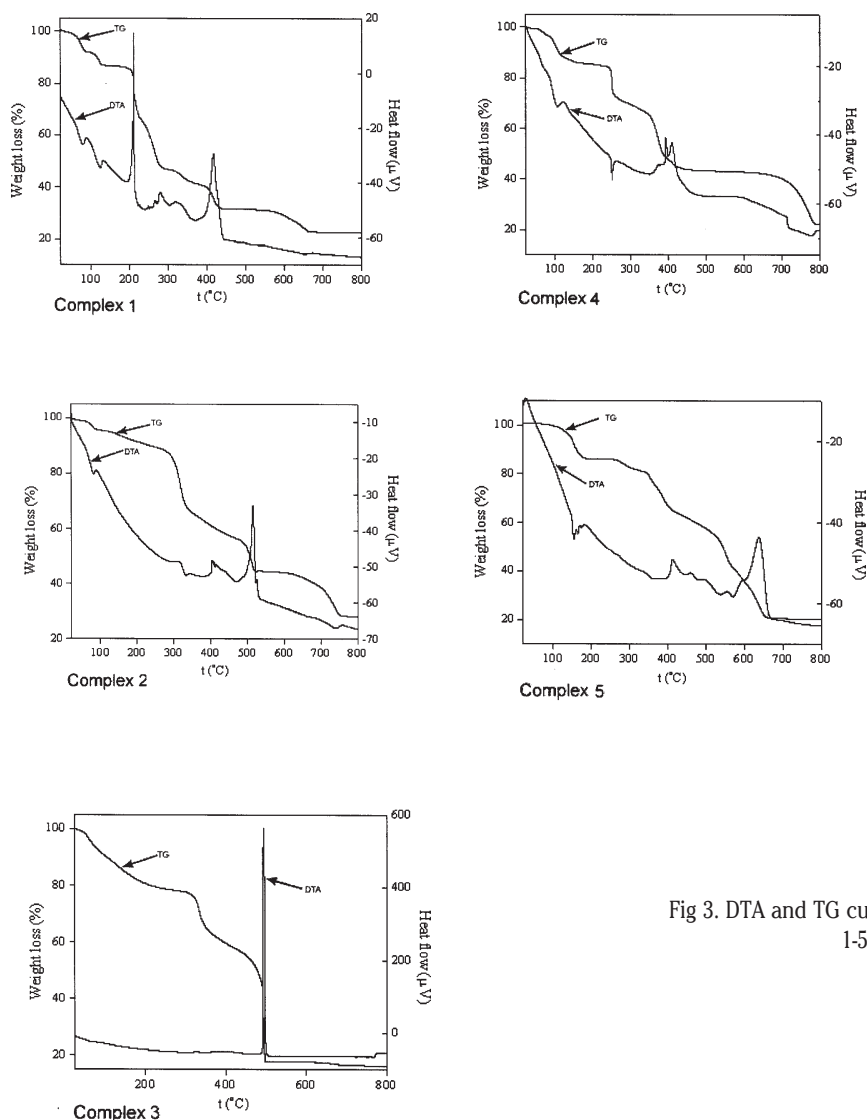

Fig 3. DTA and TG curves of complexes 1-5
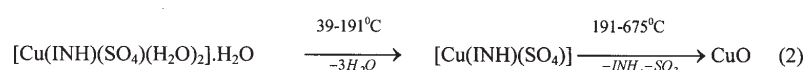
Table 4
THERMAL ANALYSIS DATA FOR THE COMPLEXES

Complex		Decomp temp (^{0}C)		Lost fragment	Weight loss (%)	
		Initial	Final		Theor	Exp
1	[Cu(INH)(SO$_4$)(H$_2$O)$_2$].H$_2$O	39	191	-3H$_2$O	15.409	14.6
		191	314	-INH	39.100	39.417
		314	675	-SO$_3$	22.809	23.275
		675	800	residuum CuO	22.680	22.708
2	[Co(INH) (SO$_4$) (H$_2$O)$_2$]$_2$	30	248	-4H$_2$O	10.98	10.034
		248	534	-2INH	41.796	42.795
		534	800	residuum 2CoSO$_4$	47.27	46.171
3	[Ni(INH)(SO$_4$)(H$_2$O)$_2$]$_2$	40	150	-4H$_2$O	11.12	12.086
		150	357	-INH	21.169	21.217
		357	500	-INH	21.169	21.422
		500	800	residuum 2NiSO$_4$	46.56	45.275
4	[Mn(INH)(SO$_4$)(H$_2$O)$_2$]$_2$	35	118	-4H$_2$O	11.954	11.243
		118	344	-INH,	21.396	22.27
		344	434	-INH	21.396	21.661
		434	800	residuum 2MnSO$_4$	44.12	43.102
5	[Zn(INH)(SO$_4$)(H$_2$O)$_2$]	37	176	-2H$_2$O	10.76	11.615
		176	439	-SO$_3$	23.906	23.23
		439	666	-INH	40.98	41.08
		666	800	residuum ZnO	24.322	24.062

- the magnetic moment determined for the complex Mn (II) is 5.65 MB. This value falls in the range 5.65 - 6.10 MB, it is appropriate the Mn (II) ion, with octahedral environment [15].

Termogravimetric analysis

DTA and TG data of the investigated complexes are given in figure 3 and table 4. The DTA curves are characterized by endothermic peaks in the temperature range 35 - 248^{0}C, assigned to loss of water of coordination (inclusively water of crystallization for complex 1), and TG curves indicates loss of mass in this interval. The appearance of more than one endothermic DTA peak confirms that water is not limited isoenergetically and elimination is done in several steps [18].

In the Cu (II) and Zn (II) complexes, the final remaining residue is metal oxide, and in the Co (II), Ni (II) and Mn (II) complexes, the final remaining residue is metal sulphate. The processes of thermal decomposition for the complexes studied can be resumes as:

$$[Cu(INH)(SO_4)(H_2O)_2].H_2O \xrightarrow[-3H_2O]{39-191^0C} [Cu(INH)(SO_4)] \xrightarrow[-INH,-SO_3]{191-675^0C} CuO \quad (2)$$

$$[Co(INH)(SO_4)(H_2O)_2]_2 \xrightarrow[-4H_2O]{30-248^0C} [Co(INH)(SO_4)]_2 \xrightarrow[-2INH]{248-534^0C} 2\,CoSO_4 \quad (3)$$

$$[Ni(INH)(SO_4)(H_2O)_2]_2 \xrightarrow[-4H_2O]{40-150^0C} [Ni(INH)(SO_4)]_2 \xrightarrow[-2INH]{150-500^0C} 2NiSO_4 \quad (4)$$

$$[Mn(INH)(SO_4)(H_2O)_2]_2 \xrightarrow[-4H_2O]{35-118^0C} [Mn(INH)(SO_4)]_2 \xrightarrow[-2INH]{118-434^0C} 2MnSO_4 \quad (5)$$

$$[Zn(INH)(SO_4)(H_2O)_2] \xrightarrow[-2H_2O]{37-176^0C} [Zn(INH)(SO_4)] \xrightarrow[-INH,-SO_3]{176-666^0C} ZnO \quad (6)$$

EPR spectra

The Cu(II) complex was examined by EPR spectroscopy and the values for g$_\parallel$ and g$_\perp$ were determined for the proper magnetic field (table 5). The EPR spectra (fig. 4) and the values of the magnetic field parameters plead for an octahedral symmetry for the Cu(II) complex.
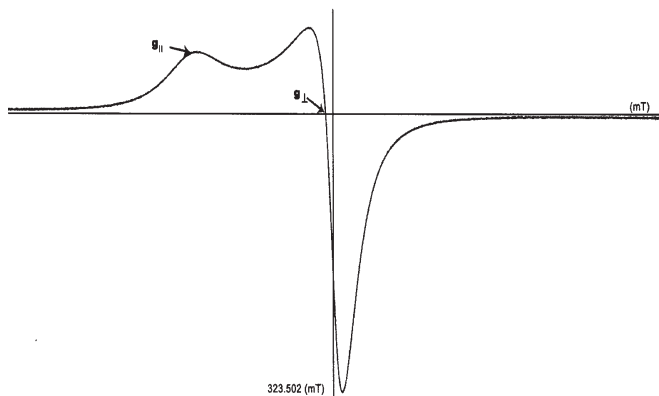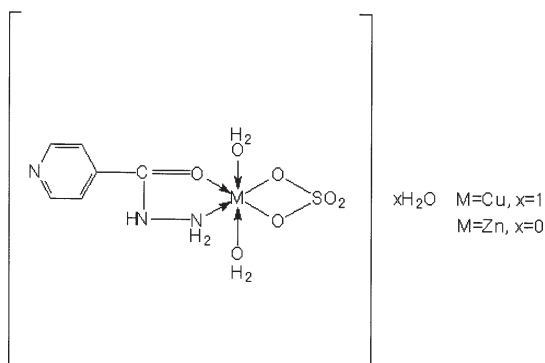
Fig 4. EPR spectrum for complex 1 at room temperature

323.502 (mT)

xH₂O M=Cu, x=1
      M=Zn, x=0

Fig 5. a. Structural formula proposed for complexes 1 and 5

M=Co²⁺, Ni²⁺, Mn²⁺
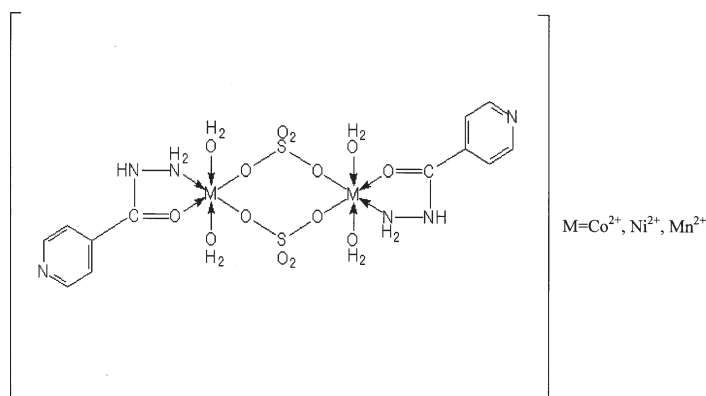
Fig 5. b. Structural formula proposed for complexes 2-4

Table 5
EPR DATA OF THE COMPLEX 1

Complex	g		H (mT)	
	g∥	g⊥	H∥	H⊥
[Cu(INH)(SO₄)(H₂O)₂].H₂O	2.3107	2.0988	291.718	321.169

The spectral (IR, EPR and UV-Vis-NIR) and magnetic data enable us to predict the possible structural formula for the metal complexes which are also supported by the thermal decomposition studies, as shown in figure 5.a and 5.b.

Conclusions

Five new complexes of Cu (II), Co (II), Ni (II), Mn (II) and Zn(II) with isoniazid (INH) were synthesized and characterized. The complexes of Cu(II) and Zn(II) are monomeric and the complexes of Co(II), Ni(II) and Mn(II) are dimeric. The spectroscopic data show that in all complexes, the metallic ion is in an octahedral environment and the ligand acts as bidentate NO, being coordinated through the imine nitrogen and carbonylic oxygen. Also, the results show that the thermal decomposition of studied complexes is consistent with the elemental and spectral analysis.

References

1.BARTMANN, K., IWAINSKI, H., KLEEBERG, H., MISON, P., OFFE, H., OTTEN, H., TETTENBORN, D., TRNKA, L., Antituberculosis Drugs, ed. K. Bartman, Springer, Berlin, 1988
2.KAYMAKCIOGLU, K. B., UNSALAN, S., KANDERMIRLI, F., ROLLAS, S., ANATHOLY, D., Eur. J. Med. Chem., **41**, 2006, p 1253
3.ISHIDATE, M., Proc. Int. Symp. On Analytical Chemistry, Birmingham University, Birmingham, 1962, p. 178
4.NAGANO, K., KINOSHITA, H., TAMURA, Z., Chem. Pharm. Bull., **11**, no. 8, 1963, p. 999
5.DONIA, A. M., EBEID, E. M., Thermochim. Acta, 131, 1988, p. 1
6.DONIA, A. M., Thermochim. Acta, **147**, 1989, p. 65
7. KRIZA, A. , MITU, L., STĂNICĂ, N., Rev. Chim. (Bucuresti)), **56,** 2005, p 137
8.MITU, L., KRIZA, A., DIANU, M., Asian Journal of Chemistry, **20,** nr.2, 2008, p 1627
9.KRIZA, A., ABABEI, L., STANICĂ, N., RĂU, I., Rev. Chim. (Bucuresti), **60**, no. 8, 2009, p 774
10.KRIZA, A. , PÎRNĂU, C., POPA, N., Rev. Chim. (Bucuresti), **52**, no. 6, 2001, p 346
11.NAKAMOTO, K., Infrared Spectra of Inorganic and Coordination Compounds. 2nd ed. New York, NY: Wiley-Interscience; 1970
12.SINGH, B., NARANG, K.K, SRIVASTAVA, R., Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, **32**, nr. 9, 2002, p 1577
13.LEVER, A.B.P, Inorg Electronic Spectroscopy, Elsevier, Amsterdam, 1984
14.KONIG, E., Structure and bonding, **9,** 1971, p 175
15.AURKIE, R., ROSAIR, G. M., GARLAND, M. T., Struct. Chem., **19**, no. 2, 2008, p 2009
16.AGARWAL, R.K., SHARMA, D., SHING, L., AGARWAL, H., Bioinorg Chem Appl., 2006, 2006, p 29238
17.SELWOOD, P. W., Magnetochemistry, Interscience Publisher, Inc., New York Interscience Publisher LTD., London, 1956, p 78
18.BORAEY, H. A., Journal of Thermal Analysis and Calorimetry, **81,** 2005, p 341